A SIMPLE MATHEMATICAL MODEL SIMULATING AMMONIA VOLATILIZATION LOSSES IN THE FIELD

R.R. Sherlock and K.M. Goh
Soil Science Department, Lincoln College, Canterbury

ABSTRACT

The efficient use of urea fertiliser in cropping and pastoral agriculture is often prejudiced by the loss of a portion of the applied nitrogen by ammonia volatilization. A simple field method for quantifying this loss is needed as the current field techniques used are labour intensive, expensive and inappropriate for many potential experimental sites.

A simple iterative computer simulation model is presented which attempts to quantify ammonia gas loss following applications of urine and urea solutions to a short, ryegrass/white clover pasture in Canterbury. The model is based on the solution chemistry of ammonia with simplifications appropriate for aqueous urea applications. Input parameters include:

(i) soil surface (0-0.5 cm) pH (preferably measured daily until pH drops to <7.5),
(ii) continuous surface air temperatures or mean daily temperatures (depending on the precision required),
(iii) rate of urea hydrolysis in the soil surface (0-2.5 cm),
(iv) the fraction of the applied nitrogen solution held up on leaf surfaces and remaining in the topsoil (0-2.5 cm) after mass flow of the solution has ceased.

Preliminary data collected from field experiments were found to verify adequately the above simulation model. These are presented and discussed.

Additional Keywords: pH, air temperature, urea fertiliser, urine patches

INTRODUCTION

With the recent construction of a urea manufacturing facility in New Zealand, an increased usage of urea fertiliser in horticulture, pastoral agriculture and forestry is widely anticipated. A factor which may potentially moderate its use, however, is the long recognised process of ammonia volatilization which can take place during, and subsequent to, hydrolysis of urea in the soil. Ammonia volatilization can occur following applications of any ammoniacal-N fertiliser. However, for urea, a preliminary hydrolysis reaction catalysed by urea in the soil generates high pH's which stimulate ammonia (NH_3) gas loss. Urea hydrolysis also occurs in urine patches in grazed pastures. Recent research on ammonia (NH_3) volatilization in New Zealand has concentrated on measuring losses from simulated urine patches using both urine and aqueous urea solutions (Holland and During, 1977; Sherlock and Goh, 1978; Ball, 1979; Ball and Keeney, 1981; Carran *et al.*, 1982; Steele and Shannon, 1982). Few direct measurements of NH_3 losses from surface applied urea prills have been made in this country.

Recent studies in South-east Queensland (Catchpoole *et al.*, 1981; 1983) indicate NH_3 gas losses from surface applied prilled urea averaged 19% over four applications made during spring, summer, autumn, and winter. Maximum loss ocurred during autumn when 42% of the nitrogen in a 94 kg N/ha application volatilized as NH_3 gas. A preliminary study at Lincoln College (unpublished data) indicated that losses approaching this magnitude may occur in Canterbury when urea prills are surface applied to pastures in autumn. Further work is underway to establish whether losses of this size are typical and also to investigate strategies to minimise them.

Unfortunately, measuring NH_3 losses directly in the field is not a task which can be carried out simply as it requires fairly sophisticated gas trapping apparatus and frequent monitoring of equipment. Also, in many potential field sites (e.g. hill country), direct aerodynamic measuring techniques would be impracticable. The laboratory testing of soils under a set of standardised conditions may provide a means of determining their relative potential to volatilize NH_3. However, the complex interactions of climate, soil type, soil moisture, temperature, soil pH, microflora and microfauna which ultimately determine the extent of NH_3 loss can only be found *in situ*.

A better assessment of the extent of this phenomenon can only be achieved with a clear understanding of the relative importance of each of these factors and the way in which they interact. Attempts at combining these and other factors into a comprehensive volatilization model have been made. However, the resulting published models are either too complex to use routinely without drastic simplifications (e.g. Parton *et al.*, 1981) or relate only to volatilization loss from flooded soils (Bouwmeester and Vlek, 1981; Vlek and Crasswell, 1981; Denmead *et al.*, 1982). What is required, therefore, is an ammonia volatilization model which can ideally take the form of a 'field test' and which would use easily measured soil properties and meteorological data as its input parameters. Such a 'field test' could be of great value in providing a rapid means of assessing the extent of nitrogen loss from both urine patches and urea fertilised pasture.

A SIMPLIFIED MODEL

A simplified NH_3 volatilization model has recently been developed independently by the authors and is represented diagrammatically in Fig. 1. It was originally designed to simulate the volatile losses of NH_3 from sheep urine patches but may prove useful in predicting volatilization losses following prilled urea applications.

In this model, all the KCl-extractable ammoniacal-N, in the topsoil (0-2.5 cm) is assumed to be in thermodynamic equilibrium with the soil/air interface and therefore subject to possible volatilization. Here, ammoniacal-N is denoted as 'NH_X' and defined as the sum of dissolved ammonium, $NH_4^+(aq)$, and ammonia, $NH_3(aq)$, in the soil solution together with ammonium ions, NH_4^+ (exchange sites) held on the exchange sites in the soil.

Inputs of NH_X into this single topsoil compartment are assumed to arise solely from *in situ* urea hydrolysis. Outputs of ammoniacal-N from the compartment are assumed to arise only by virtue of the gaseous NH_3 loss to the atmosphere.

The rates of other mechanisms which compete to remove NH_X from this compartment (e.g. plant uptake, leaching, nitrification, denitrification, and immobilization), are usually much slower than the rate of volatilization, especially over the duration of a typical volatilization event (i.e. 4-8 days following application of urea). For this reason, their combined influence in reducing the amount of NH_X in the topsoil during volatilization can often be ignored.

Equations needed to describe the model are obtained from a consideration of the following transformations which take place when urea or urine is surface applied to soil.

$$\begin{tikzcd}
 & & NH_3\,(g)\,\text{atmosphere} \\
 & NH_3\,(aq) \arrow[r, shift left, "K_h"] \arrow[d, shift left] & NH_3\,(g)\ \text{soil} \arrow[l, shift left] \arrow[u, "k_2"'] \\
\text{urea} \arrow[r, "k_1"] & NH_4^+\,(aq) \arrow[r, shift left, "D"] \arrow[u, shift left, "K_a"] & NH_4^+\,(\text{exchange sites}) \arrow[l, shift left]
\end{tikzcd} \qquad (1)$$

Where:

k_1 = first-order rate constant describing urea hydrolysis (units = $time^{-1}$)

D = dimensionless distribution ratio describing the partitioning of NH_4^+ between soil solution and soil exchange sites.

K_a = temperature and pH dependent acid dissociation constant for $NH_4^+(aq)$

K_h = dimensionless temperature dependent Henry's Law constant for $NH_3(g)$

k_2 = first-order $NH_3(g)$ volatilization constant (units = $time^{-1}$)

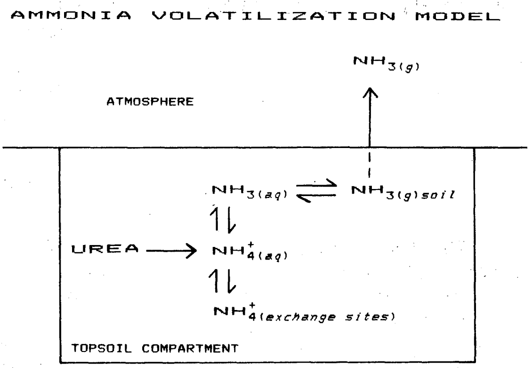

Figure 1: Diagrammatical representation of the simplified ammonia volatilization model.

Calculations based on recently published values for the equilibrium constants, K_a and K_h (Hales and Drewes, 1979), show the rate of $NH_3(g)$ volatilization to be highly dependent on both pH and temperature. The effect of these parameters are shown in Fig. 2. in which the equilibrium ratio of $NH_3(g)/NH_X(aq)$ for a system containing ammoniacal-N is plotted on a log scale against pH for several temperatures between 0 and 40 °C. This "volatilization ratio" provides directly a relative measure of the rate of $NH_3(g)$ loss from a system (e.g. urine patch or fertiliser granule) as a function of both pH and temperature assuming all other influences (e.g. soil type, amount of NH_X and windspeed) remain constant.

Under these conditions, systems with the same "volatilization ratio" should, in theory, lose $NH_3(g)$ at the same rate. For example, a hydrolysed urea fertiliser granule at pH 9.5 and temperature 0 °C (log volatilization ratio = -4.4), should lose $NH_3(g)$ at the same rate as a granule at pH 7.4 and 40 °C. Other relationships are also apparent from Fig. 2. Between pH 6 and 8.5, increasing the temperature of a system by about 10 °C increases the rate of volatilization by about a factor of 3. Similarly, increasing the pH of a system by 1 unit at constant temperature increases the rate of volatilization by a factor of 10.

These simple predictions of the direct effects of pH and temperature have been confirmed qualitatively in many laboratory investigations (Ernst and Massey, 1960; Overrein and Moe, 1967; Terman, 1979). We have used the relationships depicted in Fig. 2, together with some additional assumptions and simplifications to formulate two equations which control the input and output of NH_X in our defined topsoil compartment. A detailed description of the derivation of these equations is in preparation for publication elsewhere (Sherlock and Goh, 1983b).

Controlling Equations

The first equation describes the input of volatilizable NH_X into the topsoil compartment. This is a function of the initial amount of urea present and the rate of its subsequent hydrolysis and is given by:

$$d\,NH_x = U_o\,\{e^{-k_1 t} - e^{-k_1 (t\,+\,dt)}\} \qquad (2)$$

Where:

dt = program stepping time (usually 6 minutes)

$d\,NH_x$ = amount of NH_4^+-N generated in the topsoil in the time dt (units = % of applied N)

U_0 = amount of urea originally in the topsoil at time = 0 expressed as a percentage of the N applied

t = time after application of urea or sheep urine (units = hours)

k_1 = first-order urea hydrolysis constant (units = $hours^{-1}$)

The instantaneous rate of $NH_3(g)$ volatilization from the topsoil is given by the second equation:

$$R = \frac{k_2\ H\ NH_{x\,(total)}}{K_{h\,(mean)}\ M_v\ \ (D + 1)\ \ \{1 + \frac{10^{-pH}}{Ka}\}} \qquad (3)$$

Where:

R = NH_3-$N_{(g)}$ volatilization rate (units = % of applied N per hour)

NH_X (total) = the total KCl-extractable ammoniacal -N in the topsoil (0-2.5 cm) compartment (units = % of applied-N)

K_a = $10^{(-0.09018\ -\ 2729.92/T)}$

K_h (mean) = $10^{(-1.69\ +\ 1477.7/T\ (mean))}$

H = a temperature scaling factor for K_h i.e. H = K_h (mean)/K_h

M_V = the volumetric moisture content in the 0-2.5 cm compartment (units = cm^3/cm^3)

T (mean) = mean soil/air interface temperature during the volatilization process (units = °K)

T = instantaneous soil/air interface temperature (units = °K)

pH = instantaneous pH of surface soil (0-0.5 cm)

Running the Model

The two governing equations form the basis of a computer simulation program called NFLUX. This program is written in 'Microsoft Basic' for use on a 16K microcomputer although a version is available in 'Vax Basic'. Listings of the program together with sample runs are available from the authors.

Input Parameters

Apart from the published values for K_a and K_h (Hales and Drewes, 1979) the other input parameters required are:

(a) The urea hydrolysis constant, k_1.

This first-order rate constant describes the rate of urea hydrolysis and can be estimated from published values (e.g. Parton *et al.,* 1981) or determined by a suitable field experiment (Sherlock and Goh, 1983a).

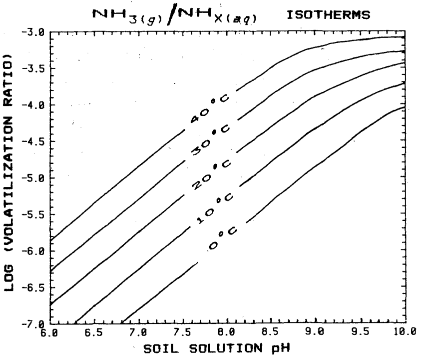

Figure 2: Plots showing log "volatilization ratio" as a function of the soil solution pH and temperature.

(b) Soil surface pH (0-0.5 cm).

As yet, the model is unable to calculate the soil surface pH as a function of time following fertiliser application. It is therefore necessary to monitor this parameter at regular intervals (e.g. once daily) during the volatilization event. Since the model actually requires discrete pH values at each iteration time (typically every 6 minutes), these are obtained by interpolation between the measured values.

(c) Estimates of the fraction of the applied N leached below 2.5 cm or held on the surface of leaves.

It is assumed that ammoniacal-N below the topsoil compartment is not subject to volatilization. Since volatilization losses are normally expressed as a percentage of the applied N, it is necessary to obtain an estimate of the applied N below the topsoil compartment otherwise volatilization losses would be overestimated.

Conversely, ammoniacal-N solution on leaf surfaces is not involved in the exchange reactions occurring in the topsoil compartment and is therefore subject to rapid and complete volatilization (McGarity and Hoult, 1971). Where urea solutions or urine are applied, hold-up of solution usually amounts to about 5% of the average 150ml simulated urination volume (Doak, 1951). Failure to allow for this results in an underestimation of losses.

Where urea is applied as prills to short pasture it seems unlikely that 'leaf-surface' volatilization would occur and, in the absence of irrigation or rain, little movement of hydrolysed NH_X would be expected below 2.5 cm. However, both these assumptions would need to be verified.

(d) Soil/air interface temperatures

These are currently supplied to the model as discrete hourly temperatures read from a shaded thermohygrograph placed at ground level in the field. Instantaneous temperatures for the controlling equations are obtained by interpolation and are calculated by the computer program.

(e) Evaluation of k_2, M_V and D

In theory, values for each of these parameters are required to solve for the volatilization rate in equation 3. Although M_V is easily measured, k_2 and D are much more difficult to evaluate. It can be shown, however, (Sherlock and Goh, 1983b) that where urea hydrolysis is not protracted (e.g. in urine patches) the rate of decline in the measured soil surface pH can be used to evaluate directly the value of: $k_2/K_{h\,(\mathrm{mean})}\,M_V\,(D+1)$.

This new composite term may be treated as a constant for the duration of the volatilization event and substituted into equation 3. Thus, a simple monitoring of the soil surface pH and temperature combined with a knowledge of the disposition of the applied nitrogen is sufficient to calculate the extent of $NH_3(g)$ volatilization using this simplified model.

Output parameters

The simulation model as currently written provides hourly calculated values of:

(a) $NH_3(g)$ loss (% applied N/hour) from the combined topsoil (0-2.5 cm) and leaf surface compartments

(b) residual NH_X (% applied N) in:
  (i) the topsoil compartment
  (ii) the leaf surface compartment and

(c) total cumulative $NH_3(g)$ loss as a function of a time.

VERIFICATION OF THE MODEL

The model was verified by comparison of the measurable output parameters with directly measured field data obtained at Lincoln College during the summer and autumn of 1982. Experiments were carried out on short ryegrass/white clover pasture established on a Templeton silt loam (Sherlock and Goh, 1983a). Volatilized $NH_3(g)$ was continuously monitored from simulated sheep urine patches using both high resolution (10-20 minute) samplings and low resolution (8 hour) samplings. Thus values were obtained for the "instantaneous" rate of $NH_3(g)$ loss and cumulative $NH_3(g)$ loss at specific sampling times. Full details of the experimental procedures will appear elsewhere (Sherlock and Goh, 1983a).

RESULTS

Excellent agreement between measured cumulative $NH_3(g)$ losses and values predicted by the simulation model was obtained. The correlation between these two sets of values for the combined 27 low resolution sampling times during summer and autumn was very highly significant (r = 0.976***). More importantly, the absolute cumulative loss values predicted by the model were very close to those actually measured. For example, the total NH_3-N loss 100 hours after urine application to pasture in the summer was measured as 21.1% of the applied N. The corresponding predicted value from the model was 20.7%. During the autumn, volatilization continued for a longer time with predicted losses after 200 hours of 22.4% and measured losses of 24.4%.

A more rigorous test of the model involves comparing measured high resolution $NH_3(g)$ loss values with predicted values. Again there was good agreement which is clearly illustrated for the summer experiment in Fig. 3. The correlation between predicted values and measured values from 58 sampling times during summer and autumn was again very highly significant (r = 0.943***). However, the model tends to slightly underestimate the measured values. This was apparent from a comparison of the means of the high resolution data which indicated that measured values were generally 10% higher than predicted. This difference between the measured and predicted means was not statistically significant.

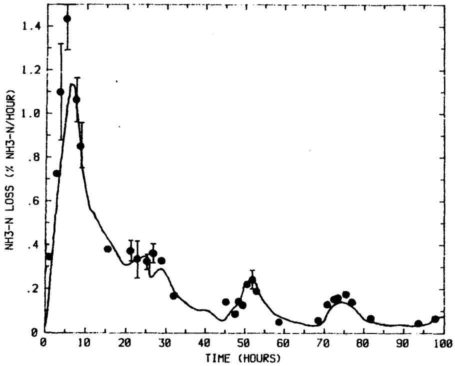

Figure 3: Rate of ammonia volatilization from urine patches in summer
(●) mean of 3 replicates
(I) standard deviation
(solid line) predicted by simulation model

DISCUSSION

Although the validating data set was obtained from only one pasture site, it provided 174 individual high resolution and 81 individual low resolution measurements and spanned two quite different seasonal situations. Thus, a wide range of fluctuating micrometeorological conditions were imposed which, together with two extremes of soil moisture, provided a very good test for the model. The extremely high correlation obtained between measured and predicted values, particularly for the low resolution data, is very encouraging.

As no soil-specific parameters were used, there appears to be no fundamental reason why the model should not work on other soil types. However, it must be cautioned that several assumptions and approximations were made, particularly in regard to the rates of other nitrogen transformations. It would be necessary to check the validity of these assumptions before applying the model to other experimental sites.

From the data currently available to us, the limitations to the usefulness of the model arise mainly from the accuracy with which the input parameters, particularly pH (0-0.5 cm), can be determined. This pH represents that of the surface within the urine patch from which volatilization to the atmosphere occurs. The values used here were from soil cores mixed with water in a 1:2.5 ratio and were recorded rapidly within 5 minutes of sampling. The requirement for rapid analysis was found necessary since pH readings changed by up to 1.0 units when the sample was left standing overnight.

The application of the present volatilization model to predicting $NH_3(g)$ losses from surface applied urea prills is currently being examined at Lincoln. Of critical importance is the characterisation of the pH in the immediate vicinity of the urea prill. A more appropriate technique in this context may be to use a portable pH meter and determine the pH directly *in situ* (e.g. Doak, 1951). This method is undergoing evaluation.

ACKNOWLEDGEMENTS

We thank the Research Division, New Zealand Ministry of Agriculture and Fisheries and the Lincoln College Research Committee for providing financial support. Our thanks also to Geoffrey Shekell and Robert Davidson for their technical assistance.

REFERENCES

Ball, P. Roger 1979. Nitrogen relationships in grazed and cut grass-clover systems. Ph.D. Thesis Massey University, Palmerston North.

Ball, P. Roger, Keeney, D.R. 1981. Nitrogen losses from urine-affected areas of a New Zealand pasture under contrasting seasonal conditions. *Proceedings of the XIV International Grasslands Congress:* 342-344.

Bouwmeester, R.J.B., Vlek, P.L.G. 1981. Rate control of ammonia volatilization from rice paddies. *Atmospheric Environment 15:* 131-140.

Carran, R.A., Ball, P.R., Theobald, P.W., Collins, M.E.G. 1982. Soil nitrogen balances in urine-affected areas under two moisture regimes in Southland. *N.Z. Journal of Experimental Agriculture 10:* 377-381.

Catchpole, V.R., Harper, L.A., Myers, R.J.K. 1981. Annual losses of ammonia from grazed pasture fertilized with urea. *Proceedings of the XIV International Grasslands Congress:* 344-347.

Catchpoole, V.R., Oxenham, D.J., Harper, L.A. 1983. Transformation and recovery of urea applied to a grass pasture in south-eastern Queensland. *Australian Journal of Experimental Agriculture and Animal Husbandry 23:* 80-86.

Denmead, O.T., Freney, J.R., Simpson, J.R., 1982. Dynamics of ammonia volatilization during furrow irrigation of maize. *Soil Science Society of America Journal 46:* 149-155.

Doak, B.W. 1951. Some chemical changes in the nitrogenous constituents of urine when voided on pasture. *Journal of Agricultural Science 32:* 162-171.

Ernest, J.W., Massey, H.F. 1960. The effects of several factors on volatilization of ammonia from urea in the soil. *Soil Science Society of America Proceedings 24:* 87-90.

Hales, J.M., Drewes, D.R. 1979. Solubility of ammonia at low concentrations. *Atmospheric Environment 13:* 1133-1147.

Holland, P.T., During, C. 1977. Movement of nitrate-N and transformations of urea-N under field conditions. *N.Z. Journal of Agricultural Research 20:* 479-488.

McGarity, J.W., Hoult, E.H. 1971. The plant component as a factor in ammonia volatilization from pasture swards. *Journal of the British Grasslands Society 26:* 31-34.

Overrein, L.N., Moe, P.G. 1967. Factors affecting urea hydrolysis and ammonia volatilization in soil. *Soil Science Society of America Proceedings 31:* 57-61.

Parton, W.J., Gould, W.D., Adamsen, F.J., Torbit, S., Woodmansee, R.G. 1981. Ammonia volatilization model. *In* "Simulation of Nitrogen Behaviour of Soil-plant Systems". Eds. M.J. Frissel and J.A. van Veen, Pudoc, Centre for Agricultural Publishing and Documentation, Wageningen, Netherlands. pp 234-244.

Sherlock, R.R., Goh, K.M. 1978. Field measurements of ammonia losses from sheep urine patches in a soil-pasture system. *In* supplement "Proceedings of Workshop on Nitrogen Transformations in Soil-pasture Systems". *N.Z. Soil News 25:* (2).

Sherlock, R.R., Goh, K.M. 1983a. Dynamics of ammonia volatilization from simulated urine patches and aqueous urea applied to pasture. I. Field experiments. *Fertilizer Research* (in press).

Sherlock, R.R., Goh, K.M. 1983b. Dynamics of ammonia volatilization from simulated urine patches and aqueous urea applied to pasture. II. Theoretical derivation of a simplied model. (Submitted for publication).

Steele, K.W., Shannon, P. 1982. Concepts relating to the nitrogen economy of a Northland intensive beef farm. *In* "Nitrogen Balances in New Zealand Ecosystems". Ed. P.W. Gander, Plant Physiology Division, DSIR, Palmerston North, New Zealand.

Terman, G.L. 1979. Volatilization losses of nitrogen as ammonia from surface-applied fertilizers, organic amendments, and crop residues. *Advances in Agronomy 31:* 189-223.

Vlek, P.L.G., Craswell, E.T. 1981. Ammonia volatilization in flooded soils. *Fertilizer Research 2:* 227-245.