ASSESSMENT OF AMMONIA VOLATILIZATION FROM FLOODED SOIL SYSTEMS

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I. INTRODUCTION

Ammonia volatilization from flooded soil systems involves a complex pathway in the terrestrial–atmospheric nitrogen (N) cycle. Ammonium N derived from natural sources (fertilized rice paddies and industrial by-products, lakes, streams, ponds, animal wastes, etc.) are potential materials for NH_3 volatilization. In recent years, losses of soil N fertility via volatilization have been identified as a major constraint to crop production, both with upland and lowland crops, particularly rice grown on flooded soils. In flooded rice culture, where ammonium (NH_4^+-N) fertilizers are broadcast directly onto the soil or water without incorporation,

NH_3 volatilization losses range from 10 to 60% of the fertilizer N applied. In contrast, where the fertilizer N is placed in the soil (e.g., 10 cm deep) by either mixing, placement, or banding techniques, NH_3 losses may be very minimal (<5%). Poor fertilizer management practices may contribute significantly to low fertilizer-use efficiency with resultant poor crop yields.

A variety of water, soil, biological, and environmental factors and management practices influence the kinetics and extent of NH_3 volatilization from flooded soil systems. Ammoniacal N concentration, pH, P_{CO_2}, alkalinity, buffering capacity, temperature, depth, turbulence, and biotic activity are several floodwater characteristics that influence NH_3 volatilization. The NH_4^+-N concentration in floodwater is influenced by N management practices such as source, timing and method of application, and water depth as well as biotic activity.

The dominant soil factors affecting NH_3 volatilization are soil pH, redox status, cation exchange characteristics, $CaCO_3$ content, soil texture, biotic activity, and fluxes affecting adsorption and desorption of NH_4^+-N at the soil–water interface. Atmospheric conditions such as windspeed, P_{NH_3}, air temperature and solar radiation also influence NH_3 volatilization. Management practices concerning the crop, water, and soil together with weather conditions prior to and after crop establishment have a direct effect on NH_3 losses.

Problems of measuring NH_3 volatilization losses to accurately reflect dynamic field conditions have long been a concern of researchers and planners. Methods used to measure NH_3 loss have been described by Fillery and Vlek (1986) and also by Harper (1988) who identify the problems associated with quantifying losses under undisturbed field conditions. They describe three micrometeorological methods that have promise, mainly eddy correlation, gradient diffusion, and mass balance.

The behavior of NH_4^+-N in flooded soil systems and the mass transfer of NH_3 across the water–air interface is a dynamic process involving numerous interactions. An understanding of the rate-controlling factors described in a simplified model will enable us to predict losses, allow simplified measurements, and subsequently aid the planning and decision making processes in controlling NH_3 losses to the atmosphere from natural systems, as well as designing more efficient fertilizer management strategies.

Only a few models have been published which analyze the floodwater chemistry and atmospheric conditions affecting NH_3 volatilization (Bouwmeester and Vlek, 1981a; Moeller and Vlek, 1982; Jayaweera and Mikkelsen, 1990a).

Several good reviews have been published which summarize the general information on NH_3 volatilization in flooded soil systems (Vlek and Cras-

well, 1981; Fillery and Vlek, 1986). Readers new to the field may wish to refer to these reviews for the early research.

II. THEORETICAL ASPECTS

Volatilization is the process by which a substance is transferred from a liquid or solid phase to a vapor phase, generally the atmosphere. Ammoniacal N occurring in a floodwater system may be transferred to the atmosphere as gaseous NH_3 across the water–air interface.

A. CHEMICAL ASPECTS

The ammonium ion, NH_4^+-N is the source of NH_3, which is formed as a N-transformation product in flooded soil, and also found following N fertilizer applications. The NH_4^+-N pool establishes an equilibrium with dissolved NH_3 gas, $NH_{3(aq)}$, which is governed by the pH of the medium. The dissociation reaction of $NH_4^+/NH_{3(aq)}$ equilibrium is of first order, whereas the association reaction is considered to be of second order (Alberty, 1983).

Volatilization of a chemical from a water body is described as a first-order process (Smith et al., 1981). Several researchers have shown that NH_3 volatilization per se follows first-order kinetics (Folkman and Wachs, 1973; Vlek and Stumpe, 1978; Moeller and Vlek, 1982).

The reaction sequence for NH_3 volatilization is as follows:

$$NH_4^+ \underset{k_a}{\overset{k_d}{\rightleftharpoons}} H^+ + NH_{3(aq)} \overset{k_{vN}}{\rightarrow} NH_{3(air)} \tag{1}$$

where
k_d = dissociation rate constant for $NH_4^+/NH_{3(aq)}$ equilibrium;
k_a = association rate constant for $NH_4^+/NH_{3(aq)}$ equilibrium; and
k_{vN} = volatilization rate constant for NH_3.

B. VOLATILIZATION ASPECTS

The transfer of NH_3 across a water–air interface is described by the two-film model proposed by Whitman (1923), a useful concept to describe the mass transfer of a gas across a liquid–gas interface (Coulson et al., 1978). According to this model, the main body of each fluid is assumed to

be well mixed by convection currents and the concentration differences are regarded as negligible except in the vicinity of the interface between the phases. On either side of the interface it is supposed that turbulent eddies die out and that there exists a thin film of fluid in each phase, the flow of which is considered to be laminar and parallel to the surface (Fig. 1). This film, however, can also be considered as a stagnant layer on either side of the interface. Most of the resistance to mass transfer, and hence most of the concentration gradient, lies in these films. Outside this layer, turbulent eddies supplement the action caused by the random motion of the molecules, and the resistance to transfer becomes progressively smaller. The basis of the theory is the assumption that the zones in which the resistance to transfer lie can be replaced by two hypothetical layers, one on each side of the interface, in which the transfer is solely by molecu-
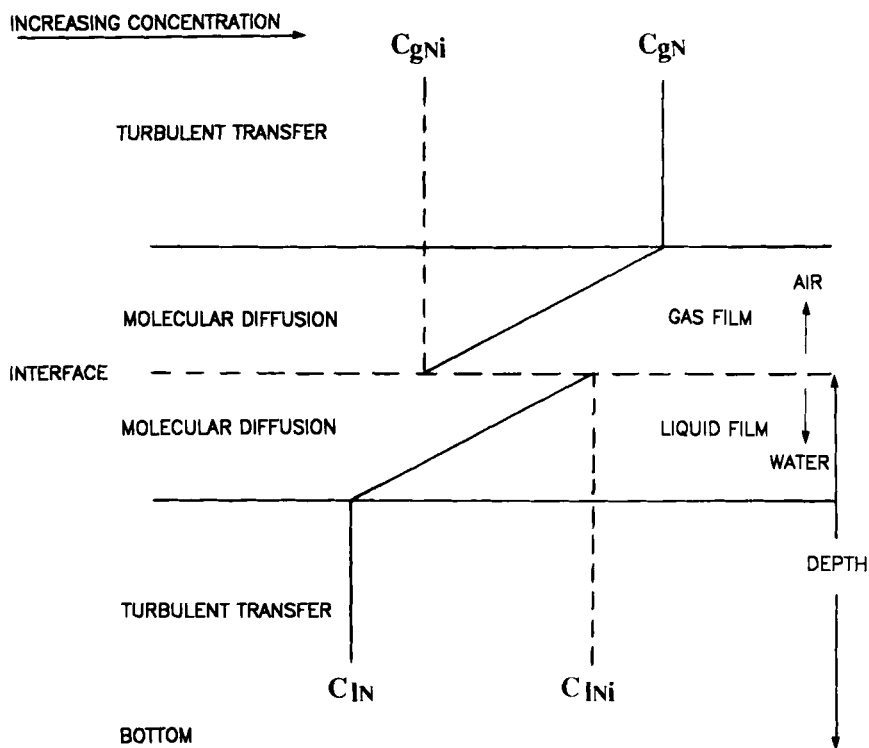

FIG. 1. Two-film model of a gas–liquid interface: C_{gN} and C_{lN}, average NH_3 concentrations in bulk gas and liquid phase, respectively; C_{gNi} and C_{lNi}, average NH_3 concentrations at the interface in gas and liquid phase, respectively. (Adapted from Liss and Slater, 1974).

lar diffusion. The concentration gradient is therefore linear in each of these layers and zero outside. 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 causes the liquid film or boundary layer to be thin; similarly, high turbulence in the gas causes the gas layer to be thin.

At the interface, there is a concentration discontinuity and NH_3 occurs at equilibrium across the interface as determined by Henry's law constant. Henry's law constant is a distribution coefficient that expresses the proportionality between the concentration of a gas dissolved in a solvent and its partial pressure (Prausnitz, 1986).

In equation form, Henry's law is

$$P = HC \qquad (2)$$

where P is the partial pressure of the gas, C is the concentration of the dissolved gas, and H is the Henry's law constant.

Henry's law constant is a function of temperature for a particular gas–solvent system. Each gas–solvent system, however, has its own unique Henry's law constant. Typically, Henry's law breaks down when partial pressure exceeds 5–10 atmospheres and/or when the dissolved concentration exceeds 3 mol percent (Prausnitz, 1986).

At the interface, there is an equilibrium, and on either side transfer is affected entirely by molecular diffusion. Diffusion occurs when the chemical experiences a drop in potential as a result of the transfer. Volatilization continues until this difference is eliminated and equilibrium is established. According to Mackay (1980), although it is possible to use chemical potential to describe volatilization, it is more convenient to use the concept of chemical fugacity or partial pressure. Therefore, the driving force of diffusion can be regarded as the partial pressure difference between the water and air for the particular gas.

Ammonia in air is in equilibrium with an aqueous solution and generally the concentration of NH_3 in water is many times greater than in the air. There is, therefore, a large concentration gradient across the interface. This, however, is not the controlling factor in the mass transfer. It is generally assumed that there is no resistance at the interface itself, where equilibrium conditions exist. However, the 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 exists. This shows that the liquid-phase or gas-phase resistance, or both, determine the overall mass transfer rate of a chemical.

The volatilization of NH_3, according to the two-film model, can be described as the diffusion of NH_3 from the bulk of floodwater to the interface, followed by transfer across the interface, and finally diffusion from the interface to the bulk of the air phase. Ammonia concentrations immediately on either side of the interface are in equilibrium, which is expressed by the Henry's law constant for NH_3.

It is interesting to note the views of Danckwerts (1970) in his book on gas–liquid reactions on the two-film model. According to Danckwerts, the two-film model is not entirely realistic and it would not be seriously contended that a discontinuity really exists near the surface, still less that it has a uniform thickness. Nevertheless, the film model incorporates an essential feature of the real system, namely, that the gas must get into the liquid by dissolution and molecular diffusion before it can be transported by convection. He further states that the predictions based on the film model are remarkably similar and sometimes identical to those based on more sophisticated models. In view of its simplicity it is often preferable to use the film model for the purposes of discussion or calculation. Liss (1973) endorsed the concepts of Danckwerts and adapted the two-film model to study gas exchange across an air–water interface. This concept has since been adapted by other researchers and has been used to predict the interfacial transfer of carbon dioxide (Liss, 1973), sulfur dioxide (Liss and Slater, 1974), and various organic chemicals (Liss and Slater, 1974; Mackay and Leiononen, 1975; Dilling, 1977; cohen et al., 1978; Southworth, 1979; Mackay et al., 1979; Rathbun and Tai, 1981; Slater and Spedding, 1981; Smith et al., 1981; Atlas et al., 1982). The two-film model simplifies the theoretical calculation of gas exchange at the air–water interface (Liss and Slater, 1974) and is the most widely used kinetic model in estimating the volatilization of chemicals (Sanders and Seiber, 1984).

III. THEORY OF AMMONIA VOLATILIZATION

The NH_3 volatilization process is directly influenced by five primary factors (Jayaweera and Mikkelsen, 1990a). They are floodwater NH_4^+-N concentration, pH, temperature, depth of floodwater, and windspeed. They have developed a theory that describes the effect of these factors on NH_3 volatilization (Fig. 2) (Jayaweera and Mikkelsen, 1990b).

The rate of NH_3 volatilization is principally a function of two parameters, (1) the $NH_{3(aq)}$ concentration in floodwater, and (2) the volatilization rate constant for NH_3, k_{vN}.

$$\text{rate of } NH_3 \text{ volatilization} = f([NH_3]_{aq}, k_{vN}) \tag{3}$$
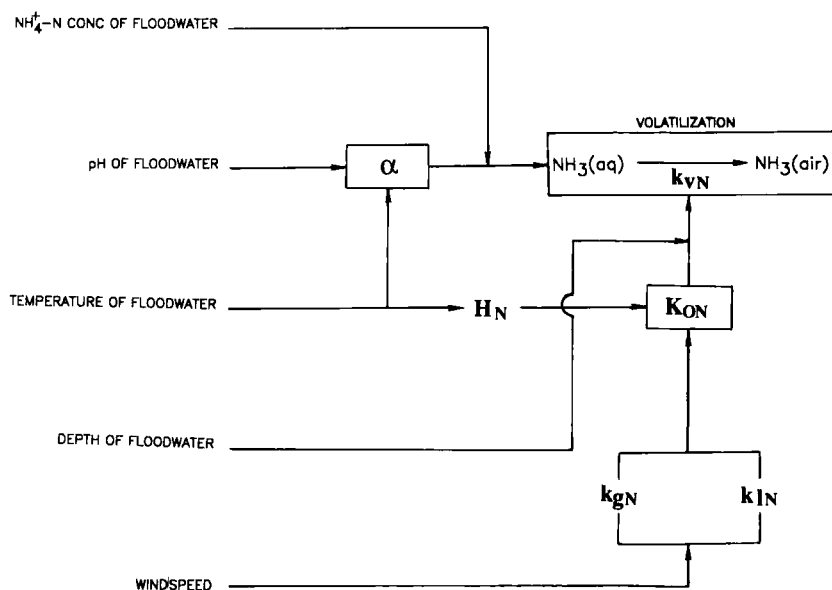
FIG. 2. Theory of NH_3 volatilization in flooded systems: α, degree of dissociation of NH_4^+; H_N, k_{vN}, K_{ON}, k_{gN}, and K_{IN} are the Henry's law constant, volatilization rate constant, overall mass transfer coefficient, and gas-phase and liquid-phase exchange constants for NH_3, respectively. (From Jayaweera and Mikkelsen, 1990b.)

Ammonia concentration in floodwater, $NH_{3(aq)}$, is determined by (1) NH_4^+-N concentration in floodwater, and (2) fraction of dissociation, α of NH_4^+. Fraction of dissociation is governed by the dissociation and association rate constants of $NH_4^+/NH_{3(aq)}$ equilibrium, and the H^+ ion concentration in the system as represented by the pH of the medium. Rate constants are ultimately determined by the temperature of the system. Therefore,

$NH_{3(aq)}$ concentration in floodwater $= f([NH_4^+\text{-}N], \text{temperature, pH})$.

$$(4)$$

The volatilization rate constant, k_{vN}, is determined by (1) the depth of floodwater, and (2) the overall mass transfer coefficient for NH_3, which is influenced by the Henry's law constant for NH_3 and liquid- and gas-phase exchange constants. Henry's law constant is a function of temperature and exchange constants, which are dependent on the windspeed. Therefore,

volatilization rate constant for NH_3 = f(water depth, temperature, windspeed). (5)

By equating Eqs. (4) and (5) to Eq. (3), we obtain

$$\text{rate of NH}_3 \text{ volatilization} = f([\text{NH}_4^+\text{-N}], \text{temperature, pH, water depth, windspeed}). \tag{6}$$

IV. FACTORS AFFECTING AMMONIA VOLATILIZATION

Ammonia volatilization in flooded rice and similar systems is influenced by a variety of water and soil characteristics, fertilizer and crop management practices, and environmental factors (Mikkelsen, 1987). Several floodwater characteristics such as $\text{NH}_4^+\text{-N}$ concentration, pH, P_{CO_2}, total alkalinity, buffering capacity, temperature, depth, turbulence, and biotic activity influence NH_3 volatilization. Soil factors affecting NH_3 volatilization are pH, redox status, $CaCO_3$ content, cation exchange capacity, soil texture, and biotic activity. Wind speed, turbulence, P_{NH_3}, air temperature, and solar radiation are several atmospheric conditions influencing NH_3 volatilization. Nitrogen source, timing, and method of application are three fertilizer management practices affecting NH_3 loss. Water management can also affect the fluxes controlling the movement of $\text{NH}_4^+\text{-N}$ between soil, water, and air.

Jayaweera and Mikkelsen (1990a) subdivided these rate-controlling factors into two categories: (1) primary factors, and (2) secondary factors.

A. PRIMARY FACTORS AFFECTING NH$_3$ VOLATILIZATION

Primary factors directly influence the process of NH_3 volatilization. Numerous secondary factors, however, modify the primary ones.

The primary factors that influence NH_3 volatilization are $\text{NH}_4^+\text{-N}$ concentration, pH, temperature, depth of floodwater, and windspeed (Jayaweera and Mikkelsen, 1990a).

1. Effect of Floodwater NH$_4^+$-N Concentration

Volatilization of NH_3 from floodwater is described as a first-order exponential decay process. Therefore, the rate of NH_3 volatilization is directly related to the concentration of aqueous NH_3, which in turn is a function of $\text{NH}_4^+\text{-N}$ concentration.

Various researchers have shown a pronounced influence of $\text{NH}_4^+\text{-N}$ concentration on overall NH_3 loss (Mikkelsen *et al.*, 1978; Vlek and

Stumpe, 1978; Terman, 1979; Vlek and Craswell, 1979; Bouwmeester and Vlek, 1981a; Denmead *et al.*, 1982; Craswell and Vlek, 1983; Fillery *et al.*, 1984; Fillery and Vlek, 1986; Mikkelsen, 1987; Jayaweera and Mikkelsen, 1990b).

Fillery and Vlek (1986) state that the quantity of NH$_4^+$-N in floodwater is an index of the potential NH$_3$ volatilization and the rate of NH$_3$ loss is partially dependent on the equilibrium vapor pressure of NH$_3$ in flood-water. Vlek and Stumpe (1978) reported that the rate of NH$_3$ volatilization is directly related to the concentration of aqueous NH$_3$ and therefore to the concentration of NH$_4^+$-N and pH. Fertilizer management, through its influence on the concentration of NH$_4^+$-N in floodwater, has a pronounced effect on the overall NH$_3$ loss (Fillery *et al.*, 1984).

Bouwmeester and Vlek (1981a), using their model, showed that the rate of NH$_3$ volatilization is increased with increasing NH$_4^+$-N concentration in floodwater. In a recently developed model by Jayaweera and Mikkelsen (1990b) they showed an increase in NH$_3$ volatilization with increasing floodwater NH$_4^+$-N concentration, under a particular pH, temperature, water depth, and windspeed (Fig. 3). Volatilization rate is increased as a result of an increase in NH$_{3(aq)}$ concentration in floodwater. They have further shown that by decreasing pH, temperature, and windspeed, and by increasing the water depth, the NH$_3$ volatilization rate is decreased at any NH$_4^+$-N concentration and vice versa (Fig. 3). A decrease in pH decreases the NH$_{3(aq)}$ concentration in floodwater; a decrease in temperature decreases both NH$_{3(aq)}$ concentration and the volatilization rate constant, whereas a decrease in windspeed and an increase in floodwater depth decreases only the volatilization rate constant (Jayaweera and Mikkelsen, 1990b). This clearly shows that the NH$_{3(aq)}$ concentration at any NH$_4^+$-N concentration is an interactive result of various factors associated with the floodwater system.

2. Effect of Floodwater pH

Ammonium/ammonia equilibrium is governed by the pH of the medium. Since NH$_3$ volatilization is directly related to the concentration of aqueous NH$_3$ in floodwater, pH plays an important role in NH$_3$ loss. By considering the chemical equilibrium of NH$_4^+$/NH$_{3(aq)}$ in floodwater, it is possible to relate pH, the equilibrium constant, K, and the concentrations as shown in Eq. (7).
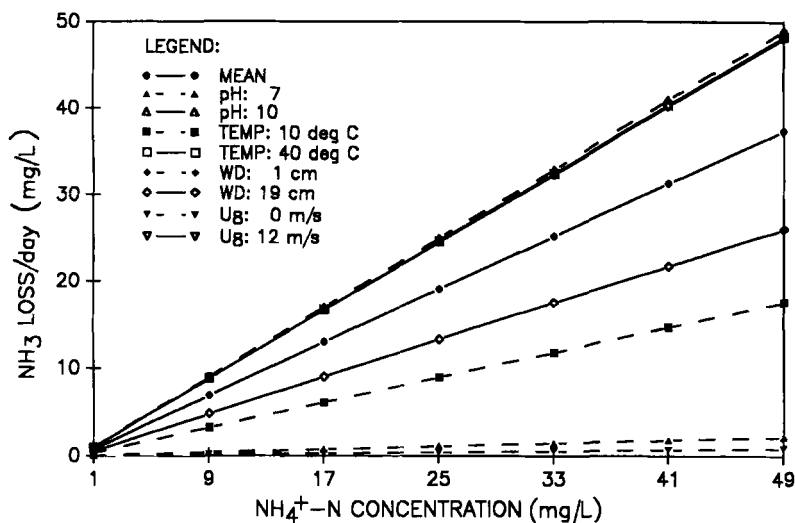
$$pH = pK + \log\frac{\alpha c}{(1 - \alpha)c} \tag{7}$$

Fig. 3. Effect of floodwater NH_4^+-N concentration on NH_3 volatilization. MEAN: pH, 8.5; TEMP (temperature), 25°C; WD (water depth), 10 cm; U_8 (windspeed at 8 m), 6 m/s. In other simulation runs, all other conditions are maintained constant at their mean values except for the listed variable.

and by rearranging, the fraction of $NH_{3(aq)}$ α in the system can be determined:

$$\alpha = \frac{10 \exp(pH - pK)}{1 + 10 \exp(pH - pK)} \qquad (8)$$

where pH is the pH of floodwater; and pK is $-\log K$.

The pK value is temperature dependent. Jayaweera and Mikkelsen (1990a) derived the following expression to compute pK as a function of absolute temperature.

$$pK(T) = 0.0897 + \frac{2729}{T} \qquad (9)$$

where pK(T) is $-\log K$, equilibrium constant for $NH_4^+/NH_{3(aq)}$ system at absolute Kelvin temperature T.

By substituting Eq. (9) into (8), they obtained the following expression to compute the fraction of NH_3 in solution as a function of pH and absolute temperature.

$$\alpha = \frac{10 \exp(pH - 0.0897 - 2729/T)}{1 + 10 \exp(pH - 0.0897 - 2729/T)} \qquad (10)$$
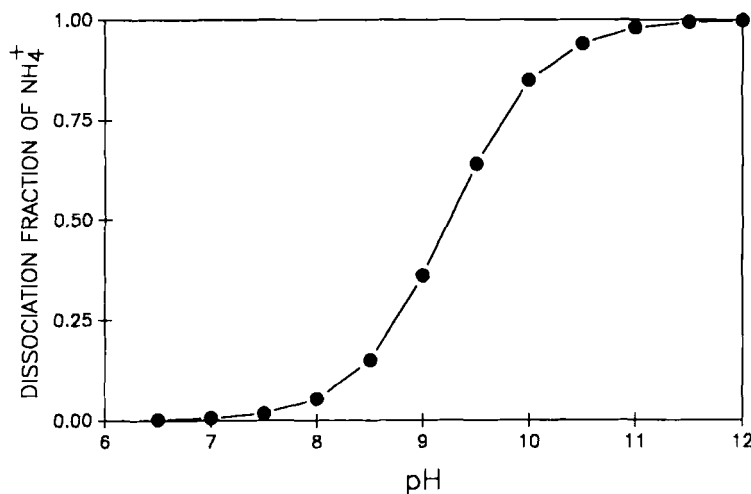
FIG. 4. Effect of pH on fraction of dissociation of NH_4^+. (From Jayaweera and Mikkelsen, 1990a.)

Figure 4 illustrates the effect of pH on the fraction of dissociation of NH_4^+ (Jayaweera and Mikkelsen, 1990a).

Numerous researchers have shown that floodwater pH has a tremendous impact on NH_3 volatilization (Vlek and Stumpe, 1978; Mikkelsen et al., 1978; Terman, 1979; Bouwmeester and Vlek, 1981a; De Datta, 1981; Vlek and Craswell, 1981; Ferrara and Avci, 1982; Pano and Middlebrooks, 1982; Denmead et al., 1982; Craswell and Vlek, 1983; Fillery et al., 1984; Fenn and Hossner, 1985; Fillery and Vlek, 1986; Jayaweera and Mikkelsen, 1990b). Fenn and Hossner (1985) reported that floodwater pH appears to be the primary contributing factor controlling NH_3 loss from flooded soils. Aqueous NH_3 in floodwater increases about tenfold per unit increase in pH in the range 7.5–9.0 (Vlek and Stumpe, 1978; Vlek and Craswell, 1981), permitting a high level of NH_3 volatilization, but when the pH value is 6.6 or less, there is no removal of NH_3 from a waste water stabilization pond (Pano and Middlebrooks, 1982). Bowmer and Muirhead (1987) reported the importance of pH by demonstrating the change in ratio of NH_3 to NH_4^+ from .056 to 5.6 (at 25°C) as the pH increases from 8.0 to 10.0.

Various models have been used to calculate NH_3 volatilization rates under different conditions such as pH. Bouwmeester and Vlek (1981a) suggested that the effects of pH, wind, and temperature on NH_3 volatilization are of the same order of magnitude. They further stated that for high pH ($> \sim 9$) the volatilization rate is controlled mainly by the transfer rate

in the liquid diffusion layer, and for low pH the volatilization rate is limited mostly by the NH_3 transfer rate in the air. Moeller and Vlek (1982) found a correlation between NH_3 loss and pH that is independent of the volatilization kinetics and this correlation was used experimentally to monitor the NH_3 volatilization. If sources of extraneous acids and bases are eliminated, the ammoniacal concentrations in solution can be determined by measuring pH. They used this method to gather volatilization data in a series of experiments.

Jayaweera and Mikkelsen (1990b), using their model, showed that an increase in solution pH increases the percentage of NH_3 loss per day (Fig. 5), as a result of an increase in $NH_{3(aq)}$ in floodwater. However, by changing other primary factors such as temperature, depth of floodwater, and windspeed, the NH_3 volatilization is varied. An increase in temperature from 10°C to 40°C increased both the $NH_{3(aq)}$ and volatilization rate constant for NH_3, k_{vN}, at various pH levels, thus increasing the NH_3 loss per day. Shallow water enhances NH_3 loss even at fairly low pH values due to the high volatilization rate constant. On the contrary, with increased water depth, NH_3 is significantly lost only at high pH values (Fig. 5). This shows
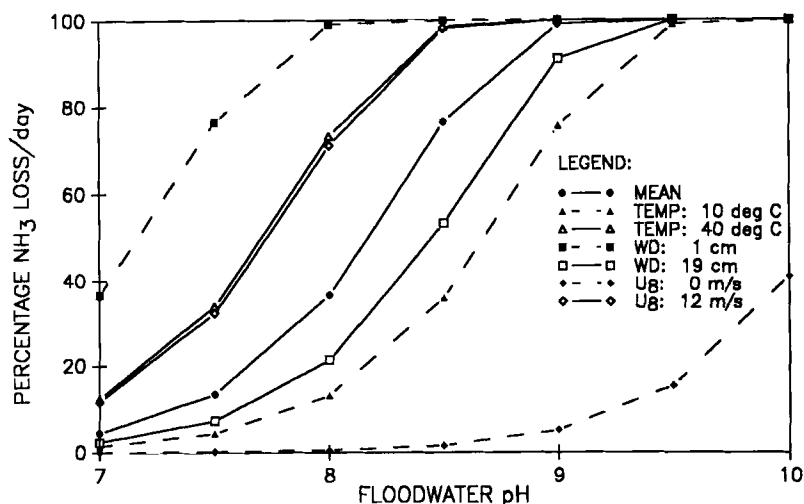

FIG. 5.   Effect of floodwater pH on NH_3 volatilization. MEAN: NH_4^+-N concentration in floodwater, 25 mg/L; pH, 8.5; TEMP (temperature), 25°C; WD (water depth), 10 cm; U_8 (windspeed at 8 m), 6 m/s. In other simulation runs, all other conditions are maintained constant at their mean values, except for the listed variable.

that even with high $NH_{3(aq)}$ concentrations in floodwater, volatilization can be controlled by low volatilization rate constants, which are achieved by increased water depth. They have further shown that the role of wind-speed is highly significant at various pH levels. At high pH values, NH_3 volatilization is maintained at low values as a result of low windspeed (Fig. 5) due to low volatilization rate constants.

3. Effect of Floodwater Temperature

Temperature affects the equilibrium constant of $NH_4^+/NH_{3(aq)}$ system (Bates and Pinching, 1949) and an increase in temperature of floodwater increases the equilibrium constant as shown by Jayaweera and Mikkelsen (1990a). Temperature also influences the Henry's law constant for NH_3, and using a mathematical model Jayaweera and Mikkelsen (1990a) computed the Henry's law constant for NH_3 as a function of floodwater temperature. The dependency of Henry's law constant on temperature for a particular gas–solvent system is well documented (Burkhard et al., 1985).

In the temperature range typical for tropical climates, NH_3 volatilization is increased by approximately 0.25% per 1°C increase in temperature, suggesting an exponential increase of NH_3 loss with temperature (Vlek and Stumpe, 1978; Terman, 1979). Vlek and Craswell (1981), however, found that at a given NH_4^+-N concentration, $NH_{3(aq)}$ concentration increases in proportion with increasing temperature, which suggests that temperature has an approximately linear effect on NH_3 volatilization.

Temperature influences the rate of NH_3 volatilization in the same order of magnitude as windspeed and pH (Bouwmeester and Vlek, 1981a). An increase in temperature increases the volatilization rate of NH_3 and the NH_3 loss per day (Fig. 6). The higher volatilization rate of NH_3 at high temperature is due to an increased floodwater $NH_{3(aq)}$ concentration and the volatilization rate constant for NH_3 (Jayaweera and Mikkelsen, 1990b).

As discussed in the theory for NH_3 volatilization, floodwater $NH_{3(aq)}$ concentration and the volatilization rate constant for NH_3 are influenced by the degree of dissociation and the Henry's law constant, respectively (Jayaweera and Mikkelsen, 1990b). They have shown that pH, depth of floodwater, and windspeed influence the NH_3 volatilization process by several orders of magnitude at various temperatures (Fig. 6). Floodwater pH controls the $NH_{3(aq)}$ concentration, while the water depth and windspeed control the volatilization rate constant for NH_3.
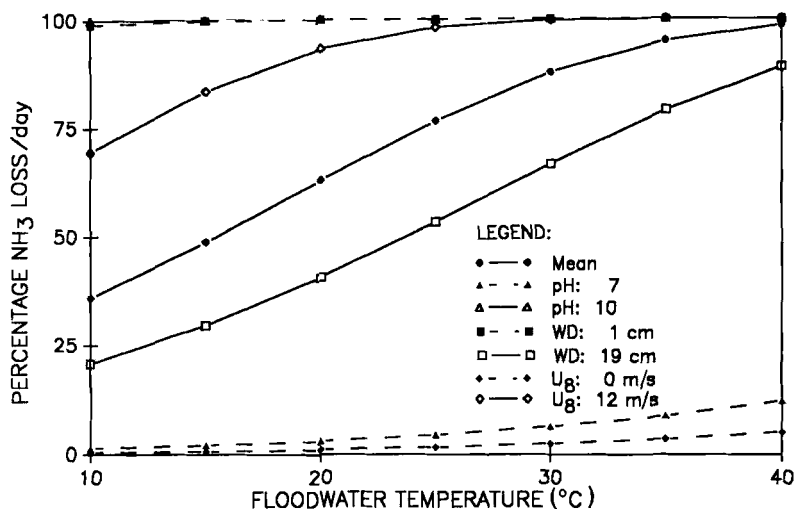
Fig. 6. Effect of floodwater temperature on NH$_3$ volatilization. MEAN: NH$_4^+$-N concentration in floodwater, 25 mg/L; pH, 8.5; TEMP (temperature), 25°C; WD (water depth), 10 cm; U$_8$ (windspeed at 8 m), 6 m/s. In other simulation runs, all other conditions are maintained constant at their mean values, except for the listed variable.

4. Effect of Water Depth

The role of depth of floodwater in NH$_3$ volatilization is twofold. Primarily it affects NH$_4^+$-ion concentration by virtue of its dilution effect. Further, it influences the volatilization relationships k_{vN} (Jayaweera and Mikkelsen, 1990a) that have not been addressed in previous research.

All transformations in an ecosystem, such as NH$_3$ transfer across the water–air interface, must obey the law of conservation of mass. To avoid any violation, therefore, it is important to consider the material balance of the system (Neely, 1980).

For interpretation, suppose there is a container of water, depth d, containing NH$_{3(aq)}$ which is volatilized from the surface via a first-order reaction process. By dimensional analysis, the material balance of this system can be determined as

$$\frac{dC_N}{dt} V = K_{ON} C_N A \tag{11}$$

where C_N is the NH$_{3(aq)}$ concentration in the solution, mol/L^3; V is the volume of the solution, L^3; A is the area of the surface, L^2; K_{ON} is the overall mass transfer coefficient for NH$_3$, L/t; L is the length; and t is the time.
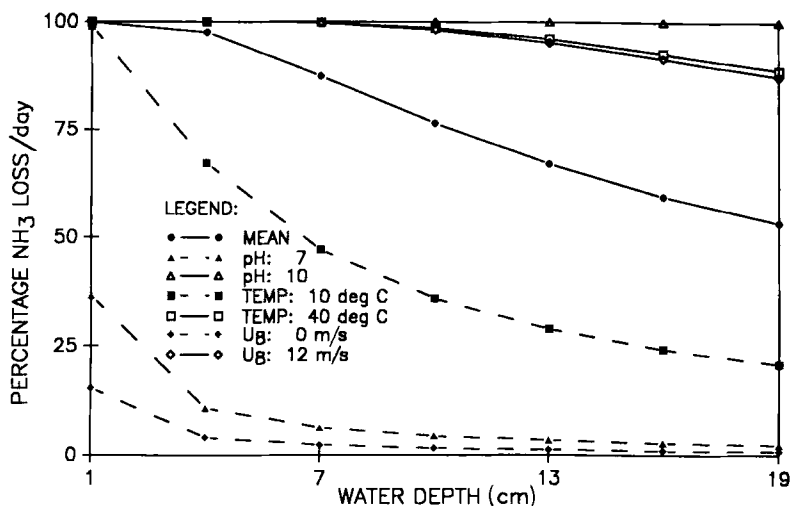
FIG. 7. Effect of floodwater depth on NH₃ volatilization. MEAN: NH₄⁺-N concentration in floodwater, 25 mg/L; pH, 8.5; TEMP (temperature), 25°C; WD (water depth), 10 cm; U₈ (windspeed at 8 m), 6 m/s. In other simulation runs, all other conditions are maintained constant at their mean values, except for the listed variable.

Dividing Eq. (11) by V yields

$$\frac{dC_N}{dt} = \frac{K_{ON}}{d} C_N \qquad (12)$$

where d is the depth of solution in the container.

The ratio K_{ON}/d is a first-order volatilization rate constant for NH₃, k_{vN}

$$k_{vN} = \frac{K_{ON}}{d} \qquad (13)$$

In the case of flooded systems, d represents the mean depth of flood-water. This relationship shows that the volatilization rate constant for NH₃ is inversely related to the depth of floodwater. The volatilization rate constant, k_{vN}, and the half-life, $t_{1/2}$ $(0.693/k_{vN})$ for NH₃ desorption are calculated as a function of floodwater depth by using the model developed by Jayaweera and Mikkelsen (1990a). An increase in depth of floodwater decreases the volatilization rate constant, k_{vN}, and increases the half life, $t_{1/2}$.

Using computer simulation runs, Jayaweera and Mikkelsen (1990b) showed that as the depth of floodwater increases from 1 to 19 cm, the volatilization rate of NH₃ loss per day decreases from 100 to 53% (Fig. 7). This is due to a decrease in volatilization rate constant, k_{vN} when other factors are maintained at constant values (NH₄⁺-N concentration,

25 mg/L; pH, 8.5; temperature, 25°C; and windspeed at 8 m height, 6 m/s). As shown in Fig. 7, at any particular water depth and at a constant NH_4^+-N concentration, an increase in pH, temperature, and windspeed increases the percentage of NH_3 loss and vice versa. It is interesting to note that, by managing the depth of floodwater, it is possible to modify NH_3 losses from flooded systems.

Thibodeaux (1979) showed the fraction of NH_3 desorbed with water depth for a small stream in southern Arkansas. For example, at pH 8.0 and temperature 60°F, nearly 90% of NH_3 is desorbed at 0.1 ft water depth, about 70% is lost at 0.5 ft, and around 20% of NH_3 is lost at a depth of 1 ft during the same duration of time. According to Thibodeaux, the volatilization of NH_3 from deep rivers is significantly lower than in small streams mainly because of water depth.

5. Effect of Windspeed

Kanwisher (1963) showed that at low windspeeds, there is little effect on the gas exchange rates until a critical value is reached. At this unique speed, the wind gets a better "grip" on the water surface. Cohen et al. (1978) also reported the importance of wind effect above a critical speed, and accordingly, above the critical speed, shear stress at the interface is large enough to set the interface and the liquid below in motion. Above the critical value, the exchange rate is supposed to increase as the square of the windspeed (Kanwisher, 1963). Broecker and Peng (1974) reported the same observations. Therefore, gusty winds may account for a large fraction of the exchange, even though they are only of short duration.

Water waves, created as a result of high windspeeds, tend to increase the interfacial area directly. However, Kinsman (1965) reported that wave height to wave length ratio is probably at most 0.143, and according to Cohen et al. (1978) this wave height to wave length ratio cannot account for more than a 4% increase in transfer rate.

Several researchers have shown that windspeed is an important environmental parameter in NH_3 volatilization. Fillery et al. (1986a) concluded that high windspeeds in the field promoted NH_3 loss and probably precluded any important N loss via nitrification–denitrification. Vlek and Stumpe (1978) reported that the relation between the loss of NH_3 from solution and the air exchange rate is curvilinear with a rapid increase in NH_3 volatilization at the lower flow rates that they tested. Several researchers observed a linear relationship between NH_3 loss and windspeed in field experiments (Fillery et al., 1984; Fillery and Vlek, 1986). Denmead et al. (1982) showed that NH_3 volatilization increased with the approxi-

mate square of windspeed in furrow irrigated maize, implying an exponential increase in NH_3 volatilization with windspeed. In a recent greenhouse study, Katyal and Carter (1989) reported that the relationship between airflow rate and NH_3 loss was logarithmic rather than linear in nature, and they concluded that this may be due to cooling of floodwater associated with high air flow rates.

These various relationships observed by researchers may be due to the variety of conditions that they encounter in their experiments. Jayaweera and Mikkelsen (1990b), by using model simulation runs, showed the effect of windspeed on NH_3 volatilization under various conditions (Fig. 8). They show clearly that the nature of the relationship changes tremendously depending on existing conditions. For example: at pH 10.0, all the NH_4^+-N in floodwater is lost at a windspeed as low as 2 m/s at 8 m height, compared to 12% loss at 12 m/s windspeed when the pH is 7.0. This illustrates that even with a high volatilization rate constant, if the $NH_{3(aq)}$ in floodwater is low, only a small amount of NH_3 is lost. Bouwmeester and Vlek (1981a), using their diffusion model found that at low windspeeds the volatilization rates are very small, and the gas-phase resistance dominates. However, with increasing windspeed the volatilization rates increase, and the liquid-phase resistance becomes more significant due to depletion of NH_3 in the
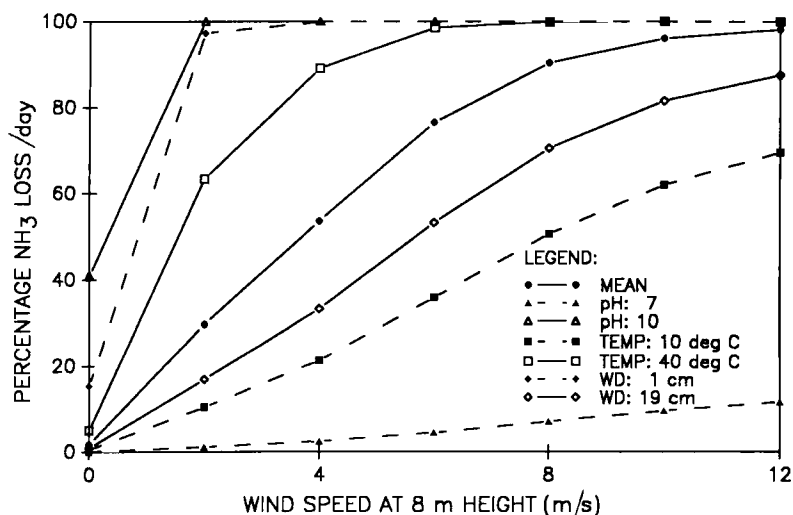

FIG. 8. Effect of windspeed on NH_3 volatilization. MEAN: NH_4^+-N concentration in floodwater, 25 mg/L; pH, 8.5; TEMP (temperature), 25°C; WD (water depth), 10 cm; U_8 (windspeed at 8 m), 6 m/s. In other simulation runs, all other conditions are maintained constant at their mean values, except for the listed variable.

surface film of the liquid phase. They reported that this shift from gas-phase resistance to liquid-phase resistance is more evident at high pH values.

Fillery and Vlek (1986) reported that there was a good fit ($R^2 = 0.90$) in the following relationship between the partial pressure of NH_3 (P_{NH_3}) in the floodwater and windspeed at 1.2 m (W_2) during the volatilization process.

$$F = k \, P_{NH_3} \, W_2 \tag{14}$$

where F is the flux of NH_3, and k is a constant.

Windspeed, however, influences the NH_3 volatilization process by virtue of its role on the volatilization rate constant (Jayaweera and Mikkelsen, 1990a,b). Other factors such as temperature, pH, and depth of floodwater, however, could vary the rate of volatilization depending on the conditions.

B. Secondary Factors Affecting Ammonia Volatilization

Secondary factors influence the primary factors in the process of NH_3 volatilization. Each primary factor is a function of several secondary factors. Thus, the NH_3 volatilization process is the overall result of numerous characteristics of soil, water, fertilizer management, and atmospheric conditions.

1. Effect of Secondary Factors on Floodwater NH_4^+-N Concentration

Ammonia volatilization is generally influenced most by the factors that influence the NH_4^+-N concentration in floodwater. Mikkelsen et al. (1978) showed that higher concentrations of NH_4^+-N in rice floodwater increased NH_3 volatilization losses. Nitrogen source, rate and method of application, soil CEC, biotic component such as urease activity, assimilation by algae, weeds, and rice, and immobilization by soil components are important secondary factors that influence NH_3 volatilization.

The source of fertilizer N plays an important role in determining the NH_4^+-N concentration in floodwater, thereby influencing the NH_3 volatilization. Urea is currently the most important fertilizer source in rice cultivation, followed by ammonium sulfate. Freney et al. (1985) reported that there is a worldwide move to use urea as the primary form of fertilizer N.

Urea is hydrolyzed by the urease enzyme to form $(NH_4)_2CO_3$ (Fenn and Hossner, 1985) and NH_4^+, whereas $(NH_4)_2SO_4$ provides NH_4^+ directly into

the system. The kinetics of urea hydrolysis in moist soils have given different results. Some researchers reported that urea hydrolysis is a first-order reaction with respect to urea concentration (Overrein and Moe, 1967; Sankhayan and Shukla, 1976). Recent studies, however, showed zero-order kinetics for urea hydrolysis (Sahrawat, 1980; Vlek and Carter, 1983). In flooded soils, Eriksen and Kjeldby (1987) reported that urea hydrolysis exhibited a zero-order reaction when urea super granules were point-placed at a 10-cm soil depth.

There are numerous reports comparing the effect of urea and $(NH_4)_2SO_4$ in NH$_3$ volatilization. When $(NH_4)_2SO_4$ is applied to puddled soil, Vlek and Stumpe (1978) observed nearly 11% of the N applied was lost as NH$_3$. Vlek and Craswell (1979), however, found a higher rate of loss (50% N applied) when urea is applied. These findings show that urea is more prone to N losses in flooded soils.

Recently, Fillery and De Datta (1986) reported NH$_3$ fluxes of up to 38 and 36% of the N applied from $(NH_4)_2SO_4$ and urea, respectively. In several other field studies, high losses of N have been detected following the application of urea and $(NH_4)_2SO_4$ (Craswell *et al.*, 1985; Katyal *et al.*, 1985; Vlek and Byrnes, 1986). These findings confirm the earlier reports of Mikkelsen *et al.* (1978) and Vlek and Craswell (1979), but contradict other studies (MacRae and Ancajas, 1970; Ventura and Yoshida, 1977; Wetselaar *et al.*, 1977; Freney *et al.*, 1981). These contradictions may be due to the differences in the alkalinity of various sources of water used to irrigate flooded rice (Vlek and Stumpe, 1978; Vlek and Craswell, 1979). Fillery *et al.* (1986b), however, in trying to explain these contradictions reported that alkalinity in floodwater as a result of evaporation and/or respiration contributed to the rapid loss of NH$_3$ following the application of $(NH_4)_2SO_4$ and urea to the floodwater.

Even though there may be the same amount of NH$_3$ loss from urea and $(NH_4)_2SO_4$, the pattern of loss differed between these fertilizers in an 8-day period. Several researchers detected NH$_3$ fluxes immediately after the application of $(NH_4)_2SO_4$ to flooded soils (Freney *et al.*, 1981; Fillery and De Datta, 1986; Fillery *et al.*, 1986b) and within 2–4 hours after the application of urea (Freney *et al.*, 1981; Simpson *et al.*, 1984; Fillery and De Datta, 1986; Fillery *et al.*, 1986b). Maximum NH$_3$ fluxes are generally observed immediately following the application of $(NH_4)_2SO_4$ (Mikkelsen *et al.*, 1978; Freney *et al.*, 1981; Fillery and De Datta, 1986; Fillery *et al.*, 1986b) or a few days after the urea application (Freney *et al.*, 1981; Fillery *et al.*, 1984, 1986b; Fillery and De Datta, 1986). The different pattern of NH$_3$ fluxes from urea and $(NH_4)_2SO_4$ were primarily due to the differences in the pattern of NH_4^+-N concentration in floodwater (Wetselaar *et al.*, 1977; Fillery *et al.*, 1986b).

There has been an interest in modifying the dissolution rate of urea by

coating the granules, adding chemical additives, by increasing the particle size of the granule, or formulation of controlled release materials.

Sulfur-coated urea (SCU), in particular, is known to be an effective N source for rice (De Datta and Gomez, 1981; De Datta et al., 1983; Flinn et al., 1984; Katyal et al., 1985; Buresh, 1987; Rao, 1987). Craswell et al. (1981) reported that NH_4^+-N concentrations in floodwater are much lower after basal incorporation of SCU than after urea applications.

Lac-coated urea (LCU), urea coated with shellac resin, however, was ineffective in reducing peak ammoniacal N levels or losses (Rao, 1987). Phosphate rock-coated urea (PRCU), an experimental material prepared by Madras Fertilizer Limited, Madras, India (Buresh, 1987), has been field evaluated with rice in India, and comparable rice yields for PRCU and urea have been reported (Singh and Yadav, 1985).

Guanyl urea sulfate (GUS) is a slowly mineralized source of N by microbial action under aerobic and anaerobic conditions (Davies, 1976; Ebisuno and Takimoto, 1981; Buresh, 1987). Ammonia formation and presumably loss were least for GUS according to Buresh (1987) who reported that the negligible NH_3 concentration in floodwater may be due to the slow mineralization and acidifying effect of GUS.

Urea phosphate, which is known to produce an acidifying effect and to reduce loss of urea N as NH_3 (Bremner and Douglas, 1971a; Stumpe et al., 1984), failed to reduce pNH_3 under flooded condition due to the stimulation of algal photosynthetic activity by added P (Buresh, 1987).

Urea-forms, which are condensation products of urea and formaldehyde, were less prone to NH_3 loss than urea in a greenhouse study with rice (Carter et al., 1986) and in a field study (Buresh, 1987). This may be due to the slow release of N from urea forms through microbial action (Corke and Robinson, 1966).

Rao (1987) reported that urea supergranules (USG), spherical granules of 1 g each, reduced the peak NH_4^+-N levels to <2 g/m^3 and N losses to 3.9%. Eriksen and Kjeldby (1987) reported that NH_3 volatilization was noticeably reduced by the surface application of urea calcium nitrate (UCN) on flooded soil as compared with USG. According to them, the total N loss from USG after 30 days was 17% of applied urea, but when the same amounts of urea and nitrogen were applied as UCN this loss was reduced to 3% and 6%, respectively.

Rate of N application obviously should control the amount of NH_4^+-N that comes into the floodwater. Vlek and Craswell (1979) reported that reduced N application rates reduced NH_3 volatilization by lowering the level of NH_4^+-N in floodwater. MacRae and Ancajas (1970), in a laboratory study, found that an increased application of both $(NH_4)_2SO_4$ and urea resulted in increased losses of NH_3 through volatilization. Fenn and Hossner (1985) reported the same.

Method of N fertilizer application influences the ammoniacal N concentration in floodwater (Fillery *et al.*, 1984) and therefore plays an important role in NH_3 volatilization. Basically, there can be three ways of applying fertilizer N to flooded soils: (1) broadcast application; (2) broadcast and incorporation; and (3) deep placement. Broadcast applications can be done in several different ways. They are: broadcast as a basal dose, broadcast as a top-dressing at different stages of crop growth, or broadcast and incorporate the fertilizer material into the soil. Deep placement is a practice that places the fertilizer in the reduced layer of the flooded soil so that the concentration of urea and NH_4^+ in floodwater remains essentially zero. This can be done in several ways, namely soil injection, mud ball placement, drill placement, band placement, or point placement.

In the last decade, there have been numerous papers published on aspects of N fertilizer management. Mikkelsen *et al.* (1978) reported considerable losses of NH_3 when urea and $(NH_4)_2SO_4$ were applied directly to floodwater, but less than 1% of the total N applied was volatilized when N fertilizer was placed at a depth of 10–12 cm. In a paper presented at the 14th International Congress of Soil Science, Kyoto, Japan (August 12–18, 1990), Rolston and his co-workers in a simulation study showed that the amount of NH_3 volatilization is affected by windspeed for the cases of NH_4^+-N fertilizer applied to the floodwater and incorporated into the soil (Fig. 9) (Rolston *et al.*, 1990). Deep placement reduces the NH_3 volatilization largely by reducing the NH_4^+-N level in floodwater. Vlek and Craswell (1979), MacRae and Ancajas (1970), Fillery *et al.* (1984), and Ericksen *et al.* (1985) reported the same.

Uniform placement of prilled urea and point placement of urea super granules have given low total N (urea + NH_4^+-N) concentration in floodwater and demonstrates that these methods can be used to reduce N losses in lowland rice production (Cao *et al.*, 1984).

The highest concentrations of NH_4^+-N and highest level of NH_3 have been detected when urea or $(NH_4)_2SO_4$ was applied to floodwater 2–4 weeks after the transplanting Fillery *et al.*, 1984, 1986b). Rao (1987) found the highest concentrations of NH_4^+-N in floodwater and NH_3 loss when granular urea was applied wholly as a basal dose.

Higher total N concentration in floodwater was recorded after split application (2/3 basal-broadcast and incorporated, and 1/3 top-dressed, 5–7 days before panicle initiation) than in band placement of urea, indicating greater potential for NH_3 volatilization (Cao *et al.*, 1984). Rao (1987), however, reported that a split urea application (1/2 at transplanting, 1/4 each at 21 days and 42 days after transplanting of rice) reduced peak NH_4^+-N levels and NH_3 volatilization losses. The differences in their conclusions may be due to timing and amount of split application. The observations of Cao *et al.* (1984), however, show that substantial N
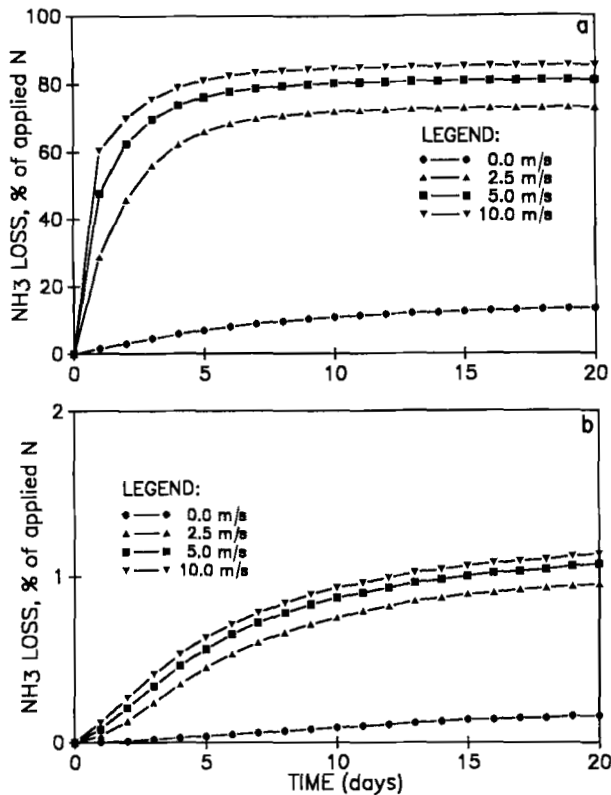
FIG. 9. Ammonia volatilization as affected by windspeed under two different fertilizer managements: (a) NH_4^+-N fertilizer applied to floodwater; and (b) NH_4^+-N fertilizer incorporated into soil. Water depth and pH are constant at 5 cm and 8.5, respectively. (Adapted from Rolston *et al.*, 1990.)

losses can still occur when N is broadcast and incorporated before transplanting.

Draining the floodwater from the soil and incorporating urea before transplanting reduced the extent of N loss (Fillery *et al.*, 1986a). Cao *et al.* (1984) also reported reduced losses and high ^{15}N recovery following a thorough incorporation of urea. However, high concentrations of NH_4^+-N are found in floodwater (Craswell *et al.*, 1981; Cao *et al.*, 1984) and substantially lower ^{15}N recoveries have been reported when incorporation is attempted without first removing the floodwater (Cao *et al.*, 1984; Craswell *et al.*, 1985). Therefore, it appears necessary to drain the floodwater from puddled soils before the application of urea if high N crop efficiency is to be achieved without deep placement of fertilizer (Fillery *et al.*, 1986a). It

is interesting to note that Buresh (1987) reported that thorough incorporation of GUS and SCU is not necessary to prevent NH_3 loss.

With all this information, it is easy to conclude that with fertilizers such as urea and $(NH_4)_2SO_4$, deep placement reduces NH_3 volatilization, and applying ammoniacal N fertilizer into floodwater can lead to large losses of gaseous N. Nonetheless, Asian farmers still frequently broadcast N fertilizer without subsequent incorporation into the soil (Mikkelsen *et al.*, 1978; De Datta, 1981). This practice may occur because small-scale farmers prefer to apply their fertilizer only after the crop is established and broadcast application is the only mode of application at that time (Freney *et al.*, 1985).

Cation exchange capacity (CEC) of a soil affects the retention capacity of a soil for cations. CEC could potentially affect NH_4^+ concentration in floodwater, which indirectly influences the extent of NH_3 loss (Vlek and Craswell, 1979; Freney *et al.*, 1983). Several researchers have found an inverse relationship of NH_3 volatilization to CEC of the soil (Overrein and Moe, 1967; Matocha, 1976; Fenn and Kissel, 1976; Fenn *et al.*, 1982; Fenn and Hossner, 1985; Mikkelsen, 1987). Recently, however, Eriksen and Kjeldby (1987) found low NH_3 loss from urea super granules in a soil with low CEC. Fleisher *et al.* (1987) in a model of NH_3 volatilization from calcareous soils reported that most NH_3 loss is due to the interactive effect of high soil pH and low CEC.

Because of the dynamic nature of soil CEC, it is easy to understand why there is no consistent agreement among researchers regarding the relationship of CEC to NH_4^+ retention.

Biotic activity in a flooded rice ecosystem could have a dominant role in controlling the NH_4^+ concentration in floodwater. Urease activity (Freney *et al.*, 1983; Mikkelsen, 1987), assimilation of NH_4^+-N by algae, weeds, and rice plant (Craswell *et al.*, 1985), and immobilization of N in the soil (Freney *et al.*, 1983) could control the NH_3 volatilization by influencing the NH_4^+ concentration.

As mentioned earlier, urease activity could follow zero-order or first-order kinetics (Overrein and Moe, 1967; Sankhayan and Shukla, 1976; Sahrawat, 1980; Vlek and Carter, 1983; Eriksen and Kjeldby, 1987). Depending on the degree of urease activity, urea can provide NH_4^+ to the flooded system. According to Fenn and Hossner (1985), NH_3 loss from flooded soils is favored by urease activity.

There have been many attempts to control the reaction rate of urease with metabolic inhibitors (Bremner and Douglas, 1971b) using toxic heavy metals and organic compounds. Vlek *et al.* (1980) showed that phenyl phosphodiamide (PPD), added at a rate of 2% (w/w) delays the appearance of NH_3 in floodwater after broadcasting urea. Application of PPD (1%

w/w) with urea inhibited urease activity for up to 3 days in a field study (Fillery and De Datta, 1986; Fillery et al., 1986c). Fillery et al. (1986c) suggested that the effect of PPD on NH_3 volatilization is largely a function of the delay in the buildup of NH_4^+-N in the floodwater and not as a result of delaying the increase in pH of floodwater as suggested by Byrnes et al. (1983). Byrnes et al. (1983) showed that PPD (1% w/w) inhibited urease activity for up to 11 days. These differences may be due to the variations in the rate of degradation of PPD under various conditions. Austin et al. (1984) showed that PPD degradation is highly dependent on pH and temperature.

From these observations it is clear that PPD seems to decompose rapidly in flooded soils. Therefore, more effective urease inhibitors are needed to minimize the accumulation of NH_4^+-N in floodwater to reduce NH_3 volatilization after urea application (Fillery and Vlek, 1986).

Nonetheless, controlling NH_3 loss by inhibiting urease enzyme is a worthy effort, but the ultimate urease inhibitor, however, should be specific to urease, inexpensive, effective in low concentrations, and should not pollute the environment.

Craswell et al. (1985) have shown that a significant quantity of ^{15}N (15% N applied) can be detected in algae and weeds after 2 weeks of urea application. This may reduce NH_3 loss by virtue of low NH_4^+-N concentration in floodwater. Craswell et al. (1981) found low NH_3 loss when N fertilizer is applied when root systems are well developed.

2. Effect of Secondary Factors on Floodwater pH

Floodwater pH is the resultant interaction of several properties including concentration of dissolved CO_2 and NH_3, biotic activity, alkalinity, pH buffering capacity, and temperature (Keeney and Sahrawat, 1986). These floodwater properties are influenced by other practices such as fertilizer management, water quality, and the stage of crop development (Mikkelsen et al., 1978).

Ponnamperuma (1978) reported that the pH of floodwater is largely a function of CO_2 concentration and HCO_3^- activity.

$$pH = 7.85 + \log (HCO_3^-) - P_{CO_2} \qquad (15)$$

Constant removal of CO_2 may increase the pH and addition of CO_2 may decrease the pH of floodwater. Mikkelsen et al. (1978) found a relationship between floodwater pH and the biotic activity. They observed a diurnal change in pH, which appears to be synchronized with the cycle of photosynthesis and respiration. They reported pH values as high as 9.5–10.0 by

midday and decreasing as much as 2–3 pH units during the night (Fig. 10). Several others reported the biotic influence on floodwater pH (Park *et al.*, 1958; Mikkelsen and De Datta, 1979; Craswell *et al.*, 1981; Morel, 1983; Fillery *et al.*, 1984). It is interesting to note that Bowmer and Muirhead (1987) were able to dampen the diurnal fluctuation in pH for 6 days, and significantly increased the ammoniacal N concentration in floodwater by using a photosynthetic inhibitor, terbutryne [2-(*tert*-butylamino)-4-(ethyl-amino)-6-(methylthio)-S-triazine].

Bouldin (1986) summarized the sequence of events that happens during the day. Photosynthesis depletes CO_2, increases pH, and increases partial
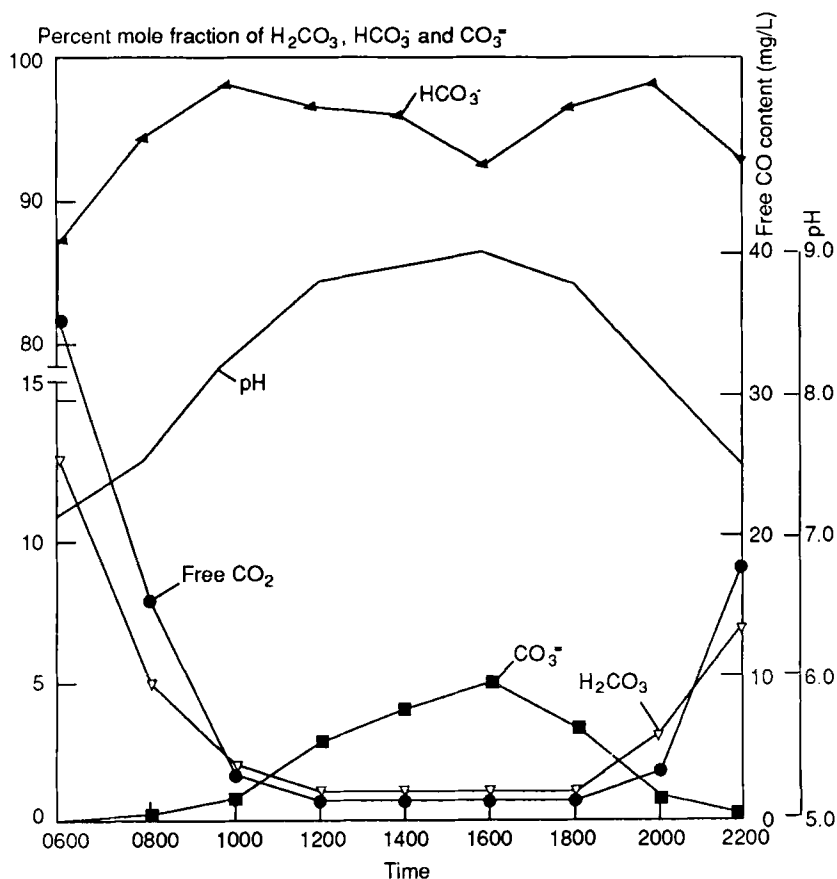

FIG. 10. Changes in the pH and components of the carbonic acid system of rice flood-water 3 days after application of N fertilizer on Maahas clay, Los Baños, Philippines, 1976 wet season. (From Mikkelsen *et al.*, 1978.)

pressure of NH_3. Therefore, NH_3 volatilization is increased during the day. At night, as respiration supplies CO_2, the sequence of events are reversed and the NH_3 volatilization is decreased.

Fillery *et al.* (1986b) reported that the algal enumerations in their study showed relatively low algal biomass. Nevertheless, they observed large fluctuations in pH of floodwater. This study shows that large algal populations are not required to increase floodwater pH to high values that support rapid NH_3 loss. Growth of algal biomass, however, is not a limitation in most rice growing ecosystems. Pantastico and Suaya (1974) reported that algal biomass is often regarded as a problem in rice floodwater in the Philippines. In Australia, large populations of diatoms and other algae sometimes smother the young rice seedlings (Dunigan and Hill, 1977), while in Bengal at least 1 million ha of transplanted rice are infested with stonewarts (Mukherji, 1968).

The alkalinity of water is a measure of its capacity to accept protons. In natural waters, the alkalinity is generally established by the concentration of HCO_3^-, CO_3^{2-}, and OH^- ions. Other species, such as NH_3, silicates, borates, and phosphates in natural waters may also contribute to the alkalinity of the system. Alkalinity and acidity are interrelated. Basically, acidity and alkalinity are a good measure of the buffering capacity of a given system.

Ammonia volatilization is an acidifying process due to the release of H^+ to the system. If there is no alkalinity in the floodwater, the pH may decrease and thereby reduces NH_3 volatilization. According to Vlek and Stumpe (1978), to sustain NH_3 volatilization, alkalinity (chiefly HCO_3^-) must be present in floodwater to buffer the production of H^+.

Several sources may provide alkalinity to floodwater. In Asia, artesian or ponded water is chiefly used as the irrigation source for dry-season rice crops (Stangel, 1979) and it may provide sufficient alkalinity to buffer the system. Vlek and Craswell (1981) reported that sufficient alkalinity can be found in areas with calcareous soils or when soils are irrigated with alkaline well waters. When N forms such as $(NH_4)_2SO_4$ or $(NH_4)_2HPO_4$ are used, irrigation water is probably the major source of alkalinity in floodwater systems (Fillery and Vlek, 1986). However, Fillery *et al.* (1986b) reported that regardless of the quality of irrigation water applied at the time of fertilizer application, the alkalinity in the floodwater can increase through evaporation or other processes. This highlights the likelihood that many flooded rice fields in Asia could contain an adequate quantity of alkalinity with modest rates of NH_3 loss from NH_4^+-N.

Urea hydrolysis produces HCO_3^- that can buffer H^+ production when urea is used as the fertilizer. Therefore, NH_3 loss from urea is less dependent on inherent alkalinity (Vlek and Craswell, 1981). Ammonium sulfate

application, on the other hand, will lead to NH_3 volatilization only if the aqueous system is alkaline (Vlek and Stumpe, 1978).

As discussed before, the various differences that had been reported (MacRae and Ancajas, 1970; Wetselaar *et al.*, 1977; Ventura and Yoshida, 1977; Mikkelsen *et al.*, 1978; Vlek and Craswell, 1979; Freney *et al.*, 1981; Craswell *et al.*, 1985; Katyal *et al.*, 1985; Fillery and De Datta, 1986; Fillery *et al.*, 1986b; Vlek and Byrnes, 1986) in NH_3 fluxes for $(NH_4)_2SO_4$ and urea may be due to the degree of buffering capacity in floodwater as a result of alkalinity in the system.

Fertilizer management and the stage of crop development influence the magnitude of diurnal fluctuations in pH of floodwater, presumably because of their effect on the algal biomass (Mikkelsen *et al.*, 1978).

Terman (1979) reported that both N and P fertilizer contribute to algal bloom accompanied by higher water pH. Urea phosphate fertilizers promoted rapid algal growth immediately following either basal incorporation or broadcast application into floodwater (Buresh, 1987). He suggested that this elevation in pH was apparently due to the stimulation of algal photosynthetic activity by added P, and it may explain the failure of a phosphoric acid amendment to urea (urea phosphate) in reducing pNH_3.

Fillery *et al.* (1986b) observed the effect of stage of crop development on the diurnal fluctuation of pH in floodwater. According to them, the diurnal fluctuations in floodwater pH were lower when urea was added 5–7 days before panicle initiation. This effect probably resulted from lower photosynthetic rates in the floodwater, since the crop canopy was appreciably more dense in the fertilized areas that had earlier received the urea 14 or 21 days after transplanting. Fillery *et al.* (1984) also detected low rates of NH_3 loss after urea was applied to flooded rice at the panicle initiation stage. According to them, aside from N uptake, it appeared that the rice crop shaded floodwater and thereby suppressed the increased pH attributed to photosynthetic activity in floodwater.

Ventura and Yoshida (1977) reported that NH_3 volatilization in flooded soil increased markedly with an increase in soil pH, which implies that soil pH has some effect on floodwater pH. MacRae and Ancajas (1970) reported the same. Vlek and Craswell (1979), however, showed that soil pH has little effect on the pH of floodwater and therefore on NH_3 volatilization.

3. Effect of Secondary Factors on Floodwater Temperature

The secondary factors that influence the temperature in floodwater have an influence on the overall NH_3 volatilization process. Temperature of

floodwater seems to be a function of solar radiation, windspeed, relative humidity, water depth, plant cover, and suspended materials in flood-water.

The solar energy is received by the waterbody in the form of short-wave radiation. A fraction of incoming solar energy is returned to space by reflection/scattering as short-wave radiation. The fraction that is returned from incoming solar radiation is known as albedo. It is interesting to note, the albedo of a natural water surface, about 6%, is the lowest of any natural surface (Hasse and Dobson, 1986). According to them, heat storage is quite different for water versus solid surfaces. In water, part of the solar energy may penetrate to several meters depth, although strong surface (0–10 cm) heat stratification usually occurs in flooded rice. In water, the turbulent motions may distribute the heat absorbed in the uppermost few centimeters throughout a deeper layer. Therefore, water surface tempera-tures respond only slowly compared to land surface temperatures. Leu-ning *et al.* (1984), however, found that thermal stratification in turbid floodwater significantly influenced rates of NH_3 loss. This may be due to a reduction in incoming solar radiation caused by suspended materials in floodwater. This shows that solar radiation, water depth, and suspended materials influence the temperature of floodwater.

Atmospheric conditions, such as windspeed and relative humidity, in-fluence the evaporation of water from a free water surface. Floodwater temperature decreased by 3°C to 15°C when airflow rate was increased from 5 to 20 L/min. Lowering of temperatures with increasing airflow rate was due to an acceleration in evaporative cooling (Katyal and Carter, 1989).

4. Effect of Secondary Factors on Water Depth

Water depth is usually a function of supply and crop management prac-tice. In irrigated agriculture, the farmer has the ability to control the water depth according to crop cultural needs. However, in rainfed agriculture during the wet season, intensity and duration of rainfall partially determine the depth of floodwater. Therefore, the depth of water can or cannot be controlled depending on the season, site, and the crop situation.

5. Effect of Secondary Factors on Windspeed

When there is a crop canopy, the effect of wind on the water surface becomes minimized. Therefore, the structure of the crop canopy is an

important secondary factor that influences the effect of windspeed on the water surface. The crop canopy also exerts a strong influence on the photosynthetic rates of the aquatic biota, which limits their effects on the water chemistry. Low rates of NH_3 loss (10–15% of the N applied) were detected after urea was applied in flooded rice at panicle initiation (Fillery *et al.*, 1984) and they concluded that dense plant canopy at panicle initiation may have restricted air exchange at the floodwater interface to minimize NH_3 volatilization.

V. METHODS OF MEASURING AMMONIA VOLATILIZATION

There are various methods available to measure NH_3 volatilization from flooded systems. These include: (1) the enclosure methods with or without air exchange; (2) micrometeorological techniques; and (3) labeled tracer techniques. The methodology used generally influences the conclusions of a study and each of these methods has its own advantages and disadvantages. There are several excellent reviews on the methodologies used in NH_3 volatilization measurements (Terman, 1979; Vlek and Craswell, 1981; Fenn and Hossner, 1985; Fillery and Vlek, 1986; Harper, 1988).

Enclosure methods are most commonly used in NH_3 volatilization measurements (Denmead, 1983). There are a variety of enclosure designs that are used to measure NH_3 losses (Harper, 1988). These methods are simple and convenient, and can be used successfully to evaluate NH_3 losses under a variety of experimental variables. The disturbance of natural conditions, however, make the interpretations of these measurements somewhat questionable in terms of actual field conditions.

Micrometeorological techniques, on the other hand, have an advantage in that they do not disturb the natural environment conditions that influence NH_3 volatilization. They provide an average integrated flux over a large area, which minimizes the sampling variability. These techniques, however, are difficult to use in practice as they are costly in instrumentation, are laborious, and are site specific and weather dependent in their application to the experimental area. There are three general types of micrometeorological methods: (1) eddy correlation; (2) gradient diffusion; and (3) mass balance (Harper, 1988).

Labeled tracer N has also been used to calculate NH_3 loss. This is an indirect measurement and consequently, all other transformations including nitrification, denitrification, runoff, leaching, and plant uptake must be precisely determined to provide meaningful values for NH_3 volatilization. As stated by Harper (1988), ^{15}N balance cannot be used to evaluate NH_3

loss from flooded soils since NH_3 volatilization and nitrification–denitrification proceed simultaneously with the addition of N to the soil.

VI. MODELS FOR PREDICTING AMMONIA VOLATILIZATION

Assessments of NH_3 volatilization can be made by understanding the system represented by a simplified model. The behavior of NH_4^+-N in flooded soil systems and the mass transfer of NH_3 across the water–air interface is a dynamic process, however, involving numerous interactions. In an NH_3 volatilization model it is vital to understand the various chemical and physical processes controlling the emission rates. Few models have been developed to predict NH_3 losses as a function of floodwater chemistry and atmospheric conditions (Bouwmeester and Vlek, 1981a; Moeller and Vlek, 1982; Jayaweera and Mikkelsen, 1990a).

A. Basic Models in Mass Transfer

When there are two phases, the mass transfer of diffusing solute takes place from the bulk fluid of one phase into the interface, and then from interface to the bulk of the second phase. The concentration of the diffusing solute is virtually constant in the bulk fluid of both phases as a result of mixing caused by turbulence. Near the interface, in the boundary layer, the turbulence diminishes, resulting in a concentration gradient as the interface is approached and the mass flux experiences a resistance due to the mechanism of diffusion. Experimental verification of the conditions at or around the interface is difficult to achieve. Therefore, to understand the mass transfer in the interface region, it is necessary to develop theoretical models and validate these with overall mass-transfer experiments.

Few basic hydrodynamic models have been presented in the literature to describe mass transfer across a gas–liquid interface. All these models represent a simplified mode of mass transfer. The mass transfer between two phases is described by three major models: (1) film model; (2) penetration theory (Higbie's model); and (3) penetration theory (Danckwerts's model).

1. Film Model

The first hydrodynamic model to describe the transport processes between two phases was the two-film model by Whitman in 1923 (see Fig. 1).

He suggested that the resistance to transfer in each phase is confined in a thin stagnant, or laminar-flow film close to the interface between the two phases, in which the fluid is turbulent. This film is assumed to have a definite but unknown thickness. The mass transfer across these films is regarded as a steady-state process of molecular diffusion and it is assumed that there is no convection in the film.

2. Penetration Theory: Higbie's Model

Higbie (1935) proposed a model to describe the hydrodynamic conditions in the liquid phase close to a gas–liquid interface. He suggested that the eddies in the fluid bring an element of fluid to the interface where it is exposed to the second phase for a definite interval of time, after which the surface element is mixed with the bulk again. Therefore, the fluid element where initial composition corresponds with that of the bulk fluid is remote from the interface, which is suddenly exposed to the second phase. This model considers the liquid surface to be composed of a large number of small elements that are being replaced by fresh elements from the bulk of the phase after a fixed time period. As the fresh liquid elements continually replace those interacting with the interface, the mass transfer is accomplished by the systematic removal of the interface.

The exposure time of such fluid elements at the interface is so short that steady-state conditions do not develop, and any mass transfer of material takes place only as a result of unsteady-state molecular diffusion.

3. Penetration Theory: Danckwerts's Model

Danckwerts (1951) improved the surface renewal model proposed by Higbie, suggesting that the fluid element can have a variable surface residence time, which is exposed to the second phase; it may vary from zero to infinity. This means that each fluid element of surface would not be exposed for a constant time period as proposed by Higbie, but rather a random distribution of times could exist. This refinement of the surface renewal model is a result of an assumption that the probability of an element of surface being destroyed and mixed with the bulk fluid was independent of how long it has been on the surface.

All three models share the feature that the rate of mass transfer is directly proportional to the concentration difference. In many instances the difference between predictions made on the basis of these three models will be less than the uncertainties about the values of the physical quantities used in the calculations, and, therefore these models can be regarded

as interchangeable for many purposes. It is merely a question of convenience concerning which of the three models is used. When numerical computations are involved, it is generally simple to use Higbie's model rather than Danckwerts's model to compute the rate of transfer per unit area of the interface. The computations relating to the film model are, of course, simpler since they involve ordinary rather than partial differential equations. In most cases, however, the film model would lead to almost the same predictions as the surface renewal models (Danckwerts, 1970).

B. Bouwmeester and Vlek Ammonia Volatilization Model

The NH_3 volatilization model developed by Bouwmeester and Vlek (1981a) has a resemblance to the penetration theories of Higbie and Danckwerts. Major difference in their analysis, however, is that the surface liquid element has a known time of exposure to the atmosphere, depending on the wind velocity and the location of the element in the rice paddy.

By considering the following chemical reaction

$$NH_4^+ \overset{k_1}{\underset{}{\rightleftharpoons}} NH_3 + H^+ \tag{16}$$

where k_1 and k_2 are the forward and reverse rate constants, Bouwmeester and Vlek (1981a) developed the following relationship to calculate the average NH_3 volatilization rate per unit area, $\overline{Q}$.

$$\overline{Q} = \frac{\overline{AN}}{\beta t_d} \left(\exp(\beta^2 D t_d) \, \text{erfc} \, \beta \sqrt{D t_d} - 1 + \frac{2}{\sqrt{\pi}} \beta \sqrt{D t_d} \right) \tag{17}$$

where $\overline{AN}$ is the ammoniacal N concentration in the bulk liquid; and $t_d = F/U_d$ is the time during which the water chemistry, wind, and water conditions are supposed to remain steady depending on the fetch, F, and surface drift velocity, U_d; and

$$\beta = k_a k_H / D(1 + R) \cdot \tag{18}$$

where k_a is the bulk transfer coefficient of NH_3 in air, k_H is the Henry's constant, and D is the molecular diffusivities; and

$$R = (H^+ \, k_2/k_1) = (H^+/K) \tag{19}$$

where H^+ is the hydrogen ion concentration in the system, and K is the equilibrium constant.

Equation (17) includes the effect of ammoniacal N concentration, pH,

temperature, wind, and fetch on the process of NH_3 volatilization. The temperature effects are reflected in the coefficients, D, k_H, and R.

In developing the model, Boumeester and Vlek (1981a) assumed that for the time (t_d) when the liquid element is at the surface, the chemical reaction does not change the pH. Hoover and Berkshire (1969) in studying the CO_2 exchange across an air–water interface also applied the same concept. They made this assumption because of the high mobility of the hydrogen ion. They argued that as the hydrogen ions have eight times the mobility of the bicarbonate ions, there would be no possibility of building up a significant concentration gradient. Therefore, the ratio NH_3/NH_4^+ is constant throughout the diffusion layer with spectator ions maintaining the electroneutrality.

Bouwmeester and Vlek (1981a) validated the model in a wind–water tunnel experiment, which simulated the flooded rice paddies. Considering the complexity of the physical and chemical processes, they reported that the validation study seems to support the numerous assumptions made in developing the basic model equation in NH_3 volatilization. Although the quantitative agreement is not fully satisfactory, the results suggest that the mathematical model may be applied to analyze the rate-controlling factors of NH_3 volatilization from rice paddies.

By simulations they found that the rate of NH_3 volatilization is increased with increasing NH_4^+-N concentration, pH, temperature, and wind velocity but is decreased with increasing fetch. The results suggest that the effects of wind, temperature, and pH on NH_3 volatilization are of the same order of magnitude. At a high pH, the volatilization rate of NH_3 is controlled by the transfer rate in the liquid diffusion layer and the effect of high windspeed is reduced. At low pH, the volatilization rate is limited mostly by the NH_3 transfer rate in the air.

C. Moeller and Vlek Ammonia Volatilization Models

Moeller and Vlek (1982) developed two mechanistic models, the pH constant model, and the pH gradient model, for the transport of NH_3 from aqueous solution to the atmosphere. These models are adaptations of the stagnant-film model used in studying gas exchange across an air–water interface (Danckwerts, 1970; Liss, 1973).

Considering Fick's first law of diffusion, and integrating over the thickness of the gas and liquid phase films, they obtained the following equations for the ammonia flux.

$$J_g = \frac{D_g}{\delta_g} ([NH_3]_g^o - [NH_3]_g^b) \tag{20}$$

where J_g is the NH_3 flux in the gas phase, D_g is the diffusion coefficient of NH_3 in air, δ_g is the thickness of the gas film, and the superscripts b and o designate the bulk and surface concentrations or activities.

$$J_l = \frac{D_l}{\delta_l} (a^b{}_{AN} - a^o{}_{AN}) \tag{21}$$

where J_l is the total ammoniacal flux in the liquid phase, D_l is the diffusion coefficient for NH_4^+ in aqueous solution, δ_l is the thickness of the liquid film, and a_{AN} is the total ammoniacal activity

$$a_{NH_3} + a_{NH_4^+} = (1 + a_{H^+}/K_1) a_{NH_3} \tag{22}$$

where K_1 is the equilibrium constant for NH_4^+/NH_3 system.

At steady-state condition, when the diffusion flux through the liquid equals that through the gas, they obtained the following expression by equating the right-hand sides of Eqs. (20) and (21) and expressing the ammonical nitrogen activity at the surface in terms of H^+, K_1 and a_{NH_3}.

$$\frac{\delta_l D_g}{D_l \delta_g} ([NH_3]_g^o - [NH_3]_g^b) = a^b{}_{AN} - (1 + a^o{}_{H^+}/K_1) a^o{}_{NH_3} \tag{23}$$

The δ_g and δ_l parameters are determined experimentally. However, to solve for $a^o{}_{NH_3}$ to calculate the flux using Eq. (21), it is necessary to determine three independent variables, $[NH_3]_g^b$, $a^o{}_H^+$, and $[NH_3]_g^o$. Therefore, they obtained three additional relationships.

By assuming that the instantaneous steady-state flux is known, they obtained the following relationship to calculate $[NH_3]_g^b$.

$$[NH_3]_g^b = JA/S \tag{24}$$

where A is the surface area of the solution and S is the airflow rate being passed over the solution (volume/time). In practice, however, J is not known without having first solved for the surface concentrations. They used an iterative procedure with the bulk gas phase NH_3 concentration set initially at zero and the surface concentration calculated in the manner described below. The NH_3 flux can then be calculated and the bulk NH_3 concentration can be determined.

By assuming that the aqueous NH_3 and gas phase NH_3 are in equilibrium at the interface, they obtained the following relationship for $[NH_3]_g^o$.

$$[NH_3]_g^o = k_H a^o{}_{NH_3}/(RT) \tag{25}$$

where k_H, R, and T are the Henry's law constant for NH_3, the gas constant, and absolute temperature, respectively.

The surface hydrogen ion activity, $a^o{}_{H^+}$ is determined by two different

methods, which differentiate the two models they developed. In the pH constant model, as assumed by Hoover and Berkshire (1969), they treated pH as a constant across the liquid film. Therefore,

$$a^o{}_{H^+} = a^b{}_{H^+}. \tag{26}$$

In the pH gradient model, by following the treatment of Quinn and Otto (1971), they developed a cubic expression for the surface hydrogen ion activity.

$$a^o{}_{H^+}{}^3 + pa^o{}_{H^+}{}^2 + qa^o{}_{H^+} + r = 0 \tag{27}$$

with

$$
\begin{aligned}
p &= a^b{}_{AN} + \frac{D_g \, \delta_l}{D_l \delta_g} \, [NH_3]^b_g + CK_l - 2\gamma[SO_4^{2-}] + \gamma(Na^+) \\
q &= -C \, K_l(2\gamma[SO_4^{2-}]) - \gamma[Na^+] - K_w \\
r &= -C \, K_l \, K_w
\end{aligned}
\tag{28}
$$

and

$$C = \frac{\delta_l D_g \, K_w}{\delta_g \, D_l \, RT} + 1 \tag{29}$$

where γ is the activity coefficient, $[Na^+]$ and $[SO_4^{2-}]$ are the spectator ion concentrations, and K_w is the equilibrium constant for water.

Moeller and Vlek (1982) tested the two stagnant-film volatilization models in a series of laboratory experiments. They employed a small volatilization chamber connected to an airflow system, an experimental technique that is suited for the investigations of the fundamental processes of NH_3 volatilization in systems artificially maintained free of CO_2.

It was evident from the experimental results that the model that assumes a pH gradient in the liquid diffusion film accurately predicts the observed volatilization rate, whereas the pH constant model does not. This indicates that the surface layer retains some importance as a resistance to volatilization at moderate and low pH. Bicarbonate and other buffers, however, can mitigate this pH gradient (Moeller and Vlek, 1982).

It is interesting to note that the effective thicknesses of the liquid- and gas-phase stagnant films calculated from NH_3 volatilization and water evaporation rates in the chamber are similar to corresponding parameters found in larger scale wind tunnel experiments. Therefore, Moeller and Vlek (1982) stated that it is possible to perform NH_3 volatilization studies in small chambers. Bouwmeester and Vlek (1981a,b) also reached a similar conclusion in their studies.

D. JAYAWEERA AND MIKKELSEN AMMONIA VOLATILIZATION MODEL

The NH_3 volatilization model developed by Jayaweera and Mikkelsen (1990a) computes the rate of NH_3 volatilization as a function of five primary factors, which include the floodwater NH_4^+-N concentration, pH, temperature, depth of floodwater, and windspeed. In previous models researchers have taken these factors into consideration but not the depth of floodwater. The role of depth of floodwater in NH_3 volatilization is twofold. It directly affects NH_4^+-N concentration by virtue of its dilution effect. Further, it influences the volatilization relationships (Jayaweera and Mikkelsen, 1990a).

1. Model Development

The ammonia volatilization model presented by Jayaweera and Mikkelsen (1990a) consists of two parts: (1) chemical aspects ($NH_4^+/NH_{3(aq)}$ equilibrium in floodwater); and (2) volatilization aspects (NH_3 transfer from floodwater across the water–air interface).

a. Chemical Aspects of the Model.   The chemical dynamics of NH_3 volatilization from floodwater is described as follows:

$$NH_4^+ \underset{k_a}{\overset{k_d}{\rightleftharpoons}} H^+ + NH_{3(aq)} \overset{k_{vN}}{\rightarrow} NH_{3(air)} \qquad (30)$$

where k_d and k_a are dissociation and association rate constants for $NH_4^+/NH_{3(aq)}$ equilibrium and k_{vN} is the first-order volatilization rate constant for NH_3.

By chemical kinetics, Jayaweera and Mikkelsen (1990a) derived the following expression to determine the rate of NH_3 volatilization from a flooded system.

$$\frac{d[NH_4^+]}{dt} = k_a \left\{ \frac{k_d\,(AN - [NH_3]_{aq}}{k_a[H^+] + k_{vN}} \right\} - k_d\,(AN - [NH_3]_{aq}) \qquad (31)$$

where AN is the ammoniacal N concentration, $[NH_3]_{aq}$ is the aqueous NH_3 concentration, and $[H^+]$ is the hydrogen ion concentration in floodwater at equilibrium.

They have estimated the rate of NH_3 volatilization by the rate of change in NH_4^+ concentration in floodwater with the assumption that no other process changes the NH_4^+ in the system. There are various processes, however, which bring NH_4^+ into floodwater, such as soil desorption, organic matter mineralization, and those which remove NH_4^+ from flood-

water, such as soil adsorption and biotic assimilation. It is assumed 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.

Equation (31) estimates the rate of NH_3 volatilization as a function of ammoniacal N concentration, aqueous NH_3 and H^+ concentration in floodwater, rate constants k_d and k_a for the $NH_4^+/NH_{3(aq)}$ equilibrium, and the volatilization rate constant for NH_3, k_{vN}.

The NH_4^+-N concentration and pH of floodwater are experimentally determined. Rate constants k_d and k_a, whose determination is discussed next, are computed in the chemical aspects of the model. Volatilization rate constant, k_{vN} is computed in the volatilization aspect of the model. Aqueous NH_3 is computed as a function of NH_4^+ concentration, pH, and temperature. The rate of NH_3 volatilization can be computed by applying these values to Eq. (31).

The rate constants at various temperatures are calculated in the model. First, the equilibrium constant, K, for the $NH_4^+/NH_{3(aq)}$ system is computed, followed by the association rate constant, k_a. Finally, the dissociation rate constant, k_d is obtained with the use of K and k_a.

By applying the Clausius–Clapeyron equation to the $NH_4^+/NH_{3(aq)}$ equilibrium, and by using the values pK at 25°C as 9.24 and $\Delta H°$ as 12,480 cal (Dean, 1986) Jayaweera and Mikkelsen (1990a) derived the following expression to compute pK at any temperature.

$$pK(T) = 0.0897 + \frac{2729}{T} \tag{32}$$

where p$K(T)$ is $-\log K$, equilibrium constant for $NH_4^+/NH_{3(aq)}$ system at absolute Kelvin temperature T. A similar equation has been derived by Bates and Pinching (1949) by a different methodology.

The association reaction between NH_3 and H^+ in water, as measured by Eigen and co-workers, is diffusion controlled (Alberty, 1983). Therefore, Jayaweera and Mikkelsen (1990a) assumed that the rate constant for the association reaction is proportional to the diffusion coefficient. By using Stokes–Einstein equation (Laidler and Meiser, 1982) and with the use of the association rate constant at 25°C (Alberty, 1983) and the viscosity of water at different temperatures (Dean, 1986), Jayaweera and Mikkelsen (1990a) developed the following relationship to compute k_a values as a function of absolute Kelvin temperature T.

$$k_a(T) = 3.8 \times 10^{11} - 3.4 \times 10^9 T + 7509700\ T^2 \tag{33}$$

By using the equilibrium relationship, the dissociation rate constant, k_d for the $NH_4^+/NH_{3(aq)}$ system at various temperatures can be computed.

$$k_d(T) = K(T) \times k_a(T) \tag{34}$$

where $K(T)$ is the antilog of $pK(T)$ at absolute Kelvin temperature T.

b. Volatilization Aspects of the Model. The volatilization aspect of the model is based on the two-film theory proposed by Whitman in 1923 and is used to compute the volatilization rate constant for NH_3, k_{vN}. The controlling factor for the mass transfer of NH_3 across the interface is the rate of diffusion through the two films on either side of the interface, where all the resistance lies. This shows the liquid phase or gas phase resistance or both, and determines the overall mass transfer rate of NH_3.

In developing this model, Jayaweera and Mikkelsen (1990a) have assumed that an $NH_4^+/NH_{3(aq)}$ equilibrium is established in the floodwater, and that NH_3 in aqueous phase diffuses from the bulk of the liquid phase to the interface across the thin film. It is assumed, although perhaps inconclusively, that the pH in the surface film remains constant. Hoover and Berkshire (1969) and Bouwmeester and Vlek (1981a) made the same assumption in their gas exchange studies. Computation of various parameters of the volatilization aspects of the model is presented as follows:

1. Determination of volatilization rate constant for NH_3, k_{vN}: By material balance of the NH_3 system, Jayaweera and Mikkelsen (1990a) showed that the volatilization rate constant for NH_3, k_{vN} is represented as a ratio:

$$k_{vN} = \frac{K_{ON}}{d} \tag{35}$$

where K_{ON} is the overall mass transfer coefficient for NH_3, and d is the mean depth of floodwater.

The relationship expressed by Eq. (35) shows that the volatilization rate constant for NH_3 is inversely related to the depth of floodwater. To estimate the volatilization rate constant, however, it is necessary to know the overall mass transfer coefficient for NH_3, K_{ON}.

2. Determination of overall mass transfer coefficient for NH_3, K_{ON}: The rate of NH_3 transfer through the gas film is the same as through a liquid film, under steady-state conditions. Since the movement through the film layers is by molecular diffusion, it can be described by Fick's first law of diffusion.

$$F_N = -D_N \frac{dC_N}{dx} \tag{36}$$

where F_N is the flux of NH_3 gas through the surface films in x direction, D_N is the molecular diffusion coefficient or diffusivity of NH_3, and dC_N/dx is the concentration gradient of NH_3 gas across the film of thickness x.

The ratio of $D_N/\Delta x$ in Eq. (36) 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.

$$k_N = - \frac{D_N}{\Delta x} \qquad (37)$$

It is possible to obtain another form of the Fick's law equation generally used in gas exchange studies by substituting Eq. (37) into Eq. (36).

$$F_N = k_N \, \Delta C_N \qquad (38)$$

where ΔC_N is the concentration difference of NH$_3$ across the layer of thickness x.

By transforming Eq. (38), the exchange constant for NH$_3$, k_N, is obtained as

$$k_N = \frac{F_N}{\Delta C_N} \qquad (39)$$

Therefore, it is seen that the exchange constant for NH$_3$, k_N, is a measure of the flux of NH$_3$ per unit concentration difference across the layer of thickness x. The value of k_N depends on many factors, of which the degree of turbulence in the fluids on both sides of the interface is important.

Under steady-state conditions and by applying Eq. (38) to the two-film situation and with the nondimensional form of Henry's law constant, Jayaweera and Mikkelsen (1990a) obtained the following expression after simplifying by introducing two constants:

$$F_N = K_{GN} \, (C_{gN} - H_{nN} \, C_{IN}) = K_{LN}[(C_{gN}/H_{nN}) - C_{IN}] \qquad (40)$$

where

$$1/K_{GN} = 1/k_{gN} + H_{nN}/k_{lN} \qquad (41)$$

and

$$1/K_{LN} = 1/k_{lN} + 1/H_{nN} \, k_{gN} \qquad (42)$$

where K_{GN} and K_{LN} are the overall gas phase and liquid phase coefficients for NH$_3$, k_{gN} and k_{lN} are the exchange constants for NH$_3$ in gas phase and liquid phase, respectively, and H_{nN} is the nondimensional Henry's law constant for NH$_3$.

The total resistance of NH$_3$ transfer can be expressed on either a gas phase, $1/K_{GN}$, or a liquid phase, $1/K_{LN}$, basis. For convenience, Jayaweera and Mikkelsen (1990a) considered $1/K_{LN}$ as the total resistance for NH$_3$ flux from a water body, and it was rearranged to determine the overall

mass transfer coefficient for NH_3, K_{ON}, which is numerically equal to the overall liquid phase coefficient for NH_3, K_{LN}.

$$K_{ON} = K_{LN} = (H_{nN} \, k_{gN} k_{lN})/(H_{nN} + k_{gN} + k_{lN}) \tag{43}$$

To estimate K_{ON}, it is necessary to determine the nondimensional Henry's law constant for NH_3, H_{nN}, and the gas and liquid phase exchange constants for NH_3, k_{gN} and k_{lN}, respectively.

3. Determination of Henry's law constant for NH_3, H_N, MPa m^3/mol: Henry's law constant is a coefficient which represents the equilibrium distribution of a material between gas and liquid phases. The Henry's law constant should be obeyed reasonably well under flooded conditions, because of relatively low concentrations of NH_3 in floodwater. Several researchers have used the Henry's law relationship in their NH_3 volatilization studies in floodwater systems (Bouwmeester and Vlek, 1981a; Moeller and Vlek, 1982; Leuning *et al.*, 1984; Jayaweera and Mikkelsen, 1990a,b).

The Henry's law constant for NH_3, H_N, in MPa m^3/mol, can be expressed in an equation form as follows:

$$H_N = \frac{P_N}{C_N} \text{ MPa } m^3/\text{mol} \tag{44}$$

where P_N is the partial pressure of NH_3 gas in MPa and C_N is the concentration of $NH_{3(aq)}$ in floodwater in mol/m^3.

a. Determination of partial pressure of NH_3 gas, P_N, MPa: Jayaweera and Mikkelsen (1990a) derived an expression to estimate the mole fraction of NH_3 in floodwater, X_N, as a function of pH and absolute temperature.

$$X_N = \frac{(C/17.03)\,(A/1 + A)}{(C/17.03)\,(A/1 + A) + (C/18.04)\,(1/1 + A) + 10^6 \, p_w/18.02} \tag{45}$$

where

$$A = 10 \exp (\text{pH} - 0.0897 - 2729/T) \tag{46}$$

C is the total NH_4^+-N concentration in floodwater, p_w is the density of water in gm/cm^3 at T, pH is the pH of floodwater, and T is the absolute Kelvin temperature of floodwater.

By using the Henry's law relationship, they obtained the following expression for the partial pressure of NH_3 in the gas phase in equilibrium with its solution.

$$P_N = 18.62 \exp (-1229/T)X_N \text{ MPa} \tag{47}$$

According to Eq. (45), the partial pressure of NH_3 in the gas phase varies with NH_4^+-N concentration, pH, and temperature of floodwater.

b. Determination of concentration of $NH_{3(aq)}$, C_N, mol/m^3: If the total ammoniacal N concentration is C mg/L, by proper conversion, the con-

centration of NH_3, C_N, can be determined in mol/m^3 (Jayaweera and Mikkelsen, 1990a).

$$C_N = (C/17.03) \frac{[10 \exp (pH - 0.0897 - 2729/T)]}{[1 + 10 \exp (pH - 0.0897 - 2729/T)]} \text{ mol/m}^3 \quad (48)$$

By using Eqs. (47) and (48), they obtained the Henry's law constant in $MPa \, m^3/mol$.

4. Determination of nondimensional Henry's law constant for NH_3, H_{nN}: Henry's law constant for NH_3, which is computed in $MPa \, m^3/mol$, H_N, can be transformed into nondimensional form as follows:

$$H_{nN} = \frac{H_N}{RT} \quad (49)$$

where R is the gas constant, 8.315×10^{-6} MPa m^3/mol/deg K, and T is absolute Kelvin temperature.

5. Determination of gas phase, k_{gN}, and liquid phase, k_{lN}, exchange constants: Exchange constants have dimensions of velocity and can be considered as the velocity at which NH_3 moves through the fluid films. The value of exchange constants k_{gN} and k_{lN} depend on the degree of turbulence in the fluids on either side of the interface, chemical reactivity of the substance, temperature, and the properties of the solute, such as diffusivity or molecular size (Liss and Slater, 1974; Mackay and Yeun, 1983). These exchange constants, however, have not yet been readily computed using basic physical principles and generally are determined empirically (Thomas, 1982).

Henry's law constant of a chemical gives some insight into the distribution of resistances in the liquid and gas films. The Henry's law constant for NH_3 varies between 4.36×10^{-6} to 6.59×10^{-6} MPa m^3 mol in the usual temperature range found in floodwater, i.e., 10–40°C (Jayaweera and Mikkelsen, 1990a). According to the model developed by Jayaweera and Mikkelsen (1990a), the process of NH_3 volatilization is therefore controlled by both gas and liquid phase resistances (Mackay et al., 1979). Liss and Slater (1974), however, suggested that the rate of NH_3 volatilization is controlled by the gas phase resistance, whereas Leuning et al. (1984) found that NH_3 fluxes were controlled by transport processes in both the atmosphere and the water.

By using the data of an experiment performed by Liss (1973) in a wind tunnel, a regression equation was developed to relate the water vapor exchange constant, k_{gW} (cm/h) and the windspeed (Jayaweera and Mikkelsen, 1990a).

$$k_{gW} = 18.5683 + 1135.89 \, U_{0.1} \quad (50)$$

where $U_{0.1}$ is the windspeed at 0.1 m above the water surface in the wind tunnel.

Jayaweera and Mikkelsen (1990a) developed a relationship between the windspeed in the wind tunnel used by Liss (1973) and the equivalent field wind speed at 8 m:

$$U_8 = 1.5686\, U_{0.1} \tag{51}$$

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

The water vapor exchange constant, k_{gW} is transformed into field situations with Eq. (51), and is adjusted to NH_3 transfer with the use of the molecular weight ratio of water and NH_3 (Liss and Slater, 1974) to obtain the gas phase exchange constant for NH_3, k_{gN} (Jayaweera and Mikkelsen, 1990a).

$$k_{gN} = 19.0895 + 742.3016\, U_8 \tag{52}$$

Similarly, the CO_2 exchange constant data of Liss (1973) were fit into a logistic equation and adjusted to field situation by Eq. (51) for the molecular weight ratios to obtain the liquid phase exchange constant for NH_3, k_{lN}.

$$k_{lN} = \{12.5853/[1 + 43.0565\, \exp\,(-0.4417\, U_8)]\}1.6075 \tag{53}$$

By using the model (Jayaweera and Mikkelsen, 1990a), k_{lN} and k_{gN} values are computed at various windspeeds; both constants show an increase with increase in windspeed.

They have developed a relationship to transform the measured windspeed at any height over a water surface to a windspeed at 8 m height by assuming a logarithmic wind profile, which is used in the NH_3 volatilization model (Jayaweera and Mikkelsen, 1990a).

$$U_8 = \frac{11.51}{\ln\,(Z/8 \times 10_{-5})}\, U_Z \tag{54}$$

where U_8 is the windspeed at 8 m height in m/s, and U_Z is the windspeed at Z m height in m/s.

It should be noted, however, that Eq. (54) is based on the assumptions of neutral stability and windspeed measurements over flat water surfaces. These assumptions may be violated at night or at times of very low or very high evapotranspiration rates, or if plant cover exists above the water surface, which would decrease the accuracy of the equation (Jayaweera et al., 1990).

2. Model Execution

The ammonia volatilization model (Jayaweera and Mikkelsen, 1990a) is executed with several input variables. They are floodwater NH_4^+-N concentration, mg/L (AMC); pH; temperature, °C (TEMP); depth of floodwater, cm (WD); windspeed, m/s (WS); and the height of wind measurement, m (WH) (Fig. 11). The model calculates the initial volatilization rate of NH_3 (VRAMI). Ammonia loss for a specific period is obtained by entering the time period 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 selected time period.

3. Sensitivity Analysis

The sensitivity analysis has been performed on the model to test the influence of various determinants on NH_3 volatilization. Floodwater NH_4^+-N concentration shows a linear relationship to NH_3 volatilization when other factors such as pH, temperature, depth of floodwater, and windspeed are kept constant. This direct relationship is due 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 Creswell, 1979; Fillery and Vlek, 1986; Jayaweera and Mikkelsen, 1990b). Therefore, in the sensitivity analysis performed by Jayaweera and Mikkelsen (1990b), the floodwater NH_4^+-N concentration is kept at a constant value of 25 mg/L.

The effect of four other factors, pH, temperature, depth of floodwater, and windspeed were tested in sensitivity analysis under these different sets of conditions. At each condition, one factor is varied while the others are kept constant. The final output, NH_3 loss per day, is shown in Fig. 12.

The sensitivity (slope) of NH_3 loss per day with respect to pH, temperature, water depth, and windspeed is shown in Table I. A detailed account of the sensitivity analysis was presented by Jayaweera and Mikkelsen (1990b).

In summary, under conditions 1, 2, and 3, pH was the most sensitive variable; temperature was the least sensitive under conditions 1 and 2; and water depth showed the least sensitivity under condition 3 (Table I, Fig. 12).

The sensitivity analysis shows clearly that it is not possible to generalize on the effect of one variable without considering the other interacting conditions. Therefore, the magnitude of NH_3 loss from floodwater can be predicted only by taking into account all five primary factors simulta-

Begin

Input
AMC, pH, TEMP, WD, WS, WH

Calculate VRAMI

Display VRAMI

Print VRAMI ?   —yes→   Print VRAMI

no

Abandon run ?   —no→   Input TIME

Successive approximation loop

Calculate NH₃ loss

Display NH₃ loss

Print NH₃ loss ?   —yes→   Print NH₃ loss

no

Another time period ?
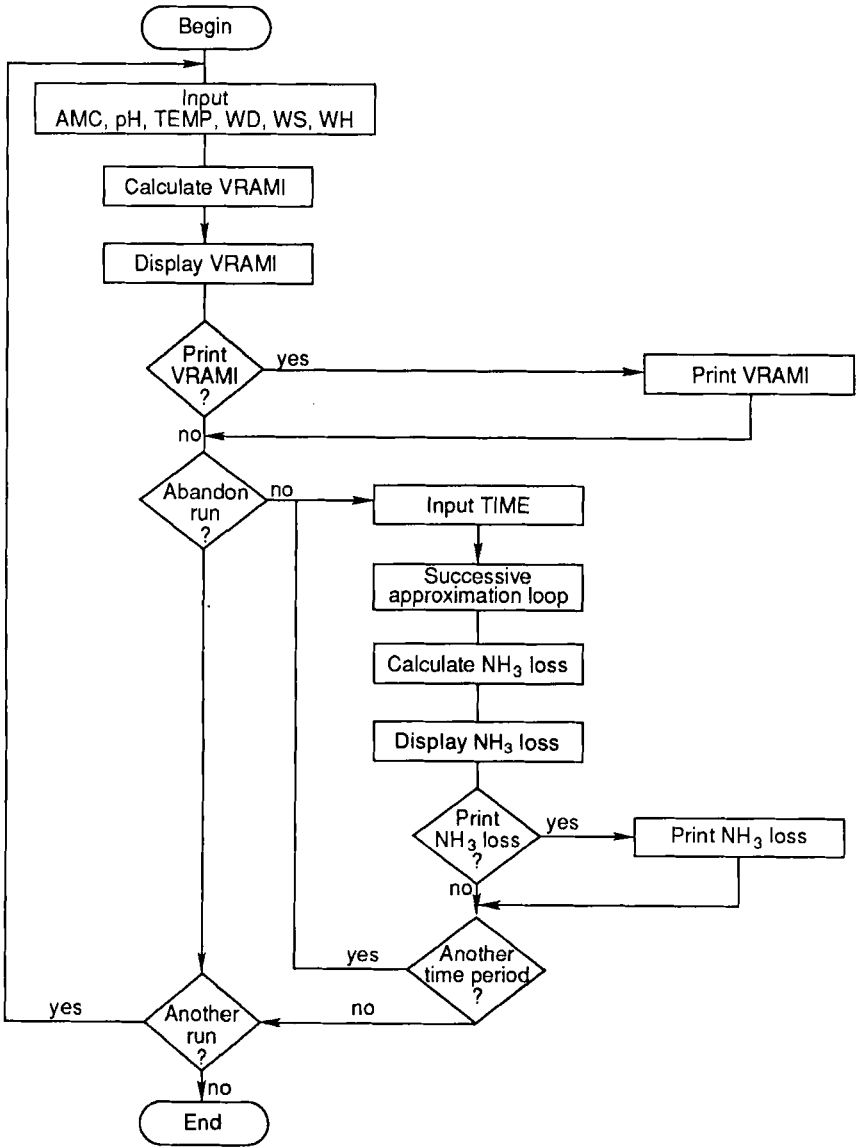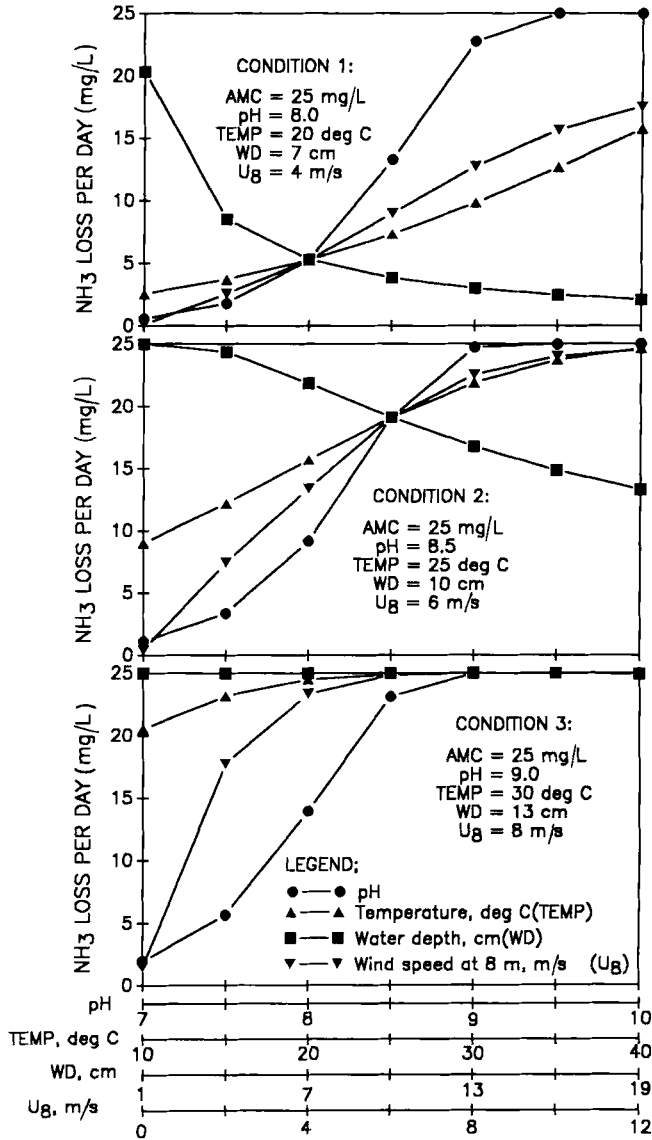
yes → Another run ?   no ← Another time period ?

yes

no

End

FIG. 11.   Flow chart for NH₃ volatilization model. (From Jayaweera and Mikkelsen, 1990b.)

FIG. 12. Sensitivity analysis for NH₃ volatilization model AMC (NH₄⁺-N concentration in floodwater). (From Jayaweera and Mikkelsen, 1990b.)

Table I

Sensitivity Analysis of Model (Slope) Affected by pH, Temperature, Depth of Floodwater, and Windspeed[a]

Condition	Percent NH₃ loss/d/unit change					
	pH[c, d, e]					
	7.25	7.75	8.25	8.75	9.25	9.75
1	2.5	7.0	16.0	19.0	4.5	0.0
2	4.5	11.6	20.0	11.3	0.5	0.0
3	7.4	16.5	18.4	3.7	0.0	0.0
	Temperature, °C[b, d, e]					
	12.5	17.5	22.5	27.5	32.5	37.5
1	0.2	0.3	0.4	0.5	0.6	0.6
2	0.6	0.7	0.7	0.6	0.4	0.2
3	0.5	0.3	0.9	0.0	0.0	0.0
	Water depth, cm[b, c, e]					
	2.5	5.5	8.5	11.5	14.5	17.5
1	−3.9	−1.1	−0.5	−0.3	−0.2	−0.1
2	−0.2	−1.0	−0.9	−0.8	−0.6	−0.5
3	0.0	0.0	0.0	0.0	0.0	0.0
	Windspeed, m/s[b, c, d]					
	1	3	5	7	9	11
1	1.2	1.4	1.9	1.5	1.5	0.9
2	3.5	3.0	2.7	1.7	0.7	0.3
3	8.1	2.8	0.8	0.0	0.0	0.0

[a] NH₄⁺-N concentration was 25 mg/L for all three conditions.
[b] pH values for conditions 1, 2, and 3 were 8.0, 8.5, and 9.0, respectively.
[c] Temperatures for conditions 1, 2, and 3 were 20, 25, and 30, respectively.
[d] Water depths for conditions 1, 2, and 3 were 7, 10, and 13, respectively.
[e] Windspeeds for conditions 1, 2, and 3 were 4, 6, and 8, respectively.

neously, which determine the $NH_{3(aq)}$ concentration and the volatilization rate constant for NH_3.

4. Model Validation

The ammonia volatilization model predicting NH_3 loss as a function of input variables was validated using a wind tunnel to simulate rice paddy conditions and direct field experiments (Fig. 13) (Jayaweera et al., 1990).

FLOODWATER NH$_4^+$—N CONC → AUTO SAMPLER → HPLC

FLOODWATER pH — SAMPLING TIME NH$_4^+$—N CONC

FLOODWATER TEMPERATURE → DATA LOGGER → COMPUTER → MODEL → NH$_3$ VOLATILIZATION
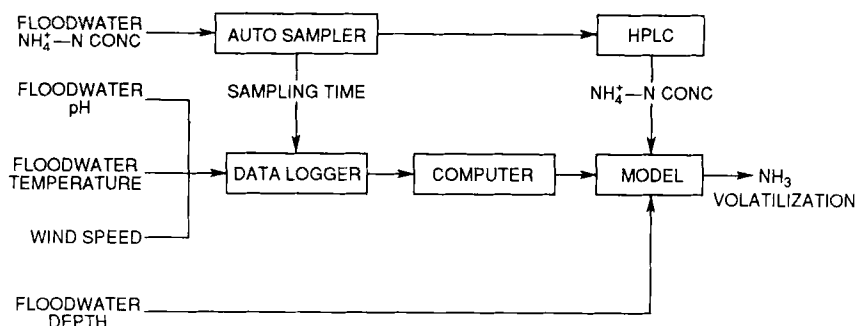
WIND SPEED

FLOODWATER DEPTH

FIG. 13. Diagrammatic representation of the experimental field setup. (From Jayaweera et al., 1990.)

There were a total of 13 wind tunnel runs to determine the effect of 5 composite combinations of variables on NH$_3$ volatilization. A central composite statistical design including mean values for each variable, as well as maximum and minimum values of each variable, were used in the experiment as described in Table II.

The solution samples collected during the wind tunnel runs show the NH$_4^+$-N depletion rate under various treatment conditions. For each run, by using first-order kinetics, a straight line was fitted after logarithmic transformed concentration values and the rate constants and half-life values of NH$_4^+$-N depletion were calculated. The highest rate constant and the shortest half-life for NH$_4^+$-N depletion were observed when the pH is 10.5 and the lowest rate constant and the largest half-life value occurred when the pH is 6.5. 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 (Jayaweera et al., 1990).

The average value for the predicted ÷ observed NH$_3$ loss for the 13 wind tunnel runs is 1.2, suggesting that on the average, the model predicted NH$_3$ loss quite close to the observed values under the experimental conditions in the wind tunnel. Linear regression of the observed NH$_3$ loss on predicted values indicates that the regression coefficient R^2 improved greatly when the high windspeed (8.9 m/s), high pH (10.5), and low pH (6.5) runs were omitted, indicating that the model has some limitations under certain conditions. Then the regression equation becomes

$$\text{observed NH}_3 = -0.43 + 0.99 \text{ (predicted NH}_3 \text{ loss)} \qquad (55)$$

with a R^2 of 0.98.

The close fit (Fig. 14) of the observed on predicted values shows that the

Table II

Experimental Details, Equivalent Field Windspeed at 8 m Height, U_8, and Observed and Predicted NH$_3$ Loss for Wind Tunnel Runs

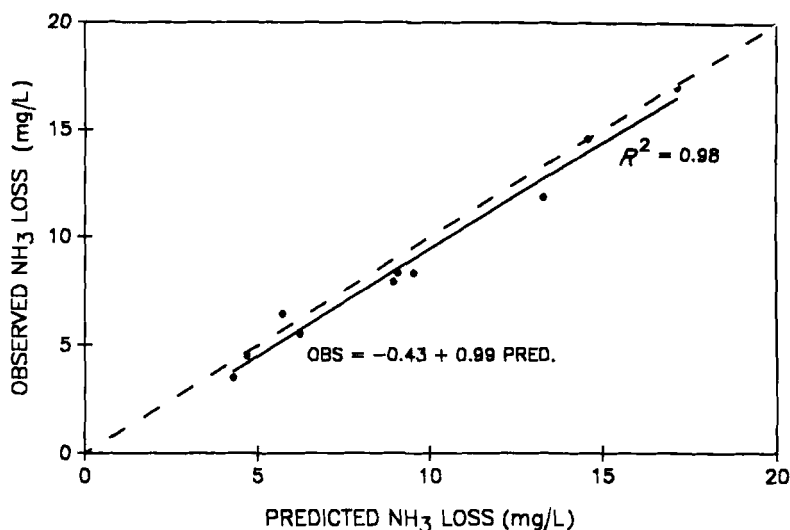| Variable (Wind tunnel run)	Initial NH$_4^+$-N conc. (mg/L)	pH	Temp. (°C)	Water depth (cm)	Free stream windspeed (m/s)	U_8 (m/s)	Observed NH$_3$ loss (mg/L)	Predicted NH$_3$ loss (mg/L)	Predicted ÷ observed
Mean (1)	52.3	8.5	25	11.0	2.9	4.4	8.3	9.5	1.1
Mean (2)	52.6	8.5	25	11.0	2.8	4.2	8.3	9.1	1.1
Mean (3)	53.2	8.5	25	11.0	2.7	4.1	7.9	8.9	1.1
NH$_4^+$-N concentration									
Low (4)	26.2	8.5	25	11.0	2.6	4.1	3.5	4.3	1.2
High (5)	102.5	8.5	25	11.0	2.7	4.1	24.8	49.8	2.0
pH									
Low (6)	52.7	6.5	25	11.0	2.6	4.1	1.8	0.1	0.1
High (7)	49.8	10.5	25	11.0	2.9	4.4	24.8	49.8	2.0
Temperature									
Low (8)	52.5	8.5	20	11.0	2.7	4.1	5.5	6.2	1.1
High (9)	53.1	8.5	30	11.0	2.9	4.4	11.8	13.3	1.1
Water depth									
Low (10)	52.7	8.5	25	6.4	2.8	4.2	14.6	14.6	1.0
High (11)	50.3	8.5	25	21.3	2.8	4.2	4.5	4.7	1.0
Windspeed at 8 m									
Low (12)	51.6	8.5	25	11.0	1.9	2.9	6.5	5.7	0.9
High (13)	52.9	8.5	25	11.0	5.3	8.2	12.2	22.3	1.8

Fig. 14. Regression of observed on predicted NH₃ loss in wind tunnel runs. (From Jayaweera *et al.*, 1990.)

model predicted NH_3 loss quite well within the range of conditions usually found in flooded systems.

Field experiments show a close agreement of predicted values with observed data collected during 3 days at two different time periods and averaged for 6 h and 24 h (Fig. 15). Regression of observed NH_4^+-N depletion data on predicted values to test the closeness of fit also showed a close agreement. However, as the averaging period is increased to 24 h, the regression slope is increased to a value slightly greater than 1.0, and the intercept decreases below 0 (Jayaweera *et al.*, 1990).

In general, it is seen that observed values from the wind tunnel and field experiments agreed closely with the predicted values from the model. By scrutinizing the data (Jayaweera *et al.*, 1990) it is established that the amount of NH_3 loss, which is a function of volatilization rate of NH_3, is quantitatively described by the concentration of $NH_{3(aq)}$ in the floodwater, which in turn is governed by NH_4^+-N concentration, pH and temperature of floodwater, and the volatilization rate constant for NH_3, k_{vN}, which is a function of temperature, water depth, and windspeed.

The NH_3 volatilization model presented by Jayaweera and Mikkelsen (1990a,b) has several unique features. It has a menu-driven computer program that can be easily executed. It requires only 5 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
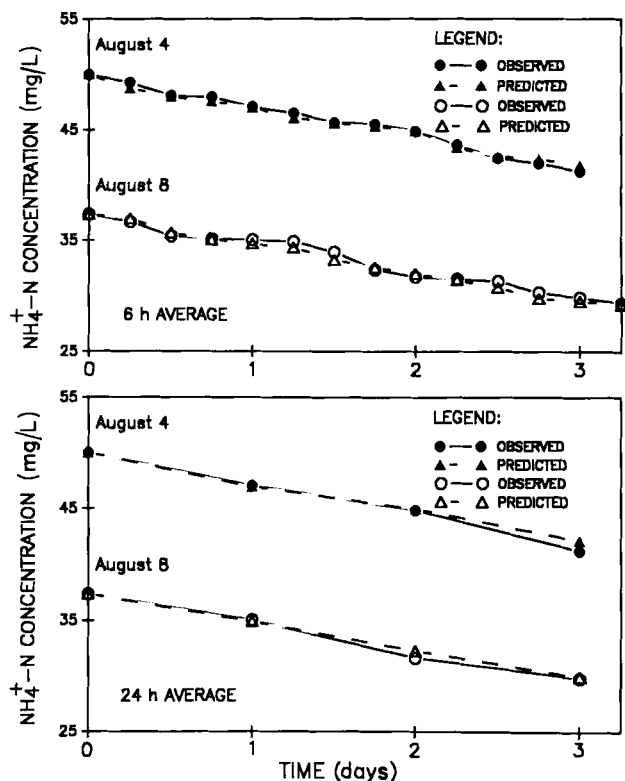
FIG. 15. Predicted and observed NH$_4^+$-N depletion in the field. (From Jayaweera *et al.*, 1990.)

are easily measurable with simple, inexpensive instrumentation. Analytical measurements are needed only for the initial foodwater 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 windspeed (Jayaweera *et al.*, 1990).

Jayaweera *et al.* (1990) concluded that the model is useful in simplifying the complex NH$_3$ volatilization process by considering only two major parameters: (1) aqueous NH$_3$ concentration; and (2) volatilization rate constant for NH$_3$ as a function of five variables, NH$_4^+$-N concentration, pH, temperature, water depth, and windspeed, which determine the volatilization rate of NH$_3$ to accurately predict the NH$_3$ loss in the range of conditions found in flooded systems.

VII. EPILOGUE

Ammonia volatilization is a major mechanism for N loss from flooded soil systems such as rice paddies, ponds, lakes, wastewater ponds, and manufacturing systems. Losses of NH_3 from rice paddies have been identified as a factor associated with low fertilizer use efficiency and reduced crop yields.

The preceeding discussion has been directed primarily to the basic aspects of NH_3 volatilization wherein NH_4^+-N concentrations in floodwater directly influence aqueous NH_3 levels and where water pH and temperature determines the fraction of NH_4^+/NH_3 dissociation. The higher the water NH_4^+-N content and water pH and temperature, the higher is the aqueous NH_3 concentration and NH_3 volatilization from floodwater. It is shown that the volatilization rate constant for NH_3 is determined by temperature, water depth, and wind speed. Elevated water temperatures, high wind speeds, and shallow water depths increase the volatilization rate constants, and consequently the quantity of NH_3 to be lost from flooded soil systems.

Theoretical aspects of the models are presented together with laboratory and field verification data in such a manner that the NH_3 volatilization process can be understood and assessments can be made of NH_3 volatilization losses. Only two parameters, aqueous NH_3 concentration and the volatilization rate constant for NH_3 as influenced by 5 variables (water NH_4^+-N concentration, pH, temperature, water depth, and wind speed), figure prominently in NH_3 volatilization process.

A knowledge of how NH_3 volatilization occurs, assessments of field losses in agricultural crop production, and an appreciation of how agronomic principles can be used will help to minimize losses. Improved crop, soil, and water management practices can be used to increase N-use efficiency (especially in flooded rice), to conserve costly fertilizer materials, and to minimize environmental pollution.

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