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Ammonia Volatilization from Flooded Soil Systems: A Computer Model. II. Theory and Model Results

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ABSTRACT

Our theory to describe the process of NH_3 volatilization from flooded systems is that the rate of NH_3 loss is principally a function of two parameters, floodwater NH_3(aq) concentration and the volatilization rate constant for NH_3, k_{vN}. These parameters are governed by five primary factors, floodwater NH_4–N concentration, pH, temperature, depth of floodwater, and wind speed. The NH_3-volatilization model is executed with five primary factors as input variables. With the input of time, it predicts the NH_3 loss for a specified period. The interactive effects of these factors were studied by individually varying one factor while maintaining the four other factors at their mean values; the same factor was also studied by maintaining a second factor at its highest and lowest values while the other three factors were kept constant at their mean values. It is seen that, by changing the existing conditions, the NH_3-volatilization losses are increased or decreased appreciably. The sensitivity analysis shows that pH is the most sensitive and temperature and water depth are the least sensitive determinants affecting NH_3 volatilization.

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

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

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

Development of the Theory

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

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

MODEL EXECUTION

The NH_3-volatilization model initially requires input data for floodwater NH_4–N concentration (AMC), pH, temperature (TEMP), depth of floodwater (WD), wind speed (WS), and the height of wind measurement (WH) (Fig. 2). The model calculates the initial volatilization rate of NH_3 (VRAMI), using mathematical equations developed by Jayaweera and Mikkelsen (1990). To determine NH_3 loss for a specific period, the time is entered as an input and the model computes the decrease in volatilization rate as a function of the time with a successive approximation loop. The final output is the predicted NH_3 loss for the time period selected.

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

The NH_3-volatilization model presented here has several unique features. It has a menu-driven computer program that can be easily executed. As previously stated, it requires only five input variables to predict NH_3 loss, and no input constants since the model computes all necessary constants depending on the variables provided. Input variables are easily measurable with simple, inexpensive instrumentation. Analytical measurements are only needed for the initial floodwater NH_4–N concentration. Depth of floodwater is measured initially and generally remains constant, thus frequent measurements are needed for only three variables: pH, temperature, and wind speed.

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

MODEL RESULTS

Effect of Floodwater Ammonium Concentration on Ammonia Volatilization

The initial floodwater NH_4–N concentration in the model was varied from 1 to 49 mg L^{-1}, in increments of 7 mg L^{-1}, while the other four parameters are maintained at their mean values. An increase in floodwater NH_4–N concentration increased the NH_3(aq) concentration linearly in the system (Table 2), while the k_{vN} was maintained at a constant value because of constant temperature, water depth, and wind speed (Jayaweera and Mikkelsen, 1990). Therefore, the increase in NH_3-volatilization rate with an increase in floodwater NH_4–N concentration (Table 2) was a function of NH_3(aq) concentration in the floodwater under the existing conditions.

The next series of model runs were performed at pH 7.0 and 10.0, while varying floodwater NH_4–N concentration from 1 to 49 mg L^{-1} and keeping the other three parameters at their mean values. Lowering

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the pH to 7.0 decreased the volatilization rate of NH_3. In contrast, elevating the pH to 10.0 increased both the rate of NH_3 volatilization and the total NH_3 loss. As shown in Table 2, at pH 7.0, the NH_3(aq) concentration in floodwater has decreased about 30 times and, at pH 10.0, it has increased about six times, compared with pH 8.5, at all floodwater NH_4–N concentrations. However, for all these runs, k_{vN} was at a constant value, indicating that pH influences NH_3(aq) in floodwater at various NH_4–N concentrations, thereby influencing the NH_3-volatilization process.

The temperature was maintained at 10 and 40 °C for the next set of runs, while varying the floodwater NH_4–N concentration from 1 to 49 mg L^{-1} and maintaining the mean value of pH, water depth, and wind speed. The NH_3 volatilization decreased at 10 °C and increased at 40 °C (Table 2). As the theory indicates, temperature influenced both NH_3(aq) in floodwater and the k_{vN}. Lowering the temperature to 10 °C decreased both the NH_3(aq) in floodwater and the k_{vN} compared with 25 °C. In contrast, when the floodwater temperature was increased to 40 °C, both the NH_3(aq) and k_{vN} increased, increasing NH_3 volatilization losses (Table 2).

The next set of runs were carried out at floodwater depths of 1 and 19 cm, with varying floodwater NH_4–N concentration and constant floodwater pH, temperature, and wind speed. At a water depth of 1 cm, 100% of NH_3 was lost in a 24-h period, compared with 77% loss at a floodwater depth of 10 cm and 53% loss at 19-cm depth at all NH_4–N concentrations. As shown in Table 2, the depth of floodwater influenced k_{vN}, but not the NH_3(aq) in the system (Jayaweera and Mikkelsen, 1990).

The next series of runs were performed at wind speeds of 0 and 12 m s^{-1} at an 8-m height above the water surface, with floodwater NH_4–N concentrations ranging from 1 to 49 mg L^{-1} while pH, temperature, and depth of floodwater were maintained at their mean values. At a wind speed of 12 m s^{-1} at the 8-m height, NH_3 volatilization was almost 100%, compared with only a 2% loss at 0 m s^{-1} at all NH_4–N concentrations. As shown in Table 2, wind speed did not influence NH_3(aq), but influenced the k_{vN}. An increase in wind speed increased the k_{vN} (Jayaweera and Mikkelsen, 1990), thus influencing NH_3 loss.

Effect of pH on Ammonia Volatilization

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

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

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

Parameter variable range	Initial NH_4–N concentration (AMC)	pH	Temperature (TEMP)	Water depth (WD)	Wind speed at 8 m (U_8)
	mg L^{-1}		°C	cm	m s^{-1}
Lowest	1	7.0	10	1	0
	9	7.5	15	4	2
	17	8.0	20	7	4
Mean	25	8.5	25	10	6
	33	9.0	30	13	8
	41	9.5	35	16	10
Highest	49	10.0	40	19	12

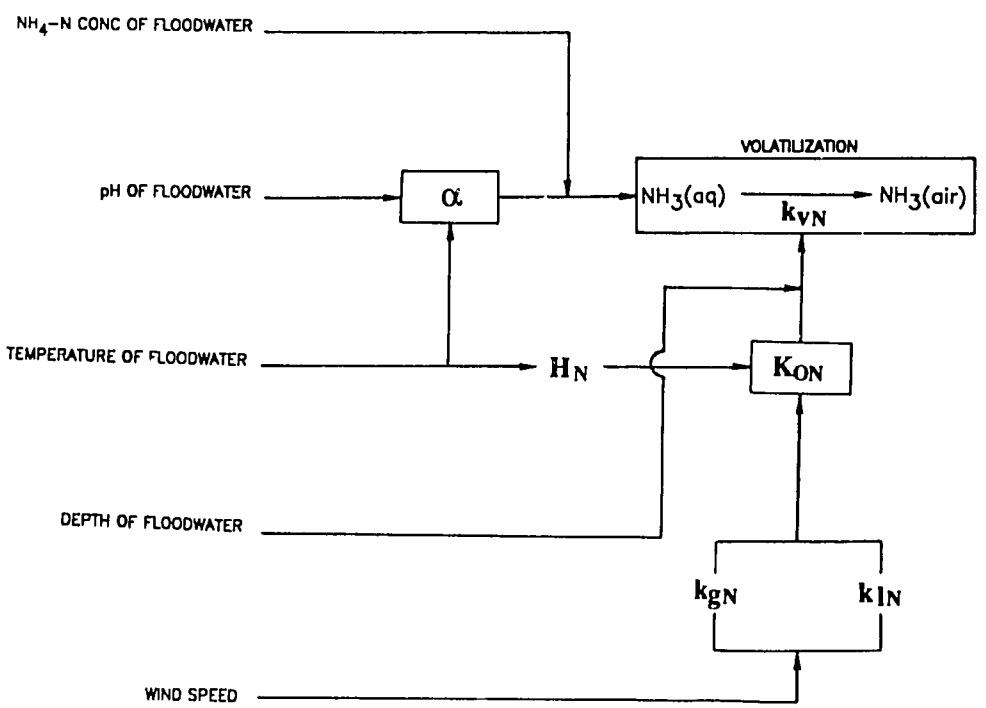

Fig. 1. Theory of NH_3 volatilization in flooded systems, where k_{vN} = volatilization rate constant for NH_3, K_{ON} = overall mass-transfer coefficient for NH_3, k_{gN} and k_{lN} = gas-liquid-exchange constants for NH_3, respectively, α = degree of dissociation of NH_4, and H_N = Henry's law constant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

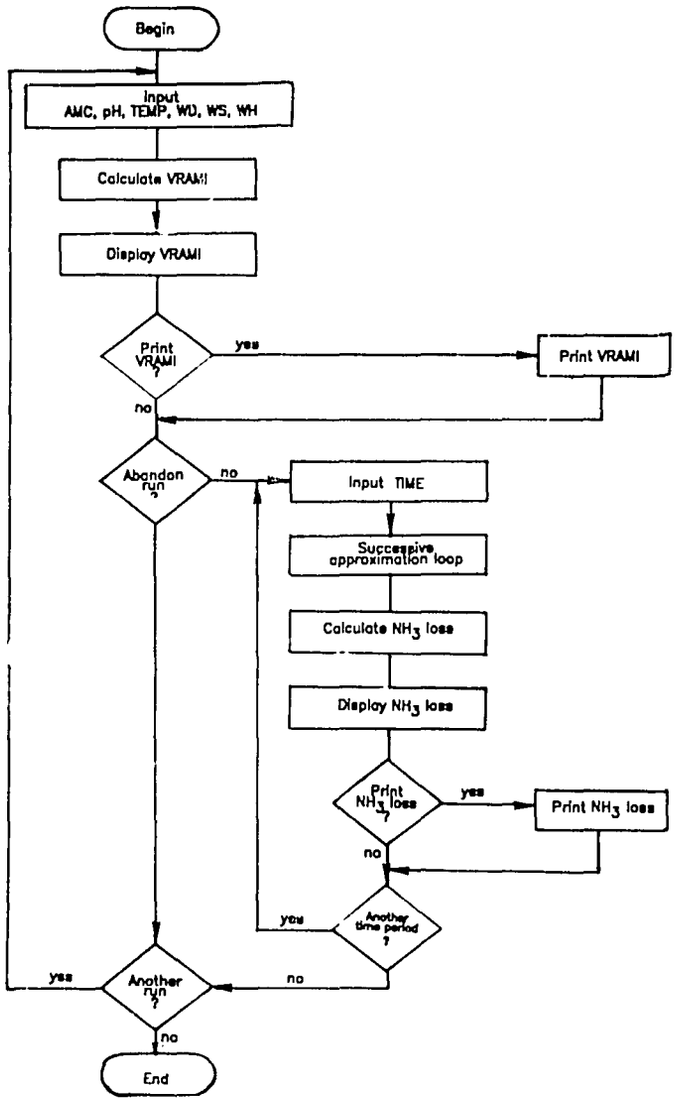

Fig. 2. Flow chart for NH_3-volatilization model, where AMC = floodwater ammoniacal-N concentration, pH = floodwater pH, TEMP = floodwater temperature, WD = floodwater depth, WS = wind speed, WH = height of wind measurement, and VRAMI = initial volatilization rate of NH_3.

Table 2. Effect of floodwater NH_4-N concentration on NH_3 volatilization.

Initial NH_4-N in floodwater	Initial NH_3(aq)	Volatilization rate constant (k_{vN})	Initial NH_3 volatilization rate[3]	NH_3 loss/day
mg L^{-1}	mol m^{-3}	s^{-1}	mol L^{-1} s^{-1}	%
pH 8.5; temperature 25 °C; water depth 10 cm; wind speed 6 m s^{-1}				
1	0.01	9.2×10^{-5}	1.7×10^{-5}	77
25	0.29	9.2×10^{-5}	4.2×10^{-4}	77
49	0.57	9.2×10^{-5}	8.2×10^{-4}	77
pH 7.0†; temperature 25 °C; water depth 10 cm, wind speed 6 m s^{-1}				
1	4.3×10^{-4}	9.2×10^{-5}	5.3×10^{-7}	4
25	1.1×10^{-2}	9.2×10^{-5}	1.3×10^{-5}	4
49	2.1×10^{-2}	9.2×10^{-5}	2.6×10^{-5}	4
pH 10.0‡; temperature 25 °C; water depth 10 cm; wind speed 6 m s^{-1}				
1	0.06	9.2×10^{-5}	5.3×10^{-4}	100
25	1.61	9.2×10^{-5}	1.3×10^{-2}	100
49	3.15	9.2×10^{-5}	2.6×10^{-2}	100
pH 8.5; temperature 10 °C†; water depth 10 cm; wind speed 6 m s^{-1}				
1	4.3×10^{-1}	8.7×10^{-5}	5.1×10^{-6}	36
25	0.11	8.7×10^{-5}	1.3×10^{-4}	36
49	0.21	8.7×10^{-5}	2.5×10^{-4}	36
pH 8.5; temperature 40 °C‡; water depth 10 cm; wind speed 6 m s^{-1}				
1	0.03	9.7×10^{-5}	4.8×10^{-5}	99
25	0.63	9.7×10^{-5}	1.2×10^{-3}	99
49	1.23	9.7×10^{-5}	2.4×10^{-3}	99
pH 8.5; temperature 25 °C; water depth 1 cm†; wind speed 6 m s^{-1}				
1	0.01	9.2×10^{-4}	1.7×10^{-4}	100
25	0.29	9.2×10^{-4}	4.2×10^{-3}	100
49	0.57	9.2×10^{-4}	8.2×10^{-3}	100
pH 8.5; temperature 25 °C; water depth 19 cm‡; wind speed 6 m s^{-1}				
1	0.01	4.9×10^{-5}	8.8×10^{-6}	53
25	0.29	4.9×10^{-5}	2.2×10^{-4}	53
49	0.57	4.9×10^{-5}	4.3×10^{-4}	53
pH 8.5; temperature 25 °C; water depth 10 cm; wind speed 0 m s^{-1}†				
1	0.01	1.1×10^{-6}	1.9×10^{-7}	2
25	0.29	1.1×10^{-6}	4.8×10^{-6}	2
49	0.57	1.1×10^{-6}	9.4×10^{-6}	2
pH 8.5; temperature 25 °C; water depth 10 cm; wind speed 12 m s^{-1}‡				
1	0.01	2.5×10^{-4}		98
25	0.29	2.5×10^{-4}		98
49	0.57	2.5×10^{-4}		98

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

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

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

When we compare the model runs at wind speeds of 12 and 0 m s^{-1} at an 8-m height, nearly 100% of NH_3 was lost per day at 12 m s^{-1} at a pH of 8.5, compared with a 41% loss at pH 10.0 when there was no wind (Table 3), which can be explained by the difference in k_{vN} values for NH_3 at the two wind speeds. This shows that, even at high pH values, low NH_3 volatilization is maintained as a result of low wind speeds.

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

Effect of Temperature on Ammonia Volatilization

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

Table 3. Effect of floodwater pH on NH_3 volatilization.

pH	Initial NH_3(aq)	Volatilization rate constant (k_{vN})	Initial NH_3 volatilization rate	NH_3 loss/day
	mol m^{-3}	s^{-1}	mol L^{-1} s^{-1}	%
NH_4-N concentration 25 mg L^{-1}; temperature 25 °C; water depth 10 cm; wind speed 6 m s^{-1}				
7.0	0.01	9.2×10^{-5}	1.3×10^{-5}	4
8.5	0.29	9.2×10^{-5}	4.3×10^{-4}	77
10.0	1.61	9.2×10^{-5}	1.3×10^{-2}	100
NH_4-N concentration 25 mg L^{-1}; temperature 10 °C†; water depth 10 cm; wind speed 6 m s^{-1}				
7.0	3.53×10^{-3}	8.7×10^{-5}	4.1×10^{-6}	1
8.5	0.11	8.7×10^{-5}	1.3×10^{-4}	36
10.0	1.2	8.7×10^{-5}	4.1×10^{-3}	100
NH_4-N concentration 25 mg L^{-1}; temperature 40 °C‡; water depth 10 cm; wind speed 6 m s^{-1}				
7.0	2.9×10^{-2}	9.7×10^{-5}	3.8×10^{-5}	12
8.5	0.63	9.7×10^{-5}	1.2×10^{-3}	99
10.0	1.77	9.7×10^{-5}	3.8×10^{-2}	100
NH_4-N concentration 25 mg L^{-1}; temperature 25 °C; water depth 1 cm†; wind speed 6 m s^{-1}				
7.0	1.07×10^{-2}	9.2×10^{-4}	1.3×10^{-4}	37
8.5	0.29	9.2×10^{-4}	4.2×10^{-3}	100
10.0	1.61	9.2×10^{-4}	0.13	100
NH_4-N concentration 25 mg L^{-1}; temperature 25 °C; water depth 19 cm‡; wind speed 6 m s^{-1}				
7.0	1.1×10^{-2}	4.8×10^{-5}	6.9×10^{-6}	2
8.5	0.29	4.8×10^{-5}	2.2×10^{-4}	53
10.0	1.61	4.8×10^{-5}	6.9×10^{-3}	100
NH_4-N concentration 25 mg L^{-1}; temperature 25 °C; water depth 10 cm; wind speed 0 m s^{-1}†				
7.0	1.07×10^{-2}	1.1×10^{-6}	1.5×10^{-7}	>1
8.5	0.29	1.1×10^{-6}	4.8×10^{-6}	1
10.0	1.61	1.1×10^{-6}	1.52×10^{-4}	41
NH_4-N concentration 25 mg L^{-1}; temperature 25 °C; water depth 10 cm; wind speed 12 m s^{-1}‡				
7.0	1.07×10^{-2}	2.5×10^{-4}	3.6×10^{-5}	12
8.5	0.29	2.5×10^{-4}	1.13×10^{-3}	98
10.0	1.61	2.5×10^{-4}	3.6×10^{-2}	100

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

Table 4. Effect of floodwater temperature on NH_3 volatilization.

Temperature	Initial NH_3(aq)	Volatilization rate constant k_{vN}	Initial NH_3 volatilization rate	NH_3 loss/day
°C	mol m^{-3}	s^{-1}	mol L^{-1} s^{-1}	%
NH_4-N concentration 25 mg L^{-1}; pH 8.5; water depth 10 cm; wind speed 6 m s^{-1}				
10	0.11	8.7×10^{-5}	1.3×10^{-4}	9
25	0.29	9.2×10^{-5}	4.2×10^{-4}	19
40	0.63	9.7×10^{-5}	1.2×10^{-3}	25
NH_4-N concentration 25 mg L^{-1}; pH 7†; water depth 10 cm; wind speed 6 m s^{-1}				
10	3.5×10^{-3}	8.7×10^{-5}	4.1×10^{-6}	1
25	1.1×10^{-2}	9.3×10^{-5}	4.2×10^{-4}	4
40	2.9×10^{-2}	9.7×10^{-5}	3.8×10^{-5}	12
NH_4-N concentration 25 mg L^{-1}; pH 10‡; water depth 10 cm; wind speed 6 m s^{-1}				
10	1.23	8.7×10^{-5}	4.1×10^{-3}	100
25	1.61	9.2×10^{-5}	1.32×10^{-2}	100
40	1.78	9.7×10^{-5}	3.79×10^{-2}	100
NH_4-N concentration 25 mg L^{-1}; pH 8.5; water depth 1 cm†; wind speed 6 m s^{-1}				
10	0.11	8.7×10^{-4}	1.3×10^{-3}	99
25	0.29	9.2×10^{-4}	4.3×10^{-3}	100
40	0.63	9.7×10^{-4}	0.01	100
NH_4-N concentration 25 mg L^{-1}; pH 8.5; water depth 19‡; wind speed 6 m s^{-1}				
10	0.11	4.6×10^{-5}	6.8×10^{-5}	21
25	0.29	4.9×10^{-5}	2.2×10^{-4}	53
40	0.63	5.1×10^{-5}	6.3×10^{-4}	89
NH_4-N concentration 25 mg L^{-1}; pH 8.5; water depth 10 cm; wind speed 0 m s^{-1}†				
10	0.11	9.1×10^{-7}	1.4×10^{-6}	>1
25	0.29	1.1×10^{-6}	4.8×10^{-6}	2
40	0.63	1.2×10^{-6}	1.5×10^{-5}	5
NH_4-N concentration 25 mg L^{-1}; pH 8.5; water depth 10 cm; wind speed m s^{-1}‡				
10	0.11	2.3×10^{-4}	3.4×10^{-4}	69
25	0.29	2.5×10^{-4}	1.1×10^{-3}	98
40	0.63	3.3×10^{-4}	4.1×10^{-3}	100

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

day (Table 4). The higher volatilization rate of NH_3 at 40 °C than at 10 °C was due to an increase in NH_3(aq) concentration in floodwater and the k_{vN} (Jayaweera and Mikkelsen, 1990).

When the model was executed at pH 10.0, with varying temperatures and the remaining variables kept constant, 100% of the NH_3 was lost per day, even at the lowest temperature (10 °C). At pH 7.0, however, even at a floodwater temperature of 40 °C, only about 12% of NH_3 was lost, which was due to the very low concentration of NH_3(aq) in the floodwater (Table 4).

When the depth of floodwater was 1 cm, even at 10 °C the NH_3 volatilization was rapid; when the floodwater depth was 19 cm, even at 40 °C, only 89% of NH_3 was lost per day. The rapid loss of NH_3 at low floodwater depths was due to a high k_{vN} (Table 4).

When there was no wind, even at 40 °C very little NH_3 was lost, compared with high volatilization losses at relatively low temperatures when the wind speed was at 12 m s^{-1} (Table 4). These differences in NH_3-volatilization rates at different wind speeds were due to variations in the k_{vN} for NH_3.

This data shows clearly that factors such as pH, depth of floodwater, and wind speed influence the NH_3-volatilization process by several orders of magnitude at various temperatures.

Effect of Water Depth on Ammonia Volatilization

The depth of floodwater was varied from 1 to 19 cm in increments of 3 cm, while the floodwater NH_4-N concentration, pH, temperature of floodwater, and wind speed were kept constant at the mean values. As the depth of floodwater increased from 1 to 19 cm, the volatilization rate of NH_3 decreased, reducing the NH_3 loss per day from 100 to 53% (Table 5). An increase in depth of floodwater did not influence the NH_3(aq) concentration in floodwater, but decreased the k_{vN} (Table 5), thus decreasing the NH_3 loss from the flooded system.

The next series of model runs were performed at pH 7.0 and 10.0, while varying floodwater depth from 1 to 19 cm with floodwater NH_4-N concentration, temperature, and wind speed kept at their mean val-

Table 5. Effect of floodwater depth on NH_3 volatilization.

Depth	Initial NH_3(aq)	Volatilization rate constant (k_{vN})	Initial NH_3 volatilization rate	NH_3 loss/day
cm	mol m^{-3}	s^{-1}	mol L^{-1} s^{-1}	%
NH_4-N concentration 25 mg L^{-1}; pH 8.5; temperature 25 °C; wind speed 6 m s^{-1}				
1	0.29	9.2×10^{-4}	4.2×10^{-3}	100
10	0.29	9.2×10^{-5}	4.2×10^{-4}	77
19	0.29	4.8×10^{-5}	2.2×10^{-4}	53
NH_4-N concentration 25 mg L^{-1}; pH 7†; temperature 25 °C; wind speed 6 m s^{-1}				
1	0.01	9.2×10^{-4}	1.3×10^{-4}	37
10	0.01	9.2×10^{-5}	1.3×10^{-5}	4
19	0.01	4.8×10^{-5}	6.9×10^{-6}	2
NH_4-N concentration 25 mg L^{-1}; pH 10‡; temperature 25 °C; wind speed 6 m s^{-1}				
1	1.6	9.2×10^{-4}	0.13	100
10	1.6	9.2×10^{-5}	1.3×10^{-5}	100
19	1.6	4.8×10^{-5}	6.9×10^{-6}	100
NH_4-N concentration 25 mg L^{-1}; pH 8.5; temperature 10 °C†; wind speed 6 m s^{-1}				
1	0.11	8.7×10^{-4}	1.3×10^{-3}	99
10	0.11	8.7×10^{-5}	1.3×10^{-4}	36
19	0.11	4.6×10^{-5}	6.8×10^{-5}	21
NH_4-N concentration 25 mg L^{-1}; pH 8.5; temperature 40 °C‡; wind speed 6 m s^{-1}				
1	0.63	9.7×10^{-4}	0.01	100
10	0.63	9.7×10^{-5}	1.2×10^{-3}	99
19	0.63	5.1×10^{-5}	6.3×10^{-4}	89
NH_4-N concentration 25 mg L^{-1}; pH 8.5; temperature 25 °C; wind speed 0 m s^{-1}†				
1	0.29	1.1×10^{-5}	4.8×10^{-5}	15
10	0.29	1.1×10^{-7}	4.8×10^{-6}	2
19	0.29	5.6×10^{-7}	2.5×10^{-6}	>1
NH_4-N concentration 25 mg L^{-1}; pH 8.5; temperature 25 °C; wind speed 12 m s^{-1}‡				
1	0.29	2.5×10^{-3}	1.1×10^{-2}	100
10	0.29	2.5×10^{-4}	1.1×10^{-3}	98
19	0.29	1.3×10^{-4}	6.0×10^{-4}	87

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

ues. When the pH of floodwater was 10.0, 100% of NH_3 was lost at all water depths ranging from 1 to 19 cm. However, when the pH was 7.0, even at 1-cm floodwater depth, nearly 37% of the NH_3 was lost and, at 19-cm depth, the NH_3 volatilization was only 2% (Table 5). This shows the interaction of NH_3(aq) concentration and k_{vN} in the process of NH_3 volatilization.

In studying the effect of temperature on NH_3 loss at different floodwater depths, it is seen that, at a water depth of 1 cm, both temperatures, 10 and 40 °C, showed the same influence on NH_3 loss, with 100% volatilizing with a period of 1 d (Table 5). At a water depth of 19 cm, however, the NH_3 loss per day decreased to 21% when the temperature of the floodwater was 10 °C, compared with 89% loss at 40 °C. Depth of floodwater plays a dominant role by allowing 100% NH_3 loss even at a floodwater temperature of 10 °C.

Wind speed had a large influence on NH_3 volatilization at different water depths. If there was no wind, i.e., at 0 m s^{-1} wind speed, at 1-cm floodwater depth, only about 15% of NH_3 was lost per day, compared with 100% loss at a wind speed of 12 m s^{-1} at an 8-m height. By increasing the depth of floodwater to 19 cm, the system lost nearly 87% of NH_3 at 12 m s^{-1} wind speed, compared with 0.9% at 0 m s^{-1}.

Table 6. Effect of wind speed at 8 m above the water surface on NH_3 volatilization.

Wind speed	Initial NH_3(aq)	Volatilization rate constant (k_{vN})	Initial NH_3 volatilization rate	NH_3 loss/day
m s^{-1}	mol m^{-3}	s^{-1}	mol L^{-1} s^{-1}	%
NH_4-N concentration 25 mg L^{-1}; pH 8.5; temperature 25 °C; water depth 10 cm				
0	0.29	1.1×10^{-6}	4.8×10^{-6}	2
6	0.29	9.2×10^{-5}	4.2×10^{-4}	77
12	0.29	2.5×10^{-4}	1.1×10^{-3}	98
NH_4-N concentration 25 mg L^{-1}; pH 7†; temperature 25 °C, water depth 10 cm				
0	0.01	1.1×10^{-6}	1.5×10^{-7}	>1
6	0.01	9.2×10^{-5}	1.3×10^{-5}	4
12	0.01	2.5×10^{-4}	3.6×10^{-5}	12
NH_4-N concentration 25 mg L^{-1}; pH 10‡; temperature 25 °C; water depth 10 cm				
0	1.61	1.1×10^{-6}	1.5×10^{-4}	41
6	1.61	9.2×10^{-5}	1.3×10^{-2}	100
12	1.61	2.5×10^{-4}	3.6×10^{-2}	100
NH_4-N concentration 25 mg L^{-1}; pH 8.5; temperature 10 °C†; water depth 10 cm				
0	0.11	9.1×10^{-7}	1.4×10^{-6}	>1
6	0.11	8.7×10^{-5}	1.3×10^{-4}	36
12	0.11	2.3×10^{-4}	3.4×10^{-4}	70
NH_4-N concentration 25 mg L^{-1}; pH 8.5; temperature 40 °C‡; water depth 10 cm				
0	0.63	1.3×10^{-6}	1.5×10^{-5}	5
6	0.63	9.7×10^{-5}	1.2×10^{-3}	99
12	0.63	2.7×10^{-4}	3.3×10^{-3}	100
NH_4-N concentration 25 mg L^{-1}; pH 8.5; temperature 25 °C; water depth 1 cm†				
0	0.29	1.1×10^{-5}	4.8×10^{-5}	15
6	0.29	9.2×10^{-4}	4.2×10^{-3}	100
12	0.29	2.5×10^{-3}	1.1×10^{-2}	100
NH_4-N concentration 25 mg L^{-1}; pH 8.5; temperature 25 °C; water depth 19 cm‡				
0	0.29	5.6×10^{-7}	2.53×10^{-6}	>1
6	0.29	4.9×10^{-5}	2.2×10^{-4}	53
12	0.29	1.3×10^{-4}	5.9×10^{-4}	87

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

The depth of floodwater plays a significant role in the process of NH_3 volatilization; however, other parameters such as pH, temperature of floodwater, and wind speed play an important role in controlling NH_3 volatilization.

Effect of Wind Speed on Ammonia Volatilization

The wind speed at an 8-m height was varied from 0 to 12 m s^{-1} while the floodwater NH_4-N concentration, pH, temperature, and depth of floodwater were maintained constant at their mean values. An increase in wind speed increased both the percent NH_3 loss per day and the k_{vN}. As shown in Table 6, the increase in wind speed did not influence NH_3(aq) concentration in the floodwater, but increased the k_{vN} as a result of increase in exchange constants for NH_3 transfer across the air-water interface (Jayaweera and Mikkelsen, 1990).

At pH 10.0, all the NH_4-N in floodwater was lost as NH_3 gas at a wind speed as low as 2 m s^{-1} at 8-m height, compared with 12% loss at 12 m s^{-1} wind speed when the pH was 7.0 (Table 6). This shows that even with a high k_{vN}, if the NH_3(aq) in floodwater is low, only a small amount of NH_3 is lost.

When the temperature of the floodwater was 40 °C, nearly 100% of NH_3 was lost at 6 m s^{-1} wind speed. In contrast, when the temperature was 10 °C, the NH_3 loss was negligible at 0 m s^{-1} at 8-m height but increased to 70% at 12 m s^{-1} (Table 6).

At a water depth of 1 cm, nearly 100% of NH_3 was lost per day even at low wind speeds, while only 87% was lost, even at 12 m s^{-1} wind speed, when the depth of floodwater was 19 cm (Table 6).

Wind speed influences the NH_3-volatilization process by virtue of its influence on k_{vN}. Temperature, pH, and depth of floodwater, however, could vary the rate of volatilization, depending on the conditions.

By analyzing the effect of various parameters on the rate of NH_3 volatilization and NH_3 loss over a given period, it is seen that (i) the floodwater NH_4–N concentration directly influences the NH_3(aq) concentration in floodwater but does not influence the k_{vN} (ii) the pH of floodwater influences only the NH_3(aq) concentration, (iii) the temperature of floodwater influences both the NH_3(aq) concentration of floodwater and the k_{vN}, and (iv) the depth of floodwater and wind speed influence only the k_{vN}.

Sensitivity Analysis

The influence of various determinants of NH_3 volatilization were tested in a sensitivity analysis. When floodwater NH_4–N concentration was increased while pH, temperature, depth of floodwater, and wind speed were kept constant, NH_3 volatilization increased linearly. This is directly related to an increase in NH_3(aq) in floodwater as a function of NH_4–N concentration, as has been reported (Vlek and Stumpe, 1978; Vlek and Craswell, 1979; Fillery and Vlek, 1986). Therefore, in the sensitivity analysis, the floodwater NH_4–N concentration was kept at a constant value of 25 mg L^{-1}.

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

Condition 1: AMC = 25 mg L^{-1}, pH = 8.0, TEMP = 20 °C, WD = 7 cm, and U_8 = 4 m s^{-1}.

Condition 2: AMC = 25 mg L^{-1}, pH = 8.5, TEMP = 25 °C, WD = 10 cm, and U_8 = 6 m s^{-1}.

Condition 3: AMC = 25 mg L^{-1}, pH = 9.0, TEMP = 30 °C, WD = 13 cm, and U_8 = 8 m s^{-1}.

where AMC = floodwater NH_4–N concentration,
pH = pH of floodwater,
TEMP = temperature of floodwater,
WD = depth of floodwater, and
U_8 = wind speed at 8-m height.

For each condition, one factor was varied while the others were kept constant. The sensitivity (slope) of NH_3 loss per day with respect to pH, temperature, water depth, and wind speed is shown in Fig. 3.

An increase in pH increased the sensitivity of NH_3 loss to values of 8.75 for Condition 1 and 8.25 for Conditions 2 and 3. A further increase in pH decreased the sensitivity. High pH values brought more NH_3(aq) into the system, but NH_3 loss also depends on the k_{vN}. This explains why the greatest sensitivity was obtained at a pH value of 8.75 under Condition 1, compared with 8.25 under Conditions 2 and 3. The sensitivity decreased due to the limitation of NH_4 concentration in solution, which supplies NH_3(aq) to the system.

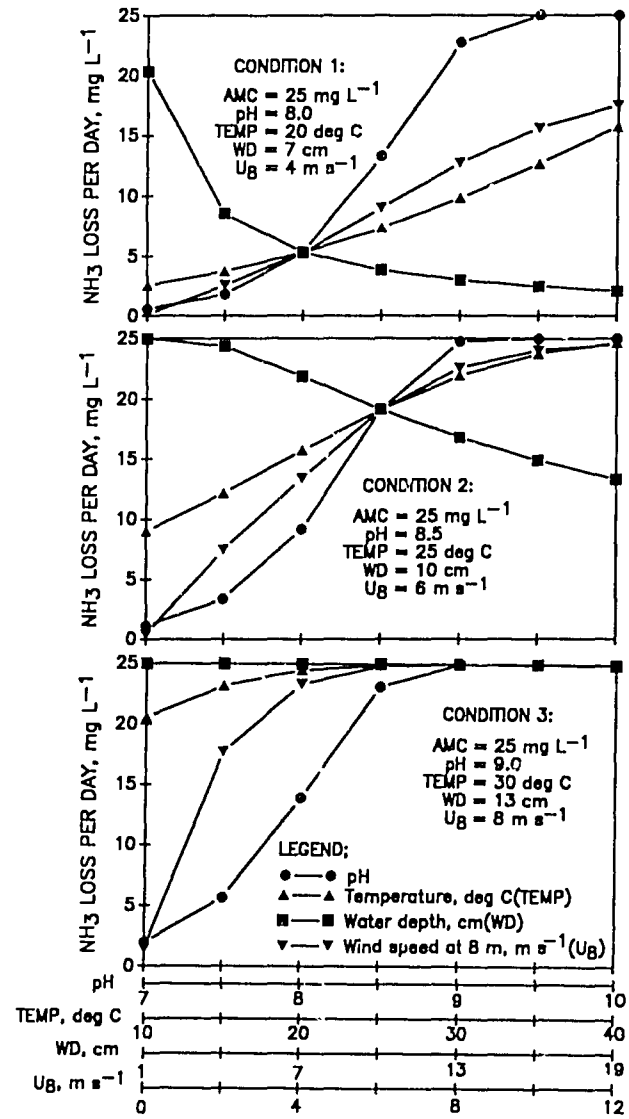

Fig. 3. Sensitivity analysis for NH_3-volatilization model, where AMC = floodwater ammoniacal-N concentration.

When the temperature increased from 10 to 40 °C under Condition 1, sensitivity increased gradually from 0.23 to 0.61; under Condition 2, sensitivity increased to a temperature of 17.5 °C and then decreased gradually; and under Condition 3, sensitivity decreased gradually. Under Condition 1, the pH and wind speed were low; when the temperature was raised, the NH_3(aq) concentration and the k_{vN} increased, thus increasing sensitivity. Under Condition 3, however, high pH and wind speed values caused high NH_3 losses; an increase in temperature decreased the sensitivity as NH_4–N concentration in the system decreased.

Increased water depth decreased the percent NH_3 loss. For each increment of water depth, however, the sensitivity of NH_3 loss varied depending on the conditions. Under Condition 1, the highest sensitivity occurred with low water depth, and sensitivity decreased as water depth increased. At a pH of 8.0 and temperature of 20 °C, a small concentration of NH_3(aq) occurred in the floodwater. Because of the shallow depth, k_{vN} increased, causing increased NH_3 volatilization, which brought high sensitivity at a shallow water