

# Ammonia Volatilisation Potentials of New Zealand Agricultural Soils Broadcast with Granular Urea

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## ABSTRACT

The potential for ammonia (NH<sub>3</sub>), loss from granular urea applied to soil can be influenced by various soil, environmental and agronomic factors. Two field experiments were conducted to investigate the soil factors influencing the volatilisation potentials of a wide range of undisturbed New Zealand soils. Sample blocks of surface soil (0-7 cm depth) were transported from various parts of New Zealand to the experimental site (Lincoln University, Canterbury) and buried at ground level in enclosures configured for active trapping of volatilised NH<sub>3</sub>. Urea granules were broadcast (@ 100 kg N ha<sup>-1</sup>) and volatilised NH<sub>3</sub> was measured in the field laboratory.

In most cases volatilisation was essentially complete 7 days following urea application. Losses ranged from 4.4 to 53.9% of the applied-N. Simple correlation tests were performed between % cumulative (7 days) NH<sub>3</sub> losses (i.e. volatilisation potentials) and 14 soil properties. The environmental conditions encountered during the study were (i) warm, rapid soil drying (Experiment No.1) and (ii) cool slow-drying (Experiment No.2) conditions. Statistically significant relationships were found between volatilisation potentials and 6 soil properties. Only the initial microsite pH (measured 8 hours following urea application) showed highly significant linear relationships ( $r > 0.94$ ;  $P < 0.05$ ) with volatilisation potential under all environmental conditions. This observation was further examined by combining all the data sets and the following relationship was obtained:

$$\text{NH}_3 \text{ loss (7 days)} = -123 + 19.8 \text{ Initial microsite pH (R}^2 = 85.4; P < 0.01)$$

It is proposed that a soil which has a high H<sup>+</sup> buffer capacity is capable of resisting the alkalinity build-up during the initial stage of the urea hydrolysis. Such a soil should have a greater rate and extent of protonation of NH<sub>3(aq)</sub> released from urea and consequently have a lower volatilisation potential than that of a soil with a lower H<sup>+</sup> supplying capacity.

The measurement of initial microsite pH 8 hours following urea application provides a more reliable and simpler technique than the standard H<sup>+</sup> buffer capacity titration method to assess the volatilisation potential of soils.

## INTRODUCTION

Ammonia (NH<sub>3</sub>) is volatilised directly from ammonium (NH<sub>4</sub><sup>+</sup>)-bearing or producing (e.g. urea) fertilisers and from the N returned in excreta during grazing. About 70% of the excreta-N is voided in the form of urea-N as urine and the NH<sub>3</sub> loss process from urine is similar to that from fertiliser urea-N. The N loss through NH<sub>3</sub> volatilisation is one of the major N loss pathways from agricultural systems and losses up to 50% of the applied-N have been reported (Field and Ball, 1982; Fenn and Hossner, 1985). Consequently, in New Zealand and elsewhere heavy emphasis has been placed on determining the potentials for the NH<sub>3</sub> loss from agricultural soils through NH<sub>3</sub> volatilisation.

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The  $\text{NH}_3$  loss from the agricultural systems varies widely because the extent of the volatilisation process is greatly influenced by the soil type, the form, fertiliser-N management practices, grazing practices and the prevailing environmental conditions. Modifying any of these factors can alter a soil's capacity to volatilise  $\text{NH}_3$ . The capacity of a soil to volatilise  $\text{NH}_3$  from a nitrogenous fertiliser or excreta applied using a particular method at a specific rate and form under specified environmental conditions is defined here as the 'volatilisation potential' of the soil. The topic of soil volatilisation potential is not new although in the past it has generally been referred to as cumulative or total  $\text{NH}_3$  loss.

Several workers have studied the factors influencing  $\text{NH}_3$  loss from urea applied to soil (e.g. Ernst and Massey, 1960; Acquaye and Cunningham, 1965; Overrein and Moe, 1967; Simpson, 1968). Others have reviewed  $\text{NH}_3$  losses from  $\text{NH}_4^+$ -bearing or producing fertilisers (Terman, 1979; Freney *et al.*, 1981 and 1983; Vlek and Craswell, 1981; Nelson, 1982; Savant and De Datta, 1982; Fenn and Hossner, 1985; Haynes and Sherlock, 1986; Freney and Black, 1988). Only recently has the concept of volatilisation potential of soils fertilised with urea become widely used and the influence of soil factors on  $\text{NH}_3$  loss and the mechanisms involved, investigated (e.g. Lyster *et al.*, 1980; Ferguson *et al.*, 1984; O'Toole *et al.*, 1985; Rachhpal-Singh and Nye, 1986; Reynolds and Wolf, 1987; Martens and Bremner, 1989; Stevens *et al.*, 1989).

To date, the majority of the field  $\text{NH}_3$  volatilisation studies on surface applied urea in New Zealand have been conducted by the Department of Soil Science, Lincoln University (e.g. Black *et al.*, 1985a & b, 1987a & b and 1989; Sherlock *et al.*, 1986 and 1989). These studies have been performed on the Templeton silt loam examining the effect of urea granule size and form, seasonal changes, microsite pH and soil moisture on the dynamics of  $\text{NH}_3$  volatilisation, and evaluating field methods for measuring  $\text{NH}_3$  loss from broadcast urea. The present study investigates the effect of different soil types on  $\text{NH}_3$  volatilisation potentials and attempts to isolate the soil factor(s) influencing  $\text{NH}_3$  loss from surface applied urea.

Many of the reported  $\text{NH}_3$  volatilisation studies have been conducted in the laboratory, although recent emphasis has been on field measurements of  $\text{NH}_3$  losses (McInnes *et al.*, 1986; Freney and Black, 1988). Nevertheless, most studies on soil properties (physical, chemical and biological) influencing the  $\text{NH}_3$  loss from surface-applied urea have been carried out under laboratory conditions. None of these studies have been performed on undisturbed soil cores obtained from the field. Since  $\text{NH}_3$  volatilisation from broadcast urea is a surface phenomenon, the present study measures  $\text{NH}_3$  losses from undisturbed soils in the field.

When several factors (i.e. environmental, agronomic and soil factors) influence  $\text{NH}_3$  losses in the field it is difficult to isolate only soil factor(s) influencing  $\text{NH}_3$  volatilisation. Thus conducting  $\text{NH}_3$  volatilisation studies at different locations and seasons adds complexity to the aim of the study by introducing a wide range of environmental effects. This present study uses a field enclosure method to monitor  $\text{NH}_3$  losses from 9 different New Zealand soils under Canterbury conditions at the Lincoln University experimental site.

## MATERIALS AND METHODS

Undisturbed blocks of topsoil (450 cm<sup>2</sup> x 7 cm) were collected from 9 different soil types in the North and South Islands of New Zealand (Table 1). The samples were brought to the experimental site (Lincoln University Sheep Breeding Unit) and each block of soil was buried at ground level along with similar blocks from the experimental site. The vegetation above the soil surface of each soil block was clipped down to 1 cm height. A random experimental design was selected using an area of 7 m x 5 m, about 3 m north of the mobile field laboratory. A mobile field laboratory was used for measuring NH<sub>3</sub> volatilisation from the soil blocks. This laboratory was previously used for measuring NH<sub>3</sub> volatilisation from urine patches by the field enclosure method (Sherlock and Goh, 1984).

The experiments were conducted in October 1988 (Experiment No. 1) and September 1989 (Experiment No.2). In both experiments the Templeton silt loam and Patumahoe clay loam were used whilst other soil types were used only once. Before the start of the trial subsamples (0-2 cm depth) were collected from the edge of each block of soil. These were air dried for 48 hours in a forced-draft cabinet at room temperature (20°C), crushed gently, passed through a 2 mm sieve and stored in polyethylene bags at room temperature. The methods for soil characterisation, soil preparation, fertiliser application (@100 kg N ha<sup>-1</sup>) NH<sub>3</sub> gas sampling, initial microsite pH measurements are described by Sherlock *et al.*, (1986) and Selvarajah *et al.*, (1989). Initial microsite pH measurements have been made 8 hours following urea application. The results reported in the study are either the average value of duplicate, triplicate or quadruplicate analyses expressed on an oven-dry basis.

## RESULTS AND DISCUSSION

### (a) Soil Characteristics:

The nine soils showed a wide range of physical, chemical and biological properties (Tables 2a & b). Both the Kaharoa sand and Onepunga sandy loam soils had very high sand contents (71 and 62% respectively) whilst the Cookson hill soil and Takapau silt loam contained high levels of organic-C (8.14 and 7.31% respectively). The Patumahoe clay loam used in Experiment 2 had a high urease activity (395 µg urea-N g<sup>-1</sup> soil h<sup>-1</sup>). This is almost 9 times higher than that observed in Experiment 1 from the same soil. This difference is attributable to an absence of vegetation cover when the Patumahoe clay loam was collected for Experiment 1, compared with an established clover cover one year later. The introduction of clover cover has also increased the organic-C content of this soil from 4.47% to 7.90%. In the Templeton soil all the properties except urease activity were similar in both experiments. The urease activity measured in Experiment 1 was much lower (80 µg urea-N g<sup>-1</sup> soil h<sup>-1</sup>) than that determined in Experiment 2 (202 µg urea-N g<sup>-1</sup> soil h<sup>-1</sup>). The high soil temperatures experienced during Experiment 1 (mean 20°C) probably caused a decrease in ureolytic population and a general decrease in urease activity. The mean soil temperature recorded during Experiment 2 was 12°C. Speir *et al.* (1980) have reported that an increase in temperature can reduce the urease activity of fallow soils.

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Table 1 Soil Descriptions

Soil Type	District	Site Location	Classification	Parent Material	Topography	Paddock History	Fertiliser or Soil Amendment
Templeton silt loam	Canterbury	Lincoln University	Recent/yellow-grey earth	Greywacke alluvium	Flat	Sheep pasture with ryegrass and clover	Nil
Kaharoa sand	Te Puke	Paengaroa	Primary podzolic soil	Kaharoa ash	Flat	Orchard (past 5 years)	1984 - liming 1985 - 1 t/ha K&P mixture
Kokotau silt loam	Wairarapa	5km south of Masterton	Yellow-grey loam	Mudstone	Flat to gentle rolling	Wheat (past 4 years)	1986/87-DAP 125kg/ha
Kairanga silt loam	Manawatu	10km east of Palmerston North	Recent soils from alluvium	Alluvium	Flat	Ryegrass seed crop (past 4 years)	45kg/ N/ha annually
Takapau heavy silt loam	Hawkes Bay	8km north of Takapau	Yellow-brown loam	Alluvium from greywacke and volcanic ash	Flat	Sheep pasture (past 10 years)	Super phosphate 250 kg/ha annually
Patumahoe clay loam	Pukekohe	6km west of Pukekohe	Brown granular clay	Hamilton ash over basalt and sediments	Flat	Dairy pasture with very poor grass/clover vegetation	Nil
Onchunga sandy loam	North Canterbury	Doctors Hills	Yellow-grey/yellow-brown earth intergrade	Siliceous sandstone	Rolling	Sheep pasture, silver tussock and beach	Nil
Waikari clay loam	North Canterbury	Waikari Basin	Rendzina	Argillaceous limestone	Rolling	Sheep pasture with ryegrass and clover	Nil
Cookson hill soils	North Canterbury	4km north Mt Cookson	Brown granular clay	Basalt, basic greywacke and some limestone	Moderately steep	Silver tussock	Nil

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Table 2a Soil Physical, Chemical and Biological Properties (Experiment No. 1)

Soil Type	Sand (%)	Silt (%)	Clay (%)	pH	HBC <sup>a</sup>	OC <sup>b</sup> (%)	TN <sup>c</sup> (%)	CEC -----(meq kg <sup>-1</sup> )-----	Ca <sup>2+</sup>	Mg <sup>2+</sup>	KCl-N <sup>d</sup> ---( $\mu\text{g NH}_4^+$ -N g <sup>-1</sup> )---	Aner.-N <sup>e</sup>	Urea hydrolysis rate ( $\mu\text{g g}^{-1} \text{h}^{-1}$ )
Templeton silt loam	41	28	31	6.15 <b>0.08</b>	21	4.03 <b>0.23</b>	0.37 <b>0.02</b>	289 <b>15</b>	43 <b>1</b>	7 <b>0</b>	26 <b>2</b>	129 <b>15</b>	80 <b>15</b>
Kaharoa sand	71	16	13	7.08 <b>0.10</b>	0	4.28 <b>0.33</b>	0.36 <b>0.03</b>	311 <b>12</b>	67 <b>8</b>	8 <b>0</b>	28 <b>3</b>	85 <b>11</b>	138 <b>8</b>
Kokotau silt loam	23	40	37	5.87 <b>0.05</b>	25	2.80 <b>0.07</b>	0.28 <b>0.01</b>	243 <b>36</b>	35 <b>0</b>	5 <b>0</b>	21 <b>0</b>	82 <b>4</b>	39 <b>10</b>
Kairanga silt loam	27	40	33	6.30 <b>0.00</b>	20	2.00 <b>0.03</b>	0.22 <b>0.01</b>	241 <b>7</b>	35 <b>2</b>	7 <b>0</b>	17 <b>1</b>	94 <b>5</b>	16 <b>10</b>
Takapau silt loam	34	57	9	5.79 <b>0.02</b>	50	7.31 <b>0.55</b>	0.69 <b>0.05</b>	422 <b>36</b>	52 <b>6</b>	7 <b>1</b>	45 <b>0</b>	187 <b>27</b>	108 <b>32</b>
Patumahoe clay loam	22	39	39	5.37 <b>0.06</b>	77	4.47 <b>0.05</b>	0.42 <b>0.01</b>	284 <b>21</b>	29 <b>1</b>	4 <b>0</b>	29 <b>1</b>	82 <b>3</b>	45 <b>9</b>
LSD (P $\leq$ 0.05)				0.71	-	1.54	0.45	33	15	4	4	11	19

Numbers quoted in **bold** are standard error of mean.a = H<sup>+</sup> buffer capacity [OH<sup>-</sup>](mmols kg<sup>-1</sup>)

b = organic-C (% by weight)

c = total-N (% by weight)

d = hydrolysable-N at 100°C in 2 M KCL ( $\mu\text{g NH}_4^+$ -N g<sup>-1</sup> dry soil)e = anaerobically mineralisable -N ( $\mu\text{g NH}_4^+$ -N g<sup>-1</sup> dry soil)

Table 2b Soil Physical, Chemical and Biological Properties (Experiment No. 2)

Soil Type	Sand (%)	Silt (%)	Clay (%)	pH	HBC <sup>a</sup>	OC <sup>b</sup> (%)	TN <sup>c</sup> (%)	CEC -----(meq kg <sup>-1</sup> )-----	Ca <sup>2+</sup>	Mg <sup>2+</sup>	KCl-N <sup>d</sup> ---( $\mu\text{g NH}_4^+$ -N g <sup>-1</sup> )---	Aner.-N <sup>e</sup> ---( $\mu\text{g NH}_4^+$ -N g <sup>-1</sup> )---	Urea hydrolysis rate ( $\mu\text{g g}^{-1} \text{h}^{-1}$ )
Templeton silt loam	41	28	31	6.27 <b>0.01</b>	17	4.26 <b>0.23</b>	0.31 <b>0.02</b>	289 <b>15</b>	45 <b>0</b>	8 <b>0</b>	23 <b>0</b>	129 <b>4</b>	202 <b>3</b>
Onepunga sandy loam	62	21	17	5.87 <b>0.01</b>	23	4.36 <b>0.33</b>	0.24 <b>0.03</b>	218 <b>2</b>	20 <b>0</b>	7 <b>0</b>	22 <b>0</b>	143 <b>12</b>	206 <b>3</b>
Waikari clay loam	32	28	40	6.62 <b>0.03</b>	18	4.60 <b>0.07</b>	0.29 <b>0.01</b>	381 <b>0</b>	92 <b>0</b>	11 <b>0</b>	18 <b>0</b>	109 <b>9</b>	140 <b>1</b>
Cookson hill soil	25	14	61	5.62 <b>0.01</b>	75	8.14 <b>0.03</b>	0.45 <b>0.01</b>	747 <b>1</b>	66 <b>0</b>	119 <b>0</b>	30 <b>0</b>	236 <b>12</b>	220 <b>1</b>
Patumahoe clay loam	24	19	57	5.69 <b>0.03</b>	42	7.90 <b>0.55</b>	0.55 <b>0.05</b>	423 <b>2</b>	47 <b>0</b>	8 <b>0</b>	41 <b>0</b>	333 <b>9</b>	395 <b>2</b>
LSD (P $\leq$ 0.05)				0.42	-	1.27	0.41	7	2	1	1	9	4

Numbers quoted in **bold** are standard error of mean.a = H<sup>+</sup> buffer capacity [OH<sup>-</sup>](mmols kg<sup>-1</sup>)

b = organic-C (% by weight)

c = total-N (% by weight)

d = hydrolysable-N at 100°C in 2 M KCL ( $\mu\text{g NH}_4^+$ -N g<sup>-1</sup> dry soil)e = anaerobically mineralisable -N ( $\mu\text{g NH}_4^+$ -N g<sup>-1</sup> dry soil)



*(b) Ammonia volatilisation losses:*

The Templeton soil lost about 40% of the applied-N within 7 days in both experiments (Tables 3a & b) which is higher than in all previous studies conducted on this soil (Sherlock *et al.*, 1986; Black *et al.*, 1987 a & b. 1989). This higher loss may be due, in part, to the shorter vegetation cover employed in the present study. The Kaharoa sand and Onepunga sandy loam soils sustained the highest NH<sub>3</sub> loss within 7 days (45.2 and 53.9% of the applied-N respectively) whilst the Patumahoe clay had the lowest loss in both experiments (4.4% in Experiment 1 and 24.3% in Experiment 2). Many workers have reported that sandy soils are susceptible for high volatilisation losses (O'Toole *et al.*, 1985; O'Toole and Morgan, 1989; Martens and Bremner, 1989). It was anticipated the alkaline Kaharoa sand would lose more NH<sub>3</sub> than the acidic Onepunga sandy loam. This is because numerous reports have shown that soils with high initial pH values sustain high NH<sub>3</sub> losses from surface applied urea (Lyster *et al.*, 1980; Beyrouthy *et al.*, 1988; O'Toole and Morgan, 1988). Moreover, NH<sub>3</sub> volatilisation from the Kaharoa sand was less than anticipated because rapid soil drying in Experiment 1 caused incomplete urea hydrolysis, which reduced the potential for NH<sub>3</sub> volatilisation (Selvarajah *et al.*, 1989). Urea hydrolysis was completed within 4 days following urea application in the soils studied in Experiment 2 (data not presented here). This is the reason for the Patumahoe soil to sustain a lower loss in Experiment 1 than that in Experiment 2. Several studies have demonstrated that rapid soil drying could inhibit urea hydrolysis process which in turn reduce the volatilisation potential (Ferguson and Kissel, 1986; McInnes *et al.*, 1986; Reynolds and Wolf, 1987).

Volatilisation loss measurements up to 14 days following urea application indicated that in both trials soils sustained about 90% of the total cumulative NH<sub>3</sub> loss within the first 7 days and majority of these soils lost about 60-80% of this 7 day cumulative loss within the first 3 days (Tables 3 a & b). These dynamics of the NH<sub>3</sub> volatilisation clearly demonstrate that when soil moisture is not limiting regardless, of the magnitude of the soil temperature, the peak volatilisation rate is attained within the first 2-3 days following urea application. This is because high NH<sub>3</sub> fluxes tend to continue until urea hydrolysis is completed or inhibited, at which time release of NH<sub>3(aq)</sub>, from urea into the soil solution also ceases. Several workers have noted that the rapid decrease in NH<sub>3</sub> flux usually coincides with the completion of urea hydrolysis (Harper *et al.*, 1983; Black *et al.*, 1987b; Kirk and Nye, 1991).

*(c) Relationships between volatilisation potentials and soil characteristics:*

Correlation tests performed between the cumulative NH<sub>3</sub> losses over 7 days and soil characteristics are shown in Table 4. Correlation analyses were carefully performed by viewing the scatter diagrams showing the relationship between every independent and dependent variable tested. Thus it was found that an outlier causing significant relationship between Mg<sup>2+</sup> content and 7 day cumulative NH<sub>3</sub> loss and clay content had better curvilinear relationship with NH<sub>3</sub> loss than that of the linear counterpart.

Whilst increasing initial soil pH, sand content and initial microsite pH appeared to increase the volatilisation potential, increasing H<sup>+</sup> buffer capacity and clay content have reduced it. Experiment 1 was carried out under warm rapid-drying conditions and Experiment 2 was conducted under cool slow-drying conditions. To rigorously examine

the overall effect of each individual soil property the data for both experiments were combined and linear correlation tests were performed as carried out previously.

**Table 3a** Cumulative NH<sub>3</sub> losses (% applied-N) (Exp. No.1)

Soil types	Days following urea application					
	1	2	3	5	7	14
<b>Templeton</b> silt loam	8.3	28.0	33.7	38.2	40.3	43.1
<b>Kaharoa</b> sand	4.6	25.8	36.6	43.5	46.5	50.1
<b>Kokotau</b> silt loam	3.2	15.5	22.3	27.7	30.0	32.8
<b>Kalranga</b> silt loam	1.6	9.9	18.8	27.3	30.7	34.6
<b>Takapau</b> heavy silt loam	1.2	8.0	13.4	18.9	22.0	26.8
<b>Patumahoe</b> clay loam	0.1	0.7	1.5	3.1	4.4	7.2
LSD ( $P < 0.05$ )	1.6	2.6	2.8	2.9	2.9	2.9

**Table 3b** Cumulative NH<sub>3</sub> losses (% applied-N) (Exp. No. 2)

Soil types	Days following urea application					
	1	2	3	5	7	14
<b>Templeton</b> silt loam	0.8	11.0	23.1	34.1	35.3	39.2
<b>Onepunga</b> sandy loam	3.0	29.6	43.8	52.8	53.9	58.2
<b>Waikari</b> clay loam	0.5	4.5	11.4	26.6	28.2	32.7
<b>Cookson</b> hill loam	0.6	6.4	14.8	26.9	28.0	31.7
<b>Patumahoe</b> clay loam	0.3	5.9	14.4	23.5	24.3	26.5
LSD ( $P < 0.05$ )	1.2	2.9	3.1	3.3	3.4	3.5



**Table 4** Linear correlation coefficients obtained from the relationship between the cumulative NH<sub>3</sub> loss and soil properties (Experiments No.1 & 2)

Soil properties	7 day NH <sub>3</sub> loss	
	Exp. No.1	Exp. No.2
Sand content (%)	0.73	0.99 <sup>++</sup>
Silt content (%)	-0.64	0.11
Clay content (%)	-0.37	-0.88 <sup>+</sup>
Native soil pH	0.89 <sup>+</sup>	-0.03
Organic-C content	-0.25	-0.62
Total-N (%)	-0.33	-0.73
Buffered CEC	-0.13	-0.62
KCl hydrolysable-N	-0.27	-0.50
Mineralisable-N	-0.03	-0.50
Urease activity	0.45	-0.10
Ca <sub>2+</sub>	0.67	-0.72
Mg <sup>2+</sup>	0.82 <sup>+</sup>	-0.30
H <sup>+</sup> buffer capacity	-0.95 <sup>++</sup>	-0.41
Initial microsite pH	0.97 <sup>++</sup>	0.94 <sup>++</sup>

Values between 0.81 and 0.92 are significant at  $P < 0.05$  level and above 0.92 are significant at  $P < 0.01$  level.

**Table 5** Linear correlation coefficients obtained from the relationship between the cumulative NH<sub>3</sub> loss and soil properties for combined data sets

Soil properties	7 day NH <sub>3</sub> loss
Sand content (%)	0.81 <sup>++</sup>
Silt content (%)	-0.48
Clay content (%)	-0.43
Native soil pH	0.56
Organic-C content	-0.26
Total-N (%)	-0.47
Buffered CEC	-0.26
KCl hydrolysable-N	-0.36
Mineralisable-N	-0.12
Urease activity	0.23
Ca <sup>2+</sup>	-0.03
Mg <sup>2+</sup>	-0.06
H <sup>+</sup> buffer capacity	-0.65 <sup>+</sup>
Initial microsite pH	0.92 <sup>++</sup>

Values between 0.60 and 0.74 are significant at  $P < 0.05$  level and above 0.74 are significant at  $P < 0.01$  level.

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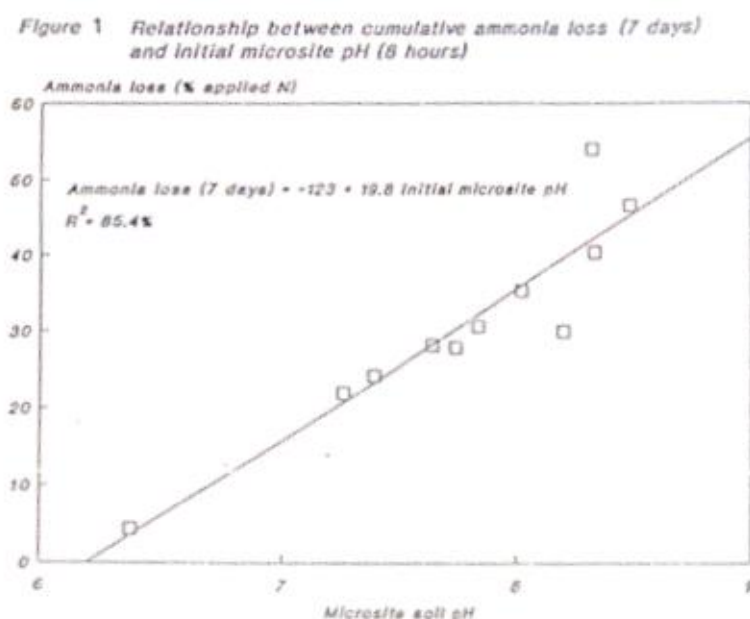
Highly significant correlations were obtained between volatilisation potentials and initial microsite pH ( $r = 0.92$ ;  $P < 0.01$ ) and sand content ( $r = 0.81$ ;  $P < 0.01$ ) (Table 5). The regression equations for these relationships are given below:

$$\text{NH}_3 \text{ loss (7 days)} = -123 + 19.8 (\text{Initial microsite pH}) \quad (R^2 = 85.4\%)$$

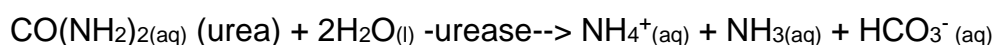
$$\text{NH}_3 \text{ loss (7 days)} = 7.54 + 0.65 (\text{Sand content \%}) \quad (R^2 = 65.5\%)$$

(d) *The chemistry of urea reaction in different soils:*

The highly significant relationship between volatilisation potential and initial microsite pH (Figure 1) is not surprising when the integrating nature of this measurement is considered.



It is well known that upon application of granular urea to soil the microsite chemistry is gradually modified by the  $\text{NH}_3$  released during the initial stages of urea hydrolysis (Figure 2). During this period a soil reaction in the microsite should indicate the resistance to the initial alkalinity build-up. The resistance against the alkalinity build-up is caused mainly by the  $\text{H}^+$  supplying capacity of soil (Ferguson et al., 1984; Rachhpal-Singh and Nye, 1986; Reynold and Wolf, 1987). The generation of the alkaline urea hydrolysis products ( $\text{NH}_3(\text{aq})$  and  $\text{HCO}_3(\text{aq})$ ) and their subsequent reaction and partial neutralisation by  $\text{H}^+$  supplying components within the soil are collectively expressed in the pH of the soil microsite. The microsite pH changes rapidly throughout the course of a volatilisation event responding to the rates of urea hydrolysis,  $\text{H}^+$  buffering and volatilisation:



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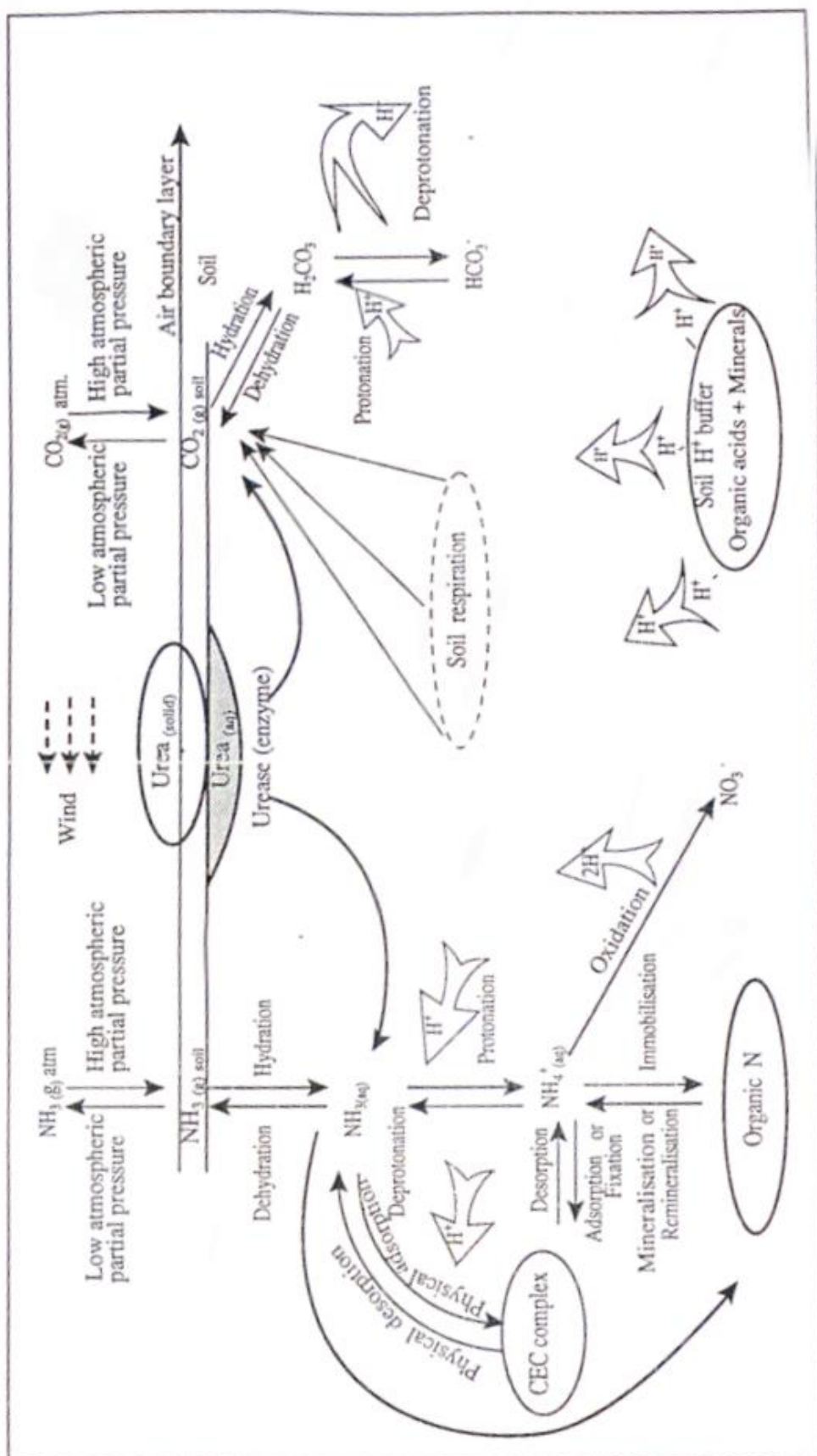


Figure 2. Diagrammatic representation of the physical, chemical and biological transformations of a urea granule applied to a bare soil surface

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In essence, the ability of a soil to resist the increase in pH caused by these alkaline products should also indicate its ability to protonate volatilisable  $\text{NH}_3(\text{aq})$ , throughout the volatilisation event and thereby resist volatilisation. When urea hydrolyses in a soil which lacks any ability to resist this increase in pH, a concentrated ammonium bicarbonate ( $\text{NH}_4\text{HCO}_3(\text{aq})$ ) solution will be produced very rapidly. For this poorly buffered soil (e.g. Kaharoa or Onepunga)  $\text{NH}_3$  volatilisation will be maximal. On the other hand, a second soil which possesses a high ability to neutralise these alkaline urea hydrolysis products (e.g. Patumahoe) will not experience the same rapid increase in microsite pH. While the maximum pH attained in this second soil may be similar to that attained by the first soil, it should maintain this pH for a shorter period of time. This must result in a greatly reduced volatilisation potential compared with the first soil which has little or no  $\text{H}^+$  supplying capacity.

The laboratory measurement of  $\text{H}^+$  buffer capacity was indeed significantly related to the overall volatilisation potentials of the soils studied (Table 5) ( $r = -0.65$ ;  $P < 0.05$ ). Several workers have already identified this relationship (Ferguson *et al.*, 1984; Rachhpal-Singh and Nye, 1986; Reynolds and Wolf, 1987). However, the laboratory assay of  $\text{H}^+$  buffer capacity was not as highly correlated to volatilisation potential as was initial microsite pH. Again this is probably not surprising when one considers the similarities and differences between these two types of measurement. In both measurements a 'titration' is being performed. In the case of the laboratory measurement of  $\text{H}^+$  buffer capacity this titration is between a strong base ( $\text{OH}^-$ ) and the  $\text{H}^+$  supplying capacity of the soil. However, for the field measurement of initial microsite pH, a titration is being performed in situ by the weakly basic urea hydrolysis products,  $\text{NH}_3(\text{aq})$  and  $\text{HCO}_3(\text{aq})$ . Consequently, these findings emphasise the future volatilisation studies conducted under most environmental conditions should include initial microsite pH measurements as an indicator for  $\text{H}^+$  buffer capacity rather than the  $\text{OH}^-$  titration method used in this study and many other studies (e.g. Ferguson *et al.*, 1984; Reynolds and Wolf, 1987; Stevens *et al.*, 1989).

The highly significant relationship between volatilisation potential and sand content (%) (Table 5) can be explained in terms of the relative abundance of chemically reactive soil components. Soils with a high sand content are less able to resist pH increases caused by urea hydrolysis than those soils with low sand content.

Of these two highly significant soil properties, initial soil microsite pH offers the best scope for development as an easily obtainable index for volatilisation potential of soils fertilised with granular urea. This measurement can be carried out easily in the field although future work may show that a laboratory based urea hydrolysis products titration is equally suitable.

## CONCLUSIONS

(1) Different soil types have different  $\text{NH}_3$  volatilisation potentials. The soils that have low chemical resistance to the alkalinity build-up caused by the urea hydrolysis products sustain high  $\text{NH}_3$  losses.

(2) Initial microsite pH measured 8 hours following urea application is a measurement which effectively integrates the individual soil properties which collectively determine the extent of chemical resistance of soil to the alkaline urea hydrolysis products.

(3) The easily measured soil property, initial microsite pH measured 8 hours following urea application, was found to be an excellent index for the  $\text{NH}_3$  volatilisation potential of unsaturated soils possessing a wide range of physical, chemical and biological properties fertilised with surface applied urea.

(4) Other soil properties (with the possible exception of sand content) were not directly related to the volatilisation potentials of soils.

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