I. Theoretical Aspects

G. R. Jayaweera* and D. S. Mikkelsen

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: NH4-N concentration, pH, temperature, depth of floodwater, and wind speed. This NH3-volatilization model is based on chemical and volatilization aspects. The chemical aspects of the model deal with the NH4+/NH3(aq) equilibrium in floodwater. Ammonium ions undergo dissociation with a first-order rate constant, while NH3(aq) and H+ undergo a diffusion-controlled association reaction with a second-order rate constant. The transfer of NH3 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 NH4+/NH3(aq) system in association with transfer of gaseous NH3 across the interface, an equation was derived to determine the rate of NH3 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 NH3. Expressions are derived to compute the Henry's law constant, gas-phase and liquid-phase exchange constant, and the overall mass-transfer coefficient for NH3.

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 NH3 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 Crawfll, 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 NH3 loss including forced-air exchange methods using enclosures with NH3 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 Houw, 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 NH4-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 NH3 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 NH4 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 NH3-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 NH3 from floodwater to the atmosphere across a water-air interface. The model presented here consists of two parts: (i) chemical aspects, NH4+/NH3(aq) equilibrium in floodwater and (ii) volatilization aspects, NH3 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 NH₃ volatilization in flooded soil systems.

Five primary factors directly influence the process of NH₃ volatilization. These include floodwater NH₄-N concentration, pH, temperature, wind velocity, and floodwater depth. The role of floodwater depth in NH₃ volatilization is twofold. It directly affects NH₄ 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 around 10 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; Freny et al., 1981; Simpson 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 NH₃ volatilization from a bare water surface and that simulates the first 14 d concentration, time. By chemical kinetics, the rate of change of NH₃ concentration in floodwater is a first-order reaction kinetics (Viek and Stumpe, 1978; Fillery and Vlek, 1986, and Mikkelsen, 1987) listed the factors that influence NH₃ volatilization in flooded soil systems. Further, by making frequent NH₃ measurements and by using these values as model inputs, any error due to this assumption will be minimized.

Thus,

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

where brackets denote concentration in water and t = time. By chemical kinetics, the rate of change of NH₃ concentration in floodwater is

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

and at steady state as

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

therefore

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

By rearranging Eq. [5],

$$[\text{NH}_3(aq)] = \frac{k_d[\text{NH}_4]}{k_d[H] + k_{vN}} \text{ [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_d[H] + k_{vN}} \right)[H] - k_d[\text{NH}_4] \text{ [7]}

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

$$AN = [\text{NH}_4] + [\text{NH}_3(aq)] + [\text{NH}_4L] \text{ [8]}

and, by ignoring ion-pair (NH₄L) formation,

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

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

By substituting Eq. [10] into Eq. [7], the rate of NH₃ volatilization can be written as

$$\frac{d[\text{NH}_4]}{dt} = k_a \left[ \frac{k_d AN - [\text{NH}_3(aq)]}{k_d[H] + k_{vN}} \right][H] - k_d[\text{NH}_4] \text{ [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 NH₃ volatilization as a function of NH₄-N, aqueous NH₃, and H⁺ concentrations in floodwater. kₐ and kₐ of NH₄-N, NH₃(aq) at equilibrium, and kₐ for NH₃ are experimentally determined. Rate constants kₐ, kₐ

CHEMICAL ASPECTS OF THE MODEL

Ammonium N contained in fertilizer or formed through urea hydrolysis is the major source of NH₃ for volatilization. Nitrogen in floodwater exists primarily in two forms: NH₄ ions and dissolved NH₃(aq). An equilibrium exists between these two forms (NH₄) is governed by the pH of the medium. The dissociation of NH₃ follows first-order reaction kinetics, whereas the association of NH₃(aq) and H⁺ exhibits a second-order reaction kinetics (Alberty, 1983).

Aqueous NH₃ is transferred across the air-water interface in the form of NH₃ 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 NH₃ volatilization from floodwater is as follows:

$$\text{NH}_4 + [\text{NH}_3(aq)] \rightarrow [\text{NH}_4][\text{NH}_3(aq)]$$

where

$$k_d = \text{dissociation rate constant for NH}_4/\text{NH}_3 \text{ equilibrium, first order,}

k_a = \text{association rate constant for NH}_4/\text{NH}_3 \text{ equilibrium, second order, and}

k_{vN} = \text{volatilization rate constant for NH}_3 \text{ first order.}

The rate of NH₃ volatilization can be estimated by the rate of change in NH₃ concentration in floodwater, with the assumption that no other processes, gases NH₄ concentration in the system. There are various

processes, however, that bring NH₄ into floodwater, such as soil desorption and organic-matter mineralization, and those that remove NH₄ 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 NH₄ concentration. Further, by making frequent NH₄ measurements and by using these values as model inputs, any error due to this assumption will be minimized.
and $k_{iN}$ 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 $k_{iN}$ 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.

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

where

- $\Delta H^0$ = change in enthalpy at standard state in the NH$_4$/NH$_3$(aq), and
- $T$ = absolute temperature.

By integrating Eq. [12] between specific limits,

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

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

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]:

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

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:

$$pK(T) = 0.0897 + (2729/T) \tag{16}$$

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 (p$K$) at different temperatures.**

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>$pK$</th>
<th>$K$</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>9.23</td>
<td>1.9 x 10^{-11}</td>
</tr>
<tr>
<td>15</td>
<td>9.56</td>
<td>2.8 x 10^{-10}</td>
</tr>
<tr>
<td>20</td>
<td>9.40</td>
<td>4.0 x 10^{-10}</td>
</tr>
<tr>
<td>25</td>
<td>9.24</td>
<td>5.7 x 10^{-10}</td>
</tr>
<tr>
<td>30</td>
<td>9.09</td>
<td>8.1 x 10^{-10}</td>
</tr>
<tr>
<td>35</td>
<td>8.95</td>
<td>1.1 x 10^{-9}</td>
</tr>
<tr>
<td>40</td>
<td>8.86</td>
<td>1.6 x 10^{-9}</td>
</tr>
</tbody>
</table>

*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 ($D$):

$$k_a \propto D \tag{17}$$

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):

$$D = C(T/\eta) \tag{18}$$

where

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

Therefore

$$D \propto \frac{T}{\eta} \tag{19}$$

By combining relationships [17] and [19],

$$k_a \propto \frac{D}{\eta} \propto \frac{T}{\eta} \tag{20}$$

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

$$\frac{k_a(T_3)}{k_a(T_1)} = \frac{T_3 k_1(T_1)}{T_1 k_1(T_3)} \tag{21}$$

where

- $k_a(T_1), k_a(T_3)$ = $k_a$ at temperatures $T_1$ and $T_3$, respectively, and
- $\eta(T_1), \eta(T_3)$ = viscosity of the medium at temperatures $T_1$ and $T_3$, 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]:

$$k_a(T) = 3.8 \times 10^{11} - 3.4 \times 10^9 T + 7.509 700 T^2 \tag{22}$$

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 \( \text{NH}_3 \) 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 \( \text{NH}_3 \) 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 \( \text{NH}_3 \).

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 \( \text{NH}_3 \) is transferred across the air-water interface, there is a drop in chemical potential, and volatilization continues until equilibrium 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 \( \text{CO}_2 \) exchange at the air-water interface, and Bouwmeester and Vlek (1981a) made the same assumption in their \( \text{NH}_3 \)-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 \( \text{NH}_3 \) 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

\[
K_{ON} = \text{overall mass-transfer coefficient for NH}_3 \text{ (in L}^2 \text{ t}^{-1})
\]

\( A = \text{area of the surface (in L}^2) \)

\( V = \text{volume of the solution (in L}^3) \)

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

\( L = \text{length, and} \)

\( t = \text{time.} \)

Dividing Eq. [24] by \( V \) yields

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

where \( d = \text{the depth of solution in the container.} \)

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**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.**

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>( k_d ) M^{-1} s^{-1}</th>
<th>( k_a ) s^{-1}</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>5.22</td>
<td>2.8 \times 10^{10}</td>
</tr>
<tr>
<td>15</td>
<td>8.96</td>
<td>3.3 \times 10^{10}</td>
</tr>
<tr>
<td>20</td>
<td>15.01</td>
<td>3.8 \times 10^{10}</td>
</tr>
<tr>
<td>25</td>
<td>25.591</td>
<td>4.3 \times 10^{10}</td>
</tr>
<tr>
<td>30</td>
<td>39.51</td>
<td>4.9 \times 10^{10}</td>
</tr>
<tr>
<td>35</td>
<td>62.29</td>
<td>5.5 \times 10^{10}</td>
</tr>
<tr>
<td>40</td>
<td>96.53</td>
<td>6.2 \times 10^{10}</td>
</tr>
</tbody>
</table>

\( ^\dagger \text{Experimental value} = 24.60 \text{ s}^{-1} \)

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

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**Fig. 1. Two-film model of a gas-liquid interface where \( C_{\text{GN}} \) and \( C_{\text{IN}} \) are concentration of \( \text{NH}_3 \) at the interface in gas and liquid phases, respectively; and \( C_{\text{GN}} \) and \( C_{\text{IN}} \) are concentration of \( \text{NH}_3 \) 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
- $dC_N/dx$ = 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

$\Delta C_N$ = 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

$$F_N = k_{SN} (C_{SN} - C_{SNi}) = k_{IN} (C_{IN} - C_{INi}) \quad [32]$$

where

- $k_{SN}$ = the exchange constant for NH$_3$ in the gas phase,
- $k_{IN}$ = the exchange constant for NH$_3$ in the liquid phase,
- $C_{SN}$ and $C_{IN}$ = the average concentration of NH$_3$ in the bulk gas and liquid phases, respectively, and
- $C_{SNi}$ and $C_{INi}$ = the concentration of NH$_3$ at the interface in the gas and liquid phases, respectively.

To obtain a direct measurement of the $k_{SN}$ and $k_{IN}$ 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 ($C_{SNi}$ and $C_{INi}$) in determining $k_{IN}$ and $k_{SN}$ values.

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

$$H_n = \frac{C_{SNi}}{C_{INi}} \quad [33]$$

where $H_n$ = nondimensional Henry’s law constant for NH$_3$, and $C_{SNi}$ and $C_{INi}$ are in g/cm$^3$ of water.

By eliminating $C_{SNi}$ and $C_{INi}$ between Eq. [32] and [33], we obtain

$$F_N = (C_{SN} - H_n C_{INi})/(1/k_{SN} + H_n/k_{IN}) = (C_{SN}/H_n) - C_{INi}/(1/k_{SN} + 1/(H_n k_{SN})) \quad [34]$$

The above expression is simplified by introducing two constants:

$$F_N = K_{GN} (C_{SN} - C_{SNi}) = K_{LN} ([C_{SN}/H_n] - C_{IN}) \quad [35]$$

where

- $K_{GN}$ = overall gas-phase coefficient for NH$_3$,
- $K_{LN}$ = overall liquid-phase coefficient for NH$_3$,

where:

$$1/K_{GN} = 1/k_{SN} + H_n/k_{IN}, \text{ and}$$

$$1/K_{LN} = 1/k_{IN} + 1/H_n k_{SN}. \quad [36]$$

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 $H_n$.

Since the term $1/K_{GN}$ of Eq. [37] can be considered as the total resistance for NH$_3$ flux from a water body, we obtain

$$F_N = k_{SN} (C_{SN} - C_{SNi}) = k_{IN} (C_{IN} - C_{INi}) \quad [32]$$

Table 3. Effect of depth of floodwater on volatilization rate constant for NH$_3$ ($k_{SN}$) and half life ($t_{1/2}$).

<table>
<thead>
<tr>
<th>Depth of floodwater (cm)</th>
<th>$k_{SN}$ (m$^{-1}$)</th>
<th>$t_{1/2}$ (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>9.2 x 10$^{-4}$</td>
<td>0.2</td>
</tr>
<tr>
<td>4</td>
<td>2.3 x 10$^{-4}$</td>
<td>0.8</td>
</tr>
<tr>
<td>7</td>
<td>1.3 x 10$^{-4}$</td>
<td>1.5</td>
</tr>
<tr>
<td>10</td>
<td>9.2 x 10$^{-5}$</td>
<td>2.1</td>
</tr>
<tr>
<td>13</td>
<td>7.1 x 10$^{-5}$</td>
<td>2.7</td>
</tr>
<tr>
<td>16</td>
<td>5.8 x 10$^{-5}$</td>
<td>3.4</td>
</tr>
<tr>
<td>19</td>
<td>4.9 x 10$^{-5}$</td>
<td>4.0</td>
</tr>
</tbody>
</table>

† Temperature = 25 ºC; wind speed = 5 m s$^{-1}$. 

JAYAWEERA & MIKKELSON: AMMONIA VOLATILIZATION FROM FLOODED SOIL SYSTEMS: I.
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 NH₃ 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 NH₃-volatilization studies in floodwater systems (Bouwmeester and Vlek, 1981a; Leuning et al., 1984). In our model, we compute $H_N$ for NH₃ in MPa m³ mol⁻¹ and, therefore, need to determine the partial pressure of NH₃ in the gas phase in equilibrium with the floodwater if we know the Henry's law constant for NH₃ in MPa per mole. The partial pressure of NH₃ in equilibrium with the floodwater can then be computed by using Eq. [42].

By considering the chemical equilibrium of NH₄/NH₃(aq) in floodwater, it is possible to relate the pH of the floodwater, $K$, and the concentrations of NH₄ and NH₃(aq) in floodwater, as shown in Eq. [39]:

$$\text{pH} = pK + \log \frac{C}{(1 - \alpha)C}$$

where $C = \text{total ammoniacal-N concentration in floodwater and, by rearrangement:}$

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

where $\alpha = \text{fraction of NH}_3(aq)$.

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

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

Equation [41] shows the fraction of NH₃ in solution as a function of pH and $T$. By using our model (Jayaweera and Mikkelsen, 1990), we calculated the fraction of NH₃(aq) in floodwater with respect to pH and temperature, which is shown in Table 4. Figure 2 illustrates the effect of pH on the fraction of dissociation of NH₃/NH₄(aq) system.

By considering the Henry's law constant for NH₃ in the form of pressure-per-mole-fraction form, we obtain

$$P_N = H_N X_N$$

where $P_N$ = partial pressure of NH₃ in the gas phase in equilibrium with the solution, and $H_N$ = Henry's law constant for NH₃ in pressure per mole fraction.

The partial pressure of NH₃ 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 NH₃ is

$$X_N = \frac{\alpha C/17.03}{(C/17.03)(1 + \alpha)}$$

where $\rho_w$ = density of water (in gm/cm³) at $T$.

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

$$X_N = \frac{(C/17.03)(1 + \alpha)}{(C/17.03)(1 + A) + (C/18.04)(1 + A) + 10\rho_w/18.02}$$

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 NH₃ in the gas phase in equilibrium with the floodwater if we know the Henry's law constant for NH₃ 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:

$$H_N = 183.8 \exp(-1229/T).$$

Table 4. Effect of wind speed at 8 m above the water surface and temperature on the overall mass-transfer coefficient for NH₃ ($K_{ON}$).

<table>
<thead>
<tr>
<th>Wind speed</th>
<th>$K_{ON}$</th>
<th>Temperature</th>
<th>$K_{ON}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>m s⁻¹</td>
<td>cm h⁻¹</td>
<td>°C</td>
<td>cm h⁻¹</td>
</tr>
<tr>
<td>1</td>
<td>0.90</td>
<td>10</td>
<td>3.12</td>
</tr>
<tr>
<td>2</td>
<td>1.32</td>
<td>15</td>
<td>3.19</td>
</tr>
<tr>
<td>4</td>
<td>1.77</td>
<td>20</td>
<td>3.25</td>
</tr>
<tr>
<td>6</td>
<td>3.31</td>
<td>25</td>
<td>3.31</td>
</tr>
<tr>
<td>8</td>
<td>5.32</td>
<td>30</td>
<td>3.37</td>
</tr>
<tr>
<td>10</td>
<td>7.33</td>
<td>35</td>
<td>3.43</td>
</tr>
<tr>
<td>12</td>
<td>9.00</td>
<td>40</td>
<td>3.48</td>
</tr>
</tbody>
</table>

† Temperature = 25 °C.
‡ Wind speed = 6 m s⁻¹.

Table 5. Effect of pH and temperature on the fraction of NH₃ (aq) in floodwater.

<table>
<thead>
<tr>
<th>pH</th>
<th>$\alpha$</th>
<th>Temperature</th>
<th>$\alpha$</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.0</td>
<td>0.01</td>
<td>10</td>
<td>0.06</td>
</tr>
<tr>
<td>7.5</td>
<td>0.02</td>
<td>15</td>
<td>0.08</td>
</tr>
<tr>
<td>8.0</td>
<td>0.05</td>
<td>20</td>
<td>0.11</td>
</tr>
<tr>
<td>8.5</td>
<td>0.15</td>
<td>25</td>
<td>0.15</td>
</tr>
<tr>
<td>9.0</td>
<td>0.36</td>
<td>30</td>
<td>0.20</td>
</tr>
<tr>
<td>9.5</td>
<td>0.64</td>
<td>35</td>
<td>0.26</td>
</tr>
<tr>
<td>10.0</td>
<td>0.85</td>
<td>40</td>
<td>0.33</td>
</tr>
</tbody>
</table>

† Temperature = 25 °C.
‡ pH = 8.5.
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 MPa m\(^3\) 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\(^{-3} \):

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

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 MPa m\(^3\) 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 MPa m\(^3\) mol\(^{-1} \), \( H_{\text{HN}} \) can be computed.

**Determination of Nondimensional Henry’s Law Constant for Ammonia**

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

\[
H_{\text{HN}} = \frac{H_N}{RT} \quad [48]
\]

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

### Table 6. Computed Henry’s law constant for \( NH_3 \) (\( H_N \)).

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>( H_N ) MPa m(^3) mol(^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>( 4.36 \times 10^{-4} )</td>
</tr>
<tr>
<td>15</td>
<td>( 4.76 \times 10^{-4} )</td>
</tr>
<tr>
<td>20</td>
<td>( 5.07 \times 10^{-4} )</td>
</tr>
<tr>
<td>25</td>
<td>( 5.47 \times 10^{-4} )</td>
</tr>
<tr>
<td>30</td>
<td>( 5.78 \times 10^{-4} )</td>
</tr>
<tr>
<td>35</td>
<td>( 6.18 \times 10^{-4} )</td>
</tr>
<tr>
<td>40</td>
<td>( 6.59 \times 10^{-4} )</td>
</tr>
</tbody>
</table>

\( \dagger \) \( NH_3 \)-N concentration = 25 mg L\(^{-1} \); 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 \( k_{N} \) and \( k_{IN} \) 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 \( H_{NH_3} \) varies between \( 4.36 \times 10^{-6} \) to \( 6.59 \times 10^{-4} \) MPa m\(^3\) 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, \( k_{N} \) and \( k_{IN} \) are computed from the data collected in a wind tunnel relating the wind speed and the water vapor exchange constant, \( k_{w} \), and the \( CO_2 \)-gas exchange constant, \( k_{SC} \) (Liss, 1973). Wind speed in the wind tunnel is transformed to equivalent field wind speed with the use of friction velocity, \( U_f \). Using Liss’ data, the following relationship is obtained:

\[
U_f = 0.0545 U_{0.1} \quad [49]
\]

where

\begin{itemize}
  \item \( U_f \) = friction velocity, in m s\(^{-1} \), and
  \item \( U_{0.1} \) = wind speed at 0.1 m above the water surface in the wind tunnel, m s\(^{-1} \).
\end{itemize}

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 \( U_f \):

\[
U_8 = 28.7823 U_f \quad [50]
\]
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:

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

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

The gas-phase exchange constant for \( \text{NH}_3 \), \( k_{\text{gas}} \), 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, \( k_{\text{gw}} \) (cm h\(^{-1}\)) and the wind speed was determined by

\[ k_{\text{gw}} = 18.5683 + 1135.98U_{0.1} \]  \[ [52] \]

This relationship is transformed into the field situation with Eq. [51] and is adjusted to \( \text{NH}_3 \) with the use of the molecular-weight (MW) ratio of water and \( \text{NH}_3 \) (Liss and Slater, 1974):

\[ k_{\text{IN}} = \left[ 12.5853/(1 + 0.4417U_8) \right]^{0.4675} \]  \[ [53] \]

Equation [53] simplifies to

\[ k_{\text{IN}} = 19.0895 + 742.3016 U_8 \]  \[ [54] \]

Similarly, the \( \text{CO}_2 \) exchange-constant data of Liss (1973) were used to estimate the liquid-phase exchange constant, \( k_{\text{IL}} \) (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,

\[ k_{\text{IN}} = \left[ 12.5853/[1 + 43.0565 \exp(-0.4417U_8)] \right]^{0.4675} \]  \[ [55] \]

Table 7 shows the computed values of \( k_{\text{IN}} \) and \( k_{\text{IL}} \) 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 a 8-m height by assuming a logarithmic wind profile:

\[ U_x = \frac{U_Z}{k} \ln \left( \frac{Z}{Z_o} \right) \]  \[ [56] \]

where

\[ U_Z = \text{wind speed, in m s}^{-1}, \text{at an anemometer height,} \ Z, \text{in m,} \]

\[ k = \text{Von Karman constant, 0.4, and} \]

\[ Z_o = \text{roughness height, in m.} \]

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

\[
\frac{U_2}{U_1} = \frac{\ln(Z_2/Z_o)}{\ln(Z_1/Z_o)} \]

\[ [57] \]

where

\[ U_2 = \text{wind speed (in m s}^{-1}\text{) at height} \ Z_2, \text{and} \]

\[ U_1 = \text{wind speed (in m s}^{-1}\text{) at height} \ Z_1. \]

According to Burns et al. (1981), the \( Z_o \), 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

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

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.

ACKNOWLEDGMENTS

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REFERENCES


II. Theory and Model Results

G. R. Jayaweera* and D. S. Mikkelsen

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 NH$_4$-N concentration and the volatilization rate constant for NH$_3$, $k_{VN}$. These parameters are governed by five primary factors, floodwater NH$_4$-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 NH$_4$-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 NH$_4$-aq concentration and $k_{VN}$.

MODEL EXECUTION

The NH$_3$-volatilization model initially requires input data for floodwater NH$_4$-N concentration (AMC), 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 NH$_4$-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 NH$_4$-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 NH$_4$-N concentration increased the NH$_4$-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 NH$_4$-N concentration (Table 2) was a function of NH$_4$-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 NH$_4$-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 NH$_3$(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 NH$_4$-N concentrations. However, for all these runs, $k_{VN}$ was at a constant value, indicating that pH influences NH$_3$(aq) in floodwater at various NH$_4$-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 NH$_4$-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 NH$_3$(aq) in floodwater and the $k_{VN}$. Lowering the temperature to 10 °C decreased both the NH$_3$(aq) in floodwater and the $k_{VN}$ compared with 25 °C. In contrast, when the floodwater temperature was increased to 40 °C, both the NH$_3$(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 NH$_4$-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 NH$_4$-N concentrations. As shown in Table 2, the depth of floodwater influenced $k_{VN}$, but not the NH$_3$(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 NH$_4$-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 NH$_4$-N concentrations. As shown in Table 2, wind speed did not influence NH$_3$(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 NH$_3$(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-

---

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$_3$, $K_N$ and $k_N =$ gas-liquid-exchange constants for NH$_n$, respectively, $\alpha =$ degree of dissociation of NH$_n$, and $H_{N} =$ Henry's law constant for NH$_n$. 

---

Table 1. Model input parameters used in the study on NH$_3$ volatilization.

<table>
<thead>
<tr>
<th>Parameter variable range</th>
<th>Initial NH$_4$-N concentration (AMC)</th>
<th>pH</th>
<th>Temperature (TEMP)</th>
<th>Water depth (WD)</th>
<th>Wind speed at 8 m (U$_w$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lowest</td>
<td>1</td>
<td>7.0</td>
<td>10</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>9</td>
<td>7.5</td>
<td>15</td>
<td>4</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>17</td>
<td>8.0</td>
<td>20</td>
<td>7</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Mean</td>
<td>25</td>
<td>8.5</td>
<td>25</td>
<td>10</td>
<td>6</td>
</tr>
<tr>
<td>33</td>
<td>9.0</td>
<td>30</td>
<td>13</td>
<td>8</td>
<td>8</td>
</tr>
<tr>
<td>41</td>
<td>9.5</td>
<td>35</td>
<td>16</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Highest</td>
<td>49</td>
<td>10.0</td>
<td>40</td>
<td>19</td>
<td>12</td>
</tr>
</tbody>
</table>
ious pH levels increased both NH₃(aq) and kᵥ, which resulted in an increase in NH₃ loss per day (Table 3).

When the depth of floodwater was 1 cm, NH₃ 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 kᵥ (9.2 × 10⁻⁴ s⁻¹; Table 3). On the contrary, at a water depth of 19 cm, 100% of NH₃ was lost per day only when the pH was raised to about 10.0, as a result of the low kᵥ (4.8 × 10⁻³ s⁻¹; Table 3). This shows that, even with high NH₃(aq) concentrations in floodwater, the volatilization can be controlled by low kᵥ, which can be achieved by higher 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 NH₃ 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 difference in kᵥ values for NH₃ at the two wind speeds. This shows that, even at high pH values, low NH₃ volatilization is maintained as a result of low wind speeds.

These model runs show that pH has the capability of increasing NH₃(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 NH₃ volatilization.

Effect of Temperature on Ammonia Volatilization

The effect of floodwater temperature on NH₃ 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 kᵥ, and the NH₃ loss per

<table>
<thead>
<tr>
<th>Initial NH₃-N in floodwater</th>
<th>Initial NH₃(aq)</th>
<th>Volatilization rate constant (kᵥ)</th>
<th>Initial NH₃-N concentration</th>
<th>NH₃ loss/day</th>
</tr>
</thead>
<tbody>
<tr>
<td>mg L⁻¹</td>
<td>mol m⁻³</td>
<td>s⁻¹</td>
<td>mol L⁻¹ s⁻¹</td>
<td>%</td>
</tr>
<tr>
<td>pH 8.5; temperature 25 °C; water depth 10 cm; wind speed 6 m s⁻¹</td>
<td>1</td>
<td>0.01</td>
<td>9.2 × 10⁻⁴</td>
<td>1.7 × 10⁻⁴</td>
</tr>
<tr>
<td>25</td>
<td>0.29</td>
<td>9.2 × 10⁻⁴</td>
<td>4.2 × 10⁻⁴</td>
<td>77</td>
</tr>
<tr>
<td>49</td>
<td>0.57</td>
<td>9.2 × 10⁻⁴</td>
<td>8.2 × 10⁻⁴</td>
<td>77</td>
</tr>
<tr>
<td>pH 7.0; temperature 25 °C; water depth 10 cm; wind speed 6 m s⁻¹</td>
<td>1</td>
<td>4.3 × 10⁻¹</td>
<td>9.2 × 10⁻⁴</td>
<td>5.3 × 10⁻⁴</td>
</tr>
<tr>
<td>25</td>
<td>1.1 × 10⁻²</td>
<td>9.2 × 10⁻⁴</td>
<td>1.3 × 10⁻⁴</td>
<td>4</td>
</tr>
<tr>
<td>49</td>
<td>2.1 × 10⁻³</td>
<td>9.2 × 10⁻⁴</td>
<td>2.6 × 10⁻⁴</td>
<td>4</td>
</tr>
<tr>
<td>pH 10.0; temperature 25 °C; water depth 10 cm; wind speed 6 m s⁻¹</td>
<td>1</td>
<td>0.06</td>
<td>9.2 × 10⁻⁴</td>
<td>5.3 × 10⁻⁴</td>
</tr>
<tr>
<td>25</td>
<td>1.61</td>
<td>9.2 × 10⁻⁴</td>
<td>1.3 × 10⁻³</td>
<td>100</td>
</tr>
<tr>
<td>49</td>
<td>3.15</td>
<td>9.2 × 10⁻⁴</td>
<td>2.6 × 10⁻⁴</td>
<td>100</td>
</tr>
<tr>
<td>pH 8.5; temperature 10 °C; water depth 10 cm; wind speed 6 m s⁻¹</td>
<td>1</td>
<td>4.3 × 10⁻¹</td>
<td>8.7 × 10⁻⁴</td>
<td>5.1 × 10⁻⁴</td>
</tr>
<tr>
<td>25</td>
<td>0.11</td>
<td>8.7 × 10⁻⁴</td>
<td>1.3 × 10⁻³</td>
<td>36</td>
</tr>
<tr>
<td>49</td>
<td>0.21</td>
<td>8.7 × 10⁻⁴</td>
<td>2.5 × 10⁻³</td>
<td>36</td>
</tr>
<tr>
<td>pH 8.5; temperature 40 °C; water depth 10 cm; wind speed 6 m s⁻¹</td>
<td>1</td>
<td>0.03</td>
<td>9.7 × 10⁻⁴</td>
<td>4.8 × 10⁻⁴</td>
</tr>
<tr>
<td>25</td>
<td>0.63</td>
<td>9.7 × 10⁻⁴</td>
<td>1.2 × 10⁻³</td>
<td>99</td>
</tr>
<tr>
<td>49</td>
<td>1.23</td>
<td>9.7 × 10⁻⁴</td>
<td>2.4 × 10⁻³</td>
<td>99</td>
</tr>
<tr>
<td>pH 8.5; temperature 25 °C; water depth 1 cm; wind speed 6 m s⁻¹</td>
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<td>0.01</td>
<td>9.2 × 10⁻⁴</td>
<td>1.7 × 10⁻⁴</td>
</tr>
<tr>
<td>25</td>
<td>0.29</td>
<td>9.2 × 10⁻⁴</td>
<td>4.2 × 10⁻⁴</td>
<td>100</td>
</tr>
<tr>
<td>49</td>
<td>0.57</td>
<td>9.2 × 10⁻⁴</td>
<td>8.2 × 10⁻⁴</td>
<td>100</td>
</tr>
<tr>
<td>pH 8.5; temperature 25 °C; water depth 19 cm; wind speed 6 m s⁻¹</td>
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<td>0.01</td>
<td>4.9 × 10⁻⁴</td>
<td>8.8 × 10⁻⁴</td>
</tr>
<tr>
<td>25</td>
<td>0.29</td>
<td>4.9 × 10⁻⁴</td>
<td>2.2 × 10⁻³</td>
<td>53</td>
</tr>
<tr>
<td>49</td>
<td>0.57</td>
<td>4.9 × 10⁻⁴</td>
<td>4.3 × 10⁻³</td>
<td>53</td>
</tr>
<tr>
<td>pH 8.5; temperature 25 °C; water depth 1 cm; wind speed 0 m s⁻¹</td>
<td>1</td>
<td>0.01</td>
<td>1.1 × 10⁻⁴</td>
<td>1.9 × 10⁻⁴</td>
</tr>
<tr>
<td>25</td>
<td>0.29</td>
<td>1.1 × 10⁻⁴</td>
<td>4.8 × 10⁻⁴</td>
<td>2</td>
</tr>
<tr>
<td>49</td>
<td>0.57</td>
<td>1.1 × 10⁻⁴</td>
<td>9.4 × 10⁻⁴</td>
<td>2</td>
</tr>
<tr>
<td>pH 8.5; temperature 25 °C; water depth 10 cm; wind speed 12 m s⁻¹</td>
<td>1</td>
<td>0.01</td>
<td>2.5 × 10⁻⁴</td>
<td>36</td>
</tr>
<tr>
<td>25</td>
<td>0.29</td>
<td>2.5 × 10⁻⁴</td>
<td>98</td>
<td></td>
</tr>
<tr>
<td>49</td>
<td>0.57</td>
<td>2.5 × 10⁻⁴</td>
<td>98</td>
<td></td>
</tr>
</tbody>
</table>

† 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 kᵥN (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 13% 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 kᵥN (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 kᵥN for NH₃.

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>NH₃-N losses %</th>
<th>NH₃-N losses %</th>
<th>NH₃-N losses %</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>25</td>
<td>3</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>40</td>
<td>7</td>
<td>7</td>
<td>7</td>
</tr>
</tbody>
</table>

Table 3. Effect of floodwater pH on NH₃ volatilization.

<table>
<thead>
<tr>
<th>pH</th>
<th>Initial NH₄-N (mg L⁻¹)</th>
<th>Volatilization rate constant (kᵥN)</th>
<th>Initial NH₃ volatilization rate</th>
<th>NH₃ loss/day (mg L⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.0</td>
<td>0.01 9.2 × 10⁻⁴</td>
<td>1.3 × 10⁻⁴</td>
<td>4 mg L⁻¹·s⁻¹</td>
<td></td>
</tr>
<tr>
<td>8.5</td>
<td>0.29 9.2 × 10⁻⁴</td>
<td>4.3 × 10⁻⁴</td>
<td>77 mg L⁻¹·s⁻¹</td>
<td></td>
</tr>
<tr>
<td>10.0</td>
<td>1.61 9.2 × 10⁻⁴</td>
<td>1.3 × 10⁻³</td>
<td>44 mg L⁻¹·s⁻¹</td>
<td></td>
</tr>
</tbody>
</table>

Table 4. Effect of floodwater temperature on NH₃ volatilization.

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>NH₃-N losses %</th>
<th>NH₃-N losses %</th>
<th>NH₃-N losses %</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>25</td>
<td>3</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>40</td>
<td>7</td>
<td>7</td>
<td>7</td>
</tr>
</tbody>
</table>

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 kᵥN (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-
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 5. Effect of floodwater depth on NH₃ volatilization.

<table>
<thead>
<tr>
<th>Depth (cm)</th>
<th>NH₃(aq) concentration (mg L⁻¹)</th>
<th>Volatilization rate constant ($k_{VN}$) (mol L⁻¹ s⁻¹)</th>
<th>Initial NH₃ loss (%/day)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>25</td>
<td>1.10</td>
<td>100</td>
</tr>
<tr>
<td>10</td>
<td>25</td>
<td>1.10</td>
<td>100</td>
</tr>
<tr>
<td>19</td>
<td>25</td>
<td>1.10</td>
<td>100</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Wind speed (m s⁻¹)</th>
<th>NH₃(aq) concentration (mg L⁻¹)</th>
<th>Volatilization rate constant ($k_{VN}$) (mol L⁻¹ s⁻¹)</th>
<th>Initial NH₃ loss (%/day)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>25</td>
<td>1.10</td>
<td>100</td>
</tr>
<tr>
<td>6</td>
<td>25</td>
<td>1.10</td>
<td>100</td>
</tr>
<tr>
<td>12</td>
<td>25</td>
<td>1.10</td>
<td>100</td>
</tr>
</tbody>
</table>

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 NH₃-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 $k_{VN}$. As shown in Table 6, the increase in wind speed did not influence $k_{VN}$ 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 NH₃-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 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 NH$_3$ was lost at 6 m s$^{-1}$ wind speed. In contrast, when the temperature was 10 °C, the NH$_3$ loss was negligible at 0 m s$^{-1}$, but increased to 70% at 12 m s$^{-1}$ (Table 6).

At a water depth of 1 cm, nearly 100% of NH$_3$ 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 NH$_3$-volatilization process by virtue of its influence on $k_{N\text{H}_3}$. 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 NH$_3$ volatilization and NH$_3$ loss over a given period, it is seen that (i) the floodwater NH$_4$-N concentration directly influences the NH$_3$(aq) concentration in floodwater but does not influence the $k_{N\text{H}_3}$ (ii) the pH of floodwater influences only the NH$_3$(aq) concentration, (iii) the temperature of floodwater influences both the NH$_3$(aq) concentration of floodwater and the $k_{N\text{H}_3}$, and (iv) the depth of floodwater and wind speed influence only the $k_{N\text{H}_3}$.

**Sensitivity Analysis**

The influence of various determinants of NH$_3$ volatilization were tested in a sensitivity analysis. When floodwater NH$_4$-N concentration was increased while pH, temperature, depth of floodwater, and wind speed were kept constant, NH$_3$ volatilization increased linearly. This is directly related to an increase in NH$_3$(aq) in floodwater as a function of NH$_4$-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 NH$_4$-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 $U_s$ = 4 m s$^{-1}$.

Condition 2: AMC = 25 mg L$^{-1}$, pH = 8.5, TEMP = 25 °C, WD = 10 cm, and $U_s$ = 6 m s$^{-1}$.

Condition 3: AMC = 25 mg L$^{-1}$, pH = 9.0, TEMP = 30 °C, WD = 13 cm, and $U_s$ = 8 m s$^{-1}$.

Where AMC = floodwater NH$_4$-N concentration,

pH = pH of floodwater,

TEMP = temperature of floodwater,

WD = depth of floodwater, and

$U_s$ = wind speed at 8-m height.

For each condition, one factor was varied while the others were kept constant. The sensitivity (slope) of NH$_3$ 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 NH$_3$ 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 NH$_3$(aq) into the system, but NH$_3$ loss also depends on the $k_{N\text{H}_3}$. 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 NH$_4$ concentration in solution, which supplies NH$_3$(aq) to the system.

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 NH$_3$(aq) concentration and the $k_{N\text{H}_3}$ increased, thus increasing sensitivity. Under Condition 3, however, high pH and wind speed values caused high NH$_3$ losses; an increase in temperature decreased the sensitivity as NH$_4$-N concentration in the system decreased.

Increased water depth decreased the percent NH$_3$ loss. For each increment of water depth, however, the sensitivity of NH$_3$ 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 NH$_3$(aq) occurred in the floodwater. Because of the shallow depth, $k_{N\text{H}_3}$ increased, causing increased NH$_3$ volatilization, which brought high sensitivity at a shallow water depth.

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 measured to study the interactive effects of NH$_3$-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 NH$_3$-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 $r^2$ 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 NH$_3$(aq) concentration and the volatilization rate constant for NH$_3$, which are dependent on five variables: floodwater NH$_3$ 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.

AMMONIA VOLATILIZATION is a complex process wherein NH$_3$ gas present in floodwater is transferred 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: NH$_3$-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-
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 (NH₄)₂SO₄ of varied concentrations (from 25 to 100 mg L⁻¹ Table I. Experimental details, friction speed (U), roughness height (Z), equivalent field wind speed at 8-m height (U₄), and observed and predicted NH₃ loss for wind-tunnel runs.

<table>
<thead>
<tr>
<th>Wind tunnel run</th>
<th>Description (variable)</th>
<th>Initial NH₄-N conc.</th>
<th>pH</th>
<th>Temperature</th>
<th>Water depth</th>
<th>Free-stream wind speed</th>
<th>U₄</th>
<th>Z</th>
<th>U₄</th>
<th>NH₃ loss</th>
<th>Predicted / Observed ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Mean</td>
<td>52.32 8.5</td>
<td>25</td>
<td>11.0</td>
<td>2.88</td>
<td>0.166</td>
<td>0.014</td>
<td>4.41</td>
<td>9.33</td>
<td>9.52</td>
<td>1.14</td>
</tr>
<tr>
<td>2</td>
<td>Mean</td>
<td>52.59 8.5</td>
<td>25</td>
<td>11.0</td>
<td>2.76</td>
<td>0.150</td>
<td>0.008</td>
<td>4.23</td>
<td>8.32</td>
<td>9.06</td>
<td>1.09</td>
</tr>
<tr>
<td>3</td>
<td>Mean</td>
<td>53.22 8.5</td>
<td>25</td>
<td>11.0</td>
<td>2.70</td>
<td>0.144</td>
<td>0.007</td>
<td>4.14</td>
<td>7.91</td>
<td>8.93</td>
<td>1.13</td>
</tr>
<tr>
<td>4</td>
<td>Low</td>
<td>26.24 8.5</td>
<td>25</td>
<td>11.0</td>
<td>2.64</td>
<td>0.128</td>
<td>0.003</td>
<td>4.05</td>
<td>3.49</td>
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<td>25</td>
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<td>2.70</td>
<td>0.140</td>
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<td>25</td>
<td>11.0</td>
<td>2.64</td>
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<td>52.50 8.5</td>
<td>25</td>
<td>11.0</td>
<td>2.70</td>
<td>0.123</td>
<td>0.002</td>
<td>4.14</td>
<td>5.52</td>
<td>6.21</td>
<td>1.13</td>
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<td>9</td>
<td>High</td>
<td>53.05 8.5</td>
<td>30</td>
<td>11.0</td>
<td>2.88</td>
<td>0.136</td>
<td>0.003</td>
<td>4.41</td>
<td>11.83</td>
<td>13.30</td>
<td>1.12</td>
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<td>10</td>
<td>Water depth</td>
<td>Low</td>
<td>52.67 8.5</td>
<td>6.42 2.76 0.158</td>
<td>0.012</td>
<td>4.23</td>
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<td>14.58</td>
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<tr>
<td>11</td>
<td>High</td>
<td>50.32 8.5</td>
<td>25</td>
<td>21.28 2.76 0.158</td>
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<td>12</td>
<td>Wind speed at 8 m</td>
<td>Low</td>
<td>51.61 8.5</td>
<td>25 11.0 1.91 0.281</td>
<td>0.019</td>
<td>2.93</td>
<td>6.45</td>
<td>5.72</td>
<td>0.89</td>
<td></td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>High</td>
<td>52.93 8.5</td>
<td>25</td>
<td>11.0 5.34 0.153</td>
<td>0.005</td>
<td>8.19</td>
<td>12.22</td>
<td>22.25</td>
<td>1.82</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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

\[ U_z = \frac{U_*}{k} \ln \left( \frac{Z}{Z_0} \right) \quad [1] \]

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

\[ \ln Z = \left( \frac{k}{U_*} \right) U_z + \ln Z_0 \quad [2] \]

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 0.006 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 \( U_8/U_* \) was fairly constant over all the wind-tunnel runs with an average of 0.0531, where \( U_8 \) is the wind speed in the axial center of the wind tunnel:

\[ \frac{U_8}{U_*} = 0.0531 \quad [3] \]

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:

\[ U_8 = 1.5283 U_* \quad [5] \]

Using Eq. [5], the free-stream wind speeds of different 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 NH₄⁻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 NH₄⁻N depletion. The calculated rate constants and half-life values, which describe the NH₄⁻N depletion rate, are shown in Table 2.

The highest rate constant for NH₄⁻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 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.
is acceptable (Thomas, 1982). Linear regression of the observed NH₃ 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 conditions usually found in flooded rice systems.

As discussed in Jayaweera and Mikkelsen (1990b), NH₃ volatilization per se is primarily dependent on two parameters, aqueous NH₃ concentration, NH₃(aq), and the volatilization rate constant for NH₃, $k_{VN}$. Table 4 shows the effect of five variables on NH₃ loss in wind-tunnel experiments. It is important to note that, when we compare values in Tables 1 and 4, the initial NH₄-N coicentration and the wind speed could not be maintained an an exact fixed value (Tables 1 and 4); however, the experimental values were always close to the target val. es.

The initial NH₃(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 low- and high-temperature runs. The difference in NH₃(aq) is dependent on the fraction of the dissociation of NH₄ to NH₃ (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 NH₄(aq) in the system from 0.44 to 0.82 (Table 4). Therefore, the volatilization rate of NH₃ in low- and high-NH₄-N-concentration runs, low- and high-pH runs, and low- and high-temperature runs were brought about by the influence of these variables on NH₃(aq) in the system. The higher the intensity of each variable, the higher the NH₃(aq) and, in turn, the higher the NH₃ loss, and vice versa.

In several of the wind-tunnel runs, the NH₃ loss was determined by the $k_{VN}$. The lower the $k_{VN}$, the lower the volatilization rate of NH₃, which decreased the amount of NH₃ loss, and vice versa.

### Table 3. Tests of slope = 1.0 and intercept = 0 from regression of observed on predicted NH₃ loss in wind-tunnel runs.

<table>
<thead>
<tr>
<th>Regression details</th>
<th>$r^2$</th>
<th>Slope</th>
<th>Intercept</th>
</tr>
</thead>
<tbody>
<tr>
<td>All wind tunnel runs (i.e., 13 runs)</td>
<td>0.86</td>
<td>0.46</td>
<td>3.86</td>
</tr>
<tr>
<td>All wind tunnel runs except high-pH and high-wind-speed runs</td>
<td>0.97</td>
<td>0.92</td>
<td>0.38</td>
</tr>
<tr>
<td>All wind tunnel runs except high- and low-pH and high-wind-speed runs</td>
<td>0.98</td>
<td>0.99</td>
<td>-0.43</td>
</tr>
</tbody>
</table>

### Table 4. Effect of model inputs on volatilization rate of NH₃, aqueous NH₃ concentration [NH₃(aq)], volatilization rate constant ($k_{VN}$), and other parameters in predicting NH₃ loss in wind-tunnel experiments. Mean is the average of three runs.

| Wind-tunnel run† | Initial volatilization rate | $k_{VN}$ | $k_d$ | $\alpha$ | NH₃(aq) | $H_m$§ | $k_{VN}$|| $K_{MN}$|| $K_{MN}$|| $k_{VN}$ |
|------------------|----------------------------|----------|-------|---------|--------|------|--------|-------|-------|-------|------|-------|
| Mean (avg. of 3) | 4.7 X 10⁻⁶ | 4.3 X 10⁻⁹ | 24.6 | 0.15 | 0.61 | 5.5 X 10⁻⁴ | 2.7 | 3181 | 4.9 X 10⁻⁴ | 1.9 |
| NH₄-N conc. mg L⁻¹ | | | | | | | | | | |
| Low 26.24 | 2.2 X 10⁻⁶ | 4.3 X 10⁻⁹ | 24.6 | 0.15 | 0.30 | 5.5 X 10⁻⁴ | 2.5 | 3025 | 4.5 X 10⁻⁴ | 1.8 |
| High 102.54 | 8.7 X 10⁻⁶ | 4.3 X 10⁻⁹ | 24.6 | 0.15 | 1.19 | 5.5 X 10⁻⁴ | 2.6 | 3092 | 4.7 X 10⁻⁴ | 1.9 |
| pH | | | | | | | | | | |
| Low 6.5 | 4.3 X 10⁻⁶ | 4.3 X 10⁻⁹ | 24.6 | 0.002 | 0.007 | 5.5 X 10⁻⁴ | 2.5 | 3025 | 4.5 X 10⁻⁴ | 1.8 |
| High 10.5 | 4.6 X 10⁻⁶ | 4.3 X 10⁻⁹ | 24.6 | 0.95 | 3.57 | 5.5 X 10⁻⁴ | 2.8 | 3293 | 5.1 X 10⁻⁴ | 2.0 |
| Temperature, °C | | | | | | | | | | |
| Low 20 | 3.1 X 10⁻⁶ | 3.8 X 10⁻⁹ | 15.0 | 0.11 | 0.44 | 3.1 X 10⁻⁴ | 2.6 | 3092 | 4.6 X 10⁻⁴ | 1.8 |
| High 30 | 7.1 X 10⁻⁶ | 4.9 X 10⁻⁹ | 39.5 | 0.20 | 0.82 | 5.8 X 10⁻⁴ | 2.8 | 3293 | 5.2 X 10⁻⁴ | 2.1 |
| Water depth, cm | | | | | | | | | | |
| Low 6.42 | 7.9 X 10⁻⁶ | 4.3 X 10⁻⁹ | 24.6 | 0.15 | 0.61 | 5.5 X 10⁻⁴ | 2.6 | 3159 | 8.3 X 10⁻⁴ | 1.9 |
| High 21.29 | 2.3 X 10⁻⁶ | 4.3 X 10⁻⁹ | 24.6 | 0.15 | 0.58 | 5.5 X 10⁻⁴ | 2.6 | 3159 | 2.5 X 10⁻⁴ | 1.9 |
| Wind speed at 8 m, ms⁻¹ | | | | | | | | | | |
| Low 2.93 | 2.8 X 10⁻⁶ | 4.3 X 10⁻⁹ | 24.6 | 0.15 | 0.60 | 5.5 X 10⁻⁴ | 1.6 | 2194 | 3.0 X 10⁻⁴ | 1.2 |
| High 8.18 | 1.3 X 10⁻⁶ | 4.3 X 10⁻⁹ | 24.6 | 0.15 | 0.61 | 5.5 X 10⁻⁴ | 9.4 | 6099 | 1.4 X 10⁻⁴ | 5.5 |

† Refer to Table 1 for details on wind-tunnel runs.
§ Association rate constant for NH₃
† Liquid-transfer exchange constant
§ Fraction of dissociation
# Henry's law constant for NH₃
|| Gas-transfer exchange constant
|| Overall mass-transfer coefficient for NH₃

mean values (Table 4). This shows that depth of water in the tank and the wind speed did not influence the concentration of NH₃(aq). However, low- and high-NH₄-N runs, low- and high-pH runs, and low- and high-temperature runs did influence the NH₃(aq) in the system. At the low value of each of these variables, the initial NH₃(aq) was lower than the mean, and vice versa. As shown in Table 4, in low- and high-NH₄-N runs, the difference in NH₃(aq) was due to the difference in the initial NH₄-N concentrations (Jayaweera and Mikkelsen, 1990b). In low- and high-pH runs, NH₃(aq) is dependent on the fraction of the dissociation of NH₄ to NH₃(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 NH₃(aq) are due to changes in the association and dissociation rate constants, $k_{VN}$ and $k_{MN}$, respectively, which influence the degree of dissociation of NH₄ to NH₃ (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 NH₄(aq) in the system from 0.44 to 0.82 (Table 4). Therefore, the volatilization rate of NH₃ in low- and high-NH₄-N-concentration runs, low- and high-pH runs, and low- and high-temperature runs were brought about by the influence of these variables on NH₃(aq) in the system. The higher the intensity of each variable, the higher the NH₃(aq) and, in turn, the higher the NH₃ loss, and vice versa.
NH₃-N runs and low- and high-pH runs, the average was 4.7 × 10⁻³ s⁻¹, which is comparable with the average mean value of 4.9 × 10⁻³ 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 kᵥN differed from the average mean value. These differences were due to entirely different causes (Jayaweera and Mikkelsen, 1990a, b).

Henry's law constant of NH₃, HₑN, is a function of temperature (Jayaweera and Mikkelsen, 1990a). Therefore, as the temperature increased, the HₑN also increased, rising from 5.07 × 10⁻⁶ MPa m³ mol⁻¹ at 20 °C to 5.47 × 10⁻⁶ MPa m³ mol⁻¹ at 25 °C and 5.78 × 10⁻⁶ MPa m³ mol⁻¹ at 30 °C. The change in HₑN changed the overall mass-transfer coefficient for NH₃, KₒN, and the kᵥN. At 20 °C, the kᵥN decreased to 4.6 × 10⁻² s⁻¹ and, at 30 °C, it increased to 5.2 × 10⁻² s⁻¹ relative to the average mean value of 4.9 × 10⁻² s⁻¹ at 25 °C. In low-and high-water-depth runs, the KₒN 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 NH₃, k₉N, and kᵥN, respectively. However, due to differences in water depth, the kᵥN was higher for a depth of 6.42 cm, compared with a mean depth of 11.0 cm, and kₒN was lower at a depth of 21.28 cm (Table 4).

In the low- and high-wind-velocity runs, the kᵥN was influenced through the k₉N and kₒN. When the wind speed was 1.9 m s⁻¹, kₒN, k₉N, and KₒN were low; and when the wind speed was high (5.3 m s⁻¹), these exchange constants were high (Table 4), thereby influencing the kᵥN. A decrease in kᵥN decreases the volatilization rate of NH₃, thereby decreasing the amount of NH₃ 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 NH₃ loss. These values were also compared with observed NH₄-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 values with observed data from the field study. Regression of observed NH₄-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 NH₃(aq), the kᵥN, and the volatilization rate of NH₃ 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 NH₃ loss, which is a func-

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**Table 5. Tests of slope = 1.0 and intercept = 0 from regression of observed on predicted NH₄-N depletion in the field experiment with different averaging periods.**

<table>
<thead>
<tr>
<th>Experimental period</th>
<th>Averaging period</th>
<th>r²</th>
<th>Slope</th>
<th>Intercept</th>
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<td>4 to 7 August</td>
<td>6 h</td>
<td>0.99</td>
<td>1.07</td>
<td>-3.30</td>
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<td></td>
<td>12 h</td>
<td>0.99</td>
<td>1.08</td>
<td>-4.15</td>
</tr>
<tr>
<td></td>
<td>24 h</td>
<td>0.99</td>
<td>1.12</td>
<td>-5.58</td>
</tr>
<tr>
<td>8 to 11 August</td>
<td>6 h</td>
<td>0.99</td>
<td>0.95</td>
<td>1.76</td>
</tr>
<tr>
<td></td>
<td>12 h</td>
<td>0.98</td>
<td>1.00</td>
<td>0.02</td>
</tr>
<tr>
<td></td>
<td>24 h</td>
<td>0.99</td>
<td>1.05</td>
<td>-1.79</td>
</tr>
</tbody>
</table>

---

**Fig. 5. Regression of observed on predicted NH₃ loss in wind-tunnel runs.**

**Fig. 6. Predicted and observed NH₄-N depletion in the field.**
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 NH$_3$(aq) in floodwater is governed by NH$_4$-N concentration in the floodwater, the pH, and the temperature. Ammonia-N concentration directly influences the floodwater NH$_3$(aq), whereas pH and temperature influence NH$_3$(aq) through the fraction of dissociation of NH$_4$-N. The higher the NH$_4$-N content, pH, and temperature, the higher the NH$_3$(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 NH$_3$(aq) concentration and $k_{vN}$, as functions of five variables: NH$_4$-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.

## ACKNOWLEDGMENTS

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## REFERENCES


