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Ammonia Volatilization from Flooded Soil Systems: A Computer Model. I. Theoretical Aspects

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ABSTRACT

Ammonia volatilization from flooded rice (*Oryza sativa* L.) is a major mechanism for N loss and poor fertilizer use efficiency. Ammonia volatilization is influenced by five primary factors: $\text{NH}_4\text{-N}$ concentration, pH, temperature, depth of floodwater, and wind speed. This NH_3 -volatilization model is based on chemical and volatilization aspects. The chemical aspects of the model deal with the $\text{NH}_4/\text{NH}_3(\text{aq})$ equilibrium in floodwater. Ammonium ions undergo dissociation with a first-order rate constant, while $\text{NH}_3(\text{aq})$ and H undergo a diffusion-controlled association reaction with a second-order rate constant. The transfer of NH_3 across the water-air interface of flooded soil systems is characterized by a first-order volatilization rate constant. By utilizing the chemical dynamics of the $\text{NH}_4/\text{NH}_3(\text{aq})$ system in association with transfer of gaseous NH_3 across the interface, an equation was derived to determine the rate of NH_3 volatilization from flooded systems as a function of the five primary factors. The chemical aspects of the model include the derivation of association and dissociation rate constants. The volatilization aspects of the model, which is based on the two-film theory, allows it to compute the volatilization rate constant for NH_3 . Expressions are derived to compute the Henry's law constant, gas-phase and liquid-phase exchange constant, and the overall mass-transfer coefficient for NH_3 .

AMMONIA VOLATILIZATION from flooded-rice soils is a major mechanism for N loss and a cause of low fertilizer use efficiency by rice. Recent reviews on NH_3 volatilization from flooded-rice soils indicate that losses of ammoniacal-N fertilizer applied directly to floodwater may vary from 10 to 50% of the amount applied (Mikkelsen and De Datta, 1979; Vlek and Cra-swell, 1981; Fillery and Vlek, 1986; Mikkelsen, 1987). Losses, however, are site and soil-management specific; thus, disparities may exist in reported rates of volatilization, depending on rate-controlling factors and methods of measurement. Various techniques have been used to measure NH_3 loss including forced-

air exchange methods using enclosures with NH_3 traps and micrometeorological techniques such as energy balance (Denmead et al., 1974, 1976), mass balance (Denmead et al., 1977; Beauchamp et al., 1978), and aerodynamic techniques (Lemon and van Houtte, 1980). The former, although simple in methodology, is not representative of natural field conditions, while the latter require elaborate instrumentation and are very labor intensive.

The behavior of $\text{NH}_4\text{-N}$ in flooded soil systems and its transfer across the water-air interface is a very dynamic process involving numerous interactions. An understanding of these rate-controlling factors is essential to the development of a model that accurately predicts losses, allows simplified measurements of NH_3 loss, and subsequently allows design of more efficient fertilizer-management practices.

There are only a few models that characterize the floodwater chemistry and atmospheric conditions affecting NH_3 volatilization. Bouwmeester and Vlek (1981a) developed a model based on the penetration theories of Higbie and Danckwerts (e.g., Danckwerts, 1970). Moeller and Vlek (1982) used the same theories with inclusion of a pH gradient in the liquid diffusion layer for model development.

The NH_3 -volatilization model developed here is based on the two-film model of mass transfer (Whitman, 1923), which has been adapted to environmental problems by Liss (1973) and, later, by other researchers (Liss and Slater, 1974; Mackay and Leinonen, 1975; Dilling, 1977; Cohen et al., 1978; Southworth, 1979; Mackay et al., 1979; Rathbun and Tai, 1981; Smith et al., 1981; Atlas et al., 1982). The predictions on gaseous volatilization based on the film model, which is the most widely used kinetic model for estimating the volatilization of chemicals (Sanders and Seiber, 1984), are similar to those based on more sophisticated models (Danckwerts, 1970).

Ammonia volatilization is the transfer of NH_3 from floodwater to the atmosphere across a water-air interface. The model presented here consists of two parts: (i) chemical aspects, $\text{NH}_4/\text{NH}_3(\text{aq})$ equilibrium in floodwater and (ii) volatilization aspects, NH_3 transfer from floodwater across the water-air interface.

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MODEL DEVELOPMENT

Ammonia volatilization from a flooded soil system is a complex process, influenced by water, soil, and fertilizer characteristics, and also by environmental and crop-management practices (Mikkelsen, 1987). Excellent reviews by Terman (1979), Vlek and Craswell (1981), Fenn and Hossner (1985), Fillery and Vlek (1986), and Mikkelsen (1987) list the factors that influence NH_3 volatilization in flooded soil systems.

Five primary factors directly influence the process of NH_3 volatilization. These include floodwater $\text{NH}_4\text{-N}$ concentration, pH, temperature, wind velocity, and floodwater depth. The role of floodwater depth in NH_3 volatilization is twofold. It directly affects NH_4 ion concentration by virtue of its dilution. Further, it influences the volatilization relationships, which have not been addressed in previous research. These primary factors, however, are further influenced by several other factors, referred to as secondary factors.

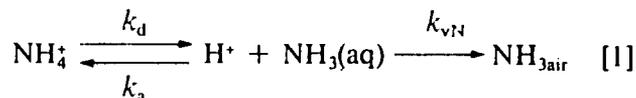
Ammonia volatilization from flooded rice typically ceases about 7 to 14 d after fertilizer application, depending on the N source, method of application, and management (Ventura and Yoshida, 1977; Mikkelsen et al., 1978; Vlek and Stumpe, 1978; Mikkelsen and De Datta, 1979; Freney et al., 1981; Simpson et al., 1984; Fillery et al., 1984; Fillery and De Datta, 1986). In transplanted and direct-seeded rice cultures, within the first 14 d, crops have generally been fertilized but have not emerged appreciably from the floodwater. Therefore, a model that predicts the rate of NH_3 volatilization from a bare water surface and that simulates the first 14 d of rice culture, the most critical period of NH_3 volatilization, encompasses the main sequence of events. Our model will not address the midseason NH_3 losses where split N applications are made.

CHEMICAL ASPECTS OF THE MODEL

Ammonium N contained in fertilizer or formed through urea hydrolysis is the major source of NH_3 for volatilization. Nitrogen in floodwater exists primarily in two forms: NH_4 ions and dissolved $\text{NH}_3(\text{aq})$. An equilibrium exists between these two forms that is governed by the pH of the medium. The dissociation of NH_4 follows first-order reaction kinetics, whereas the association of $\text{NH}_3(\text{aq})$ and H exhibits a second-order kinetics (Alberty, 1983).

Aqueous NH_3 is transferred across the air-water interface in the form of NH_3 gas, which follows first-order reaction kinetics (Vlek and Stumpe, 1978; Moeller and Vlek, 1982) and can be characterized by a first-order rate constant.

The chemical dynamics of NH_3 volatilization from floodwater is as follows:



where

k_d = dissociation rate constant for NH_4/NH_3 equilibrium, first order,

k_a = association rate constant for NH_4/NH_3 equilibrium, second order, and

k_{vN} = volatilization rate constant for NH_3 , first order.

The rate of NH_3 volatilization can be estimated by the rate of change in NH_4 concentration in floodwater, with the assumption that no other processes changes NH_4 concentration in the system. There are various

processes, however, that bring NH_4 into floodwater, such as soil desorption and organic-matter mineralization, and those that remove NH_4 from floodwater, such as soil adsorption and biotic assimilation. It is assumed here that these processes quickly equilibrate and subsequently affect little change in floodwater NH_4 concentration. Further, by making frequent NH_4 measurements and by using these values as model inputs, any error due to this assumption will be minimized. Thus,

$$\frac{d[\text{NH}_4]}{dt} = k_a[\text{NH}_3(\text{aq})][\text{H}] - k_d[\text{NH}_4] \quad [2]$$

where brackets denote concentration in water and t = time. By chemical kinetics, the rate of change of $\text{NH}_3(\text{aq})$ is given as

$$\frac{d[\text{NH}_3(\text{aq})]}{dt} = k_d[\text{NH}_4] - k_a[\text{NH}_3(\text{aq})][\text{H}] - k_{vN}[\text{NH}_3(\text{aq})] \quad [3]$$

and at steady state as

$$\frac{d[\text{NH}_3(\text{aq})]}{dt} = 0 \quad [4]$$

therefore

$$k_d[\text{NH}_4] - k_a[\text{NH}_3(\text{aq})][\text{H}] - k_{vN}[\text{NH}_3(\text{aq})] = 0 \quad [5]$$

By rearranging Eq. [5],

$$[\text{NH}_3(\text{aq})] = \frac{k_d[\text{NH}_4]}{k_a[\text{H}] + k_{vN}} \quad [6]$$

and by substituting Eq. [6] into Eq. [2],

$$\frac{d[\text{NH}_4]}{dt} = k_a \left(\frac{k_d[\text{NH}_4]}{k_a[\text{H}] + k_{vN}} \right) [\text{H}] - k_d[\text{NH}_4] \quad [7]$$

The ammoniacal-N concentration in floodwater at equilibrium (AN) is the sum of the various species in the system:

$$\text{AN} = [\text{NH}_4] + [\text{NH}_3(\text{aq})] + [\text{NH}_4\text{L}] \quad [8]$$

and, by ignoring ion-pair (NH_4L) formation,

$$\text{AN} = [\text{NH}_4] + [\text{NH}_3(\text{aq})] \text{ and, therefore,} \quad [9]$$

$$[\text{NH}_4] = \text{AN} - [\text{NH}_3(\text{aq})] \quad [10]$$

By substituting Eq. [10] into Eq. [7], the rate of NH_3 volatilization can be written as

$$\frac{d[\text{NH}_4]}{dt} = k_a \left\{ \frac{k_d(\text{AN} - [\text{NH}_3(\text{aq})])}{k_a[\text{H}] + k_{vN}} \right\} [\text{H}] - k_d(\text{AN} - [\text{NH}_3(\text{aq})]) \quad [11]$$

In all these derivations, the activity coefficient for various species is assumed to be unity. Therefore, the activity is represented by the equilibrium concentration of each species (denoted by brackets).

Equation [11] estimates the rate of NH_3 volatilization as a function of $\text{NH}_4\text{-N}$, aqueous NH_3 , and H concentrations in floodwater, k_a and k_d of $\text{NH}_4/\text{NH}_3(\text{aq})$ at equilibrium, and k_{vN} for NH_3 .

The $\text{NH}_4\text{-N}$ concentration and pH of the floodwater are experimentally determined. Rate constants k_d , k_a

and k_{vN} are computed in the model. Aqueous NH_3 is computed as a function of NH_4 concentration, pH, and temperature. By applying these values to Eq. [11], the rate of NH_3 volatilization can be estimated. Rate constants k_d and k_a for the $NH_4/NH_3(aq)$ equilibrium are computed in the chemical aspects of the model. The rate constant k_{vN} is computed in the volatilization aspect of the model.

Determination of Association and Dissociation Rate Constants

This model is designed to perform at any natural temperature range and has the capability of computing the rate constants at various temperatures in a series of steps. First, the equilibrium constant, K , for the $NH_4/NH_3(aq)$ system is computed as a function of temperature, then k_a is determined. Finally, k_d is obtained with the use of K and k_a .

Determination of the Equilibrium Constant

The K for the $NH_4/NH_3(aq)$ equilibrium is computed as a function of the temperature of the floodwater by applying the Clausius-Clapeyron equation to the equilibrium system.

$$\frac{d \ln K}{dT} = \frac{\Delta H^0}{RT^2} \quad [12]$$

where

H^0 = change in enthalpy at standard state in the $NH_4/NH_3(aq)$, and
 T = absolute temperature.

By integrating Eq. [12] between specific limits,

$$\int_{K_1}^{K_2} d \ln K = \Delta \frac{\Delta H^0}{R} \int_{T_1}^{T_2} T^{-2} dT \quad [13]$$

$$\ln \frac{K_2}{K_1} = \frac{\Delta H^0 \Delta T}{RT_1 T_2} \quad [14]$$

where

K_1 = the equilibrium constant for the $NH_4/NH_3(aq)$ system at absolute temperature T_1 ,
 K_2 = the equilibrium constant for the $NH_4/NH_3(aq)$ system at absolute temperature T_2 ,

$$\Delta T = T_2 - T_1.$$

By transformation of Eq. [14], we obtain Eq. [15]:

$$pK_2 = pK_1 - \frac{\Delta H^0 T}{2.303RT_1 T_2} \quad [15]$$

By using Eq. [15], pK at 25 °C = 9.24, and $\Delta H^0 = 2982.8$ J (Dean, 1986), an equation is derived by regression analysis to compute pK at any temperature, an equation similar to that of Bates and Pinching (1949) derived by a different methodology:

$$pK(T) = 0.0897 + (2729/T) \quad [16]$$

where $pK(T) = -\log K$ at absolute Kelvin temperature T .

The computed pK and K for the $NH_4/NH_3(aq)$ system at different temperatures are given in Table 1.

Table 1. Computed equilibrium constant (K) for $NH_4/NH_3(aq)$ system and its negative log (pK) at different temperatures.

Temperature °C	pK	K
10	9.73	1.9×10^{-10}
15	9.56	2.8×10^{-10}
20	9.40	4.0×10^{-10}
25	9.24	5.7×10^{-10}
30	9.09	8.1×10^{-10} †
35	8.95	1.1×10^{-9}
40	8.80	1.6×10^{-9}

† Calculated value = experimental value (Alberty, 1983).

Determination of the Association Rate Constant

The association reaction between NH_3 and H in water, as measured by Eigen and coworkers, is diffusion controlled (Alberty, 1983). Therefore, it is assumed that the rate constant for the association reaction is proportional to the diffusion coefficient (D):

$$k_a \propto D \quad [17]$$

For a particular species, D is a function of temperature and viscosity of the medium as shown by the Stokes-Einstein equation (Laidler and Meiser, 1982)

$$D = C(T/\eta) \quad [18]$$

where

C = a constant, $k/6\pi r$
 k = Boltzmann constant,
 η = viscosity of the medium, and
 r = radius of the particle.

Therefore

$$D \propto \frac{T}{\eta} \quad [19]$$

By combining relationships [17] and [19],

$$k_a \propto D \propto \frac{T}{\eta} \quad [20]$$

This relationship can be transformed to an equation form by equating at two different temperatures:

$$\frac{k_a(T_2)}{k_a(T_1)} = \frac{T_2 \eta(T_1)}{T_1 \eta(T_2)} \quad [21]$$

where

$k_a(T_1), k_a(T_2)$ = k_a at temperatures T_1 and T_2 , respectively, and
 $\eta(T_1), \eta(T_2)$ = viscosity of the medium at temperatures T_1 and T_2 , respectively.

With the use of k_a at 25 °C (Alberty, 1983) and the viscosity of water at different temperatures (Dean, 1986), a relationship was developed by regression using Eq. [21]:

$$k_a(T) = 3.8 \times 10^{11} - 3.4 \times 10^9 T + 7.5097007 T^2 \quad [22]$$

The computed k_a values at different temperatures are given in Table 2.

Determination of Dissociation Rate Constant

By using the K relationship, the k_d for the $NH_4/NH_3(aq)$ system at various temperatures can be computed:

$$k_d(T) = K(T) k_a(T) \quad [23]$$

using $k_a(T)$ from Eq. [22].

The computed k_d values at different temperatures are given in Table 2.

The k_a and k_d computed at various temperatures are used in Eq. [11] to determine the rate of NH_3 loss from a flooded system.

VOLATILIZATION ASPECTS OF THE MODEL

The volatilization aspect of the model is based on the two-film theory (Whitman, 1923), which assumes that the main body of each fluid is homogeneous by convection currents, and concentration differences are regarded as negligible except in the vicinity of the liquid-gas interface. On either side of the interface, it is assumed that turbulent eddies are negligible and a thin film of fluid exists in each phase, in which the flow is considered to be laminar and parallel to the surface (Fig. 1). Most of the resistance to mass transfer and, hence, most of the concentration gradient lies in those films. The basis of the model assumes that the zones in which the resistance to transfer lies can be described by two hypothetical layers, one on either side of the interface, in which the transfer is solely by molecular diffusion. Under given conditions of turbulence, however, the layer thicknesses vary both spatially and temporally (Liss and Slater, 1974). According to Smith and Bomberger (1979), high turbulence in the liquid phase causes the liquid film or boundary layer to be thin; similarly, high turbulence in the gas phase causes the gas layer to be thin.

At the interface, there is a concentration discontinuity and NH_3 is at equilibrium across the interface as determined by Henry's law constant. It is generally assumed that no resistance exists at the interface itself, where equilibrium conditions develop. However, measurements of concentration profiles show that there is a diffusion resistance for gas exchange and it lies in the film on either side of the interface (Coulson et al., 1978; Mackay et al., 1979). Therefore, the controlling factor is the rate of diffusion through the two films, where all the resistance lies. This shows that liquid-phase or gas-phase resistance, or both, determines the overall mass-transfer rate of NH_3 .

In developing our model, we assumed that a $\text{NH}_4/\text{NH}_3(\text{aq})$ equilibrium exists in the floodwater, and that $\text{NH}_3(\text{aq})$ diffuses from the bulk of the liquid to the interface across the thin film. As NH_3 is transferred across the air-water interface, there is a drop in chemical potential, and volatilization continues until equilibrium is achieved.

Table 2. Computed dissociation (k_d) and association (k_a) rate constant for the $\text{NH}_4/\text{NH}_3(\text{aq})$ system at different temperatures.

Temperature °C	k_d s ⁻¹	k_a M ⁻¹ s ⁻¹
10	5.22	2.8×10^{10}
15	8.96	3.3×10^{10}
20	15.01	3.8×10^{10}
25	25.59†	$4.3 \times 10^{10} \ddagger$
30	39.51	4.9×10^{10}
35	62.29	5.5×10^9
40	96.53	6.2×10^{10}

† Experimental value = 24.60 s^{-1} .

‡ Experimental value = $4.3 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ (Alberty, 1983).

librium is achieved. It is assumed, although perhaps inconclusively, that the pH in the surface film remains constant. Hoover and Berkshire (1969) assumed the same in their study of CO_2 exchange at the air-sea interface, and Bouwmeester and Vlek (1981a) made the same assumption in their NH_3 -volatilization model. This assumption may hold true in a situation where the pH changes that probably occur at the surface may be compensated for by other effects.

Determination of the Volatilization Rate Constant for Ammonia

When NH_3 is transferred across the air-water interface, it should obey the law of conservation of mass; therefore, the material balance of the system should be considered (Neely, 1980). For interpretation, suppose there is a container with water of depth d containing $\text{NH}_3(\text{aq})$, which is volatilized from the surface via a first-order reaction process. A material balance on this system, which can be determined by dimensional analysis, is given as

$$\frac{dC_N}{dt} V = K_{ON} C_N A \quad [24]$$

where

K_{ON} = overall mass-transfer coefficient for NH_3 (in $L t^{-1}$),

A = area of the surface (in L^2),

V = volume of the solution (in L^3),

C_N = $\text{NH}_3(\text{aq})$ concentration in the solution (in $\text{mol } L^{-3}$),

L = length, and

t = time.

Dividing Eq. [24] by V yields

$$\frac{dC_N}{dt} = \frac{K_{ON}}{d} C_N \quad [25]$$

where d = the depth of solution in the container.

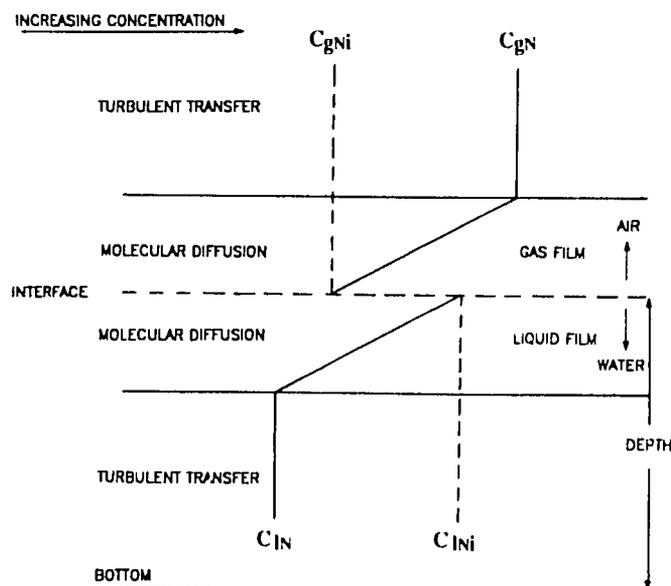


Fig. 1. Two-film model of a gas-liquid interface where C_{gN} and C_{lN} = concentration of NH_3 at the interface in gas and liquid phases, respectively; and C_{gN} and C_{lN} = concentration of NH_3 in bulk gas and liquid phases, respectively.

By dimensional analysis, it is seen that the ratio of K_{ON} and d is a first-order k_{vN} for NH_3 :

$$k_{vN} = \frac{K_{ON}}{d} \quad [26]$$

By extrapolating into a field situation, d can be considered as the mean depth of floodwater.

The relationship expressed by Eq. [25] shows that the k_{vN} for NH_3 is inversely related to d . To estimate the k_{vN} , we need the K_{ON} for NH_3 .

Our model calculates k_{vN} as a function of d (Jayaweera and Mikkelsen, 1990). Table 3 shows the effect of d on k_{vN} and the half-life of NH_4 depletion from floodwater, $t_{1/2}$.

$$t_{1/2} = 0.693/k_{vN} \quad [27]$$

According to Table 3, an increase in d decreases k_{vN} , which thereby increases $t_{1/2}$.

Determination of the Overall Mass Transfer Coefficient for NH_3

The rate of transfer of NH_3 through the gas film is the same as through a liquid film under steady state. Since the movement through the film layers is by molecular diffusion, it can be described by Fick's first law of diffusion:

$$F_N = -D_N \frac{dC_N}{dx} \quad [28]$$

where:

F_N = flux of NH_3 gas through the surface film (in mol $L^{-2} t^{-1}$)

D_N = molecular diffusion coefficient or diffusivity of NH_3 (in $L^2 t^{-1}$), and

$\frac{dC_N}{dx}$ = concentration gradient of NH_3 gas across the film of thickness x .

The ratio of $D_N/\Delta x$ in Eq. [28] can be considered as a constant, k_N , under a given set of conditions and is the exchange constant for NH_3 gas, which has the dimensions of velocity, [L] $[t]^{-1}$.

$$k_N = -D_N/\Delta x \quad [29]$$

By substituting Eq. [29] into Eq. [28], we obtain another form of the Fick's law equation generally used in gas-exchange studies:

$$F_N = k_N \Delta C_N \quad [30]$$

where

ΔC_N = concentration difference of NH_3 across the film of thickness x .

By transforming Eq. [30], we can define k_N as

$$k_N = F_N/\Delta C_N \quad [31]$$

According to Eq. [31], k_N is a measure of the flux of NH_3 per unit concentration difference across the film layer of thickness x . The value of k_N depends on many factors, among which the degree of turbulence in the fluids on both sides of the interface is important.

Under steady-state conditions for NH_3 transfer across the air-water interface, and applying Eq. [30] to the two-film situation, we obtain

$$F_N = k_{gN} (C_{gN} - C_{gNi}) = k_{lN} (C_{lNi} - C_{lN}) \quad [32]$$

where

k_{gN} = the exchange constant for NH_3 in the gas phase,

k_{lN} = the exchange constant for NH_3 in the liquid phase,

C_{gN} and C_{lN} = the average concentration of NH_3 in the bulk gas and liquid phases, respectively, and

C_{gNi} and C_{lNi} = the concentration of NH_3 at the interface in the gas and liquid phases, respectively.

To obtain a direct measurement of the k_{lN} and k_{gN} requires measurement of NH_3 at the interface, the determination of which has been difficult (Coulson et al., 1978). However, if the exchanging gas obeys Henry's law, we can eliminate the concentration requirement at the interface (C_{gNi} and C_{lNi}) in determining k_{lN} and k_{gN} values.

Henry's law constant, in its nondimensional form, can then be defined as

$$H_{nN} = \frac{C_{gNi}}{C_{lNi}} \quad [33]$$

where H_{nN} = nondimensional Henry's law constant for NH_3 , and C_{gNi} and C_{lNi} are in g/cm^3 of water.

By eliminating C_{gNi} and C_{lNi} between Eq. [32] and [33], we obtain

$$F_N = (C_{gN} - H_{nN}C_{lN}) / (1/k_{gN} + H_{nN}/k_{lN}) = [(C_{gN}/H_{nN}) - C_{lN}] / [1/k_{lN} + 1/(H_{nN}k_{gN})] \quad [34]$$

The above expression is simplified by introducing two constants:

$$F_N = K_{GN} (C_{gN} - H_{nN}C_{lN}) = K_{LN} [(C_{gN}/H_{nN}) - C_{lN}] \quad [35]$$

where

K_{GN} = overall gas-phase coefficient for NH_3 ,
 K_{LN} = overall liquid-phase coefficient for NH_3 ,

where:

$$1/K_{GN} = 1/k_{gN} + H_{nN}/k_{lN}, \text{ and} \quad [36]$$

$$1/K_{LN} = 1/k_{lN} + 1/H_{nN}k_{gN}. \quad [37]$$

The total resistance to NH_3 transfer can be expressed on either a gas-phase ($1/K_{GN}$) or a liquid-phase ($1/K_{LN}$) basis. According to Eq. [36] and [37], the total resistance depends on K_{gN} , k_{lN} , and H_{nN} .

Since the term $1/K_{LN}$ of Eq. [37] can be considered as the total resistance for NH_3 flux from a water body,

Table 3. Effect of depth of floodwater on volatilization rate constant for NH_3 (k_N) and half life ($t_{1/2}$).

Depth of floodwater	k_N †	$t_{1/2}$
cm	s ⁻¹	h
1	9.2×10^{-4}	0.2
4	2.3×10^{-4}	0.8
7	1.3×10^{-4}	1.5
10	9.2×10^{-5}	2.1
13	7.1×10^{-5}	2.7
16	5.8×10^{-5}	3.4
19	4.9×10^{-5}	4.0

† Temperature = 25 °C; wind speed = 5 m s⁻¹.

Eq. [37] can be rearranged to determine K_{ON} , which is numerically equal to K_{LN} .

$$K_{ON} = K_{LN} = (H_{nN}k_{gN}k_{iN})/(H_{nN}k_{gN} + k_{iN}) \quad [38]$$

To estimate K_{ON} , we need H_{nN} , k_{gN} , and k_{iN} .

Henry's law constant is a function of temperature and k_{gN} and k_{iN} values are dependent on wind speed; therefore, K_{ON} becomes a function of both temperature and wind speed. The K_{ON} is calculated by the model by varying the temperature and the wind speed (Jayaweera and Mikkelsen, 1990) as shown in Table 4. It is interesting to note that the temperature effect is very small from 20 to 40 °C, the range of interest in most cases.

Determination of Henry's Law Constant for Ammonia

Henry's law constant is a coefficient that represents the equilibrium distribution of a material between the gas and liquid phases.

Because of relatively low concentrations of NH_3 in floodwater, the Henry's law constant should be obeyed reasonably well under flooded conditions. Several researchers have used the Henry's law relationship in their NH_3 -volatilization studies in floodwater systems (Bouwmeester and Vlek, 1981a; Leuning et al., 1984). In our model, we compute H_N for NH_3 in MPa m^3 mol^{-1} and, therefore, need to determine the partial pressure of NH_3 in the gas phase in equilibrium with solution in MPa and the NH_3 concentration in solution in $mol\ m^{-3}$.

By considering the chemical equilibrium of $NH_4^+/NH_3(aq)$ in floodwater, it is possible to relate the pH of the floodwater, K , and the concentrations of NH_4^+ and $NH_3(aq)$ in floodwater, as shown in Eq. [39]:

$$pH = pK + \log \frac{\alpha C}{(1 - \alpha)C} \quad [39]$$

where C = total ammoniacal-N concentration in floodwater and, by rearrangement:

$$\alpha = \frac{10 \exp(pH - pK)}{10 \exp(pH - pK) + 1} \quad [40]$$

where α = fraction of $NH_3(aq)$.

The pK value is temperature dependent. By substituting an expression that we derived (Eq. [16]) to compute pK as a function of T , we obtain

$$\alpha = \frac{10 \exp(pH - 0.0897 - 2729/T)}{10 \exp(pH - 0.0897 - 2729/T) + 1} \quad [41]$$

Equation [41] shows the fraction of NH_3 in solution as a function of pH and T . By using our model (Jayaweera and Mikkelsen, 1990), we calculated the fraction of $NH_3(aq)$ in floodwater with respect to pH and temperature, which is shown in Table 5. Figure 2 illustrates the effect of pH on the fraction of dissociation of $NH_4^+/NH_3(aq)$ system.

By considering the Henry's law constant for NH_3 in the form of pressure-per-mole-fraction form, we obtain

$$P_N = H_N X_N \quad [42]$$

Table 4. Effect of wind speed at 8 m above the water surface and temperature on the overall mass-transfer coefficient for NH_3 (K_{ON}).

Wind speed	K_{ON}^\dagger	Temperature	K_{ON}^\ddagger
$m\ s^{-1}$	$cm\ h^{-1}$	°C	$cm\ h^{-1}$
1	0.90	10	3.12
2	1.32	15	3.19
4	1.77	20	3.25
6	3.31	25	3.31
8	5.32	30	3.37
10	7.33	35	3.43
12	9.00	40	3.48

† Temperature = 25 °C.

‡ Wind speed = 6 $m\ s^{-1}$.

Table 5. Effect of pH and temperature on the fraction of $NH_3(aq)$ (α) in floodwater.

pH	α^\dagger	Temperature	α^\ddagger
		°C	
7.0	0.01	10	0.06
7.5	0.02	15	0.08
8.0	0.05	20	0.11
8.5	0.15	25	0.15
9.0	0.36	30	0.20
9.5	0.64	35	0.26
10.0	0.85	40	0.33

† Temperature = 25 °C.

‡ pH = 8.5.

where

P_N = partial pressure of NH_3 in the gas phase in equilibrium with the solution, and

H_N = Henry's law constant for NH_3 in pressure per mole fraction.

X_N = mole fraction of NH_3 in solution.

The partial pressure of NH_3 in equilibrium with the solution can then be computed by using Eq. [42].

If C (in mg/L) is the total ammoniacal N concentration, the mole fraction of NH_3 is

$$X_N = \frac{\alpha C/17.03}{\alpha C/17.03 + (1 - \alpha)C/18.04 + 10^6 \rho_w/18.02} \quad [43]$$

where ρ_w = density of water (in gm/cm^3) at T .

By substituting Eq. [40] into Eq. [42], we can estimate X_N as a function of pH and T :

$$X_N = \frac{(C/17.03)(A/1 + A)}{(C/17.03)(A/1 + A) + (C/18.04)(1/1 + A) + 10^6 \rho_w/18.02} \quad [44]$$

where $A = 10 \exp(pH - 0.0897 - 2729/T)$.

Equation [44] computes X_N in floodwater as a function of total ammoniacal-N concentration, pH, and temperature of the floodwater. According to Eq. [42], we can estimate the partial pressure of NH_3 in the gas phase in equilibrium with the floodwater if we know the Henry's law constant for NH_3 in MPa per mole fraction form. Therefore, we compute H_N in MPa per mole fraction.

Click and Reed (1975) developed an expression to relate H_N to absolute Rankine degrees. In this model, their expression has been modified to suit absolute Kelvin:

$$H_N = 183.8 \exp(-1229/T) \quad [45]$$

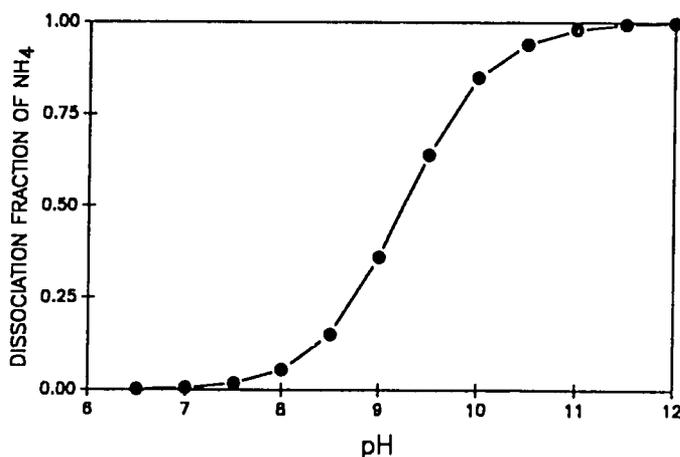


Fig. 2. Effect of pH on fraction of dissociation of $NH_4/NH_3(aq)$ system.

By substituting Eq. [45] and [44] into Eq. [42], P_N can be obtained:

$$P_N = 18.62 \exp(-1229/T) X_N \text{ MPa.} \quad [46]$$

According to this relationship, P_N varies with total ammoniacal-N concentration, pH, and temperature of the floodwater.

Determination of the Concentration of Aqueous Ammonia

The C_N is determined in mol m^{-3} to calculate the Henry's law constant in $\text{MPa m}^3 \text{mol}^{-1}$. Equation [41] computes the fraction of NH_3 in $NH_4/NH_3(aq)$ equilibrium as a function of pH and temperature. If C is in mg L^{-1} , by proper conversion, C_N can be determined in mol m^{-3} :

$$C_N = (C/17.03) \frac{10 \exp(\text{pH} - 0.0897 - 2729/T)}{10 \exp(\text{pH} - 0.0897 - 2729/T) + 1} \quad [47]$$

According to Eq. [47], the C_N in the floodwater depends on C , pH, and temperature.

By using Eq. [46] and [47], we can obtain the Henry's law constant in $\text{MPa m}^3 \text{mol}^{-1}$ for our model (Jayaweera and Mikkelsen, 1990). As shown in Table 6, H_N is a function of floodwater temperature, wherein an increase in temperature increases H_N . The dependency of H on temperature for a particular gas/solvent system is well documented (Burkhard et al., 1985).

With the use of H_N in $\text{MPa m}^3 \text{mol}^{-1}$, H_{nN} can be computed.

Determination of Nondimensional Henry's Law Constant for Ammonia

The Henry's law constant that is computed in $\text{MPa m}^3 \text{mol}^{-1}$ can be transformed into nondimensional form to be used in Eq. [38] as

$$H_{nN} = \frac{H_N}{RT} \quad [48]$$

where R , the gas constant, is $8.315 \times 10^{-6} \text{ MPa m}^3 \text{mol}^{-1} \text{K}^{-1}$.

Table 6. Computed Henry's law constant for NH_3 (H_N).

Temperature		$H_N \dagger$
°C		$\text{MPa m}^3 \text{mol}^{-1}$
10		4.36×10^{-6}
15		4.76×10^{-6}
20		5.07×10^{-6}
25		5.47×10^{-6}
30		5.78×10^{-6}
35		6.18×10^{-6}
40		6.59×10^{-6}

$\dagger NH_4\text{-N concentration} = 25 \text{ mg L}^{-1}$; $\text{pH} = 8.5$.

Determination of Gas-Phase and Liquid-Phase Exchange Constants

Exchange constants k_e have the dimension of velocity and can be considered as the velocity at which NH_3 moves through the fluid films. The value of k_{gN} and k_{lN} depend on the degree of turbulence in the fluids on either side of the interface, the chemical reactivity of the substance, and the temperature and properties of the solute, such as diffusivity or molecular size (Liss and Slater, 1974; Mackay and Yeun, 1983).

The reciprocal of k_e is a measure of the resistance to gas transfer. The relative importance of the gas- and liquid-phase resistances for the exchange of any particular gas can be estimated if we obtain numerical values for the k_e . These k_e , however, cannot yet be readily computed using basic physical principles, and generally are determined empirically (Thomas, 1982).

The values of H for different chemicals give some insight into the distribution of resistances in the liquid and gas films. In the usual temperature range found in floodwater, i.e., 10 to 40 °C, the H_N for NH_3 varies between 4.36×10^{-6} to $6.59 \times 10^{-6} \text{ MPa m}^3 \text{mol}^{-1}$ (Table 6). According to our model, therefore, the process of NH_3 volatilization is controlled by both gas- and liquid-phase resistances (Mackay et al., 1979). Liss and Slater (1974), however, suggested that the gas phase controls the rate of NH_3 volatilization. On the contrary, Leuning et al. (1984) found experimentally that NH_3 -volatilization rates were controlled by transfer processes in the water as well as in the air.

In our model, k_{gN} and k_{lN} are computed from the data collected in a wind tunnel relating the wind speed and the water vapor exchange constant, k_{gw} and the CO_2 -gas exchange constant, k_{IC} (Liss, 1973). Wind speed in the wind tunnel is transformed to equivalent field wind speed with the use of friction velocity, U . Using Liss' data, the following relationship is obtained:

$$U = 0.0545 U_{0.1} \quad [49]$$

where

U = the friction velocity, in m s^{-1} , and
 $U_{0.1}$ = the wind speed at 0.1 m above the water surface in the wind tunnel, m s^{-1} .

By using the mean roughness height of 0.008 cm (Jayaweera et al., 1990) and by assuming a logarithmic wind profile, a relationship is developed between the wind speed at an 8-m height, U_8 , and U :

$$U_8 = 28.7823U. \quad [50]$$

Table 7. Computed gas-phase exchange constants for NH_3 (k_{gN}) and liquid-phase exchange constant (k_{lN}) as a function of wind speed at 8 m above the water surface.

Wind speed	k_{gN}	k_{lN}
m s ⁻¹	cm h ⁻¹	
1	19	0.46
2	1504	2.20
4	2988	2.42
6	4473	5.01
8	5958	8.96
10	7442	13.31
12	8927	16.65

By equating the friction velocity in Eq. [49] and [50], the following equation is obtained to relate the wind-tunnel speed and the equivalent field wind speed at 8 m:

$$U_8 = 1.5686U_{0.1} \quad [51]$$

This is in close agreement with the relationship developed by Bouwmeester and Vlek (1981b).

The gas-phase exchange constant for NH_3 , k_{gN} , was determined by using the water-vapor exchange constant at different wind speeds. By using the data of Liss (1973), a regression equation relating the water-vapor exchange constant, k_{gW} (cm h⁻¹) and the wind speed was determined by

$$k_{gW} = 18.5683 + 1135.98U_{0.1} \quad [52]$$

This relationship is transformed into the field situation with Eq. [51] and is adjusted to NH_3 with the use of the molecular-weight (MW) ratio of water and NH_3 (Liss and Slater, 1974):

$$k_{gN} = [18.0683 + 1135.98(U_8/1.5686)](MW_{\text{H}_2\text{O}}/MW_{\text{NH}_3})^{1/2} \quad [53]$$

Equation [53] simplifies to

$$k_{gN} = 19.0895 + 742.3016 U_8 \quad [54]$$

Similarly, the CO_2 exchange-constant data of Liss (1973) were used to estimate the liquid-phase exchange constant for NH_3 , k_{lN} (in cm h⁻¹), as a function of U_8 using Eq. [51], and accounting for the molecular-weight ratio.

The data were fit to a logistic equation,

$$k_{lN} = \{12.5853/[1 + 43.0565 \exp(-0.4417U_8)]\}1.6075 \quad [55]$$

Table 7 shows the computed values of k_{lN} and k_{gN} by using the model at various wind speeds; both constants show increases with increases in wind speed.

Wind speeds measured at any height in the field may be adjusted to an 8-m height by assuming a logarithmic wind profile:

$$U_z = \frac{U_*}{k} \ln \frac{z}{Z_0} \quad [56]$$

Where:

U_z = wind speed, in m s⁻¹, at an anemometer height, z , in m,

k = Von Karman constant, 0.4, and

Z_0 = roughness height, in m.

By considering wind speeds at two different heights, Z_1 and Z_2 , Eq. [56] can be transformed into

$$\frac{U_2}{U_1} = \frac{\ln(Z_2/Z_0)}{\ln(Z_1/Z_0)} \quad [57]$$

where

U_2 = wind speed (in m s⁻¹) at height Z_2 , and
 U_1 = wind speed (in m s⁻¹) at height Z_1 .

According to Burns et al. (1981), the Z_0 of a flat water surface is generally on the order of 1 mm, but, from the data collected in this study, we calculated it more precisely as .08 mm (Jayaweera et al., 1990). So Eq. [57] becomes

$$U_8 = \frac{11.51}{\ln(Z/8 \times 10^{-5})} U_z \quad [58]$$

Equations [55] to [57] are based on the assumptions of neutral stability and wind-speed measurements over a flat water surface. These assumptions may be violated at night, at times of very low or very high evapotranspiration rates, or if plant cover exists above the water surface, any of which would decrease the accuracy of these equations.

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Ammonia Volatilization from Flooded Soil Systems: A Computer Model.

II. Theory and Model Results

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ABSTRACT

Our theory to describe the process of NH_3 volatilization from flooded systems is that the rate of NH_3 loss is principally a function of two parameters, floodwater $\text{NH}_3(\text{aq})$ concentration and the volatilization rate constant for NH_3 , k_{vN} . These parameters are governed by five primary factors, floodwater $\text{NH}_4\text{-N}$ concentration, pH, temperature, depth of floodwater, and wind speed. The NH_3 -volatilization model is executed with five primary factors as input variables. With the input of time, it predicts the NH_3 loss for a specified period. The interactive effects of these factors were studied by individually varying one factor while maintaining the four other factors at their mean values; the same factor was also studied by maintaining a second factor at its highest and lowest values while the other three factors were kept constant at their mean values. It is seen that, by changing the existing conditions, the NH_3 -volatilization losses are increased or decreased appreciably. The sensitivity analysis shows that pH is the most sensitive and temperature and water depth are the least sensitive determinants affecting NH_3 volatilization.

THE VOLATILIZATION OF NH_3 from flooded rice culture is a complex process influenced by characteristics of the soil, water, fertilizer, management practices, and environmental conditions. Vlek and Craswell (1979) reported that up to 50% of the urea applied to puddled Crowley soil (fine, montmorillonitic, thermic Typic Albaqualfs) was volatilized as NH_3 , which significantly affects fertilizer use efficiency and, ultimately, crop yields.

The theoretical aspects of a computer model used to estimate NH_3 losses from flooded soil systems was presented by Jayaweera and Mikkelsen (1990).

A theory has been developed to describe the process of NH_3 volatilization from flooded systems and the results obtained by various simulation runs of the model.

Development of the Theory

Five primary factors govern NH_3 volatilization (Jayaweera and Mikkelsen, 1990). Our model theory describes the effects of these factors. Ammonium concentration, temperature, and pH determine the $\text{NH}_3(\text{aq})$ concentration of floodwater. Depth of floodwater, temperature, and wind speed determine the k_{vN} across the water-air interface (Fig. 1).

Based on this information, our theory states that the rate of NH_3 volatilization is a function of two parameters, floodwater $\text{NH}_3(\text{aq})$ concentration and k_{vN} .

MODEL EXECUTION

The NH_3 -volatilization model initially requires input data for floodwater $\text{NH}_4\text{-N}$ concentration (AMC),

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pH, temperature (TEMP), depth of floodwater (WD), wind speed (WS), and the height of wind measurement (WH) (Fig. 2). The model calculates the initial volatilization rate of NH_3 (VRAMI), using mathematical equations developed by Jayaweera and Mikkelsen (1990). To determine NH_3 loss for a specific period, the time is entered as an input and the model computes the decrease in volatilization rate as a function of the time with a successive approximation loop. The final output is the predicted NH_3 loss for the time period selected.

The model simulations are performed as follows: (i) a single parameter is varied, maintaining the other four parameters fixed at their mean values; (ii) the same variable is tested by maintaining a second parameter at its lowest and highest value while the other three parameters are kept constant at their mean values. The input variables are selected (Table 1) to suit the range of conditions that exist in most rice-growing ecosystems.

The NH_3 -volatilization model presented here has several unique features. It has a menu-driven computer program that can be easily executed. As previously stated, it requires only five input variables to predict NH_3 loss, and no input constants since the model computes all necessary constants depending on the variables provided. Input variables are easily measurable with simple, inexpensive instrumentation. Analytical measurements are only needed for the initial floodwater $\text{NH}_4\text{-N}$ concentration. Depth of floodwater is measured initially and generally remains constant, thus frequent measurements are needed for only three variables: pH, temperature, and wind speed.

The model results are computed with the objective of determining the interactive effect of the five input parameters on the rate of NH_3 loss.

MODEL RESULTS

Effect of Floodwater Ammonium Concentration on Ammonia Volatilization

The initial floodwater $\text{NH}_4\text{-N}$ concentration in the model was varied from 1 to 49 mg L^{-1} , in increments of 7 mg L^{-1} , while the other four parameters are maintained at their mean values. An increase in floodwater $\text{NH}_4\text{-N}$ concentration increased the $\text{NH}_3(\text{aq})$ concentration linearly in the system (Table 2), while the k_{vN} was maintained at a constant value because of constant temperature, water depth, and wind speed (Jayaweera and Mikkelsen, 1990). Therefore, the increase in NH_3 -volatilization rate with an increase in floodwater $\text{NH}_4\text{-N}$ concentration (Table 2) was a function of $\text{NH}_3(\text{aq})$ concentration in the floodwater under the existing conditions.

The next series of model runs were performed at pH 7.0 and 10.0, while varying floodwater $\text{NH}_4\text{-N}$ concentration from 1 to 49 mg L^{-1} and keeping the other three parameters at their mean values. Lowering

the pH to 7.0 decreased the volatilization rate of NH_3 . In contrast, elevating the pH to 10.0 increased both the rate of NH_3 volatilization and the total NH_3 loss. As shown in Table 2, at pH 7.0, the $\text{NH}_3(\text{aq})$ concentration in floodwater has decreased about 30 times and, at pH 10.0, it has increased about six times, compared with pH 8.5, at all floodwater $\text{NH}_4\text{-N}$ concentrations. However, for all these runs, k_{vN} was at a constant value, indicating that pH influences $\text{NH}_3(\text{aq})$ in floodwater at various $\text{NH}_4\text{-N}$ concentrations, thereby influencing the NH_3 -volatilization process.

The temperature was maintained at 10 and 40 °C for the next set of runs, while varying the floodwater $\text{NH}_4\text{-N}$ concentration from 1 to 49 mg L^{-1} and maintaining the mean value of pH, water depth, and wind speed. The NH_3 volatilization decreased at 10 °C and increased at 40 °C (Table 2). As the theory indicates, temperature influenced both $\text{NH}_3(\text{aq})$ in floodwater and the k_{vN} . Lowering the temperature to 10 °C decreased both the $\text{NH}_3(\text{aq})$ in floodwater and the k_{vN} compared with 25 °C. In contrast, when the floodwater temperature was increased to 40 °C, both the $\text{NH}_3(\text{aq})$ and k_{vN} increased, increasing NH_3 volatilization losses (Table 2).

The next set of runs were carried out at floodwater depths of 1 and 19 cm, with varying floodwater $\text{NH}_4\text{-N}$ concentration and constant floodwater pH, temperature, and wind speed. At a water depth of 1 cm, 100% of NH_3 was lost in a 24-h period, compared with 77% loss at a floodwater depth of 10 cm and 53% loss at 19-cm depth at all $\text{NH}_4\text{-N}$ concentrations. As shown in Table 2, the depth of floodwater influenced k_{vN} , but not the $\text{NH}_3(\text{aq})$ in the system (Jayaweera and Mikkelsen, 1990).

The next series of runs were performed at wind speeds of 0 and 12 m s^{-1} at an 8-m height above the

water surface, with floodwater $\text{NH}_4\text{-N}$ concentrations ranging from 1 to 49 mg L^{-1} while pH, temperature, and depth of floodwater were maintained at their mean values. At a wind speed of 12 m s^{-1} at the 8-m height, NH_3 volatilization was almost 100%, compared with only a 2% loss at 0 m s^{-1} at all $\text{NH}_4\text{-N}$ concentrations. As shown in Table 2, wind speed did not influence $\text{NH}_3(\text{aq})$, but influenced the k_{vN} . An increase in wind speed increased the k_{vN} (Jayaweera and Mikkelsen, 1990), thus influencing NH_3 loss.

Effect of pH on Ammonia Volatilization

A series of model runs were performed to study the effect of pH on NH_3 volatilization (Table 3), varying pH from 7.0 to 10.0 while the other variables were maintained at constant mean values. An increase in pH increased the percentage NH_3 loss per day as a result of an increase in $\text{NH}_3(\text{aq})$ in floodwater because of its influence on the degree of dissociation (Jayaweera and Mikkelsen, 1990).

An increase in temperature from 10 to 40 °C at var-

Table 1. Model input parameters used in the study on NH_3 volatilization.

Parameter variable range	Initial $\text{NH}_4\text{-N}$ concentration (AMC) mg L^{-1}	pH	Temperature (TEMP) °C	Water depth (WD) cm	Wind speed at 8 m (U_8) m s^{-1}
Lowest	1	7.0	10	1	0
	9	7.5	15	4	2
	17	8.0	20	7	4
Mean	25	8.5	25	10	6
	33	9.0	30	13	8
	41	9.5	35	16	10
Highest	49	10.0	40	19	12

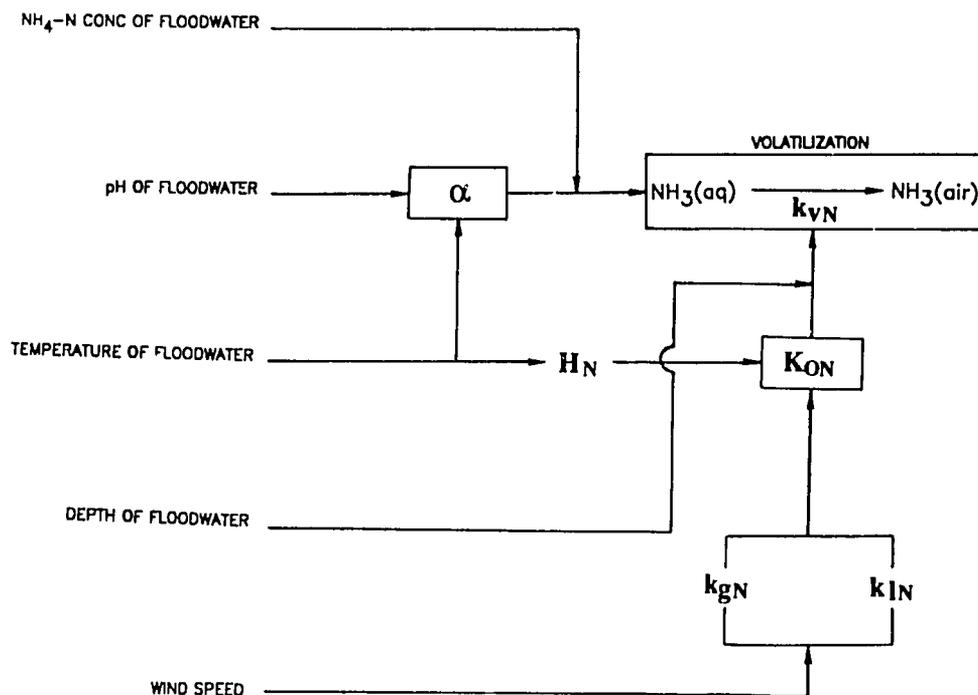


Fig. 1. Theory of NH_3 volatilization in flooded systems, where k_{vN} = volatilization rate constant for NH_3 , K_{ON} = overall mass-transfer coefficient for NH_3 , k_{gN} and k_{IN} = gas-liquid-exchange constants for NH_3 , respectively, α = degree of dissociation of NH_4 , and H_{N} = Henry's law constant for NH_3 .

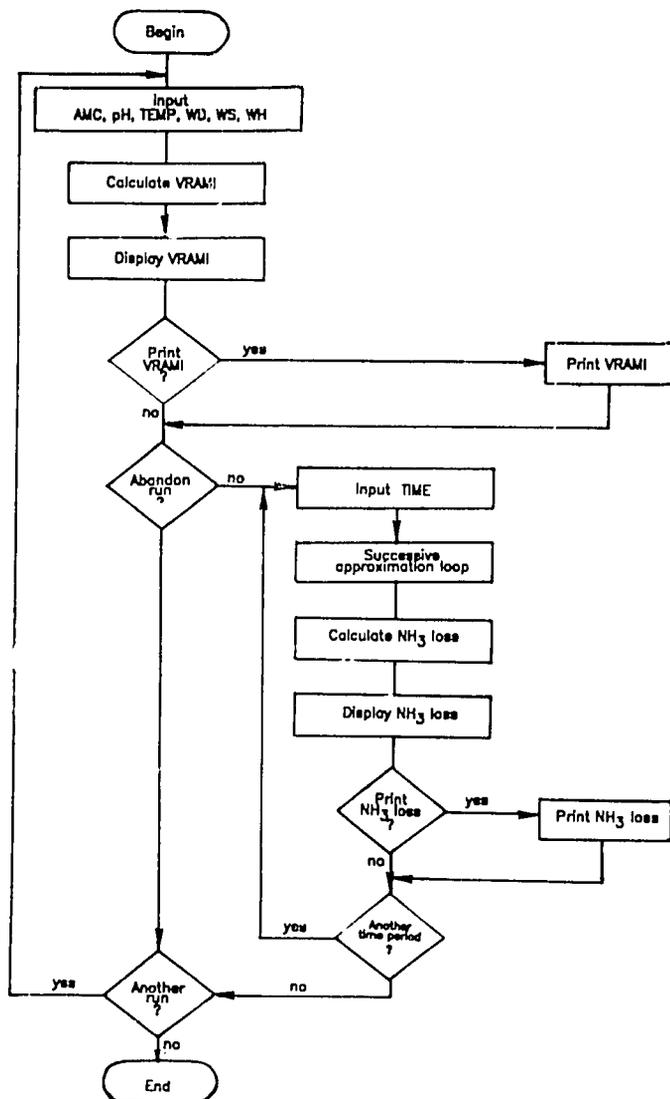


Fig. 2. Flow chart for NH_3 -volatilization model, where AMC = floodwater ammoniacal-N concentration, pH = floodwater pH, TEMP = floodwater temperature, WD = floodwater depth, WS = wind speed, WH = height of wind measurement, and VRAMI = initial volatilization rate of NH_3 .

ious pH levels increased both $\text{NH}_3(\text{aq})$ and k_{vN} , which resulted in an increase in NH_3 loss per day (Table 3).

When the depth of floodwater was 1 cm, NH_3 was lost at a very high rate, reaching nearly 100% per day at about pH 8.5 (Table 3). This large loss at a fairly low pH was due to the high k_{vN} ($9.2 \times 10^{-4} \text{ s}^{-1}$; Table 3). On the contrary, at a water depth of 19 cm, 100% of NH_3 was lost per day only when the pH was raised to about 10.0, as a result of the low k_{vN} ($4.8 \times 10^{-5} \text{ s}^{-1}$; Table 3). This shows that, even with high $\text{NH}_3(\text{aq})$ concentrations in floodwater, the volatilization can be controlled by low k_{vN} , which can be achieved by high water depths.

When we compare the model runs at wind speeds of 12 and 0 m s^{-1} at an 8-m height, nearly 100% of NH_3 was lost per day at 12 m s^{-1} at a pH of 8.5, compared with a 41% loss at pH 10.0 when there was no wind (Table 3), which can be explained by the dif-

Table 2. Effect of floodwater $\text{NH}_4\text{-N}$ concentration on NH_3 volatilization.

Initial $\text{NH}_4\text{-N}$ in floodwater	Initial $\text{NH}_3(\text{aq})$	Volatilization rate constant (k_{vN})	Initial NH_3 volatilization rate [†]	NH_3 loss/day
mg L^{-1}	mol m^{-3}	s^{-1}	$\text{mol L}^{-1} \text{ s}^{-1}$	%
pH 8.5; temperature 25 °C; water depth 10 cm; wind speed 6 m s^{-1}				
1	0.01	9.2×10^{-5}	1.7×10^{-5}	77
25	0.29	9.2×10^{-5}	4.2×10^{-4}	77
49	0.57	9.2×10^{-5}	8.2×10^{-4}	77
pH 7.0†; temperature 25 °C; water depth 10 cm, wind speed 6 m s^{-1}				
1	4.3×10^{-4}	9.2×10^{-5}	5.3×10^{-7}	4
25	1.1×10^{-2}	9.2×10^{-5}	1.3×10^{-5}	4
49	2.1×10^{-2}	9.2×10^{-5}	2.6×10^{-5}	4
pH 10.0‡; temperature 25 °C; water depth 10 cm; wind speed 6 m s^{-1}				
1	0.06	9.2×10^{-5}	5.3×10^{-4}	100
25	1.61	9.2×10^{-5}	1.3×10^{-2}	100
49	3.15	9.2×10^{-5}	2.6×10^{-2}	100
pH 8.5; temperature 10 °C†; water depth 10 cm; wind speed 6 m s^{-1}				
1	4.3×10^{-4}	8.7×10^{-5}	5.1×10^{-6}	36
25	0.11	8.7×10^{-5}	1.3×10^{-4}	36
49	0.21	8.7×10^{-5}	2.5×10^{-4}	36
pH 8.5; temperature 40 °C‡; water depth 10 cm; wind speed 6 m s^{-1}				
1	0.03	9.7×10^{-5}	4.8×10^{-5}	99
25	0.63	9.7×10^{-5}	1.2×10^{-3}	99
49	1.23	9.7×10^{-5}	2.4×10^{-3}	99
pH 8.5; temperature 25 °C; water depth 1 cm†; wind speed 6 m s^{-1}				
1	0.01	9.2×10^{-4}	1.7×10^{-4}	100
25	0.29	9.2×10^{-4}	4.2×10^{-3}	100
49	0.57	9.2×10^{-4}	8.2×10^{-3}	100
pH 8.5; temperature 25 °C; water depth 19 cm‡; wind speed 6 m s^{-1}				
1	0.01	4.9×10^{-5}	8.8×10^{-6}	53
25	0.29	4.9×10^{-5}	2.2×10^{-4}	53
49	0.57	4.9×10^{-5}	4.3×10^{-4}	53
pH 8.5; temperature 25 °C; water depth 10 cm; wind speed 0 m s^{-1}†				
1	0.01	1.1×10^{-6}	1.9×10^{-7}	2
25	0.29	1.1×10^{-6}	4.8×10^{-6}	2
49	0.57	1.1×10^{-6}	9.4×10^{-6}	2
pH 8.5; temperature 25 °C; water depth 10 cm; wind speed 12 m s^{-1}‡				
1	0.01	2.5×10^{-4}		98
25	0.29	2.5×10^{-4}		98
49	0.57	2.5×10^{-4}		98

† Lowest value for this parameter.

‡ Highest value for this parameter.

ference in k_{vN} values for NH_3 at the two wind speeds. This shows that, even at high pH values, low NH_3 volatilization is maintained as a result of low wind speeds.

These model runs show that pH has the capability of increasing $\text{NH}_3(\text{aq})$ in floodwater by increasing the degree of dissociation at high pH values. Other parameters such as wind speed, depth of floodwater, and temperature, however, play an important role in the process of NH_3 volatilization.

Effect of Temperature on Ammonia Volatilization

The effect of floodwater temperature on NH_3 volatilization was determined by varying the temperature from 10 to 40 °C while the other four parameters were maintained at constant mean values. An increase in temperature increased the k_{vN} and the NH_3 loss per

Table 3. Effect of floodwater pH on NH₃ volatilization.

pH	Initial NH ₃ (aq) mol m ⁻³	Volatilization rate constant (k _{vN}) s ⁻¹	Initial NH ₃ volatilization rate mol L ⁻¹ s ⁻¹	NH ₃ loss/day %
NH ₄ -N concentration 25 mg L ⁻¹ ; temperature 25 °C; water depth 10 cm; wind speed 6 m s ⁻¹				
7.0	0.01	9.2 × 10 ⁻⁵	1.3 × 10 ⁻⁵	4
8.5	0.29	9.2 × 10 ⁻⁵	4.3 × 10 ⁻⁴	77
10.0	1.61	9.2 × 10 ⁻⁵	1.3 × 10 ⁻²	100
NH ₄ -N concentration 25 mg L ⁻¹ ; temperature 10 °C†; water depth 10 cm; wind speed 6 m s ⁻¹				
7.0	3.53 × 10 ⁻¹	8.7 × 10 ⁻⁵	4.1 × 10 ⁻⁶	1
8.5	0.11	8.7 × 10 ⁻⁵	1.3 × 10 ⁻⁴	36
10.0	1.2	8.7 × 10 ⁻⁵	4.1 × 10 ⁻³	100
NH ₄ -N concentration 25 mg L ⁻¹ ; temperature 40 °C‡; water depth 10 cm; wind speed 6 m s ⁻¹				
7.0	2.9 × 10 ⁻²	9.7 × 10 ⁻⁵	3.8 × 10 ⁻⁵	12
8.5	0.63	9.7 × 10 ⁻⁵	1.2 × 10 ⁻¹	99
10.0	1.77	9.7 × 10 ⁻⁵	3.8 × 10 ⁻²	100
NH ₄ -N concentration 25 mg L ⁻¹ ; temperature 25 °C; water depth 1 cm‡; wind speed 6 m s ⁻¹				
7.0	1.07 × 10 ⁻²	9.2 × 10 ⁻⁴	1.3 × 10 ⁻⁴	37
8.5	0.29	9.2 × 10 ⁻⁴	4.2 × 10 ⁻¹	100
10.0	1.61	9.2 × 10 ⁻⁴	0.13	100
NH ₄ -N concentration 25 mg L ⁻¹ ; temperature 25 °C; water depth 19 cm‡; wind speed 6 m s ⁻¹				
7.0	1.1 × 10 ⁻²	4.8 × 10 ⁻⁵	6.9 × 10 ⁻⁶	2
8.5	0.29	4.8 × 10 ⁻⁵	2.2 × 10 ⁻⁴	53
10.0	1.61	4.8 × 10 ⁻⁵	6.9 × 10 ⁻³	100
NH ₄ -N concentration 25 mg L ⁻¹ ; temperature 25 °C; water depth 10 cm; wind speed 0 m s ⁻¹ †				
7.0	1.07 × 10 ⁻²	1.1 × 10 ⁻⁶	1.5 × 10 ⁻⁷	>1
8.5	0.29	1.1 × 10 ⁻⁶	4.8 × 10 ⁻⁶	1
10.0	1.61	1.1 × 10 ⁻⁶	1.52 × 10 ⁻⁴	41
NH ₄ -N concentration 25 mg L ⁻¹ ; temperature 25 °C; water depth 10 cm; wind speed 12 m s ⁻¹ ‡				
7.0	1.97 × 10 ⁻²	2.5 × 10 ⁻⁴	3.6 × 10 ⁻⁵	12
8.5	0.29	2.5 × 10 ⁻⁴	1.13 × 10 ⁻¹	98
10.0	1.61	2.5 × 10 ⁻⁴	3.6 × 10 ⁻²	100

† Lowest value for this parameter.
‡ Highest value for this parameter.

Table 4. Effect of floodwater temperature on NH₃ volatilization.

Temperature °C	Initial NH ₃ (aq) mol m ⁻³	Volatilization rate constant k _{vN} s ⁻¹	Initial NH ₃ volatilization rate mol L ⁻¹ s ⁻¹	NH ₃ loss/day %
NH ₄ -N concentration 25 mg L ⁻¹ ; pH 8.5; water depth 10 cm; wind speed 6 m s ⁻¹				
10	0.11	8.7 × 10 ⁻⁵	1.3 × 10 ⁻⁴	9
25	0.29	9.2 × 10 ⁻⁵	4.2 × 10 ⁻⁴	19
40	0.63	9.7 × 10 ⁻⁵	1.2 × 10 ⁻³	25
NH ₄ -N concentration 25 mg L ⁻¹ ; pH 7‡; water depth 10 cm; wind speed 6 m s ⁻¹				
10	3.5 × 10 ⁻³	8.7 × 10 ⁻⁵	4.1 × 10 ⁻⁶	1
25	1.1 × 10 ⁻²	9.3 × 10 ⁻⁵	1.2 × 10 ⁻⁴	4
40	2.9 × 10 ⁻²	9.7 × 10 ⁻⁵	3.8 × 10 ⁻³	12
NH ₄ -N concentration 25 mg L ⁻¹ ; pH 10‡; water depth 10 cm; wind speed 6 m s ⁻¹				
10	1.23	8.7 × 10 ⁻⁵	4.1 × 10 ⁻³	100
25	1.61	9.2 × 10 ⁻⁵	1.32 × 10 ⁻²	100
40	1.78	9.7 × 10 ⁻⁵	3.79 × 10 ⁻²	100
NH ₄ -N concentration 25 mg L ⁻¹ ; pH 8.5; water depth 1 cm‡; wind speed 6 m s ⁻¹				
10	0.11	8.7 × 10 ⁻⁴	1.3 × 10 ⁻³	99
25	0.29	9.2 × 10 ⁻⁴	4.3 × 10 ⁻³	100
40	0.63	9.7 × 10 ⁻⁴	0.01	100
NH ₄ -N concentration 25 mg L ⁻¹ ; pH 8.5; water depth 19‡; wind speed 6 m s ⁻¹				
10	0.11	4.6 × 10 ⁻⁵	6.8 × 10 ⁻⁵	21
25	0.29	4.9 × 10 ⁻⁵	2.2 × 10 ⁻⁴	53
40	0.63	5.1 × 10 ⁻⁵	6.3 × 10 ⁻⁴	89
NH ₄ -N concentration 25 mg L ⁻¹ ; pH 8.5; water depth 10 cm; wind speed 0 m s ⁻¹ †				
10	0.11	9.1 × 10 ⁻⁷	1.4 × 10 ⁻⁶	>1
25	0.29	1.1 × 10 ⁻⁶	4.8 × 10 ⁻⁶	2
40	0.63	1.2 × 10 ⁻⁶	1.5 × 10 ⁻⁵	5
NH ₄ -N concentration 25 mg L ⁻¹ ; pH 8.5; water depth 10 cm; wind speed 12 m s ⁻¹ ‡				
10	0.11	2.3 × 10 ⁻⁴	3.4 × 10 ⁻⁴	69
25	0.29	2.5 × 10 ⁻⁴	1.1 × 10 ⁻³	98
40	0.63	3.3 × 10 ⁻⁴	4.1 × 10 ⁻³	100

† Lowest value for this parameter.
‡ Highest value for this parameter.

day (Table 4). The higher volatilization rate of NH₃ at 40 °C than at 10 °C was due to an increase in NH₃(aq) concentration in floodwater and the k_{vN} (Jayaweera and Mikkelsen, 1990).

When the model was executed at pH 10.0, with varying temperatures and the remaining variables kept constant, 100% of the NH₃ was lost per day, even at the lowest temperature (10 °C). At pH 7.0, however, even at a floodwater temperature of 40 °C, only about 12% of NH₃ was lost, which was due to the very low concentration of NH₃(aq) in the floodwater (Table 4).

When the depth of floodwater was 1 cm, even at 10 °C the NH₃ volatilization was rapid; when the floodwater depth was 19 cm, even at 40 °C, only 89% of NH₃ was lost per day. The rapid loss of NH₃ at low floodwater depths was due to a high k_{vN} (Table 4).

When there was no wind, even at 40 °C very little NH₃ was lost, compared with high volatilization losses at relatively low temperatures when the wind speed was at 12 m s⁻¹ (Table 4). These differences in NH₃-volatilization rates at different wind speeds were due to variations in the k_{vN} for NH₃.

This data shows clearly that factors such as pH, depth of floodwater, and wind speed influence the NH₃-volatilization process by several orders of magnitude at various temperatures.

Effect of Water Depth on Ammonia Volatilization

The depth of floodwater was varied from 1 to 19 cm in increments of 3 cm, while the floodwater NH₄-N concentration, pH, temperature of floodwater, and wind speed were kept constant at the mean values. As the depth of floodwater increased from 1 to 19 cm, the volatilization rate of NH₃ decreased, reducing the NH₃ loss per day from 100 to 53% (Table 5). An increase in depth of floodwater did not influence the NH₃(aq) concentration in floodwater, but decreased the k_{vN} (Table 5), thus decreasing the NH₃ loss from the flooded system.

The next series of model runs were performed at pH 7.0 and 10.0, while varying floodwater depth from 1 to 19 cm with floodwater NH₄-N concentration, temperature, and wind speed kept at their mean val-

Table 5. Effect of floodwater depth on NH₃ volatilization.

Depth	Initial NH ₃ (aq)	Volatilization rate constant (k_{vN})	Initial NH ₃ volatilization rate	NH ₃ loss/day
cm	mol m ⁻³	s ⁻¹	mol L ⁻¹ s ⁻¹	%
NH ₄ -N concentration 25 mg L ⁻¹ ; pH 8.5; temperature 25 °C; wind speed 6 m s ⁻¹				
1	0.29	9.2×10^{-4}	4.2×10^{-3}	100
10	0.29	9.2×10^{-5}	4.2×10^{-4}	77
19	0.29	4.8×10^{-5}	2.2×10^{-4}	53
NH ₄ -N concentration 25 mg L ⁻¹ ; pH 7†; temperature 25 °C; wind speed 6 m s ⁻¹				
1	0.01	9.2×10^{-4}	1.3×10^{-4}	37
10	0.01	9.2×10^{-5}	1.3×10^{-5}	4
19	0.01	4.8×10^{-5}	6.9×10^{-6}	2
NH ₄ -N concentration 25 mg L ⁻¹ ; pH 10‡; temperature 25 °C; wind speed 6 m s ⁻¹				
1	1.6	9.2×10^{-4}	0.13	100
10	1.6	9.2×10^{-5}	1.3×10^{-5}	100
19	1.6	4.8×10^{-5}	6.9×10^{-6}	100
NH ₄ -N concentration 25 mg L ⁻¹ ; pH 8.5; temperature 10 °C†; wind speed 6 m s ⁻¹				
1	0.11	8.7×10^{-4}	1.3×10^{-3}	99
10	0.11	8.7×10^{-5}	1.3×10^{-4}	36
19	0.11	4.6×10^{-5}	6.8×10^{-5}	21
NH ₄ -N concentration 25 mg L ⁻¹ ; pH 8.5; temperature 40 °C‡; wind speed 6 m s ⁻¹				
1	0.63	9.7×10^{-4}	0.01	100
10	0.63	9.7×10^{-5}	1.2×10^{-3}	99
19	0.63	5.1×10^{-5}	6.3×10^{-4}	89
NH ₄ -N concentration 25 mg L ⁻¹ ; pH 8.5; temperature 25 °C; wind speed 0 m s ⁻¹ †				
1	0.29	1.1×10^{-3}	4.8×10^{-3}	15
10	0.29	1.1×10^{-7}	4.8×10^{-6}	2
19	0.29	5.6×10^{-7}	2.5×10^{-6}	>1
NH ₄ -N concentration 25 mg L ⁻¹ ; pH 8.5; temperature 25 °C; wind speed 12 m s ⁻¹ ‡				
1	0.29	2.5×10^{-3}	1.1×10^{-2}	100
10	0.29	2.5×10^{-4}	1.1×10^{-3}	98
19	0.29	1.3×10^{-4}	6.0×10^{-4}	87

† Lowest value for this parameter.

‡ Highest value for this parameter.

ues. When the pH of floodwater was 10.0, 100% of NH₃ was lost at all water depths ranging from 1 to 19 cm. However, when the pH was 7.0, even at 1-cm floodwater depth, nearly 37% of the NH₃ was lost and, at 19-cm depth, the NH₃ volatilization was only 2% (Table 5). This shows the interaction of NH₃(aq) concentration and k_{vN} in the process of NH₃ volatilization.

In studying the effect of temperature on NH₃ loss at different floodwater depths, it is seen that, at a water depth of 1 cm, both temperatures, 10 and 40 °C, showed the same influence on NH₃ loss, with 100% volatilizing with a period of 1 d (Table 5). At a water depth of 19 cm, however, the NH₃ loss per day decreased to 21% when the temperature of the floodwater was 10 °C, compared with 89% loss at 40 °C. Depth of floodwater plays a dominant role by allowing 100% NH₃ loss even at a floodwater temperature of 10 °C.

Wind speed had a large influence on NH₃ volatilization at different water depths. If there was no wind, i.e., at 0 m s⁻¹ wind speed, at 1-cm floodwater depth, only about 15% of NH₃ was lost per day, compared with 100% loss at a wind speed of 12 m s⁻¹ at an 8-m height. By increasing the depth of floodwater to 19 cm, the system lost nearly 87% of NH₃ at 12 m s⁻¹ wind speed, compared with 0.9% at 0 m s⁻¹.

Table 6. Effect of wind speed at 8 m above the water surface on NH₃ volatilization.

Wind speed	Initial NH ₃ (aq)	Volatilization rate constant (k_{vN})	Initial NH ₃ volatilization rate	NH ₃ loss/day
m s ⁻¹	mol m ⁻³	s ⁻¹	mol L ⁻¹ s ⁻¹	%
NH ₄ -N concentration 25 mg L ⁻¹ ; pH 8.5; temperature 25 °C; water depth 10 cm				
0	0.29	1.1×10^{-6}	4.8×10^{-6}	2
6	0.29	9.2×10^{-5}	4.2×10^{-4}	77
12	0.29	2.5×10^{-4}	1.1×10^{-3}	98
NH ₄ -N concentration 25 mg L ⁻¹ ; pH 7†; temperature 25 °C; water depth 10 cm				
0	0.01	1.1×10^{-6}	1.5×10^{-7}	>1
6	0.01	9.2×10^{-5}	1.3×10^{-5}	4
12	0.01	2.5×10^{-4}	3.6×10^{-5}	12
NH ₄ -N concentration 25 mg L ⁻¹ ; pH 10‡; temperature 25 °C; water depth 10 cm				
0	1.61	1.1×10^{-6}	1.5×10^{-4}	41
6	1.61	9.2×10^{-5}	1.3×10^{-2}	100
12	1.61	2.5×10^{-4}	3.6×10^{-2}	100
NH ₄ -N concentration 25 mg L ⁻¹ ; pH 8.5; temperature 10 °C†; water depth 10 cm				
0	0.11	9.1×10^{-7}	1.4×10^{-6}	>1
6	0.11	8.7×10^{-5}	1.3×10^{-4}	36
12	0.11	2.3×10^{-4}	3.4×10^{-4}	70
NH ₄ -N concentration 25 mg L ⁻¹ ; pH 8.5; temperature 40 °C‡; water depth 10 cm				
0	0.63	1.3×10^{-6}	1.5×10^{-5}	5
6	0.63	9.7×10^{-5}	1.2×10^{-3}	99
12	0.63	2.7×10^{-4}	3.3×10^{-3}	100
NH ₄ -N concentration 25 mg L ⁻¹ ; pH 8.5; temperature 25 °C; water depth 1 cm†				
0	0.29	1.1×10^{-3}	4.8×10^{-3}	15
6	0.29	9.2×10^{-4}	4.2×10^{-3}	100
12	0.29	2.5×10^{-3}	1.1×10^{-2}	100
NH ₄ -N concentration 25 mg L ⁻¹ ; pH 8.5; temperature 25 °C; water depth 19 cm‡				
0	0.29	5.6×10^{-7}	2.53×10^{-6}	>1
6	0.29	4.9×10^{-5}	2.2×10^{-4}	53
12	0.29	1.3×10^{-4}	5.9×10^{-4}	87

† Lowest value for this parameter.

‡ Highest value for this parameter.

The depth of floodwater plays a significant role in the process of NH₃ volatilization; however, other parameters such as pH, temperature of floodwater, and wind speed play an important role in controlling NH₃ volatilization.

Effect of Wind Speed on Ammonia Volatilization

The wind speed at an 8-m height was varied from 0 to 12 m s⁻¹ while the floodwater NH₄-N concentration, pH, temperature, and depth of floodwater were maintained constant at their mean values. An increase in wind speed increased both the percent NH₃ loss per day and the k_{vN} . As shown in Table 6, the increase in wind speed did not influence NH₃(aq) concentration in the floodwater, but increased the k_{vN} as a result of increase in exchange constants for NH₃ transfer across the air-water interface (Jayaweera and Mikkelsen, 1990).

At pH 10.0, all the NH₄-N in floodwater was lost as NH₃ gas at a wind speed as low as 2 m s⁻¹ at 8-m height, compared with 12% loss at 12 m s⁻¹ wind speed when the pH was 7.0 (Table 6). This shows that even with a high k_{vN} , if the NH₃(aq) in floodwater is low, only a small amount of NH₃ is lost.

When the temperature of the floodwater was 40 °C, nearly 100% of NH₃ was lost at 6 m s⁻¹ wind speed. In contrast, when the temperature was 10 °C, the NH₃ loss was negligible at 0 m s⁻¹ at 8-m height but increased to 70% at 12 m s⁻¹ (Table 6).

At a water depth of 1 cm, nearly 100% of NH₃ was lost per day even at low wind speeds, while only 87% was lost, even at 12 m s⁻¹ wind speed, when the depth of floodwater was 19 cm (Table 6).

Wind speed influences the NH₃-volatilization process by virtue of its influence on *k_{vN}*. Temperature, pH, and depth of floodwater, however, could vary the rate of volatilization, depending on the conditions.

By analyzing the effect of various parameters on the rate of NH₃ volatilization and NH₃ loss over a given period, it is seen that (i) the floodwater NH₄-N concentration directly influences the NH₃(aq) concentration in floodwater but does not influence the *k_{vN}* (ii) the pH of floodwater influences only the NH₃(aq) concentration, (iii) the temperature of floodwater influences both the NH₃(aq) concentration of floodwater and the *k_{vN}*, and (iv) the depth of floodwater and wind speed influence only the *k_{vN}*.

Sensitivity Analysis

The influence of various determinants of NH₃ volatilization were tested in a sensitivity analysis. When floodwater NH₄-N concentration was increased while pH, temperature, depth of floodwater, and wind speed were kept constant, NH₃ volatilization increased linearly. This is directly related to an increase in NH₃(aq) in floodwater as a function of NH₄-N concentration, as has been reported (Vlek and Stumpe, 1978; Vlek and Craswell, 1979; Fillery and Vlek, 1986). Therefore, in the sensitivity analysis, the floodwater NH₄-N concentration was kept at a constant value of 25 mg L⁻¹.

The effect of the four other factors were tested under three different sets of conditions as follows:

Condition 1: AMC = 25 mg L⁻¹, pH = 8.0, TEMP = 20 °C, WD = 7 cm, and U₈ = 4 m s⁻¹.

Condition 2: AMC = 25 mg L⁻¹, pH = 8.5, TEMP = 25 °C, WD = 10 cm, and U₈ = 6 m s⁻¹.

Condition 3: AMC = 25 mg L⁻¹, pH = 9.0, TEMP = 30 °C, WD = 13 cm, and U₈ = 8 m s⁻¹.

where AMC = floodwater NH₄-N concentration,
 pH = pH of floodwater,
 TEMP = temperature of floodwater,
 WD = depth of floodwater, and
 U₈ = wind speed at 8-m height.

For each condition, one factor was varied while the others were kept constant. The sensitivity (slope) of NH₃ loss per day with respect to pH, temperature, water depth, and wind speed is shown in Fig. 3.

An increase in pH increased the sensitivity of NH₃ loss to values of 8.75 for Condition 1 and 8.25 for Conditions 2 and 3. A further increase in pH decreased the sensitivity. High pH values brought more NH₃(aq) into the system, but NH₃ loss also depends on the *k_{vN}*. This explains why the greatest sensitivity was obtained at a pH value of 8.75 under Condition 1, compared with 8.25 under Conditions 2 and 3. The sensitivity decreased due to the limitation of NH₄ concentration in solution, which supplies NH₃(aq) to the system.

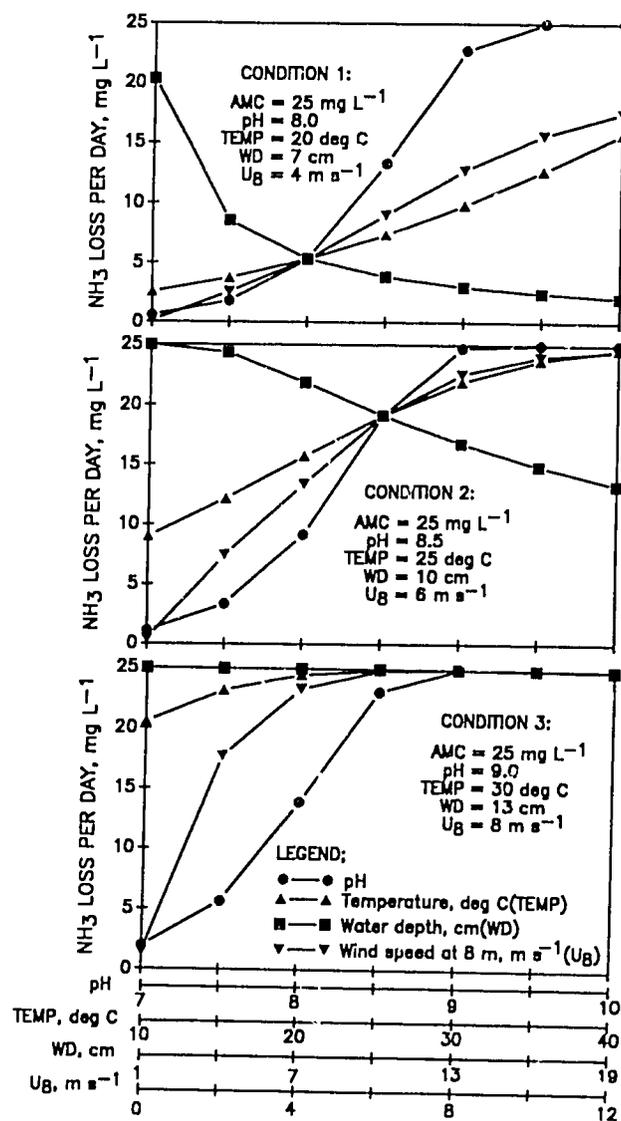


Fig. 3. Sensitivity analysis for NH₃-volatilization model, where AMC = floodwater ammoniacal-N concentration.

When the temperature increased from 10 to 40 °C under Condition 1, sensitivity increased gradually from 0.23 to 0.61; under Condition 2, sensitivity increased to a temperature of 17.5 °C and then decreased gradually; and under Condition 3, sensitivity decreased gradually. Under Condition 1, the pH and wind speed were low; when the temperature was raised, the NH₃(aq) concentration and the *k_{vN}* increased, thus increasing sensitivity. Under Condition 3, however, high pH and wind speed values caused high NH₃ losses; an increase in temperature decreased the sensitivity as NH₄-N concentration in the system decreased.

Increased water depth decreased the percent NH₃ loss. For each increment of water depth, however, the sensitivity of NH₃ loss varied depending on the conditions. Under Condition 1, the highest sensitivity occurred with low water depth, and sensitivity decreased as water depth increased. At a pH of 8.0 and temperature of 20 °C, a small concentration of NH₃(aq) occurred in the floodwater. Because of the shallow depth, *k_{vN}* increased, causing increased NH₃ volatilization, which brought high sensitivity at a shallow water

depth. Under Condition 3, a change in water depth did not affect sensitivity to NH_3 loss. Under this condition, a high pH, temperature, and wind speed caused high NH_3 loss; an increase in water depth did not affect the NH_3 loss.

The sensitivity of NH_3 loss as a function of wind speed depends on the other conditions of the system. Under Condition 1, sensitivity increased until a wind speed of 7 m s^{-1} was reached, and then decreased. Because the pH and temperature were relatively low under Condition 1, $\text{NH}_3(\text{aq})$ concentration in floodwater was also low. An increase in wind speed, however, caused an increase in k_{vN} , thereby increasing sensitivity. An increase in wind speed beyond 7 m s^{-1} , however, decreased sensitivity due to the limitation of NH_4 concentration in the floodwater. Under Conditions 2 and 3, an increase in wind speed decreased the sensitivity of NH_3 loss. These conditions, i.e., high pH and high temperature, provide more $\text{NH}_3(\text{aq})$ to the floodwater. Even at low wind speeds, the k_{vN} is sufficient to bring more $\text{NH}_3(\text{aq})$ into the atmosphere; therefore, sensitivity is high at low wind speeds. Under Condition 3, an increase in wind speed beyond 7 m s^{-1} did not affect percent NH_3 loss. This was due to the limitation of NH_4 concentration in the floodwater.

Under all conditions, pH was the most sensitive variable, temperature was least sensitive under Con-

ditions 1 and 2, and water depth showed the least sensitivity under Condition 3 (Fig. 3).

The sensitivity analysis shows that it is not possible to generalize on the effect of one variable without considering the other existing conditions. Therefore, the magnitude of NH_3 loss from floodwater can be predicted only by taking into account simultaneously all five primary factors (Jayaweera and Mikkelsen, 1990) that determine the $\text{NH}_3(\text{aq})$ concentration and the k_{vN} .

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Ammonia Volatilization from Flooded Soil Systems: A Computer Model. III. Validation of the Model

G. R. Jayaweera,* D. S. Mikkelsen, and K. T. Paw U.

ABSTRACT

An NH_3 -volatilization model predicting NH_3 loss as a function of five input variables was validated using a wind tunnel to simulate rice paddy conditions and direct field experiments. A total of five variables in a central composite statistical design were compared to study the interactive effects of $\text{NH}_4\text{-N}$ concentration, pH, temperature, wind speed, and water depth. Experiments were also conducted in a flooded rice field with polypropylene basins placed at water level. Samples were collected every hour for determination of $\text{NH}_4\text{-N}$ concentration. Temperature, pH, and wind speed were recorded continuously, and water depth was constant. Wind-tunnel data showed that the model predicted observed values with excellent accuracy in the range of conditions found in flooded rice systems. The regression of predicted NH_3 loss on observed losses resulted in an r^2 of 0.98 and a regression slope of 0.99. Field experiments also showed very close agreement between predicted and experimental values with 6-, 12-, and 24-h averages of pH, temperature, and wind speed. The model validation confirmed the theory that NH_3 volatilization is a function of $\text{NH}_3(\text{aq})$ concentration and the volatilization rate constant for NH_3 , which are dependent on five variables: floodwater NH_4 concentration, pH, temperature, water depth, and wind speed. The model is theoretically sound and predicts NH_3 loss with a high level of accuracy using a menu-driven computer program with easily measurable variables, and can be used in comparison studies of NH_3 loss at the same site.

ferred across the air-water interface to the atmosphere. Ammonia volatilization can be an important mechanism of N-fertilizer loss in flooded rice production and may account for losses up to 50% of the N applied (Fillery and Vlek, 1986). A computer model has been developed to predict NH_3 loss from a flooded system as a function of several floodwater variables and wind speed (Jayaweera and Mikkelsen, 1990a,b). The model described can be executed with five input variables: $\text{NH}_4\text{-N}$ concentration, pH, temperature, depth of floodwater, and wind speed at a known height. The model was validated through experiments conducted in a wind tunnel and in the field.

MATERIALS AND METHODS

Wind-Tunnel Experiment

There were a total of 13 wind-tunnel runs to determine the effect of five composite combinations of variables on NH_3 volatilization. A central composite statistical design in-

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AMMONIA VOLATILIZATION is a complex process wherein NH_3 gas present in floodwater is trans-

volving mean values as well as maximum and minimum values of each variable was used as described in Table 1.

The wind-tunnel experiments were carried out in the Hydraulic Laboratory wind tunnel at the University of California, Davis. This is a U-shaped, open-end wind tunnel where wind is driven by a propeller fan at the inlet of the tunnel. Air is taken into the tunnel, passed through several

vanes and screens, and then over the water surface in the test section.

The wind-tunnel test section (Fig. 1) included a metal tank (245 by 61 by 22 cm) imbedded in the section floor. The depth of the tank for different runs was adjusted with foam plastic inserts placed under polyethylene film. A solution of $(\text{NH}_4)_2\text{SO}_4$ of varied concentrations (from 25 to 100 mg L^{-1}

Table 1. Experimental details, friction speed (U_*), roughness height (Z_0), equivalent field wind speed at 8-m height (U_8), and observed and predicted NH_3 loss for wind-tunnel runs.

Wind tunnel run	Description (variable)	Initial $\text{NH}_4\text{-N}$ conc. mg L^{-1}	pH	Temperature $^\circ\text{C}$	Water depth cm	Free-stream wind speed m s^{-1}	U_*	Z_0 cm	U_8 m s^{-1}	NH_3 loss mg L^{-1}		Predicted/Observed ratio
										Observed	Predicted	
1	Mean	52.32	8.5	25	11.0	2.88	0.166	0.014	4.41	8.33	9.52	1.14
2	Mean	52.59	8.5	25	11.0	2.76	0.150	0.008	4.23	8.32	9.06	1.09
3	Mean	53.22	8.5	25	11.0	2.70	0.144	0.007	4.14	7.51	8.93	1.13
	$\text{NH}_4\text{-N}$ conc.											
4	Low	26.24	8.5	25	11.0	2.64	0.128	0.003	4.05	3.49	4.27	1.22
5	High	102.54	8.5	25	11.0	2.70	0.140	0.006	4.14	24.77	49.79	2.01
	pH											
6	Low	52.69	6.5	25	11.0	2.64	0.149	0.010	4.05	1.83	0.09	0.05
7	High	49.79	10.5	25	11.0	2.88	0.131	0.002	4.41	24.77	49.79	2.01
	Temperature											
8	Low	52.50	8.5	25	11.0	2.70	0.123	0.002	4.14	5.52	6.21	1.13
9	High	53.05	8.5	30	11.0	2.88	0.136	0.003	4.41	11.83	13.30	1.12
	Water depth											
10	Low	52.67	8.5	25	6.42	2.76	0.158	0.012	4.23	14.59	14.58	1.00
11	High	50.32	8.5	25	21.28	2.76	0.158	0.012	4.23	4.52	4.68	1.04
	Wind speed at 8 m											
12	Low	51.61	8.5	25	11.0	1.91	0.281	0.019	2.93	6.45	5.72	0.89
13	High	52.93	8.5	25	11.0	5.34	0.153	0.005	8.19	12.22	22.25	1.82

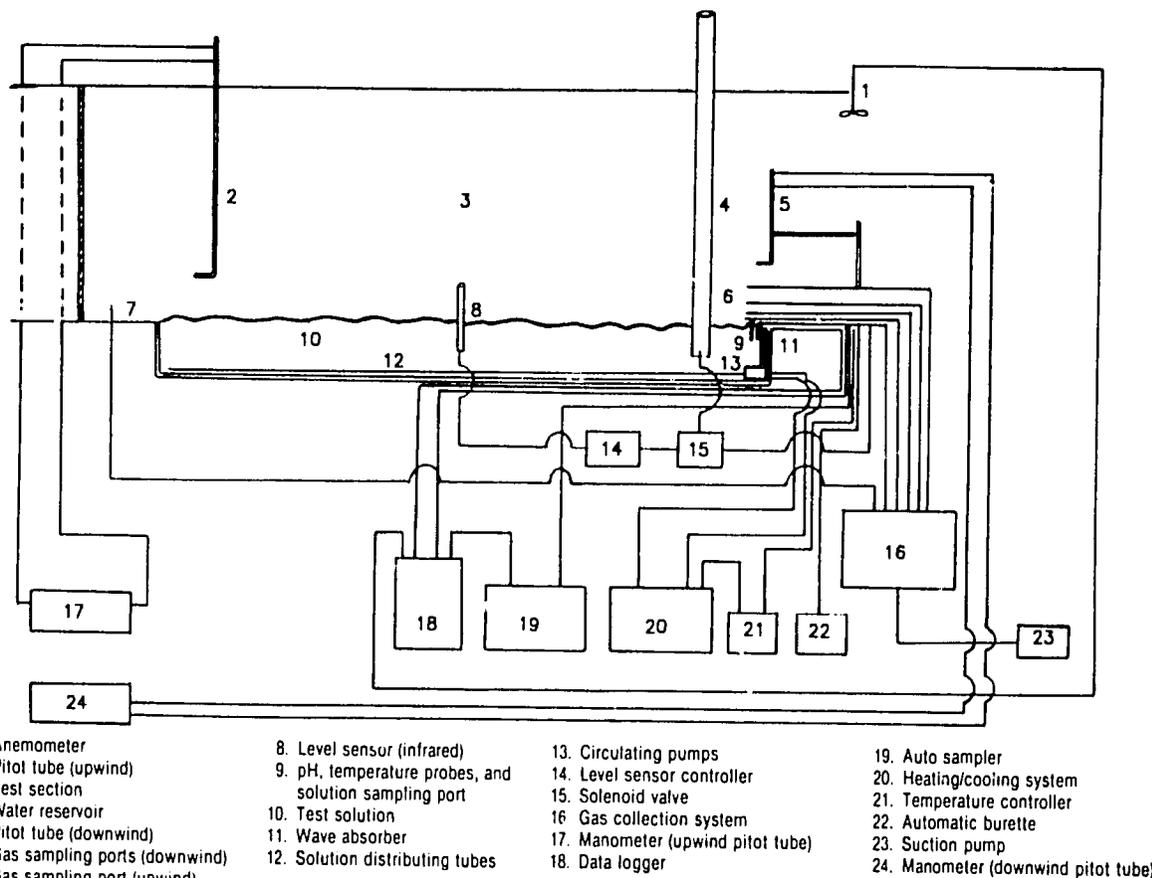


Fig. 1. Schematic view of wind-tunnel test section.

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for different runs) was placed in the tank lined with 5-mil (0.127-mm) polyethylene plastic. The tank water level was maintained by a constant-level device using an infrared level sensor, activating a solenoid valve, to transfer water from a reservoir. This device was also used to determine the total amount of water lost. The solution in the tank was well mixed and maintained at a constant temperature by circulating the solution with three pumps, each at a rate of 20 L min^{-1} , through plastic coils placed in a heating/cooling bath and then back through three perforated submerged tubes extending over the entire length of the tank. The heating/cooling system was connected to a temperature-control unit (YSI Model 71A; Yellow Springs Instrument Co., Yellow Springs, CO), and regulated by a thermistor probe placed in the solution. The heating was done with six 1000-W heating elements and cooling was controlled by two Blue M portable cooling units (Model PCC-24A-2, Blue M Equipment, Blue Island, IL). The pH of the tank solution was maintained at a constant value by titrating acid or base with an automatic burette.

Wind-speed profiles were measured at the upwind and downwind end of the test section by two pitot tubes of Prandtl design, mounted on a vertical traversing mechanism. The wind measurements were taken at 1-, 2-, 4-, 8-, and 16-cm heights. A wave absorber was fixed at the downwind end of the tank to dissipate wave energy and minimize reflection. Wet- and dry-bulb temperatures were measured by thermistor probes (Campbell Scientific Model 10i, Logan, UT) at two heights at the downwind end of the tank and at the inlet to the wind tunnel, and recorded in a data logger (Campbell Scientific Model CR21).

Each wind-tunnel run was conducted over a 6-h time period. Ammoniacal-N concentration, pH, temperature, and wind velocity were monitored over the course of the experiment. Ammoniacal-N concentration was measured by sampling the tank solution every 20 min using a custom-built autosampler device. Samples of approximately 7 mL were collected at the downwind end of the tank through a thin nylon plastic tube with the tip protected to prevent any particles from blocking the sampling tube. Vacutainers (Monoject, Sherwood Medical, St. Louis, MO) of 7-mL capacity placed in a rotating tray were pierced by a needle connected to the sampling tube and the sample was pulled into the Vacutainer by suction.

Solution pH, temperature, and wind speed were recorded continuously during the wind-tunnel run with a four-channel data logger (Rustrak-Ranger, Gulton Industries, East Greenwich, RI). The pH was measured with a combination pH electrode, and temperature was measured with a glass-covered thermistor probe in the solution (0–1-cm depth) at the downwind end of the tank. Wind speed was measured by a cup anemometer (Met-one 014 A, Campbell Scientific) placed at the downwind end of the tunnel. The pH electrode, thermistor probe, and the anemometer were interfaced with

the data logger through a custom-built pH meter and pod types POD-03 and POD-24 (Gulton, Graphic Instruments), respectively. The time of solution sampling was recorded in the fourth channel of the data logger. The data logger was downloaded at the end of each wind-tunnel run to an IBM PC-type computer.

Air samples were drawn at 1-, 2-, 4-, 8-, and 16-cm heights above the water surface at 30 cm from the downwind end of the tank and also at the upwind end as the control throughout the experiment. These samples were drawn by a suction pump at a rate of approximately 1 L min^{-1} (the exact value was found by calibration through a flowmeter with a control valve and a solution trap of 30 mL 0.1 M H_2SO_4).

Tank-solution samples were collected (nine samples collected at different places and averaged) from the tank just before and after each experimental run. Autosampler-collected samples for $\text{NH}_4\text{-N}$ analyses were immediately acidified and analyzed along with H_2SO_4 air-collection-trap samples by high-pressure liquid chromatography (Abshahi et al., 1988).

Field Experiment

The field experiment was conducted at the Rice Research Facility of the University of California, Davis. Circular polypropylene basins of 105-cm diameter and 15-cm depth were placed in duplicate in a flooded field so that the edge of each basin was just above the floodwater surface. One hundred and twenty liters of $(\text{NH}_4)_2\text{SO}_4$ solutions ($\text{NH}_4\text{-N}$ concentration: 50 mg L^{-1}) were placed in each pan and exposed to the natural conditions found in a rice field.

Solution $\text{NH}_4\text{-N}$ concentration, pH, temperature, and wind speed were measured as illustrated in the diagrammatic representation of the experimental setup (Fig. 2). Ammonium-N concentration in the water basin was monitored by sampling every hour using a custom-built battery-operated autosampler. A Rustrak-Ranger datalogger recorded the time of sampling, pH, temperature (0–1-cm depth), and wind speed at 2 m above the water surface using the instruments described above. The evaporative losses were adjusted for periodically with distilled water and the basin solution level was maintained at 15-cm depth throughout the experiment by a conductivity device that gave an audible signal when the water level reached the probe.

Solution samples were acidified and $\text{NH}_4\text{-N}$ concentrations were determined by high-pressure liquid chromatography (Abshahi et al., 1988). The data logger was downloaded periodically to an IBM PC-type computer.

RESULTS AND DISCUSSION

Wind-Tunnel Validation

Wind-speed profiles, taken at the downwind and upwind end of the test section, showed no significant

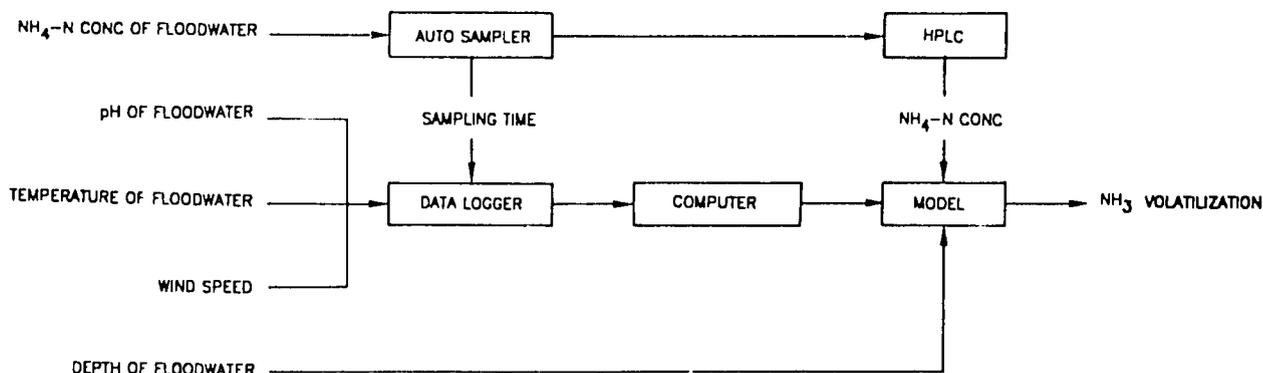


Fig. 2. Diagrammatic representation of the experimental setup.

difference; therefore, all the wind calculations used the wind profiles from the downwind end. A typical wind-speed profile is shown in Fig. 3. In all the wind-tunnel runs, a vertical mean logarithmic speed profile was assumed:

$$U_z = (U_* / k) \ln(Z / Z_0) \quad [1]$$

where

- U_z = the wind velocity at height Z ,
- U_* = the friction velocity,
- k = the Von-Karman constant, 0.4, and
- Z_0 = the roughness height.

Extrapolation of the wind-tunnel results to the processes occurring in a natural environment is possible if characteristics of the vertical wind profile are known. Therefore, we transformed Eq. [1] to a linear form as

$$\ln Z = (k / U_*) U_z + \ln Z_0 \quad [2]$$

Using Eq. [2], U_* and Z_0 were computed. A typical plot obtained after logarithmic transformation is shown in Fig. 4. The average r^2 value of regression for all the wind-tunnel runs was 0.98 with the data points in a straight line, which implied that the wind-tunnel boundary layer was well developed in all experimental runs. Calculated friction velocities and roughness lengths are shown in Table 1. Overall in the wind-tunnel runs, the mean value of Z_0 is 0.008 cm, which compares well with other data (0.007 cm) for air flow over water surfaces (Liss, 1973). These values fall well within the range found in other air-sea interface research (Smith, 1970). The ratio of U_* / U_x was fairly constant over all the wind-tunnel runs with an average of 0.0531, where U_x is the wind speed in the axial center of the wind tunnel:

$$U_* / U_x = 0.0531 \quad [3]$$

The following relationship has developed between the wind speed at 8-m height, U_8 , and U_* (Jayaweera and Mikkelsen, 1990a).

$$U_8 = 28.7823 U_* \quad [4]$$

By combining Eq. [3] and [4], the free-stream speed of the wind tunnel can be converted to the equivalent field wind speed at a height of 8 m:

$$U_8 = 1.5283 U_x \quad [5]$$

Using Eq. [5], the free-stream wind speeds of dif-

ferent runs in the wind tunnel were transformed into equivalent 8-m-height field wind speeds as shown in Table 1. This calculated field wind speed was used as an input in the model.

The solution samples collected every 20 min during a 6-h period in the wind tunnel show that $\text{NH}_4\text{-N}$ concentration in the tank decreases at different rates depending on the treatment variables. For each run, by using first-order kinetics, a straight line was fit after logarithmic-transformation of concentration values, and the rate constant was calculated for $\text{NH}_4\text{-N}$ depletion. The calculated rate constants and half-life values, which describe the $\text{NH}_4\text{-N}$ depletion rate, are shown in Table 2.

The highest rate constant for $\text{NH}_4\text{-N}$ depletion and the shortest half-life occurred when the pH was 10.5; the lowest rate constant and the highest half-life value occurred when the pH was 6.5. In the wind-tunnel runs, it is interesting to note that the rate constant almost doubled from 0.00028 to 0.00054 when the temperature was increased from 20 to 30 °C, which is common for chemical reactions. As shown in Table 2, the greater the water depth and the lower the wind speed, the lower the rate constant became, with the result of increasing the half-life, and vice versa.

The observed NH_3 loss in the wind-tunnel runs and the values predicted by the model over a 6-h period are shown in Table 1. The model overpredicted NH_3 loss at high pH (10.5) and at a high wind speed (8.9 m s^{-1} at 8-m height) by a factor of 1.8 to 2 times, which

Table 2. Rate constants and half lives for $\text{NH}_4\text{-N}$ depletion in the solution for wind-tunnel runs. (Refer to Table 1 for details on wind-tunnel runs.)

Wind tunnel run	Rate constant	Half life
	min ⁻¹	h
1. Mean (1)	0.00049	23.57
2. Mean (2)	0.00048	24.06
3. Mean (3)	0.00040	28.88
4. $\text{NH}_4\text{-N}$ conc.-low	0.00039	29.62
5. $\text{NH}_4\text{-N}$ conc.-high	0.00043	26.86
6. pH-low	0.00008	144.38
7. pH-high	0.00190	6.08
8. Temperature-low	0.00028	41.25
9. Temperature-high	0.00054	21.39
10. Water depth-low	0.00075	15.40
11. Water depth-high	0.00027	42.78
12. Wind speed-low	0.00041	28.17
13. Wind speed-high	0.00069	16.74

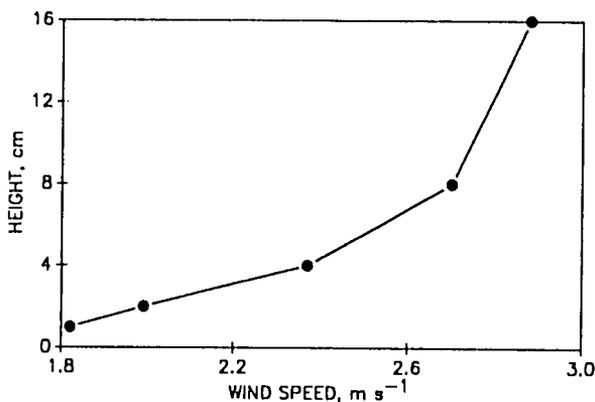


Fig. 3. Typical wind-speed profile in the wind tunnel.

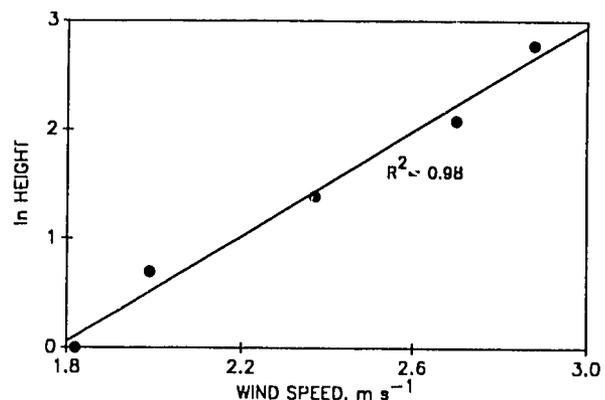


Fig. 4. Typical wind-speed profile in the wind tunnel after logarithmic transformation.

is acceptable (Thomas, 1982). Linear regression of the observed NH_3 loss on the predicted values is reported in Table 3. The regression coefficient, r^2 , improved greatly when the high-pH run was omitted. Further improvements can be seen when the extremes of high wind speed and low pH were also omitted, and a regression equation with $r^2 = 0.98$ was obtained. This shows, however, that the model has some limitations at high wind speed and high pH. The close fit (Fig. 5) of the observed on the predicted values shows that the model predicts NH_3 loss quite well within the range of conditions usually found in flooded rice systems.

As discussed in Jayaweera and Mikkelsen (1990b), NH_3 volatilization per se is primarily dependent on two parameters, aqueous NH_3 concentration, $\text{NH}_3(\text{aq})$, and the volatilization rate constant for NH_3 , k_{vN} . Table 4 shows the effect of five variables on $\text{NH}_3(\text{aq})$ and k_{vN} in the wind-tunnel experiments. It is important to note that, when we compare values in Table 4, the initial $\text{NH}_4\text{-N}$ concentration and the wind speed could not be maintained at an exact fixed value (Tables 1 and 4); however, the experimental values were always close to the target values.

The initial $\text{NH}_3(\text{aq})$ concentration was maintained at 0.61 mol m^{-3} in the low- and high-water-depth runs, low- and high-wind-speed runs, and in runs using

mean values (Table 4). This shows that depth of water in the tank and the wind speed did not influence the concentration of $\text{NH}_3(\text{aq})$. However, low- and high- $\text{NH}_4\text{-N}$ runs, low- and high-pH runs, and low- and high-temperature runs did influence the $\text{NH}_3(\text{aq})$ in the system. At the low value of each of these variables, the initial $\text{NH}_3(\text{aq})$ was lower than the mean, and vice versa. As shown in Table 4, in low- and high- $\text{NH}_4\text{-N}$ runs, the difference in $\text{NH}_3(\text{aq})$ was due to the difference in the initial $\text{NH}_4\text{-N}$ concentrations (Jayaweera and Mikkelsen, 1990b). In low- and high-pH runs, $\text{NH}_3(\text{aq})$ is dependent on the fraction of the dissociation of NH_4 to $\text{NH}_3(\text{aq})$. At pH 6.5, the fraction of dissociation is negligible (0.0018); but at pH 10.5, the fraction increases to 0.85, compared with 0.15 at pH 8.5 (all other wind-tunnel runs). In low- and high-temperature runs, the differences in $\text{NH}_3(\text{aq})$ are due to changes in the association and dissociation rate constants, k_{aN} and k_{dN} , respectively, which influence the degree of dissociation of NH_4 to NH_3 (Jayaweera and Mikkelsen, 1990a,b). It is interesting to note that, as temperature increased from 20 to 30 °C, the degree of dissociation increased approximately twofold from 0.11 to 0.20, and nearly doubled the initial $\text{NH}_3(\text{aq})$ in the system from 0.44 to 0.82 (Table 4). Therefore, the volatilization rate of NH_3 in low- and high- $\text{NH}_4\text{-N}$ -concentration runs, low- and high-pH runs, and low- and high-temperature runs were brought about by the influence of these variables on $\text{NH}_3(\text{aq})$ in the system. The higher the intensity of each variable, the higher the $\text{NH}_3(\text{aq})$ and, in turn, the higher the NH_3 loss, and vice versa.

In several of the wind-tunnel runs, the NH_3 loss was determined by the k_{vN} . The lower the k_{vN} , the lower the volatilization rate of NH_3 , which decreased the amount of NH_3 loss, and vice versa. For low- and high-

Table 3. Tests of slope = 1.0 and intercept = 0 from regression of observed on predicted NH_3 loss in wind-tunnel runs.

Regression details	r^2	Slope	Intercept
All wind tunnel runs (i.e., 13 runs)	0.86	0.46	3.86
All wind tunnel runs except high-pH and high-wind-speed runs	0.97	0.92	0.38
All wind tunnel runs except high- and low-pH and high-wind-speed runs	0.98	0.99	-0.43

Table 4. Effect of model inputs on volatilization rate of NH_3 , aqueous NH_3 concentration [$\text{NH}_3(\text{aq})$], volatilization rate constant (k_{vN}), and other parameters in predicting NH_3 loss in wind-tunnel experiments. Mean is the average of three runs.

Wind-tunnel run†	Initial volatilization rate	$k_{\text{a}}\ddagger$	$k_{\text{d}}\S$	$\alpha\parallel$	$\text{NH}_3(\text{aq})$	$H_{\text{N}}\#$	$k_{\text{LN}}\dagger\dagger$	$k_{\text{GN}}\ddagger\dagger$	$K_{\text{ON}}\S\S$	k_{vN}	
	$\text{mg L}^{-1} \text{ s}^{-1}$	$\text{M}^{-1} \text{ s}^{-1}$	s^{-1}		mol m^{-3}	$\text{MPa m}^3 \text{ mol}^{-1}$	cm h^{-1}			s^{-1}	
Mean (avg. of 3)	4.7×10^{-4}	4.3×10^{10}	24.6	0.15	0.61	5.5×10^{-4}	2.7	3181	4.9×10^{-3}	1.9	
$\text{NH}_4\text{-N}$ conc. mg L^{-1}											
4 Low	26.24	2.2×10^{-4}	4.3×10^{10}	24.6	0.15	0.30	5.5×10^{-4}	2.5	3025	4.5×10^{-3}	1.8
5 High	102.54	8.7×10^{-4}	4.3×10^{10}	24.6	0.15	1.19	5.5×10^{-4}	2.6	3092	4.7×10^{-3}	1.9
pH											
6 Low	6.5	4.3×10^{-6}	4.3×10^{10}	24.6	0.002	0.007	5.5×10^{-4}	2.5	3025	4.5×10^{-3}	1.8
7 High	10.5	4.6×10^{-3}	4.3×10^{10}	24.6	0.95	3.57	5.5×10^{-4}	2.8	3293	5.1×10^{-3}	2.0
Temperature, °C											
8 Low	20	3.1×10^{-4}	3.8×10^{10}	15.0	0.11	0.44	5.1×10^{-4}	2.6	3092	4.6×10^{-3}	1.8
9 High	30	7.1×10^{-4}	4.9×10^{10}	39.5	0.20	0.82	5.8×10^{-4}	2.8	3293	5.2×10^{-3}	2.1
Water depth, cm											
10 Low	6.42	7.9×10^{-4}	4.3×10^{10}	24.6	0.15	0.61	5.5×10^{-4}	2.6	3159	8.3×10^{-3}	1.9
11 High	21.28	2.3×10^{-4}	4.3×10^{10}	24.6	0.15	0.58	5.5×10^{-4}	2.6	3159	2.5×10^{-3}	1.9
Wind speed at 8 m, ms^{-1}											
12 Low	2.93	2.8×10^{-4}	4.3×10^{10}	24.6	0.15	0.60	5.5×10^{-4}	1.6	2194	3.0×10^{-3}	1.2
13 High	8.18	1.3×10^{-3}	4.3×10^{10}	24.6	0.15	0.61	5.5×10^{-4}	9.4	6099	1.4×10^{-4}	5.5

† Refer to Table 1 for details on wind-tunnel runs.

‡ Association rate constant for NH_3 .

§ Dissociation rate constant for NH_4 .

|| Fraction of dissociation

Henry's law constant for NH_3 .

†† Liquid-transfer exchange constant

‡‡ Gas-transfer exchange constant

§§ Overall mass-transfer coefficient for NH_3 .

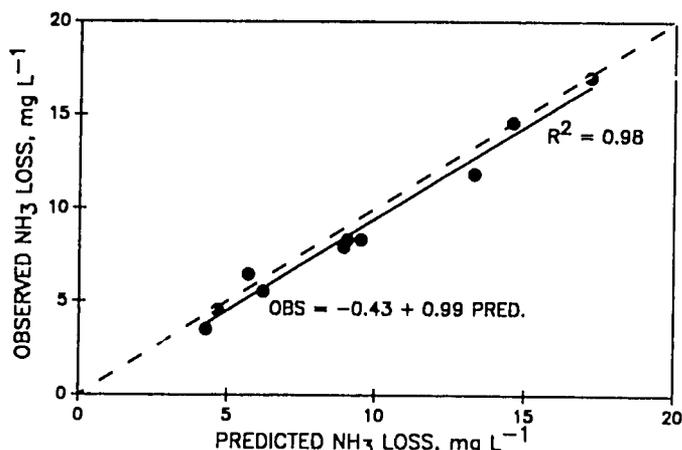


Fig. 5. Regression of observed on predicted NH_3 loss in wind-tunnel runs.

$\text{NH}_4\text{-N}$ runs and low- and high-pH runs, the average was $4.7 \times 10^{-5} \text{ s}^{-1}$, which is comparable with the average mean value of $4.9 \times 10^{-5} \text{ s}^{-1}$ (Table 4). However, in low- and high-temperature runs, low- and high-water-depth runs, and low- and high-wind-velocity runs, the k_{vN} differed from the average mean value. These differences were due to entirely different causes (Jayaweera and Mikkelsen, 1990a,b).

Henry's law constant of NH_3 , H_N , is a function of temperature (Jayaweera and Mikkelsen, 1990a). Therefore, as the temperature increased, the H_N also increased, rising from $5.07 \times 10^{-6} \text{ MPa m}^3 \text{ mol}^{-1}$ at 20°C to $5.47 \times 10^{-6} \text{ MPa m}^3 \text{ mol}^{-1}$ at 25°C and $5.78 \times 10^{-6} \text{ MPa m}^3 \text{ mol}^{-1}$ at 30°C . The change in H_N changed the overall mass-transfer coefficient for NH_3 , K_{ON} , and the k_{vN} . At 20°C , the k_{vN} decreased to $4.6 \times 10^{-2} \text{ s}^{-1}$ and, at 30°C , it increased to $5.2 \times 10^{-2} \text{ s}^{-1}$ relative to the average mean value of $4.9 \times 10^{-5} \text{ s}^{-1}$ at 25°C . In low- and high-water-depth runs, the K_{ON} remained constant at 1.9 cm h^{-1} , which is the same as the average mean value. This is due to having the same Henry's law constants and liquid- and gas-phase exchange constants for NH_3 , k_{iN} and k_{gN} , respectively. However, due to differences in water depth, the k_{vN} was higher for a depth of 6.42 cm, compared with a mean depth of 11.0 cm, and k_{vN} was lower at a depth of 21.28 cm (Table 4).

In the low- and high-wind-velocity runs, the k_{vN} was influenced through the k_{iN} and k_{gN} . When the wind speed was 1.9 m s^{-1} , k_{iN} , k_{gN} , and K_{ON} were low; and when the wind speed was high (5.3 m s^{-1}), these exchange constants were high (Table 4), thereby influencing the k_{vN} . A decrease in k_{vN} decreases the volatilization rate of NH_3 , thereby decreasing the amount of NH_3 loss, and vice versa.

Field Validation

The pH, temperature, and wind-speed data collected from rice paddies were recorded continuously in the data logger and averaged for 6, 12, and 24 h to predict NH_3 loss. These values were also compared with observed $\text{NH}_4\text{-N}$ -depletion data, gathered during 3 d at two different time periods and averaged for 6 and 24 h. Figure 6 shows the close agreement of predicted

Table 5. Tests of slope = 1.0 and intercept = 0 from regression of observed on predicted $\text{NH}_4\text{-N}$ depletion in the field experiment with different averaging periods.

Experimental period	Averaging period	r^2	Slope	Intercept
4 to 7 August	6 h	0.99	1.07	-3.30
	12 h	0.99	1.08	-4.15
	24 h	0.99	1.12	-5.58
8 to 11 August	6 h	0.99	0.95	1.76
	12 h	0.98	1.00	0.02
	24 h	0.99	1.05	-1.79

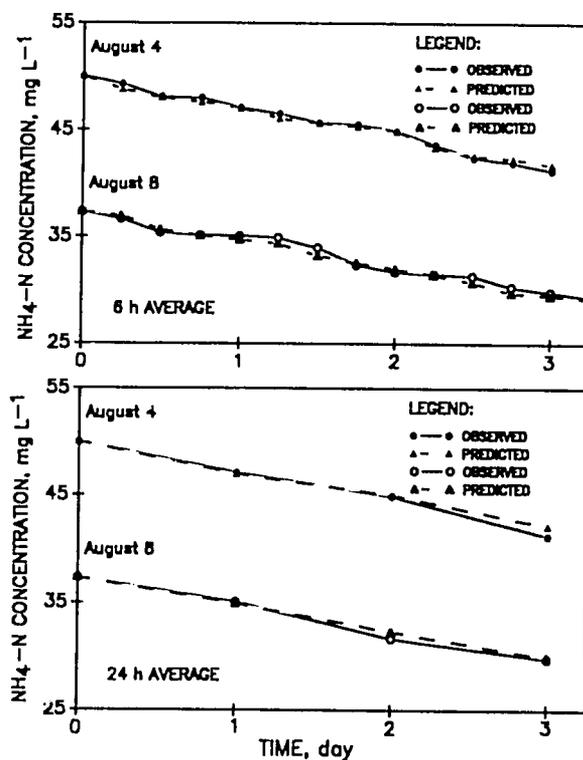


Fig. 6. Predicted and observed $\text{NH}_4\text{-N}$ depletion in the field.

values with observed data from the field study. Regression of observed $\text{NH}_4\text{-N}$ -depletion values on predicted values to test the closeness of fit also showed the close agreement of observed and predicted values (Table 5). As the averaging time was increased to 24 h, the regression slope increased to slightly greater than one, and the intercept decreased below zero (Table 5). Since there is slight deviation, however, the predictions done with values from the 24-h averaging period are well within the acceptable range. It is important to note that, during the first set of field-study comparisons studied on 4 August, 12:18 h, the 1-h average values for pH varied from 7.84 to 8.11, while temperature varied from 14.9 to 28.8°C and wind speed varied from 0.8 to 3.4 m s^{-1} . The change in concentration of $\text{NH}_3(\text{aq})$, the k_{vN} , and the volatilization rate of NH_3 as a function of model inputs with 1-h average of pH, temperature, and wind speed in the field experiment is shown in Table 6. In the second set of comparisons, started on 8 August, 6:28 h, pH varied from 7.90 to 8.10, temperature from 14.6 to 27.1°C , and wind speed from 1.3 to 3.8 m s^{-1} .

By scrutinizing the wind-tunnel and field experimental data, the amount of NH_3 loss, which is a func-

Table 6. Effect of model inputs on aqueous NH_3 concentration [$\text{NH}_3(\text{aq})$], volatilization rate constant (k_{vN}) and NH_3 volatilization rate for the field experiment (6-h averages).

Time	$\text{NH}_4\text{-N}$ conc.	pH	Temperature	Water depth	Wind speed at 2-m height	Initial $\text{NH}_3(\text{aq})$	k_{vN}	Initial volatilization rate
h	mg L ⁻¹		°C	cm	m s ⁻¹	mol m ⁻³	s ⁻¹	mg L ⁻¹ s ⁻¹
0	50.0	7.90	28.47	15	2.26	0.21	2.0×10^{-5}	5.8×10^{-5}
6	48.76	7.93	21.98	15	2.11	0.14	1.8×10^{-5}	3.5×10^{-5}
12	48.01	8.06	15.71	15	1.33	0.12	1.2×10^{-5}	1.9×10^{-5}
18	47.60	8.11	17.14	15	1.54	0.14	1.4×10^{-5}	2.6×10^{-5}
24	47.02	7.84	28.75	15	2.07	0.17	1.8×10^{-5}	4.4×10^{-5}
30	46.07	7.88	20.94	15	1.56	0.11	1.4×10^{-5}	2.1×10^{-5}
36	45.62	8.04	15.05	15	0.97	0.10	9.7×10^{-6}	1.3×10^{-5}
42	45.33	8.05	18.07	15	1.18	0.13	1.1×10^{-5}	2.0×10^{-5}
48	44.91	7.87	26.84	15	3.44	0.16	3.4×10^{-5}	7.3×10^{-5}
54	43.36	7.98	20.11	15	2.54	0.12	2.2×10^{-5}	3.7×10^{-5}
60	42.56	8.08	14.86	15	0.83	0.10	8.8×10^{-6}	1.2×10^{-5}

tion of volatilization rate of NH_3 , can be quantitatively described by the concentration of $\text{NH}_3(\text{aq})$ in the floodwater, which, in turn, is governed by $\text{NH}_4\text{-N}$ concentration, pH, and temperature, and by the k_{vN} , which is a function of temperature, water depth, and wind speed.

SUMMARY AND CONCLUSIONS

The theoretical NH_3 -volatilization model described by Jayaweera and Mikkelsen (1990a,b) was validated in a variable controlled wind tunnel and in the field. In the wind-tunnel experiments, the regression of observed on predicted NH_3 loss yields observed NH_3 loss = $-0.43 + 0.99$ (predicted NH_3 loss), with a r^2 of 0.98. It should be noted, however, that some data were omitted in obtaining this regression. In the field experiment, using a similar regression for two sets of comparisons of experimental and predicted values, the slope was close to 1.0 and the intercept near zero. By averaging the pH, temperature, and wind-speed data in the field over 6-, 12-, and 24-h periods, it is possible to obtain predictions that are quite accurate. Observed values from the wind-tunnel and field experiments agreed closely with the predicted values from the model.

The model calculations shown that $\text{NH}_3(\text{aq})$ in floodwater is governed by $\text{NH}_4\text{-N}$ concentration in the floodwater, the pH, and the temperature. Ammoniacal-N concentration directly influences the floodwater $\text{NH}_3(\text{aq})$, whereas pH and temperature influence $\text{NH}_3(\text{aq})$ through the fraction of dissociation of $\text{NH}_4\text{-N}$. The higher the $\text{NH}_4\text{-N}$ content, pH, and temperature, the higher the $\text{NH}_3(\text{aq})$ in floodwater, thus increasing the volatilization rate of NH_3 and NH_3 loss. Further, the k_{vN} is governed by temperature, water depth, and wind speed. A high temperature and high

wind speed, together with low water depths, increases the k_{vN} , thus increasing the amount of NH_3 loss.

The model is useful in understanding the complex NH_3 -volatilization process by considering only two parameters, aqueous $\text{NH}_3(\text{aq})$ concentration and k_{vN} , as functions of five variables: $\text{NH}_4\text{-N}$ concentration, pH, temperature, water depth, and wind speed, which determine the volatilization rate of NH_3 . This model allows accurate prediction of NH_3 loss in the range of conditions found in flooded rice systems.

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