DYNAMICS OF AMMONIA VOLATILIZATION AND NITROUS OXIDE PRODUCTION FROM URINE PATCHES IN GRAZED PASTURES

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ABSTRACT

A continuously aspirated enclosure method was used to measure ammonia (NH_3) volatilization from simulated sheep urine patches in a perennial ryegrass (*Lolium perenne*) / white clover (*Trifolium repens*) pasture in the field during summer, autumn and winter periods. Volatilization was essentially complete after 100 - 200 hours. Mean volatilization losses from urine treated plots were 22.2% of the applied nitrogen (N) in summer, 24.6% in autumn and 12.2% in winter. Corresponding losses from the urea treated plots were 17.9%, 28.9% and 8.5%. Seasonal differences were significant ($P \leq 0.05$) for both N sources, but differences between N sources during any particular season were not significant. Repeated applications of urine or aqueous urea to the same area of pasture were made during summer to simulate the possible effects of high stocking rates and sheep camp areas. Significantly greater ($P \leq 0.05$) subsequent volatilization losses were produced, averaging 29.6 and 37.5% from the second and third applications, respectively.

Theoretical considerations were presented for the development of a simplified $NH_{3(g)}$ volatilization model appropriate to urine patches. Volatilization rate was calculated to be directly proportional to the amount of ammoniacal-N in the topsoil, and inversely proportional to soil moisture content and the extent of exchange reactions with the charged sites on the soil colloids. Temperature and pH also markedly affect the rate of ammonia volatilization but in a non-linear manner. An increase in either of these parameters was calculated to increase the rate of ammonia volatilization. It was shown that the dominant factor determining the rate of $NH_{3(g)}$ volatilization is the soil surface pH. Input data for calculating $NH_{3(g)}$ losses are: a knowledge of the disposition of the applied N within the soil profile; the rate of urea hydrolysis in the topsoil; and soil surface pH and temperature measurements throughout the duration of a volatilization

event. The model was verified using field experimental data from the present study and also published data from independent sources. It was considered that the model offers the potential for determining $NH_{3(g)}$ volatilization losses following urine or aqueous urea applications to short pasture in non-leaching, non-nitrifying environments.

Field, growth cabinet and laboratory measurements of nitrous oxide (N_2O) emissions from simulated urine patches were also conducted. A sensitive electron-capture gas chromatographic procedure was combined with a short duration enclosure method to monitor the build-up of N_2O in the enclosed headspace above the pasture surface. In a field experiment, plots received aqueous solutions containing 7.2 g N as either sheep urine, calcium nitrate or ammonium sulphate and after 10 days lost 6.4, 6.8 and 7.7 mg of the applied N respectively. A control plot treated with distilled water released 1.1 mg N_2O-N during the same period. Diurnal fluctuations in N_2O emission rates from both N treated and untreated control plots were significantly correlated ($r \geq 0.980$) with soil temperature (10 cm depth) although the magnitude of the temperature fluctuations ($\pm$ 2°C) were insufficient by themselves to produce the large (e.g. 10 fold) variations in daily N_2O emission rates observed. Fluxes of N_2O from untreated pasture soil ranged from 0 - 2.1 mg $N_2O\ m^{-2}\ day^{-1}$.

In growth cabinet and laboratory experiments, N_2O emissions were measured from blocks of freshly cut pasture soil (165 x 165 x 150 mm) treated with aqueous solutions containing 0.5 g N as either sheep urine, calcium nitrate, ammonium sulphate or urea. Pasture blocks watered to 27.5% average soil moisture content lost significantly more ($P \leq 0.05$) N_2O than blocks maintained at 14.0% average soil moisture content but within each moisture regime, differences in total N_2O-N losses between treatments were not significant. Peak emissions occurred on the days following watering with similar patterns of release apparent from each N source.

Emission rates of N_2O immediately following sheep urine applications to blocks of fresh pasture soil were significantly greater ($P \leq 0.05$) than initial rates of production from similar applications of aqueous calcium nitrate, ammonium sulphate or urea. The magnitude of the initial pulse of N_2O from the sheep urine was unrelated to soil moisture content and amounted to about 30% of the N_2O loss from each simulated urine patch (i.e. 0.1% of the applied urine-N).

Measured N_2O losses from sheep urine and inorganic N fertilizers (ammonium sulphate, calcium nitrate and urea) were small with maximum losses estimated at < 2% of the applied N after 3 months. It was concluded that direct gaseous N_2O emissions from typical silt-loam pasture soils in Canterbury are of little agronomical importance.

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INTRODUCTION

Modern technology is being used increasingly to improve crop yields and combat the chronic food shortage brought about by the continuing increase in world population. Plants require more nitrogen than any other nutrient element present in the soil and its availability is often rate-limiting on growth. It has been estimated that the rate of nitrogen input to the biosphere through the combined use of industrially-fixed nitrogen fertilizer and cultivated legumes is currently about double the total rate of nitrogen fixation by biological and other sources before human intervention (Delwiche, 1977). Thus, human activities have produced or have the potential for producing significant changes in the amounts and rates of exchange of nitrogen between the various compartments of the nitrogen cycle. The resulting changes may be manifested locally (e.g. increased crop yields in response to fertilizer inputs), regionally (e.g. eutrophication of lakes and rivers) and globally (e.g. the possible increase in nitrous oxide concentration in the atmosphere), (Keeney, 1982). The challenge to mankind is to increase food production through more efficient utilization of fixed nitrogen without producing adverse environmental problems. This can only be achieved by a better understanding of the mechanisms which promote the loss of fixed nitrogen from agricultural systems.

Grassland ecosystems based on improved grass-legume pastures and domesticated herbivors are of comparatively recent anthropogenic origin. Research has shown that the urine-affected areas within grazed pastures form focal points for the loss of fixed nitrogen as volatile ammonia gas and for leaching as nitrate (Ball *et al.*, 1979). In addition, they are also the probable focal points for the gaseous loss of fixed nitrogen

by denitrification (Carran *et al.*, 1982) and nitrification.

While the factors which influence ammonia volatilization and denitrification have been the subject of many laboratory studies and are well documented, there have been very few attempts to identify and rationalize the interaction of these factors under field conditions. The two main objectives of the present study were:

(1) to isolate and quantify the factors which promote ammonia volatilization from simulated urine patches under field conditions, and

(2) to assess the importance of nitrous oxide production from urine-affected pasture soil.

Methodological problems associated with the simultaneous measurement of both ammonia and nitrous oxide emissions from soils together with the differences in their mechanisms of production, provided a convenient division of this study into two sections: firstly a series of field measurements to produce the necessary data bases for the development of a simplified ammonia volatilization model and secondly, a series of field and laboratory measurements to compare nitrous oxide production from urine-affected soil with untreated soil and soil treated with solutions of various inorganic nitrogen fertilizers.

P A R T I

DYNAMICS OF AMMONIA VOLATILIZATION FROM SIMULATED URINE PATCHES AND AQUEOUS UREA APPLIED TO PASTURE

CHAPTER 1

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CHAPTER 1

REVIEW OF LITERATURE

1.1 INTRODUCTION

Ammonia volatilization is the term commonly used to describe the process by which gaseous ammonia is released from the soil surface to the atmosphere. It can take place whenever free ammonia (i.e. $NH_{3(g)}$ and $NH_{3(aq)}$) is present near the soil surface. Such conditions can arise at the sites of microbial decomposition of dead plants and animals, in animal excreta (e.g. dung and urine patches), and following surface applications of ammoniacal fertilizers and sewage sludge. Volatilization losses can be significant and under certain conditions may amount to more than 50% of the nitrogen (N) applied to a soil surface. Generally, losses increase with increases in pH and temperature and are greatest in soils with a low cation exchange capacity.

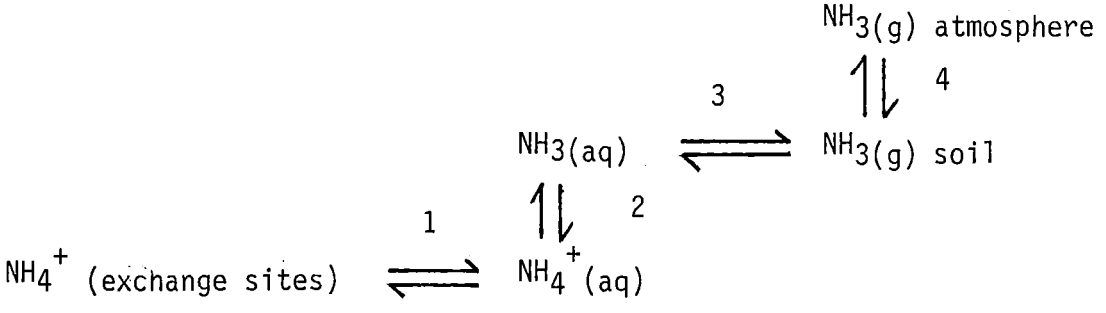
While the generation of ammonia in soil is often the result of biological activity (e.g. hydrolysis of urea by urease), its subsequent loss by volatilization is primarily a physico-chemical process controlled by factors such as soil pH, buffer capacity, temperature and windspeed. However, the ultimate extent of N loss via volatilizaton in any particular situation depends not only on these factors but also on several other chemical, physical and biological mechanisms which compete to remove ammoniacal-N from the system. These include nitrification, plant uptake, immobilization, and ammonium fixation.

This chapter is not intended as a comprehensive review of the literature on ammonia volatilizaton. For that, the reader should consult Terman (1979) or Nelson (1982). Rather, it is an attempt to present the current knowledge and understanding of ammonia volatilization through a discussion of the basic mechanism and a review of the factors which modify and confound it.

1.2 AMMONIA EQUILIBRIA

Ammonia exchange between the soil surface and the atmosphere may be represented by the sequence of coupled equilibria as shown in Figure 1.1. These equilibria indicate that the soil solution can

Figure 1.1 Ammonia Equilibria



act as both a source and sink for atmospheric $NH_{3(g)}$. Whether $NH_{3(g)}$ is absorbed or volatilized is determined by the concentration gradient of the gas above the soil surface (Vlek and Craswell, 1981; Denmead *et al.*, 1982). The $NH_{3(g)}$ flux, F, into or out of the soil surface is given by:

$$F = k \times (NH_{3(g)soil} - NH_{3(g)atmosphere}) \qquad [1.1]$$

where '$NH_{3(g)soil}$' is the $NH_{3(g)}$ concentration in equilibrium with the soil solution, '$NH_{3(g)atmosphere}$' is the $NH_{3(g)}$ concentration of the

bulk atmosphere and 'k' is an exchange coefficient and is constant at constant windspeed (Vlek and Craswell, 1981). The influence of varying windspeed is discussed separately later.

Ambient atmospheric $NH_{3(g)}$ concentrations are normally very low and in pollution free areas rarely exceed 2-6 μg NH_3-N m^{-3} (N.R.C. Subcommittee on Ammonia, 1979). No direct measurements of equilibrium $NH_{3(g)soil}$ concentrations have been reported but calculations by Vlek and Craswell (1981) show $NH_{3(aq)}$ concentrations of 0.5 ppm or greater are sufficient to promote volatilization. These workers maintained that where $NH_{3(g)}$ volatilization is a problem, such levels of $NH_{3(aq)}$ are easily reached. Under these conditions, '$NH_{3(g)soil}$' is likely to greatly exceed '$NH_{3(g)atmosphere}$' whereupon equation [1.1] can be simplified to:

$$F = k \times NH_{3(g)soil} \qquad [1.2]$$

Therefore, at constant windspeed under conditions promoting high volatilization rates, the $NH_{3(g)}$ flux from the soil surface should be directly proportional to '$NH_{3(g)soil}$'.

Thus, ammoniacal-N added to the soil from whatever source may be subject to loss as $NH_{3(g)}$. The actual magnitude of any loss depends on the concentration of '$NH_{3(g)soil}$' which in turn depends on the total concentration of ammoniacal-N species, the values of the individual equilibrium constants (Figure 1.1) and the rate of attainment of equilibrium at each stage. Factors which can influence any or all of these separate equilibria can therefore influence the magnitude of $NH_{3(g)}$ loss. Likewise, all strategies designed to limit volatilization losses attempt to manipulate these equilibria either directly or indirectly to reduce the '$NH_{3(g)soil}$' concentration at the soil/air interface.

1.2.1 Major Factors Affecting NH_3 Equilibria

1.2.1.1 pH and buffer capacity

The concentration of $NH_{3(aq)}$ is highly dependent on pH. This pH effect is primarily felt in equilibrium 2 (Figure 1.1) and has been represented by various workers (e.g. Jewitt, 1942; Wahhab *et al.*, 1957; Du Plessis and Kroontje, 1964; Lyster *et al.*, 1980) with the equation:

$$NH_4^+ + OH^- \rightleftharpoons NH_3 + H_2O \qquad [1.3]$$

An increase in pH (i.e. an increase in hydroxide ion concentration) drives the equilibrium to the right thereby producing more NH_3.

Alternatively, the following simple derivation may be employed (Freney *et al.*, 1981) where the equilibrium between $NH_{3(aq)}$ and $NH_4^+(aq)$ is represented by the equation:

$$NH_4^+(aq) + H_2O \overset{Ka}{\rightleftharpoons} NH_{3(aq)} + H_3O^+(aq) \qquad [1.4]$$

in which the acid dissociation constant, Ka, is given by

$$Ka(NH_4^+) = \frac{NH_{3(aq)} \cdot H_3O^+(aq)}{NH_4^+(aq)} = 3.9\times10^{-10} \text{ at } 20°C \qquad [1.5]$$

Thus:

$$pKa(NH_4^+) = pH + \log \frac{NH_4^+(aq)}{NH_{3(aq)}} \qquad [1.6]$$

Since pKa is a constant at a particular temperature (Hales and Drewes, 1979), the ratio of $NH_4^+(aq)$ to $NH_{3(aq)}$ is determined by the pH of the soil solution. The fraction of the aqueous ammoniacal-N present as $NH_{3(aq)}$ at pH 6, 7, 8 and 9 may be calculated using equation [1.6] and is approximately 0.0004, 0.004, 0.04 and 0.3 respectively. Thus, more of the ammoniacal-N exists as $NH_{3(aq)}$ and is therefore potentially volatilizable as the soil pH increases.

Equation [1.6] is an oversimplification since it fails to consider the influence of ambient CO_2 levels, possible ion-pair formation with HCO_3^- ion and is valid only for dilute solutions. However, a more rigorous treatment of the equilibrium by Vlek and Craswell (1981) showed departures from the ideal behaviour predicted by equation [1.6] only become significant above pH 9.3. Such high pH values are only rarely observed under natural conditions.

Du Plessis and Kroontje (1964) attempted to use equation [1.6] to directly calculate the total amount of ammoniacal-N present as $NH_{3(aq)}$ and therefore able to be volatilized. In laboratory experiments, $NH_{3(g)}$ losses for a range of 5 soils (pH 4.5 - 7.1) at 9 rates of ammonium sulphate increased linearly with calculated $NH_{3(aq)}$ concentration as expected. However, measured losses for each of these treatments were about 12 times higher than predicted. This apparent contradiction with theory has been interpreted by others (e.g. Freney *et al.*, 1981) as indicating the influence of other factors apart from pH. This is not necessarily the case and illustrates a possible point of confusion in this type of work, namely the distinction between 'rate of volatilization' and 'extent of volatilization'.

As stated earlier, the rate of volatilization is proportional to the $NH_{3(g)}$ concentration gradient above the soil surface. Most laboratory measurements of $NH_{3(g)}$ losses (including those of Du Plessis and Kroontje, 1964) have employed aspirated enclosures in which $NH_{3(g)}$ evolved into an enclosed headspace above the soil surface is continuously swept away and absorbed in a separate chemical trap. With sufficient airflow through the headspace so as not to limit volatilization (Vlek and Craswell, 1981), or where the flushing air is $NH_{3(g)}$ free (Du Plessis and Kroontje, 1964), the rate of $NH_{3(g)}$ loss should be directly proportional

to the $NH_{3(g)soil}$ concentration. At constant temperature, $NH_{3(g)soil}$ is itself directly proportional to the $NH_{3(aq)}$ concentration calculated by equation [1.6]. The results of Du Plessis and Kroontje (1964) clearly show that the total losses in 48 hours were directly proportional to the calculated $NH_{3(aq)}$ concentrations and are therefore in agreement with equation [1.6]. However, the actual amount of $NH_{3(g)}$ volatilized under these conditions depends not only on pH but also on the time of aspiration (Terman, 1979). If Du Plessis and Kroontje had aspirated their enclosures for only 4 hours instead of the 48 hours used, their measurements and predictions may have been much closer. Indeed, Avnimelech and Laher (1977) maintain that if $NH_{3(g)}$ is totally absent from the air used to flush a headspace then all the ammoniacal-N in the soil would eventually volatilize.

A large number of laboratory and field experiments by many workers have demonstrated the essential validity of equation [1.6] by showing that $NH_{3(g)}$ losses increase as soil pH increases (e.g. Wahhab *et al.*, 1957; Volk, 1959; Ernst and Massey, 1960; Watkins *et al.*, 1972; Lyster *et al.*, 1980). However, interpretation of the direct effects of pH in many of these experiments is often difficult. More often than not, the original soil pH was assumed to characterize the pH throughout the duration of $NH_{3(g)}$ loss. Such assumptions are not always correct. For example, Avnimelech and Laher (1977) postulated that the volatilization of ammonia could be described by the equation:

$$NH_4^+ \longrightarrow NH_3\uparrow + H^+ \qquad [1.7]$$

and therefore must be accompanied by a net acidification of the system. Consequently, unless the soil is well buffered the pH should drop and the rate of volatilization should decrease. They concluded that original soil pH is of prime importance in controlling the extent of

volatilization only when the buffer capacity of the soil is high or when the concentration of $NH_4^+{}_{(aq)}$ is low. Conversely, the buffer capacity of the soil can become the dominant factor controlling the process when both the original soil pH and the initial $NH_4^+{}_{(aq)}$ concentration are high.

The role of original soil pH becomes clouded where the ammoniacal-N source itself (e.g. urea) can alter the soil solution pH. Urea, either as solid granules or animal urine is rapidly hydrolysed in most soils in accordance with the equation:

$$CO(NH_2)_2 + 2H_2O \longrightarrow 2NH_4^+ + CO_3^{2-} \qquad [1.8]$$

The carbonate ions then undergo hydrolysis resulting in a localized area of elevated pH.

$$CO_3^{2-} + H_2O \rightleftharpoons HCO_3^- + OH^- \qquad [1.9]$$

Ammonia can be volatilized from these areas even though the soil immediately adjacent may be acid. This takes place irrespective of the original pH of the soil. For example, in field studies of $NH_{3(g)}$ volatilization from urine patches, localized pH increases of about 2 units were found to accompany urea hydrolysis (Vallis *et al.*, 1982). Temporal changes in soil surface pH coincided with changes in mean daily $NH_{3(g)}$ fluxes. The maximum rates of $NH_{3(g)}$ loss coincided with maximum soil surface pH and declined slowly thereafter as pH declined.

In some studies, original soil pH has been shown to relate to losses from urea. For example, Watkins *et al.* (1972) showed total $NH_{3(g)}$ losses following urea fertilizer applications to 5 forest soils were positively related to the original soil pH. This occurred even though the pH 20 days after application remained elevated on average by 2 units. However, in a laboratory study of volatilization following

the application of urea fertilizer to 6 widely different Irish soils, Lyster *et al.* (1980) showed total volatilization losses were unrelated to original soil pH and were instead related to the maximal pH values reached after all the urea had hydrolysed i.e. 2 - 3 days after fertilizer application.

It appears from these and other studies that original soil pH is not by itself a good indicator of potential $NH_{3(g)}$ loss particularly where urea fertilizer is applied.

1.2.1.2 Temperature

The constants controlling equilibria (2) and (3) in Figure 1.1 are both temperature dependent. Henry's law constant, Kh, which describes the partitioning of NH_3 between the aqueous and gas phases (equilibrium (3)) is given by:

$$Kh = \frac{NH_{3(aq)}}{NH_{3(g)soil}} \qquad [1.10]$$

and has been determined experimentally as:

$$\log_{10} Kh = -1.69 + 1477.7/T \qquad [1.11]$$

where 'T' is the absolute temperature and 'Kh' is the dimensionless ratio of molar concentrations (Hales and Drewes, 1979). The acid dissociation constant, Ka, equation [1.4] has also been determined experimentally as:

$$\log_{10} Ka = -0.09018 - 2729.92/T \qquad [1.12]$$

An expression which combines equilibria (2) and (3) is:

$$NH_{3(g)soil} = \frac{Ka.AN}{Kh\ ([H_3O^+] + Ka)} \qquad [1.13]$$

where 'AN' is the total aqueous ammoniacal-N concentration (i.e. $AN = NH_{3(aq)} + NH_4^+{}_{(aq)}$) (Vlek and Craswell, 1981).

Equation [1.13] is useful in several ways. For example, the ratio '$NH_{3(g)soil}/AN$' (referred to here as the "volatilization ratio") may be calculated directly and provides a relative measure of the rate of $NH_{3(g)}$ volatilization from a system as a function of both pH and temperature assuming all other influences (e.g. soil type, rate of N application and windspeed) remain constant (see Figure 1.2). Under these conditions, systems with the same "volatilization ratio" should, in theory lose $NH_{3(g)}$ at the same rate (Sherlock and Goh 1983c). For example, a hydrolysed urea fertilizer 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 (Figure 1.2).

Figure 1.2

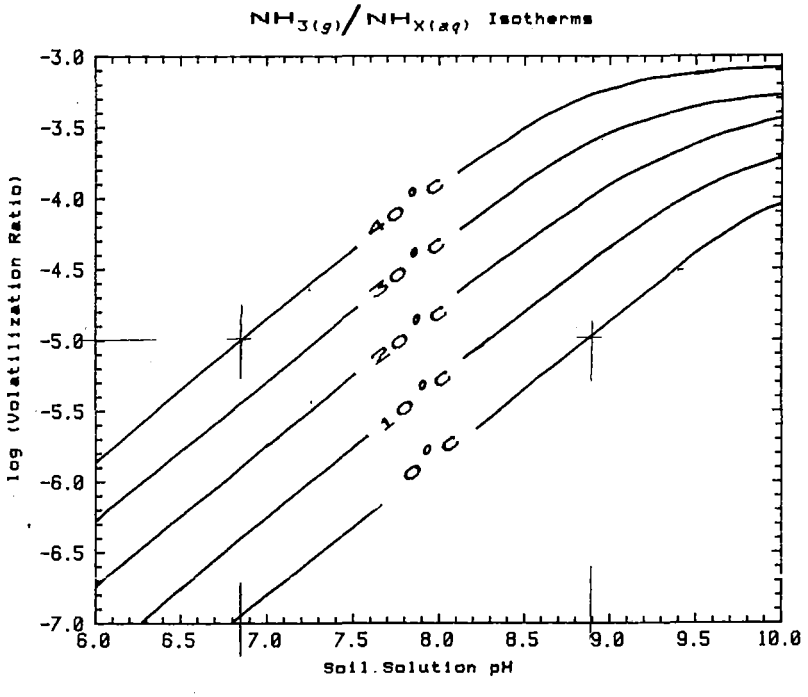


Figure 1.2. Plots showing log "volatilization ratio" as a function of the soil solution pH and temperature.

For a system at some constant pH between pH 6 and 8.5, increasing the temperature by 10°C should increase the rate of volatilization by about a factor of 3 (see Figure 1.2). Experimental confirmation of this can be found in the work of Hoff *et al.* (1981). They measured the rate of $NH_{3(g)}$ loss in the field at constant windspeed every 3 hours for the 7 days following the surface application of liquid swine manure. In the 6 hour period between 17 and 23 hours after application, soil solution ammoniacal-N concentrations and pH would have changed little. During this period, however, air temperatures rose 10°C from 20 to 30°C and $NH_{3(g)}$ fluxes rose from 0.5 to 1.5 kg $Nha^{-1}hr^{-1}$, exactly as predicted by equation [1.13]. The same pattern was repeated the following day (see Figure 3 in Hoff *et al.*, 1981).

Aerodynamic techniques were employed by Beauchamp *et al.* (1978, 1982) to measure $NH_{3(g)}$ fluxes from surface applications of sewage sludge and liquid dairy manure. The effect of temperature on the rate of $NH_{3(g)}$ volatilization was again apparent from the distinctive diurnal $NH_{3(g)}$ flux patterns which were closely related to air temperature variations and unrelated to variations in ambient windspeeds.

In the example cited above, a relatively simple relationship existed between temperature and rate of $NH_{3(g)}$ loss which appeared to be consistent with equation [1.13]. However, most reports of the effects of temperature on volatilization have simply involved measuring total net loss at various constant temperatures (Wahhab *et al.*, 1957; Volk, 1959; Ernst and Massey, 1960; Watkins *et al.*, 1972; Lyster *et al.*, 1980). Under these conditions, any simple temperature relationship would very likely be confounded by a host of other effects

(e.g. temporal variations in pH and differential moisture loss). Consequently, in these studies no simple unifying relationship of the type above was apparent. However, without exception they all showed that loss of $NH_{3(g)}$ following applications of urea or NH_4^+ salts to soil increases with increasing temperature.

Another possible effect of temperature is to directly influence the rate of attainment of the various equilibria shown in Figure 1.1. Increasing the temperature may also indirectly decrease volatilization losses by increasing the rates of biological processes (e.g. nitrification and immobilization) which operate to remove ammoniacal-N from the system. No data are currently available to verify these speculations.

1.2.1.3 Ammoniacal-N concentration

The rate of $NH_{3(g)}$ loss from aqueous solution at constant temperature was shown to be directly proportional to the total ammoniacal-N concentration provided pH was constant or remained sufficiently high (i.e. >10) such that all the ammoniacal-N existed as $NH_{3(aq)}$ (Vlek and Stumpe, 1978). This finding is in accordance with equations [1.2] and [1.13] and implies a similar relationship might exist between total $NH_{3(g)}$ losses and the amounts of urea or ammonium fertilizers applied to a soil. A linear relationship between the rate of fertilizer application and total $NH_{3(g)}$ loss has been shown in a number of studies (Chao and Kroontje, 1964; Hargrove *et al.*, 1977; Hoff *et al.*, 1981). In other studies, percentage losses increased as rates of application increased (Wahhab *et al.*, 1957; Volk, 1959; Kresge and Satchell, 1960; Lyster *et al.*, 1980). This

non-linear relationship occurred mainly for urea and probably results from an indirect pH effect. Increasing the rate of urea application would be expected to induce increased soil surface pH's which in turn would mean a higher proportion of the ammoniacal-N would be in the form of volatilizable $NH_{3(aq)}$.

Of major importance in determining the soil solution $NH_4^+{}_{(aq)}$ concentration is the cation exchange capacity of a soil. Many laboratory experiments have shown that coarse textured (sandy) soils volatilize more of the applied ammoniacal-N than fine textured soils (Wahhab *et al.*, 1957; Gasser, 1964; Fenn and Kissel, 1976). The lower CEC of the coarse textured soils means a smaller percentage of the NH_4^+ cations would be bound to the exchange sites (see equilibrium 1 in Figure 1.1). Thus, coarse textured soils would have a higher percentage of the NH_4^+ ions in soil solution compared with fine textured soils and this would be reflected in their enhanced ability to volatilize $NH_{3(g)}$.

When other soluble cations are applied along with an ammoniacal fertilizer, competition for the exchange sites can result. For example, soluble calcium may depress normal adsorption of NH_4^+ on exchange sites leading to enhanced $NH_{3(g)}$ losses (Fenn *et al.*, 1982). It might well be that similar competition between K^+ and NH_4^+ occurs in the urine patches of grazing herbivors since urine contains almost equivalent amounts of potassium and nitrogen (Richards and Wolton, 1976). However, no data are available to test this speculation.

Many other mechanisms can induce changes in the ammoniacal-N concentration and thereby affect the chain of equilibria which determine

the extent of $NH_{3(g)}$ loss. The more obvious include: plant uptake, nitrification, denitrification, leaching, immobilization, and the fixation of NH_4^+ by clay minerals in non-exchangeable forms. All these mechanisms would tend to decrease the ammoniacal-N concentration in soil solution and so reduce $NH_{3(g)}$ losses. Some are able to be manipulated beneficially. For example, Fleisher and Hagin (1981) have demonstrated in the laboratory a strategy to reduce volatilization losses through stimulation of the nitrification mechanism. Soils were pre-incubated with a small amount of ammonium sulphate several days before receiving a larger application of urea. The usual time lag between urea hydrolysis and the onset of nitrification was eliminated with the result that nitrate was formed more rapidly than in controls which had received no pre-treatment. This reduced the ammoniacal-N concentration in the soil solution and approximately halved the $NH_{3(g)}$ losses from 20% to 11%. The opposite effect can also be induced. Bundy and Bremner (1974) used N-serve to retard nitrification of the NH_4^+ produced by urea hydrolysis with the result that $NH_{3(g)}$ losses were enhanced.

Other techniques which have been investigated are the use of urease inhibitors (Moe, 1967) and slow release agents (e.g. sulphur coated urea) (Vlek and Craswell, 1979). These techniques work by retarding the rate of urea hydrolysis thereby preventing a rapid build up in ammoniacal-N. Similar effects have been observed following urea applications to soils partially sterilized by heat (Volk, 1970).

Placement of the fertilizer below the soil surface or thoroughly incorporating it into the topsoil may also help to reduce the ammoniacal-N concentration of the soil solution at the soil surface

and thereby reduce $NH_{3(g)}$ loss. This has been consistently demonstrated in placement experiments by a number of workers (Wahhab *et al.*, 1957; Ernst and Massey, 1960; Overrein and Moe, 1967; Fenn and Kissel, 1976; Vlek and Craswell, 1979; Hoff *et al.*, 1981).

1.2.1.4 Soil moisture content and moisture loss

Examination of equation [1.13] suggests a simple relationship should exist between initial soil moisture content and the rate of volatilization. Ammoniacal-N concentrations at high moisture contents should be lower than at low moisture contents leading to lower $NH_{3(g)}$ losses from wetter soils. This has been shown in a number of studies (Martin and Chapman, 1951; Wahhab *et al.*, 1957; Fenn and Escarzaga, 1976). Other workers have found the opposite effect occurs (Volk, 1959; Ernst and Massey, 1960; Kresge and Satchell, 1960).

Unfortunately, interpretation of these results is often confounded by simultaneous water loss. Loss of water would tend to maintain or possibly increase ammoniacal-N concentrations over time and lead to greater losses than if no drying of the soil occurred. This appears to have taken place in several studies in which definite relationships between water and $NH_{3(g)}$ losses were observed (Jewitt, 1942; Wahhab *et al.*, 1957). Accordingly, it has been suggested that moisture loss is mandatory for $NH_{3(g)}$ loss to occur (e.g. Wahhab *et al.*, 1957). This is not the case since others have shown that $NH_{3(g)}$ may still be lost in substantial amounts under non-drying conditions (Ernst and Massey, 1960; Terry *et al.*, 1978).

The rate of moisture loss may also affect the extent of $NH_{3(g)}$ loss in other ways. It has been suggested that the rapid drying of moist soil could produce $NH_4^+{}_{(aq)}$ concentrations sufficient to inhibit nitrification thereby increasing $NH_{3(g)}$ losses (Terry *et al.*, 1978; Lyster *et al.*, 1980). Conversely, the slow drying of soils might allow time for the nitrification process to reduce the ammoniacal-N concentration and help acidify the system resulting in a net reduction in $NH_{3(g)}$ losses (Terry *et al.*, 1978).

In the case of urea fertilizers, low initial soil moisture content or rapid drying immediately after fertilizer application could slow the rate of urea dissolution, and hydrolysis could be impeded. This could lead to the low $NH_{3(g)}$ losses observed at low moisture contents in a number of experiments (e.g. Ernst and Massey, 1960).

The loss of soil moisture is necessarily accompanied by a net upwards movement of water to the soil surface. This would help transport dissolved ammoniacal-N to the soil surface where volatilization could then take place. Fenn and Escarzaga (1977) showed that initially wet soil lost more $NH_{3(g)}$ than initially dry soil even though large amounts of water were added to both soils shortly after application of the solid fertilizer. They suggested that in the dry soil, dissolved $NH_4^+{}_{(aq)}$ was adsorbed wherever the water moved whereas in the initially wet soil $NH_4^+{}_{(aq)}$ would tend to remain in the large soil pores. Convection to the soil surface would tend to proceed via the large pores and thereby transport more $NH_4^+{}_{(aq)}$ to the surface of the initially wet soil. Thus, the rate of convection of soil moisture to the soil surface could be important in determining the ultimate rate of $NH_{3(g)}$ loss from the soil surface.

A similar mechanism may operate where fertilizer solution or animal urine is applied to soil. For example, Vallis *et al.* (1982) found in field experiments that 14.4% of urine-N was volatilized from dry soil whereas 28.8% was lost from moist soil. The mean temperatures were similar for both experiments. Quin (1982) has suggested that the depth of urine penetration increased rather than decreased under declining soil moisture due to channeling down large soil pores, cracks and worm holes. Such factors are rarely considered in laboratory experiments.

1.2.1.5 Windspeed

The previous sections have examined the various factors which can influence $NH_{3(g)}$ volatilization mainly through their effects on the equilibria in Figure 1.1. The equations derived and discussed thus far assumed the attainment and maintenance of equilibrium conditions throughout the system, and in particular at the soil solution/air interface. Vlek and Craswell (1981) have described the net result of these factors on the dynamics of aqueous ammonia chemistry as constituting the "volatilization potential" of the system. They maintained the actual $NH_{3(g)}$ loss rates would be further influenced by environmental factors (e.g. windspeed and rainfall), which affect the magnitude of "k", the volatilization exchange coefficient (see equation [1.1]). Of these, the most important is windspeed.

The effect of windspeed on the rate of volatilization from well-drained soils is somewhat ambiguous and will be discussed later. It has been clearly demonstrated, however, that increasing the windspeed over a flooded soil surface increases the $NH_{3(g)}$ volatilization

rate (Vlek and Stumpe, 1978; Bouwmeester and Vlek, 1981; Denmead *et al.*, 1982; Moeller and Vlek, 1982). A mathematical volatilization model appropriate to flooded soils developed by Bouwmeester and Vlek (1981) predicted an almost linear increase in volatilization rate with increasing windspeed. These investigators were able to distinguish 3 rate controlling factors which may provide an insight also into the factors which limit volatilization from well-drained soils. They were: the reaction rate of equation [1.7], the transfer resistance in the liquid phase, and the transfer resistance in the gas phase. At very low wind velocities the gas phase resistance dominates and the volatilization rate is controlled by the rate of $NH_{3(g)}$ transfer away from the solution surface. At higher windspeeds, the volatilization rate is controlled mainly by the transfer rate of NH_3 through the diffusion layer at the surface of the solution. Only at very high pH does the volatilization rate become insensitive to increases in windspeed. The model assumed the transport of NH_3 to the water surface relied on molecular diffusion only and that this was independent of windspeed. Subsequently, Denmead *et al.* (1982) demonstrated an exponential increase in volatilization rate with increasing windspeed from flooded soil under field conditions. These investigators suggested that there could be considerable resistance to transport of $NH_{3(aq)}$ in the liquid phase and that the enhanced volatilization in high winds could be due to better mechanical mixing of the surface water, a factor not considered in the volatilization model. They further suggested that this mixing would tend to avoid the development of a region at the floodwater surface depleted of $NH_{3(aq)}$ which might limit the volatilization rate.

No such mechanical mixing is possible in the case of well-drained soils. The movement of NH_3 to the soil surface as stated by Freney *et al.* (1982) occurs by diffusion in the liquid or vapour phases, or by convection if the soil solution is also moving, although, when the ammonia is located close to the soil surface diffusion alone is the most likely transport mechanism. The effect of windspeed on rate of NH_3 diffusion in well-drained, non-saturated soils would be more difficult to assess and much more difficult to model than for flooded soils particularly since the micro-environment within the surface soil may itself have a large influence. For example, the parameters pH and temperature are unlikely to be spatially constant and variations would affect the partitioning of all forms of ammoniacal-N which in turn would affect the net rate of NH_3 diffusion.

Sealed aspirated enclosures have been used by several groups to determine the effect of windspeed (or airflow rate) under controlled laboratory or greenhouse conditions. Both Watkins *et al.* (1972) and Kissel *et al.* (1977) showed that total $NH_{3(g)}$ losses increased with increasing airflow but reached an asymptote at some particular flowrate. Maximum loss from ammonium sulphate applied to a calcareous soil was achieved using flowrates at or above 15 exchange volumes per minute (Kissel *et al.*, 1977) while a flow of only 0.8 volumes per minute was needed to realize maximum losses from urea applied to the organic horizon of a forest soil (Watkins *et al.*, 1972). Clearly in these two examples simulated windspeed was not rate limiting once a particular minimum value was exceeded.

Hoff *et al.* (1978) used enclosures based on the Kissel design to measure the $NH_{3(g)}$ loss from liquid swine manure under field and greenhouse conditions. They concluded that when the enclosures were

open to the atmosphere, ambient air movement stimulated $NH_{3(g)}$ release which then exceeded the measured loss during the enclosed sampling periods. This resulted in an underestimation of the total $NH_{3(g)}$ loss. Alternatively, it is reasonable to conclude that when the enclosures were closed, the flowrate during the $NH_{3(g)}$ collection periods would have limited the rate of $NH_{3(g)}$ release.

"Free-field" measurement techniques are not confounded by the modifying influences of enclosures. Denmead *et al.* (1974) used a micrometeorological approach to measure the $NH_{3(g)}$ fluxes from a pasture grazed by sheep. They reported specific data for two experimental periods on successive days when the windspeeds at 1 metre were 0.9 and 3 m s^{-1} respectively. While this windspeed difference created large differences in the $NH_{3(g)}$ concentration profiles above the surface of the pasture, the actual $NH_{3(g)}$ fluxes were almost identical on both days (i.e. 1.5 mg m^{-2} hr^{-1}). Thus, windspeed appeared to have little effect on the rate of $NH_{3(g)}$ loss. Similar conclusions were reached by Beauchamp *et al.* (1978, 1982). They used an aerodynamic method to measure gaseous losses from field applications of sewage sludge and liquid dairy cattle manure. The work involved 5 separate field experiments each lasting 5-7 days and in none was a relationship between windspeed and $NH_{3(g)}$ flux discernable. As remarked upon earlier (section 1.2.1.2) the fluxes were most closely related to air temperature. These workers suggested that volatilization from the liquid dairy cattle manure was diffusion controlled and was limited by depletion of ammoniacal-N at sites from which volatilization was possible. Windspeed presumably had little effect on this diffusion process.

Before the development of "free-field" techniques, most direct measurements of $NH_{3(g)}$ loss carried out in the field utilized enclosures in which aspiration rates were often sufficiently low to be rate limiting. Sometimes static units were employed which relied on internal acid traps to collect $NH_{3(g)}$. The rate limiting factor in these systems was probably the transfer resistance through the air which in turn would be related to the surface area of the acid trap. Clearly, results obtained using such techniques may not relate well to results obtained using unconfined plots.

Vlek and Craswell (1981) have stressed that where enclosures are used for direct field measurements from flooded soils they are best confined to assessing fertilizer management on the potential for $NH_{3(g)}$ volatilization and then only when the airflow employed is sufficient so that gas phase resistance does not dominate the volatilization process. However, it appears that for well-drained soils suitable enclosures utilizing high aspiration rates may provide a good indication of losses under non-enclosed conditions. Unfortunately, no direct comparisons between "free-field" and enclosure methods have been reported to test this possibility.

1.3 EFFECTS OF PLANTS

Plants are capable of playing both active and passive roles in ammonia volatilization. Some plants are known to both actively absorb and emit $NH_{3(g)}$ through their stomata (Kresge and Satchell, 1960; Denmead *et al.*, 1976, 1978; Stutte *et al.*, 1979; Farquhar *et al.*, 1980; Lemon and Van Houtte, 1980; Cowling and Lockyer, 1981). At

the same time, leaves may provide an essentially exchange free surface upon which hydrolysis of urea and subsequent volatilization of $NH_{3(g)}$ can take place (Doak, 1952; Volk, 1959; Simpson and Melsted, 1962; McGarity and Hoult, 1971; Watkins *et al.*, 1972).

1.3.1 Active Role of Plants

Hutchinson *et al.* (1972) showed that young plants grown in growth chambers under optimum conditions acted as an almost infinite sink for $NH_{3(g)}$. However, these and other experiments were usually carried out with chamber $NH_{3(g)}$ concentrations well in excess of normal ambient levels. When lower and more realistic concentrations were used (i.e. 3-5 μg NH_3 m^{-3}) it has been shown that some leaves, particularly those undergoing senescence, could also release $NH_{3(g)}$ (e.g. Farquhar *et al.* 1979). Stutte *et al.* (1979) used a sensitive pyro-chemiluminescent technique to quantify the N content of transpired soybean leaf vapour. Although this technique did not distinguish the form of the N detected, the amount released was not insignificant and was estimated at 45 kg N ha^{-1} over the growing season. Using an aerodynamic technique which did not disturb natural field conditions, Lemon and Van Houtte (1980) demonstrated that uptake of $NH_{3(g)}$ through the stomata of soybean leaves was concentration dependent. At high ambient concentrations healthy leaves could absorb $NH_{3(g)}$ while at low concentrations $NH_{3(g)}$ could be released. They concluded that in some respects NH_3 behaved very much like CO_2 and advanced the hypothesis that this mechanism allowed NH_3 to move by the wind from areas of high N status to areas of low status N. More recently, Harper *et al.* (1983)

have measured a diurnal $NH_{3(g)}$ flux cycle above a short Nandi Setaria pasture in Queensland, Australia. Atmospheric $NH_{3(g)}$ was absorbed by the plant-soil system during daytime hours with generally a small efflux occurring at night. These authors could only speculate that the major $NH_{3(g)}$ sink was plant tissue since the major absorption period was during sunlight when plant activity was at its highest and leaf stomata were open. Subsequently, when urea fertilizer was applied, this diurnal flux pattern reversed and maximum efflux occurred during the day.

Using a similar aerodynamic technique Denmead *et al.* (1976) demonstrated that $NH_{3(g)}$ was released from the soil surface of an ungrazed 70 cm high ryegrass/clover pasture only to be absorbed by the plant canopy above. They calculated that the amounts absorbed were too large for stomatal uptake alone and suggested that $NH_{3(g)}$ dissolved in water films on the plant leaf surfaces and was subsequently absorbed and metabolized. In later experiments with maize plants they showed that leaf absorption of $NH_{3(g)}$ by a short crop constituted only about 4% of that volatilized while absorption by a tall crop was 15% (Denmead *et al.*, 1982). It appears therefore, that the height and density of the crop canopy is an important factor in net $NH_{3(g)}$ exchange between a crop and the atmosphere.

1.3.2 Passive Role of Plants

Crop height and density are also important factors in determining the fraction of an applied fertilizer solution that might be intercepted before it reaches the soil surface. Intercepted solution may undergo a number of transformations. In the case of aqueous urea, direct stomatal uptake of urea can occur (Yamada *et al.*, 1965). However, leaf surfaces

may also possess considerable urease activity and direct volatilization of the hydrolysis products has been demonstrated (Doak, 1952; Volk, 1959; Simpson and Melsted, 1962; McGarity and Hoult, 1971; Watkins *et al.*, 1972). Volatilization from the moisture films on leaves may even be greater than from the soil surface itself. This is because leaf surfaces possess only a limited cation exchange capacity (CEC) and low buffering capacity with the result that high concentrations of $NH_{3(aq)}$ may be produced. Litter surfaces may also be important in this regard. For example, approximately 30% of the urea-N applied as solution to bluegrass leaves taken from an established sod volatilized as $NH_{3(g)}$. This was generally twice that volatilized from the leaves of other grasses grown from seed in pots and over three times that volatilized from a bare soil surface (Simpson and Melsted, 1962). These differences were attributed by the investigators to the greater urease activity of residual organic matter from previous plant growth present in the established bluegrass sod which would have intercepted some of the applied solution.

These factors are very relevant to grazed pasture ecosystems since a high percentage of the nitrogen in voided animal urine is in the form of urea (Richards and Wolton, 1976). Doak (1952) estimated that hold-up of sheep urine on the surfaces of ryegrass leaves could amount to 36% of the green weight of the leaves. Estimates based on this indicate that volatilization from intercepted urine on leaf and plant litter surfaces might consitute a significant portion of the total $NH_{3(g)}$ volatilized from urine patches.

1.4 VOLATILIZATION FROM CALCAREOUS SOILS

The presence of calcium carbonate in soil is reported to stimulate volatilization of $NH_{3(g)}$ from applied ammoniacal fertilizers. The effect is not primarily related to the original soil pH as might be expected but rather depends on the nature of the anion associated with the applied NH_4^+ cation (Terman and Hunt, 1964). The anions, F^-, SO_4^{2-}, and HPO_4^{2-} all produce sparingly soluble calcium salts whereas the calcium salts of Cl^-, NO_3^- and I^- are all highly soluble. It was shown (Fenn and Kissel, 1973) that the addition of NH_4F, $(NH_4)_2SO_4$ and $(NH_4)_2HPO_4$ to a calcareous Black Houston clay soil at a rate equivalent to 550 kg NH_4-N ha^{-1} produced volatilization losses of 68%, 55% and 51% respectively whereas application of NH_4Cl, NH_4NO_3 and NH_4I under the same conditions resulted in losses of only 18%, 18% and 16% respectively. Soil pH changes closely paralleled changes in the rate of $NH_{3(g)}$ loss.

1.4.1 Reaction Mechanism

Fenn and Kissel (1973) proposed that ammonium salts could react with calcium carbonate in calcareous soils to form either soluble or insoluble calcium salts. The general equation they presented to describe this mechanism was:

$$X\ (NH_4)_zY\ +\ N\ CaCO_{3(s)} \rightleftharpoons N\ (NH_4)_2CO_3\ +\ Ca_nY_x \qquad [1.14]$$

where 'Y' refers to the anion associated with the NH_4^+ cation, 'Z' and 'X' are stoichiometric coefficients and 'n', 'x' and 'z' are dependent upon the valencies of the anions and cations. They further suggested that if the calcium salt 'Ca_nY_x' was insoluble, e.g. $CaSO_4$ then equilibrium [1.14] would proceed to the right to favour the formation of unstable ammonium carbonate, $(NH_4)_2CO_3$, which would then

decompose producing $NH_{3(g)}$ and $CO_{2(g)}$ and H_2O. In a subsequent study, Feagley and Hossner (1978) showed that the ratio of volatile reaction products was more consistent with the formation of ammonium bicarbonate, NH_4HCO_3. Also at no time did the pH of the calcareous systems under study ever exceed 8.4 and consequently $(NH_4)_2CO_3$ was unlikely to be formed.

Whatever the precise mechanism, the important outcome is that the anion of the NH_4^+ fertilizer can influence the soil pH. It does so by encouraging the dissolution of $CaCO_{3(s)}$ through the formation of an insoluble calcium salt. Depending on the buffering capacity of the soil, the subsequent hydrolysis of the CO_3^{2-} ion (equation [1.9]) may increase the soil solution pH. If this occurs then the amount of ammoniacal-N present as $NH_{3(aq)}$ increases with the net result being an increase in $NH_{3(g)}$ volatilization rate from the soil surface. The solubility of the possible calcium salt reaction product can therefore indirectly influence the soil pH and is consequently a major factor in determining the ultimate extent of $NH_{3(g)}$ production from calcareous soils.

1.4.2 Major Factors Affecting NH_3 Volatilization in Calcareous Soils

1.4.2.1 Particle size

According to the previous discussion, the rate of increase in soil pH should be related to the rate of precipitation of the sparingly soluble calcium salt and to the rate of dissolution of calcium carbonate. It might be expected, therefore, that the calcium carbonate particle size would influence the rate of dissolution and

hence the ultimate extent of $NH_{3(g)}$ loss. This was confirmed by Ryan *et al.* (1981) who found a highly significant correlation between the amount of clay sized calcium carbonate and $NH_{3(g)}$ loss following the addition of $(NH_4)_2SO_4$ to non-calcareous soils ammended with ground limestone.

1.4.2.2 Rate of application

Increasing the rate of application of an insoluble salt forming fertilizer (e.g. $(NH_4)_2SO_4$) produced an increase in the total percentage $NH_{3(g)}$ loss (Fenn and Kissel, 1974). However, a constant percentage loss resulted when increasing rates of NH_4NO_3 were used. These findings are again consistent with the predicted effect of a pH increase accompanying CO_3^{2-} hydrolysis. That is, an increase in the amount of insoluble salt formed leading to an increase in the amount of CO_3^{2-} hydrolysis and an increase in pH. Unfortunately, pH measurements were not reported to confirm this (Fenn and Kissel, 1974).

1.4.2.3 Losses from urea

A better understanding of the peculiarities characterising $NH_{3(g)}$ volatilization following applications of ammonium salts has led to renewed interest in the reactions of urea with calcareous soils. Fenn and Miyamoto (1981a) showed that KCl extractable Ca^{2+} and Mg^{2+} levels decreased near the sites of urea hydrolysis. This was accompanied by the precipitation of $MgCO_3$ and $CaCO_3$, the enhanced adsorption of NH_4^+ on exchange sites and a reduction in $NH_{3(g)}$ losses. The reaction between the urea hydrolysis product, CO_3^{2-}, and exchangeable Ca^{2+} and Mg^{2+} presumably led to a decrease in the extent of CO_3^{2-} hydrolysis. This reaction was subsequently investigated as a possible means of reducing

volatile losses from urea in both calcareous and non-calcareous soils (Fenn *et al.*, 1981b, 1981c). The deliberate addition of soluble Ca^{2+} salts along with urea enhanced the precipitation of carbonates and led to a decrease in both pH and $NH_{3(g)}$ losses.

1.5 AMMONIA VOLATILIZATION FROM FLOODED SOILS

The fountain experiment, well known to all who have studied chemistry, is a dramatic demonstration of the high solubility of $NH_{3(g)}$. In fact, NH_3 is the most soluble gas known and it is tempting to think that a soil flooded with water would serve as an almost infinite sink for the gas and that any volatilization to the atmosphere would therefore be negligible. This is not supported by results of recent field experiments. Recent research has demonstrated that considerable amounts of nitrogen fertilizers applied to flooded soils may be lost as $NH_{3(g)}$. For example, Vlek and Craswell (1979) showed that up to 50% of urea, surface applied to floodwater, was lost as $NH_{3(g)}$ within 2-3 weeks. This is all the more significant since over 80% of the N fertilizer now used on wetland rice soils in the tropics is reported to be urea (Vlek and Craswell, 1981).

The dynamics of $NH_{3(g)}$ loss from aqueous solution and flooded soil has been the subject of several recent investigations (Mikkelsen *et al.*, 1978; Vlek and Stumpe, 1978; Vlek and Craswell, 1979; Bouwmeester and Vlek, 1981; Craswell *et al.*, 1981; Denmead *et al.*, 1982; Moeller and Vlek, 1982) and also the subject of a comprehensive review (Vlek and Craswell, 1981). This work has greatly expanded current understanding. It appears that the same factors which

determine the extent of volatilization from well drained soils also operate in flooded soils (Freney *et al.*, 1981). In addition, there are several other factors which have been identified which may be unique to the flooded system, some of which are discussed below.

1.5.1 Major Factors Affecting Volatilization in Flooded Soils

1.5.1.1 Bicarbonate buffering

Vlek and Stumpe (1978) showed that in order for ammonia volatilization to proceed, buffering substances needed to be present to prevent the acidification of the floodwater resulting from the conversion of NH_4^+ to NH_3 (see equation [1.7]). The only proton acceptor capable of that at the typical pH's of floodwater and also present in sufficient quantity is bicarbonate (HCO_3^-). Volatilization of $NH_{3(g)}$ from a flooded system can therefore be represented by the equation:

$$NH_4^+{}_{(aq)} + HCO_3^-(aq) \longrightarrow NH_{3(g)} + CO_{2(g)} + H_2O \qquad [1.15]$$

Following the hydrolysis of applied urea, the floodwater will contain both $NH_4^+{}_{(aq)}$ and $HCO_3^-(aq)$ and behave as a dilute ammonium bicarbonate solution buffered at a pH of about 8. This pH is sufficient to sustain volatilization and will be maintained so long as stoichiometrically equivalent amounts of $NH_{3(g)}$ and $CO_{2(g)}$ are evolved (equation [1.15]). The upper limit to volatilization is then determined by the amount of HCO_3^- in the floodwater (Vlek and Craswell, 1981). Once the HCO_3^- is depleted, any further volatilization will acidify the floodwater and lower the pH. The fraction of the ammoniacal-N present as $NH_{3(aq)}$ will reduce and the volatilization rate will drop accordingly. However, as HCO_3^- concentrations decrease,

the buffering capacity of the floodwater also decreases and may be influenced by photosynthetic activity accompanying any surface algal growth (Mikkelsen *et al.*, 1978; Vlek and Craswell, 1981). Algal photosynthesis will tend to raise the pH and thereby increase $NH_{3(g)}$ losses.

Losses of $NH_{3(g)}$ from ammonium sulphate or ammonium nitrate fertilized soils will normally be lower than from urea fertilized soils because high $HCO_3^-{}_{(aq)}$ concentrations are not induced by the fertilizer itself. However, losses from these fertilizers may become substantial where alternative sources of HCO_3^- are available (e.g. calcareous soils or alkaline well water) (Vlek and Craswell, 1981).

1.5.1.2 Nitrification

As mentioned previously, the extent of volatilization in soils may be influenced by the rate of nitrification (Fleisher and Hagin, 1981). Nitrification can only take place under oxidizing conditions and in the case of flooded soils these only occur at the aerobic water/air interface. Consequently, the rate of nitrification will depend on the rate of diffusion of NH_4^+ to this aerobic layer (Reddy *et al.*, 1976) and will be much slower than under well-drained conditions. Nitrification is therefore not an efficient mechanism for reducing high $NH_4^+{}_{(aq)}$ concentrations in flooded soils and is unlikely to contribute significantly to reducing $NH_{3(g)}$ losses.

1.5.1.3 Urease activity

Urea broadcast on the surface of flooded soil must diffuse to a site of sufficient urease activity at the soil surface before

hydrolysis can occur. In order to be volatilized, the $NH_4^+{}_{(aq)}$ thus formed must diffuse back to the floodwater surface. It might be expected, therefore, that this would greatly retard the volatilization process relative to a well-drained soil receiving a similar broadcast application. This may be the case but the total extent of $NH_{3(g)}$ loss from broadcast urea can still be severe (Vlek and Craswell, 1979). A better strategy is to incorporate the urea into the soil. This allows the urea to hydrolyse rapidly and be retained as NH_4^+ on exchange sites within the soil thus preventing back diffusion to the floodwater surface. The use of sulphur coated urea or urea supergranules placed at depth (e.g. 8 cm) has also been shown to markedly reduce losses (Vlek and Craswell, 1979).

1.5.1.4 Windspeed

Finally, as was discussed previously, volatilization losses from flooded soils increase with increasing windspeed. In rice paddies which are flooded for long periods there would appear to be little scope for overcoming the effects of high winds. However, where flooding is intermittent and controllable some of the effects of wind might be combatted. For example, Denmead *et al.* (1982) suggested flood irrigation with water containing dissolved $NH_{3(aq)}$ should preferentially be carried out at night when wind speeds are usually low. They also showed that the rate of $NH_{3(g)}$ loss from a flood irrigated short maize crop was about 7 times that from a tall crop. Crop height is therefore an important factor in moderating the effects of high winds.

1.6 VOLATILIZATION FROM URINE PATCHES IN GRAZED PASTURES

1.6.1 The Urine Patch

It has been estimated that 85-95% of the N ingested by grazing herbivors is excreted (Henzell and Ross, 1973) and most of this is voided as urine in localized patches on the soil surface (Doak, 1952). Urine is a concentrated N solution (approx. 10 g N l^{-1} of which 80-90% is urea) and the effective rate of application within urine patches is often greater than the equivalent of 500 kg N ha^{-1}. This is generally much higher than that following the surface application of artificial N fertilizers to pastures (0-100 kg N ha^{-1}) (Ball, 1982). In most soils, urea is rapidly hydrolysed to ammoniacal-N under the action of the enzyme, urease, in accordance with the reactions described earlier (see equations [1.8] and [1.9] in section 1.2.1.1) The rise in soil solution pH which accompanies the formation of these high concentrations of ammoniacal-N will favour the formation of $NH_{3(aq)}$ and make the loss of some $NH_{3(g)}$ almost inevitable (O'Connor, 1981).

As a direct consequence of the manner by which they are formed, urine patches represent a very inefficient mechanism for the recycling of nutrient within a grazed pasture ecosystem. For example, Jackman (1960) assumed random distribution of sheep and estimated that only 30% of a grazed pasture carrying 19 sheep ha^{-1} would receive a direct urine influence every year. In reality, the deposition of urine-N may be even less extensive than this since the gregarious habits of some breeds may lead to the development of preferred camping areas affected by disproportionate amounts of excreta (Floate, 1981).

Minor changes in topology or shelter might also lead to camping behaviour (O'Connor, 1981). Urine patches therefore provide concentrated focal points within the pasture from which $NH_{3(g)}$ volatilization can take place.

Another suggested consequence of the aggregation of labile nitrogen in urine patches is that application rates are usually much too high for effective plant utilization. For example, apparent recovery of urine-N by pasture was investigated under cool-moist, warm-moist, and warm-dry conditions at Palmerston North, New Zealand and was shown to be 55%, 30% and 11% respectively (Ball and Keeney, 1981). Soil total-N was not increased significantly which led these authors to conclude that substantial losses of urine-N had occurred and that the more intensively farmed grass-clover systems in New Zealand may be in negative N balance. These views were supported by another study carried out in Southland, New Zealand in which Carran *et al.* (1982) showed that after 130 days 30% and 40% of the urine-N applied to dry and wet pasture soils respectively remained unaccounted for. In that study, measurements were also made of herbage uptake (15% and 22% for the dry and wet treatments respectively), $NH_{3(g)}$ volatilization (36% and 17% respectively) and NH_4^+ fixation by clay minerals (10% for both treatments). Since leaching was not implicated, these authors concluded that denitrification was the other principal mechanism of loss. Denitrification is discussed as a possible loss mechanism in Part II of this thesis.

Before denitrification can take place, it must be preceded by nitrification of the ammonical-N. Nitrification within urine patches provides a mechanism for the formation and accumulation of nitrite (NO_2^-) (Doak, 1952). It has been demonstrated both in laboratory

experiments (e.g. Bundy and Bremner, 1974) and in growth cabinet studies (Barlow, 1974) that NO_2^- can form nitric oxide (NO) and nitrogen dioxide (NO_2) through chemo-denitrification reactions (see section 6.4). The subsequent evolution of these gases to the atmosphere may augment $NH_{3(g)}$ volatilization losses from urine patches although the limited data available suggest contributions via this mechanism are small. For example, Barlow (1974) reported losses of $NO_{(g)}$ and $NO_{2(g)}$ from urine patches of less than 2% of the applied N and in the Southland field experiments discussed earlier (Carran *et al.*, 1982), no chemo-denitrification products were detected.

1.6.2 Measurements and Methodology

Methods currently available for measuring $NH_{3(g)}$ losses from urine patches and urine affected pasture may be broadly classed as either direct or indirect. Direct measurements include the use of volatilization chambers or suitably aspirated enclosures as well as micrometeorological and aerodynamic methods which do not induce modifications in the micro-environment of the pasture surface. Indirect methods use dry matter yields plus the N accounted for in other soil and plant fractions to infer potential $NH_{3(g)}$ losses.

1.6.2.1 Direct measurements

Most studies dealing with $NH_{3(g)}$ volatilization have employed aspirated chambers or enclosures (see sections 1.2.1.1 and 1.2.1.5). These have also been used in several studies to measure losses from simulated urine patches. The first to attempt this in the field was

Doak (1952). An inverted metal cylinder served as the volatilization chamber. Air was aspirated through the headspace and the liberated $NH_{3(g)}$ was trapped in sulphuric acid. The mean loss in 72 hours from 3 experiments was 12.1%.

Two factors which influenced the design of subsequent field systems were a need for temperature control and the need to eliminate the tendency for $NH_{3(g)}$ to dissolve in the condensate which collects on the inside surface of the enclosure and the air conduits. McGarity and Rajaratnam (1973) overcame these problems with a chamber that used sunshades for temperature control and a heating element on the transparent interior surface to eliminate condensate. They used it to measure the loss of $NH_{3(g)}$ following the application of urine to a pasture soil in the field and found that only 6.5% of the urine-N (applied at 118 kg N ha^{-1}) volatilized during a 6 day period. Later modifications introduced a refrigerated cooling coil and fan to moderate temperature and to serve as an additional $NH_{3(g)}$ trap (Hoult *et al.*, 1974). Unfortunately, this meant that the system could only be employed under growth cabinet or greenhouse conditions.

The need for air cooling could be reduced if higher airflow rates were employed. The 32 l min^{-1} flowrate (1 air-change per 45 seconds) used by Ball *et al.* (1979) eliminated the need for active cooling but still required the passive assistance of sunshades to maintain internal chamber temperatures within 1.5°C of ambient. The high air flowrate also meant that only minor amounts of NH_3 dissolved in any condensate present (Ball *et al.*, 1979). In studies carried out at Palmerston North with this chamber, measured loss of $NH_{3(g)}$ from simulated urine patches was 16, 66 and 5% of the urine-N applied to pasture under warm-moist, warm-dry and cool-moist conditions

respectively (Ball, 1982). Carran *et al.* (1982) used the same system for the Southland study discussed earlier.

The necessity for cooling was dispensed with entirely in the design of Kissel *et al.* (1977) which combined a small enclosure (headspace volume approximately 1 litre) with a high airflow rate (approximately 20 l min^{-1}). This design was used for the field experiments reported in chapter 2 of this thesis. The latest reported refinement in chamber design made provision for the throttling of airflow rates to more closely approximate ambient windspeeds (Vallis *et al.*, 1982) (see section 1.2.1.4).

A direct method for estimating $NH_{3(g)}$ loss from grazed and ungrazed pastures has also been described (Denmead *et al.*, 1974, 1977). The basic technique has been used extensively in micrometeorology for measuring the rates of gas exchange (e.g. evaporation) above natural surfaces. To calculate $NH_{3(g)}$ fluxes with the technique requires the measurement of a variety of micrometeorological variables (e.g. net radiation, soil heat flux, and air temperature profiles) together with simultaneous measurements of the $NH_{3(g)}$ concentration in the atmosphere at various heights above the surface of the pasture. Denmead *et al.* (1974) used the method to determine that 26% of the urine-N voided by 200 sheep uniformly grazing a 4 ha field was volatilized as $NH_{3(g)}$. The method was also used by Hutchinson *et al.* (1982) to determine $NH_{3(g)}$ volatilization rates above a large cattle feedlot in Colorado. They measured a mean vertical $NH_{3(g)}$ flux density of 1.4 kg N ha^{-1} hr^{-1} during daylight hours in spring and summer and estimated that this constituted about one-half of the urine-N deposition rate or one-fourth of the total-N deposition rate for the feedlot. This micrometeorological method has large fetch

requirements and is therefore unsuitable for studying treatment effects (e.g. rate of urine application). However, unlike the enclosure methods it does enable $NH_{3(g)}$ influx measurements to be made (Denmead *et al.*, 1976).

More recently, Beauchamp *et al.* (1978, 1982) have demonstrated a simpler aerodynamic procedure which was used to measure $NH_{3(g)}$ losses from surface applied sewage sludge and liquid dairy shed manure. It requires the application of nitrogenous substrate to the soil surface as a circular disk of at least 20 m radius. Measurements are then made (usually every 2 to 4 hours) of time averaged horizontal windspeed and vertical $NH_{3(g)}$ concentration profiles at the centre of the disk. No other micrometeorological data are required. The method has yet to be used to measure $NH_{3(g)}$ losses from grazed pasture although it would appear quite feasible and probably simpler to implement than the earlier micrometeorological approach.

1.6.2.2 Indirect measurements

A number of early New Zealand studies attempted to infer volatilization losses indirectly from herbage production (e.g. Sears, 1953). The methodology employed in these experiments has recently been strongly criticised (e.g. Ball, 1982) since it involved mixing urine and dung together and applying it uniformly to pasture plots by watering can. Pasture responses in these experiments were therefore probably greater and volatilization losses smaller than in a normal grazed pasture where the return of excrement would have been localised in patches. Ball (1982)

has also pointed out that the intimate mixing of urine and dung prior to application to the pasture effectively turns treated plots into 'small-scale compost heaps' and subsequent biological transformations are probably quite unlike those actually taking place within a urine patch.

More appropriate methodology was used by Watson and Lapins (1969). Sheep urine was applied in simulated patches to pots containing either a coarse textured sand or a sandy loam sown with grass. The pots were then set into the ground to maintain ambient soil temperatures and destructively sampled at regular intervals and analysed for N. In a series of experiments, Watson and Lapins (1969) showed that for both soil types more than half of the urine-N was unaccounted for 28-36 weeks after application with the major portion of the loss occurring rapidly during the first 2 weeks. The authors attributed the majority of the N loss to volatilization as $NH_{3(g)}$.

Similar techniques were used by Stillwell *et al.* (1981) who applied synthetic urine to confined microplots under summer field conditions in Colorado. Again, about 50% of the inorganic-N disappeared after 9 weeks. However, these workers were unable to directly measure N immobilized by plant roots or micro-organisms and were therefore unable to distinguish N immobilized within the system from N lost as $NH_{3(g)}$ or denitrification products.

To clearly make this distinction requires the use of ^{15}N labelled urea. For example, Keeney and MacGregor (1978) showed the potential for rapid immobilization when labelled aqueous urea was applied at approximately 300 kg N ha^{-1} to confined field microplots

of a ryegrass/white clover pasture at Palmerston North under dry summer conditions. After 3 days 11.6% was immobilized in the soil organic-N fraction and this remained almost constant until the completion of the experiment 3 weeks later. ^{15}N recovery after 3 weeks was about 88% but since almost quantitative recovery was obtained after 1 week it was concluded that any $NH_{3(g)}$ volatilization which occurred was reabsorbed by the plant canopy.

CHAPTER 2

MEASUREMENTS OF AMMONIA VOLATILIZATION

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CHAPTER 2

MEASUREMENTS OF AMMONIA VOLATILIZATION

2.1 INTRODUCTION

The release of nitrogen from soil by volatilization as ammonia (NH_3) is considered to be a significant pathway for nitrogen loss from both arable and pastoral systems (West, 1975; Ball *et al.*, 1979; Vlek *et al.*, 1981).

Direct field measurements of ammonia volatilization show the potential for $NH_{3(g)}$ losses where high soil pH's are induced through either hydrolysis of urea or aqueous ammonia ($NH_{3(aq)}$). The combined influence of substrate concentration, ($NH_3 + NH_4^+$), fluctuating air temperatures and air movement on the pattern of ammonia release has been reviewed (see Chapter 1). Theoretically, the $NH_{3(g)}$ flux from the surface of the soil is determined primarily by the $NH_{3(g)}$ concentration at the soil-air interface (Vlek and Craswell, 1981) which in turn is related to pH and temperature by the equation:

$$NH_{3(aq)} = NH_{x(aq)} / \{1 + 10^{(0.09018 + 2729.92 / T - pH)}\}$$

(Denmead *et al.*, 1982) where $NH_{x(aq)}$ represents the total $NH_{3(aq)} + NH_4^+{}_{(aq)}$ concentration, and T is temperature (° K). From this equation it can be seen that increasing pH, temperature and ammoniacal-N concentration all increase the $NH_{3(aq)}$ concentration and should lead to increased $NH_{3(g)}$ fluxes (see section 1.2.1).

In pastures, N is usually returned through the urine and dung of grazing animals. In Australia and New Zealand, sheep are the dominant herbivors and most of the N is voided by sheep in discrete

isolated urine patches. The immediate fate of this N is expected to depend on the dynamics of urea hydrolysis and the influence of pH, windspeed and diurnal temperature fluctuations on the soil solution chemistry of the urine patch. These factors and the methodology available for measuring $NH_{3(g)}$ losses under field conditions were reviewed in Chapter 1.

The initial objective of this study is to develop and refine a field gas sampling procedure for measuring the soluble gases NH_3 and NO_2, released from urine patches and from other nitrogenous fertilizers applied to pasture soil. This is to be followed by a series of more detailed field experiments designed to directly measure $NH_{3(g)}$ volatilization from simulated sheep urine patches using either sheep urine or urea solutions applied to pasture under varying seasonal conditions. The results obtained are rationalized with reference to rates of urea hydrolysis and the influence of pH, windspeed and diurnal temperature fluctuations on the soil solution chemistry of the urine patch. In addition, $NH_{3(g)}$ fluxes resulting from repeated additions of these N solutions to the same area of soil are measured in an attempt to simulate the situation in a heavily stocked pasture.

2.2 CALIBRATION PROCEDURES AND PRELIMINARY EXPERIMENTS

2.2.1 Materials and Methods

2.2.1.1 Volatilization chamber

An enclosure technique similar to that of Kissel *et al.* (1977) was used to measure $NH_{3(g)}$ volatilization. It consisted of a cylindrical PVC volatilization chamber (23 cm diameter, 15 cm height) which was inserted

Figure 2.1

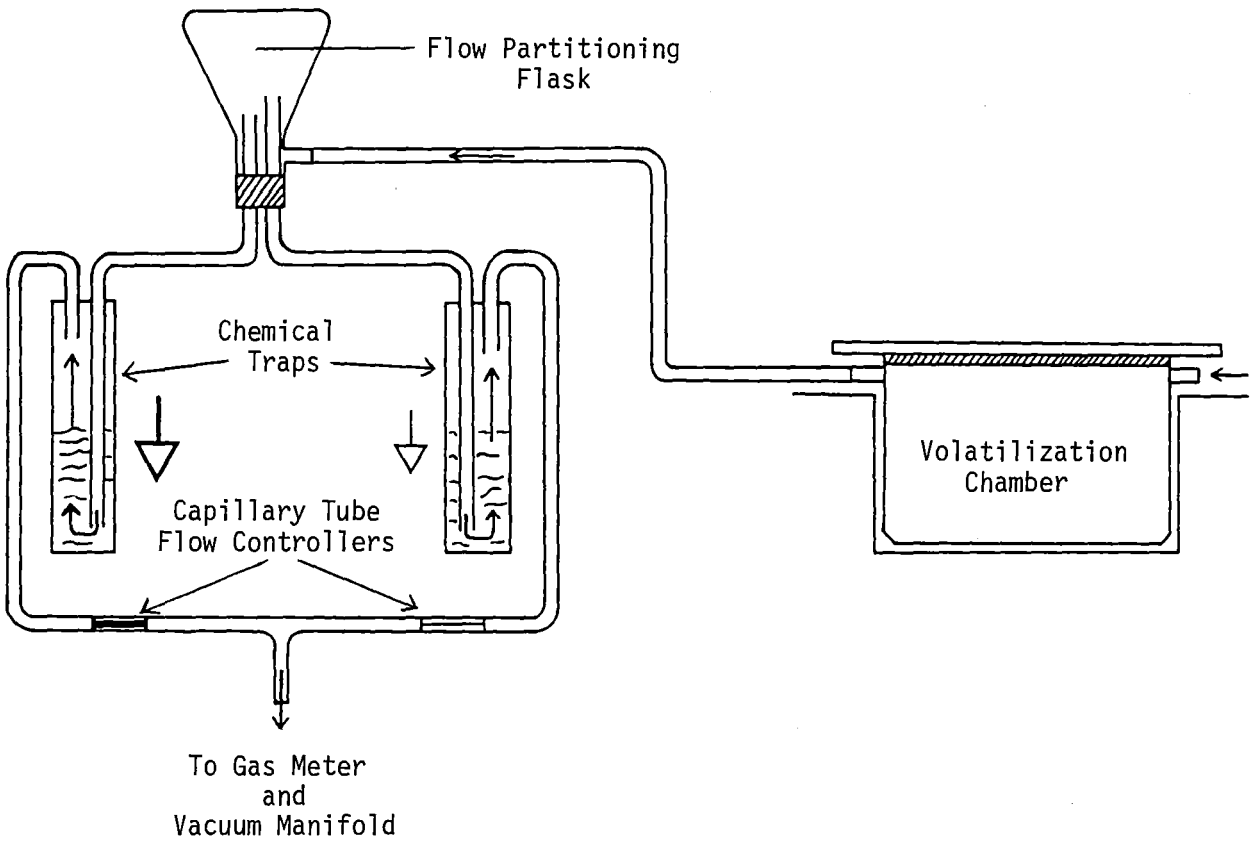


Figure 2.1 Diagram of Volatilization Chamber and Gas Trapping System used in the continuously aspirated mode.

into the soil with the top 3 cm exposed (Figure 2.1). A neoprene gasket on the rim of the exposed cylinder formed an effective seal with a clear perspex lid which was clamped over the cylinder immediately after N application. The lid was detachable and in some of the preliminary experiments an intermittant enclosure method was used (Kissel *et al.*, 1977). However, for the majority of the experiments the lid remained in place for the duration of the volatilization event (i.e. 7 - 10 days). Two holes (1 cm diameter) drilled diagonally opposite each other in the exposed cylinder wall formed the air inlet and outlet. The outlet hole was connected by 2 cm (internal diameter) flexible PVC pipe to chemical traps located in a mobile field laboratory and from there via a distribution manifold to a system of vacuum pumps. One PVC pipe was fitted with a nichrome heating element running its full length. This was to eliminate any condensate which might absorb ammonia and thereby prevent it from reaching the chemical trap. Chambers were aspirated either individually or simultaneously (section 2.2.1.2) at a constant air flow of about 21 l min^{-1} $chamber^{-1}$ (17 air exchanges min^{-1}).

2.2.1.2 Gas sampling

Two gas sampling procedures were used. The heated PVC pipe was used in conjunction with an intermittent enclosure method (Kissel *et al.*, 1977) to sample each chamber in sequence. Chambers were only sealed and aspirated during sampling periods lasting 10 - 20 minutes every 2 hours. The effluent gas was passed through 50 ml of 2% boric acid indicator solution (Bremner, 1965) contained in a 150 ml test-tube. This procedure was used exclusively to obtain high resolution $NH_{3(g)}$ flux data.

In the second procedure, the lids of the volatilization chambers were left in place and the enclosed headspaces were aspirated continuously for the duration of the experiment. The air from each chamber was partitioned in the field laboratory into two streams. A carefully monitored subsample (approx. 2.8%) was passed continuously through a gas distribution tube into 50 ml of 0.1 N triethanolamine solution. This subsample trap provided a means of monitoring the total release of gaseous $NO_{2(g)}$ and was analysed as required, usually twice daily (Levaggi *et al.*, 1973). The balance of the gas was normally pumped to waste but could be manually diverted as required through a second trap charged with a similar quantity of 2% boric acid indicator solution to absorb $NH_{3(g)}$. High resolution $NH_{3(g)}$ data during periods of rapid flux change were obtained from 10 minute samplings using the second trap. Calibration of air flows was achieved using gas meters mounted permanently in the gas lines with spot checks being made periodically using a rotameter flow meter. For the continuously aspirated procedure, the total switching time during which no air flowed through the chambers was estimated at less than 5 minutes each 24 hours.

It was not possible to directly quantify background levels of $NH_{3(g)}$ released from control plots. During sampling the absorption of ambient CO_2 in all the acid traps resulted in a slight colour change (reddening) of the indicator solutions. It was therefore necessary to use the colour of the control sample as the reference 'end-point' colour for the ammonia titrations. This automatically subtracted the control reading from the others. True $NH_{3(g)}$ backgrounds were obtained by distilling the boric acid solutions used for control plots and reabsorbing the evolved $NH_{3(g)}$ in fresh indicator solution.

The $NH_{3(g)}$ trapping efficiency at 21 l min^{-1} was confirmed by aspirating the headspace above 10 ml of 200 ppm ammonium sulphate solution made alkaline with 25 ml of a borax buffer solution (pH 9.2). Ammonia evolved over 20 minutes was passed through 2 acid traps in series. Aliquots of the trapping solutions and residual ammonium sulphate solution were distilled into 2% boric acid indicator solution (Bremner, 1965). The experiment was repeated 5 times. Recovery was quantitative (99.8 $\pm$ 1.2%) with 97% of the evolved $NH_{3(g)}$ located in the first trap. The $NH_{3(g)}$ found in the second trap probably resulted from carry-over of a small volume of boric acid from the first trap. At a flowrate of 35 l min^{-1} recovery was again quantitative but about 13% of the evolved $NH_{3(g)}$ was located in the second trap. Considering the almost total recovery using a single trap at 21 l min^{-1} it was decided to adopt that flowrate and dispense with the second trap for the field experiments.

The absorption efficiency of the triethanolamine solution is known to be flowrate dependent (Levaggi *et al.*, 1973). This was confirmed when an air sample containing $NO_{2(g)}$ was aspirated simultaneously through 6 traps in parallel. Flow rates were set at 0.55, 0.85, 1.2, 4.0, 12.5 and 20.0 litres per minute. Absorbed $NO_{2(g)}$ increased linearly with flowrate up to 1.2 l min^{-1} and then decreased sharply. At 20.0 l min^{-1} the absorption efficiency was calculated to be only 7% of that at 0.55 l min^{-1}. Therefore, for field sampling of $NO_{2(g)}$ the flowrates of the subsample traps were adjusted to approximately 0.6 l min^{-1}.

2.2.1.3 Site and soil used

A permanent ryegrass - white clover pasture site at the Lincoln College sheep stud farm was used for the study. The soil was a Templeton silt loam (a Dystric Ustochrept) representative of the dry land pasture soils of Canterbury. A detailed description of the soil appears elsewhere (Soils of New Zealand Part 3, 1968). Some pertinent soil chemical and physical properties are given in Table 2.1. The experimental site was a flat area (22 m x 11 m) immediately adjacent to a mobile field laboratory.

2.2.1.4 Temperature and flowrate

The chamber was tested under conditions most likely to generate a greenhouse effect (i.e. a midsummer cloudless day at noon). At the flowrate used during these experiments (21 l min^{-1}) a maximum air temperature increase within the chamber of 2°C was recorded using thermister probes mounted internally and externally. This differential could be lowered by increasing the flow rate but only at the expense of reducing the number of chambers sampled. The flow rate used was therefore a compromise chosen to maximize the number of chambers simultaneously aspirated while keeping induced greenhouse effects within the chambers to a tolerable level.

2.2.1.5 Preliminary field experiments

Three preliminary field experiments were carried out in October 1977, February 1978, and July 1978. They were conducted to test the field sampling system under different seasonal conditions and to obtain some initial data on the magnitude and duration of $NH_{3(g)}$ and $NO_{2(g)}$ loss from urine patches and other nitrogen fertilizers.

Table 2.1

Soil Chemical Properties

Depth (cm)	pH (soil : water 2.5 : 1)	Total - N (%)	Organic carbon (%)	C.E.C. (me kg^{-1})
0 - 2.5	6.1	0.31	4.3	158
2.5 - 20	5.8	0.21	3.0	133

In the October experiment, 6 volatilization chambers were used. Sheep urine was applied to 3 enclosed plots at 3 rates i.e. 3.5 g N/200 ml, 1.22 g N/150 ml and 0.98 g N/150 ml (1200, 400 and 220 kg N ha^{-1} respectively). Calcium nitrate and ammonium sulphate solutions were applied to 2 other plots at 1 rate only (0.91 g N/150 ml i.e. 200 kg N ha^{-1}) and the remaining control enclosure received 150 ml of distilled water. High resolution $NH_{3(g)}$ flux data was obtained for the 50 hours following application using the intermittent enclosure procedure described earlier.

Six chambers were again used in February 1978. Sheep urine was applied to 4 plots at 2 rates i.e. 1200 kg N ha^{-1} and 400 kg N ha^{-1} with the remaining 2 plots acting as controls. One plot at each rate was covered and continuously aspirated for the duration of the experiment to provide low resolution $NO_{2(g)}$ measurements as well as high resolution $NH_{3(g)}$ data. The remaining plots were sampled intermittently for $NH_{3(g)}$.

The July 1978 experiment was essentially a repeat of the February experiment except that the continuously aspirated control plot was replaced by a 400 kg N ha^{-1} aqueous urea treatment.

2.2.1.6 Urine collection and analysis

Prior to each experiment, urine was collected from ewe lambs which were fed on a diet of fresh grass and housed in metabolism cages. Individual samples were bulked, the pH was measured, a subsample was taken for chemical analysis and the remainder frozen for later use. Urea-N was determined by the method of Douglas and Bremner (1970), NH_4^+ - N by steam distillation (Bremner, 1965) and total - N by a modified semi-micro Kjeldahl method (Goh, 1972).

2.2.1.7 Environmental factors and pH

Temperature and relative humidity were continuously recorded on a shaded thermohygrograph throughout each experiment. Soil moisture was measured gravimetrically on 0 - 25 mm samples taken from outside the gas sampled enclosures and soil pH (0 - 10 mm) was measured on cores taken from the centre of each plot 3 days following fertilizer application.

2.2.2 Results

2.2.1 Gas sampling

There appeared to be little difference in the shape of the $NH_{3(g)}$ flux curves (Figure 2.2) determined by the two gas sampling procedures, although when total losses were calculated by integrating the curves, the intermittent enclosure technique consistently gave lower values (Table 2.2). One of the assumptions made with this method was that the rate of $NH_{3(g)}$ loss during periods of lid closure was the same as that when the lid was open. The results obtained suggests that this may not have been the case. This interpretation of the perceived differences is,

Figure 2.2

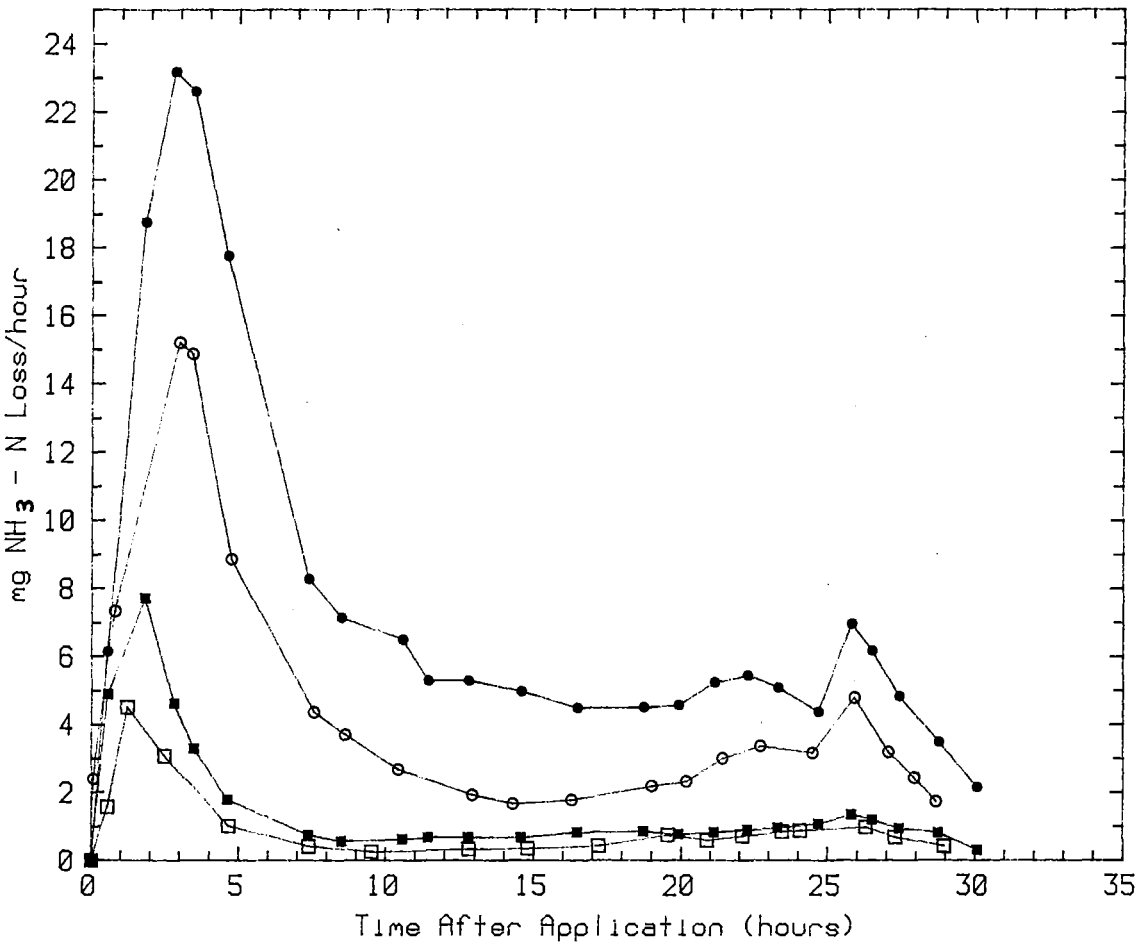


Figure 2.2 Rate of ammonia volatilization after applications of sheep urine during February 1978.

(●) 3.4 g urine-N: continuous aspiration

(■) 1.2 g urine-N: continuous aspiration

(○) 3.4 g urine-N: intermittent aspiration

(□) 1.2 g urine-N: intermittent aspiration

however, based on very limited data from unreplicated experiments and therefore may not be valid.

Condensate appeared in the unheated PVC gas delivery pipes in both the February and July experiments. Although it readily evaporated during the daytime it was collected and analysed on several occasions. Generally, the ammonia dissolved in the condensate from any particular plot was equivalent to the amount evolved in 1 hour. Condensate, when it does form is therefore only a very limited and temporary sink for volatilized $NH_{3(g)}$.

2.2.2.2 Ammonia volatilization

The results from the 3 preliminary experiments showed that easily measured amounts of ammonia volatilized from all the urine and urea treated plots while none was released from the calcium nitrate or ammonium sulphate treatments (Table 2.2). Percentage losses from urine appeared to increase with increasing rate and increasing air temperature. The time of maximum $NH_{3(g)}$ flux also appeared to be related to temperature. For example, maximum flux occurred 6 hours after application for the February experiment when the mean air temperature was 23°C and at 24 hours for the October experiment when the air temperature was only 10°C. In each of the experiments distinct diurnal fluctuations in $NH_{3(g)}$ flux were measured. These changes in flux appeared to be related to changing air temperature. Fluctuations have been observed previously in experiments reported by others (McGarity and Rajaratnam, 1973). Soil surface pH appeared to be an important factor since the limited data available suggested that $NH_{3(g)}$ losses increased with increased soil pH (Table 2.2).

Table 2.2 Percentage loss of urine - N as ammonia 30 hours after application measured by the continuously aspirated and intermittent enclosure techniques

	Soil Moisture (%)	Temperature (°C)				Surface Soil pH (0 — 1 cm)		Gas Sampling Method				
		Air (soil surface)		Soil (0 — 0.5 cm)				Intermittent			Continuous	
						urine - N applied (g)		urine - N applied (g)			urine - N applied (g)	
		Max.	Min.	Max.	Min.	3.4	1.2	3.4	1.2	0.98	3.4	1.2
October 1977	28	14.0	5.5	20.5	8.5	7.6	ND	4.0	1.1	1.6	ND	ND
February 1978	8	31.5	15.0	40.0	19.0	8.2	7.5	3.8	2.2	ND	6.9	3.6
July 1978	34	9.5	-2.0	7.5	-1.5	8.0	7.1	0.3	0.3	ND	0.4	0.5#

ND = not determined

\# = loss from 1.2 g urea - N = 0.55%

Figure 2.3

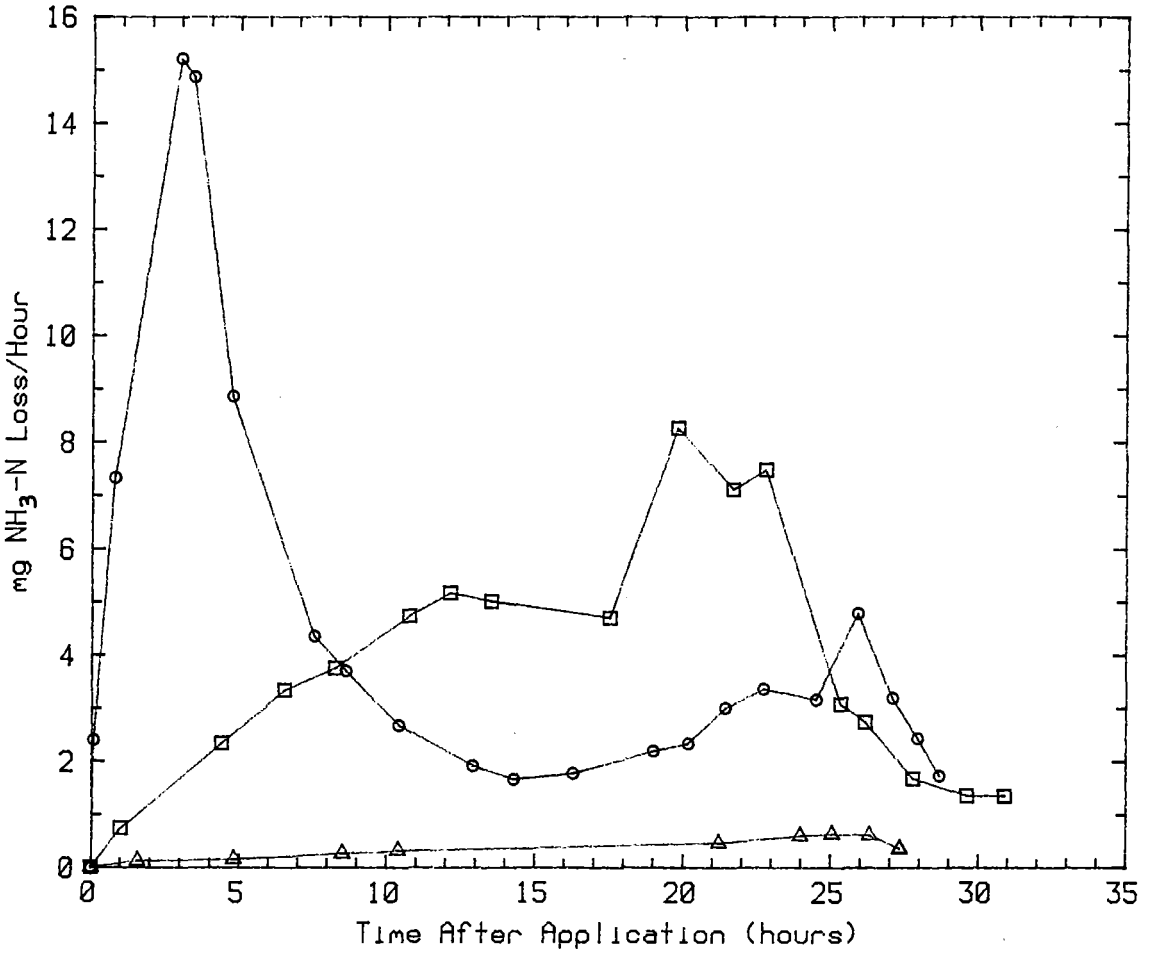


Figure 2.3 Rate of ammonia volatilization from sheep urine patches (3.4 g urine-N) using the intermittent enclosure technique in (□) October 1977, (○) February 1978 and (△) July 1978.

2.2.2.3 Nitrogen dioxide losses

No measurable quantities of $NO_{2(g)}$ were detected from any of the urine or urea treated plots during the February and July experiments. The lower limit of detection in the absorbing solution for the colorimetric analysis used was about 1 ppb. This corresponds to an upper limit of NO_2-N loss of 0.002% of the applied N over a four day period or a rate of loss equivalent to less than 0.75 kg N ha^{-1} yr^{-1}.

2.2.3 Discussion

On the basis of the results obtained in these initial experiments it was considered that the continuously aspirated technique provided a relatively simple and effective means of measuring volatilized ammonia in the field. An advantage over the intermittent enclosure method was that the subsampling procedure employed to detect $NO_{2(g)}$ could easily be modified to provide low resolution $NH_{3(g)}$ measurements while still maintaining the facility to make high resolution samplings as required. The continuously aspirated enclosures responded rapidly to temperature induced flux changes even in the presence of condensate in the unheated PVC gas pipes and therefore appeared to have minimal effect on the dynamics of ammonia volatilization.

A volatilization measurement *per se* is of only limited use in furthering an understanding of the volatilization process. Without a knowledge of the extent to which other mechanisms were utilizing the applied N, the measurements as reported here must stand in isolation. To be of any real value in this regard, volatilization measurements must at least be combined with a knowledge of the disposition of mineral-N within the soil profile together with a clearer description of temporal pH changes. Subsequent field experiments attempted to accomplish this.

2.3 FIELD EXPERIMENTS

2.3.1 Materials and Methods

2.3.1.1 Gas sampling

During 1982 ammonia volatilization experiments were continued on the same field site (section 2.2.1.3) using a modification of the system designed earlier. Three vacuum pumps were joined in parallel to provide a combined free air displacement of 260 l min^{-1}. Using this system six volatilization chambers were aspirated simultaneously at the required flowrate of 21 l min^{-1} $chamber^{-1}$ using the procedures described previously (section 2.2.1.2). A minor modification increased the subsample flowrate to approximately 6.5% of the total flow and the subsample trap was charged with 50 ml of 2% boric acid indicator to provide low resolution (twice daily) $NH_{3(g)}$ flux data.

2.3.1.2 Single application experiments

Volatilization experiments were repeated 3 times during January, May and August, hereafter referred to as the summer, autumn and winter experiments respectively. A split-plot in time design was used (Steele and Torrie, 1960). In plots sampled for $NH_{3(g)}$, sheep urine (3 replicates) and urea solutions (2 replicates) were applied at the same rate (i.e. 1.5 g total - N over an area of 300 cm^2, equivalent to 500 kg N ha^{-1}) (Table 2.3). The control plot received 150 ml of distilled water. Gas sampling was initiated immediately after application.

Table 2.3 Analysis of sheep urine used in 1982 field experiments

Sample	pH	Total - N (g N l^{-1})	NH_4^+ - N (g N l^{-1})	urea - N (g N l^{-1})
Summer				
1st application	8.60	10.1	0.5	8.5
2nd application	8.45	7.2 #	0.5	6.6
3rd application	8.45	7.2 #	0.5	6.6
Autumn	8.60	14.4	0.8	11.6
Winter	8.50	13.6	1.8	10.1

= urine amended with 6 g urea per litre before application

For both summer and autumn experiments, additional unconfined control and similarly treated plots were sampled periodically for pH, soil moisture and mineral - N. Measurements of pH were made at 5 depths (0 - 0.5, 0.5 - 1.0, 1 - 2.5, 2.5 - 5 and 5 - 10 cm) using 5 cores per treatment and a sample:water ratio of about 1 : 2.5. The pH was recorded within 5 minutes of soil sampling and again after 24 hours.

Mineral - N analyses were performed on a second series of cores after extracting fresh soil samples immediately with 100 ml of 2 mol l^{-1} KCl / phenyl mercuric acetate (PMA) (Douglas and Bremner, 1970). Sampling depths were 0 - 2.5, 2.5 - 5, 5 - 10 and 10 - 15 cm for both experiments with an additional 15 - 25 cm depth sampled during autumn. For the summer experiment soil samples were taken at 6 times (1, 5, 24, 96, 264 and 984 hours after application) while in the autumn experiment only 5 sampling times (1, 25, 48 and 192 hours and 3 months) were used.

2.3.1.3 Repeated applications experiments

During the summer experiment, sheep urine and aqueous urea (1.5 g N per 150 ml) were re-applied on two occasions to the same gas sampled plots; 16 and 30 days after the initial application.

2.3.1.4 Temperature measurement

Soil temperatures at three depths (2.5, 5.0 and 30 cm) were recorded continuously on a triple pen soil temperature recorder. Ground level air temperature and humidity were monitored using a shaded thermohygrograph and were supplemented during high resolution flux measurements by wet and dry bulb temperatures taken at 1.5 metres using a whirling sling thermometer.

2.3.1.5 Statistical analyses

Statistical analyses were performed using the GENSTAT statistics package on the Lincoln College D.E.C. "Vax" computer.

2.3.2 Results

2.3.2.1 Ammonia volatilization - single application

The detailed pattern of ammonia release from both urine and urea applications (Figure 2.4) showed that essential features were similar to those found in the preliminary experiments (section 2.2.2) and also those reported by other workers (Vallis *et al.*, 1982; Beauchamp *et al.*, 1978, 1982). These included a rapid increase in ammonia flux followed by a more gradual exponential decline. Superimposed on this general flux envelope were clearly defined temperature-induced diurnal fluctuations.

Figure 2.4

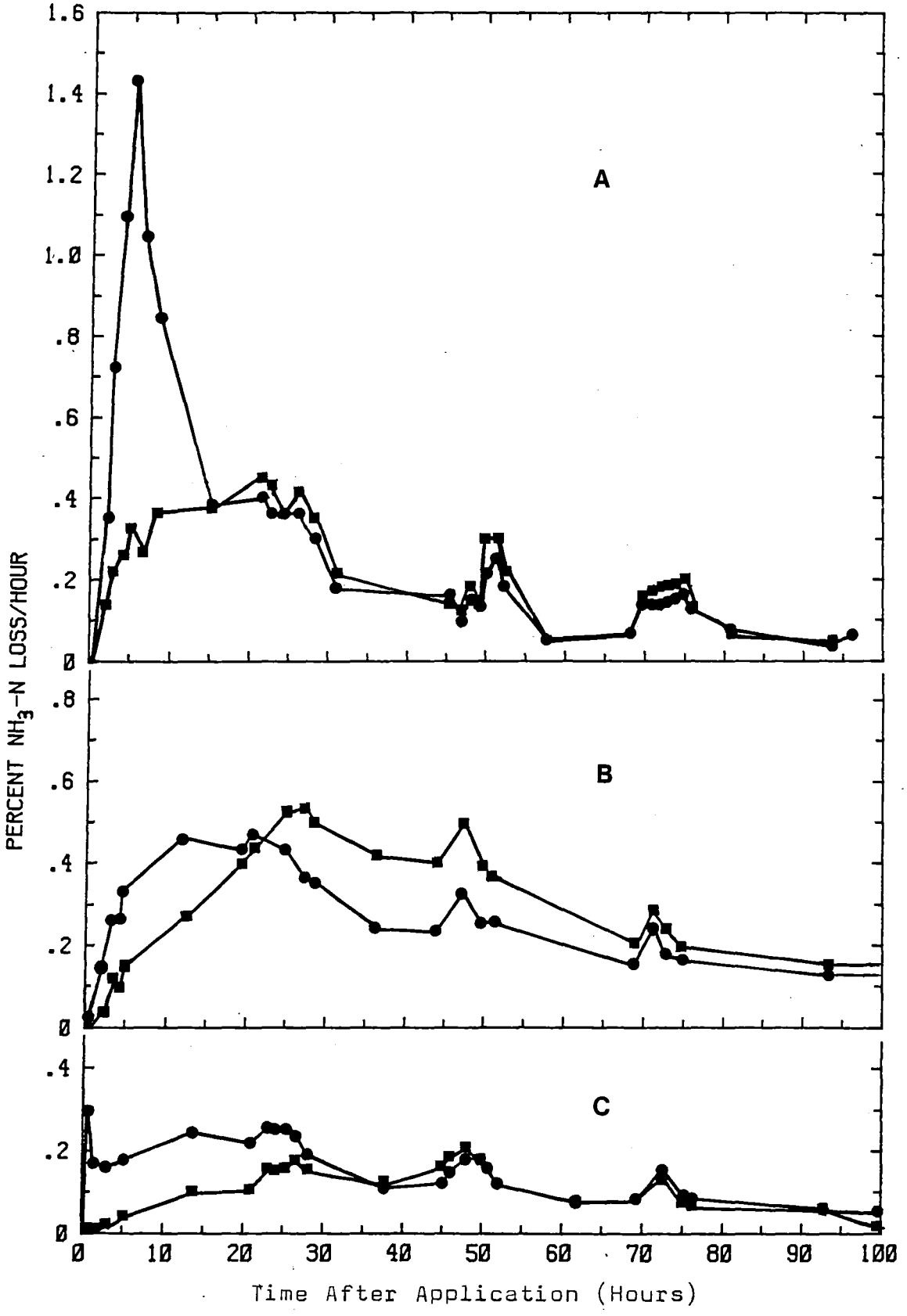

1.6
1.4
1.2
1.0
.8
.6
.4
.2
0
A
.8
.6
.4
.2
0
B
.4
.2
0
C
PERCENT NH3-N LOSS/HOUR
0
10
20
30
40
50
60
70
80
90
100
Time After Application (Hours)

Table 2.4 Percentage loss of nitrogen as volatilized ammonia in summer, autumn and winter

Season	Mean air temp °C	Soil moisture 0 - 5 cm (%) b	Duration of volatilization (hours) a	TREATMENT						
				URINE (1.5 g N)				UREA (1.5 g N)		
				replicates				replicates		
				1	2	3	mean	1	2	mean
Summer										
1st application	20.4	10.0	165	19.1	24.3	23.2	22.2	19.5	16.3	17.9
2nd application	23.5	8.4	137c	29.5	35.1	36.5	33.7	24.1	23.0	23.6
3rd application	21.5	9.4	246	39.3	34.1	41.8	38.4	39.3	32.9	36.1
Autumn	8.3	26.0	235	19.8	37.1	16.9	24.6	35.3	22.5	28.9
Winter	4.5	33.9	141	11.3	9.6	15.8	12.2	9.5	7.5	8.5

a Time taken for mean $NH_{3(g)}$ flux to decrease to < 0.5% per day.

b Field capacity = 35.0%.

c Mean flux was reduced to only 1.3% per day at time of 3rd application.

Ammonia losses were monitored until volatilization rates decreased to < 0.5% of the applied N per day. Total $NH_{3(g)}$ volatilized for all replicates together with relevant mean temperature and soil moisture data are shown in Table 2.4.

The $NH_{3(g)}$ release was calculated by summing the individual subsample measurements and also by integrating the high resolution flux curves. Both methods gave results which were in close agreement and thereby provided an internal check on the absorption efficiency of the acid traps (e.g. see Figures 2.5 and 2.6).

As can be seen from the results in Table 2.4, there was some variation between replicates for both urine and urea treated plots particularly during the autumn experiment. This could be due in part to the vigorous pasture growth present during autumn with the herbage on different plots possibly intercepting differing amounts of the applied fertilizer solutions. The greater the amount of solution intercepted, the greater and possibly the more variable the amount of $NH_{3(g)}$ that may have been volatilized from the leaf surfaces (see section 1.3.2).

Nevertheless, the split plot in time analysis (Steele and Torrie, 1960) revealed that significant ($P \leqslant 0.05$) differences occurred in total percentage $NH_{3(g)}$ losses between all seasons. There were no significant differences for total $NH_{3(g)}$ loss between urine and urea applications in the same season.

The lower evolution of $NH_{3(g)}$ during winter can be rationalized by reference to the soil solution chemistry of $NH_{3(aq)}$ and in particular the effect of temperature on the:

$$NH_4^+{}_{(aq)} + H_2O \rightleftharpoons NH_{3(aq)} + H_3O^+{}_{(aq)} \quad \text{equilibrium}$$

(see equation [1.4]). A lower temperature favours the formation of

$NH_4^+{}_{(aq)}$ thus reducing the amount of 'volatilizable' $NH_{3(aq)}$ present in the soil solution. The high soil moisture content (33.9%) would also dilute the $NH_{3(aq)}$ concentration thus further lowering the $NH_{3(g)}$ flux from the surface.

An interesting distinction between the flux patterns from the 2 N sources was a more rapid mean flux from urine than from urea during the time immediately following application (Figure 2.4). This was particularly apparent for the summer experiment when the $NH_{3(g)}$ fluxes from the urine treatments were significantly greater ($P \leqslant 0.05$) on each sampling occasion up to 10 hours after application. Thereafter mean $NH_{3(g)}$ fluxes were similar between the 2 sources of N.

Another essential difference between the 2 N sources was the time of flux maximum as defined by the flux curves especially in the summer experiment (Figure 2.4 A). The maximum $NH_{3(g)}$ flux occurred earlier for urine applications than for urea solutions of equivalent N content. This distinction between flux patterns was coincident with, and probably due to, a difference in the rate of urea hydrolysis in the two N sources and will be examined in more detail later.

2.3.2.2 Ammonia volatilization - repeated applications

Compared with the initial ammonia release (averaging 20.5% for both N sources) the repeated applications produced significantly higher losses ($P \leqslant 0.05$) averaging 29.6% and 37.5% from the second and third applications respectively (Table 2.4). These higher subsequent losses were probably due at least in part to the high initial soil pH present, which favours the formation of $NH_{3(aq)}$ from $NH_4^+{}_{(aq)}$, thereby increasing the amount of 'volatilizable' $NH_{3(aq)}$ in the soil. For example, at the time of the second application, the pH of the topsoil

(0 - 1 cm) in both N treatments was 8.0. The soil pH value could have risen even higher immediately preceding the 3rd application due to further hydrolysis thus resulting in additional losses of $NH_{3(g)}$. Another contributing factor may have been the high concentration of residual $NH_4^+{}_{(aq)}$ present in the soil from each previous aqueous N application. Upon rewetting with a subsequent application, this residual ammoniacal-N could have contributed to the ammoniacal-N concentration at the soil surface. A greater N concentration may therefore have arisen with each successive addition, thereby increasing the $NH_{3(g)}$ losses.

The rapid initial release of $NH_{3(g)}$ from urine observed earlier in the first application (Figure 2.4 A) was also found in each of the repeated applications (Figure 2.5). However, the magnitude of these initial fluxes was much higher. Maximum fluxes of 1.53% of the applied N hr^{-1} followed the 1st application but briefly exceeded 6.2 and 3.1% hr^{-1} following the second and third applications respectively. High air temperatures immediately following the second application (26°C) probably contributed to the flux by shifting the $NH_{3(aq)}$ / $NH_4^+{}_{(aq)}$ equilibrium to further favour the formation of 'volatilizable' $NH_{3(aq)}$.

It is also possible that the urease activity of the surface soil was increased following the initial application of $urea_{(aq)}$ or urine (Ladd and Jackson, 1982). If this occurred it could have led to a more rapid production of ammoniacal - N and elevated soil pH's immediately following the subsequent applications than occurred after the initial applications. This may have led in turn to greater initial $NH_{3(g)}$ fluxes.

Figure 2.5 Rate of ammonia volatilization after 3 sequential (1.5 g N) applications of sheep urine during summer 1982 and whirling-sling dry-bulb air temperatures 1.5 metres above soil surface.

Histogram = low resolution sampling

(●) = high resolution sampling (mean of 3 replicates)

(▲) = time of urine application

Figure 2.5

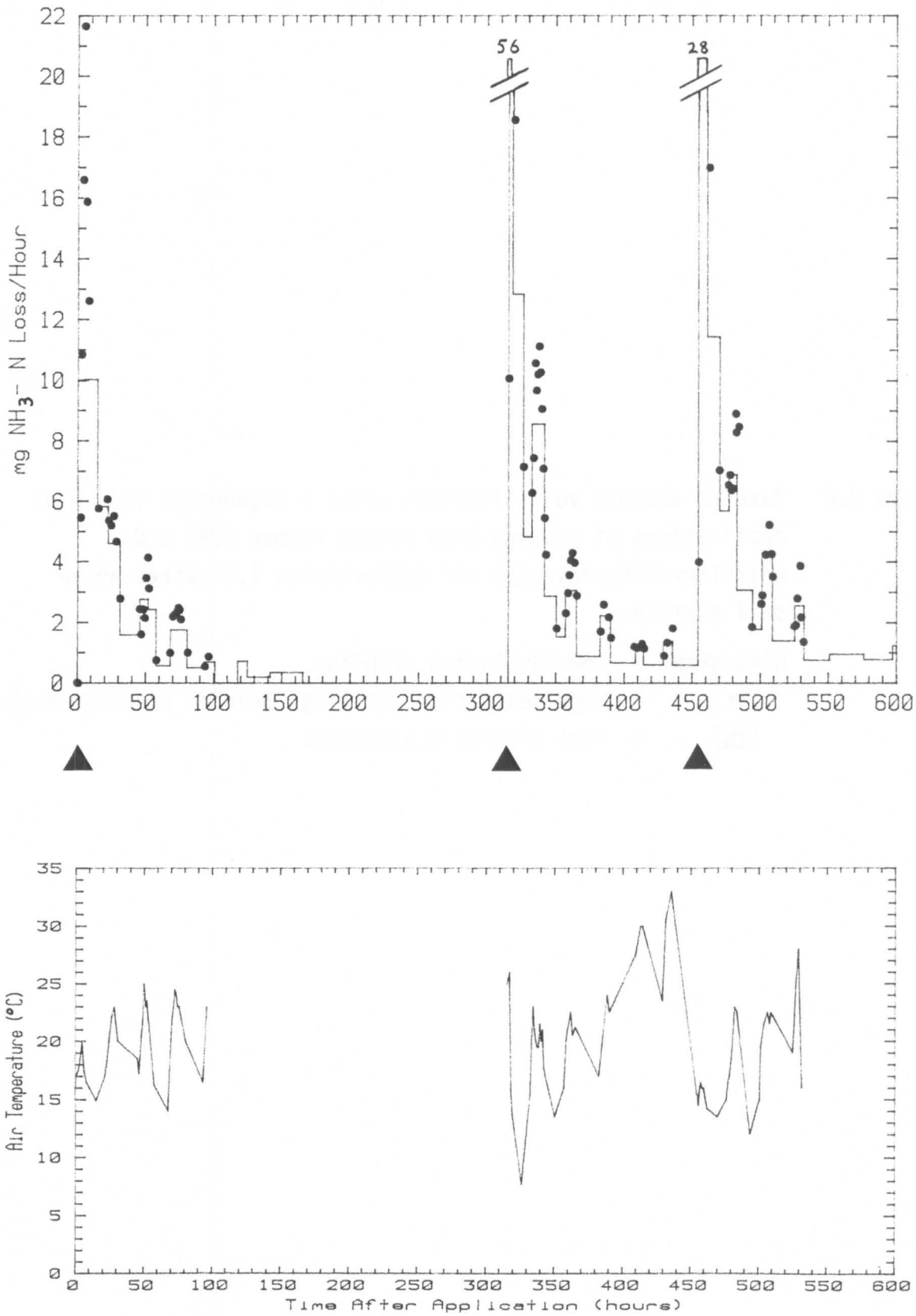
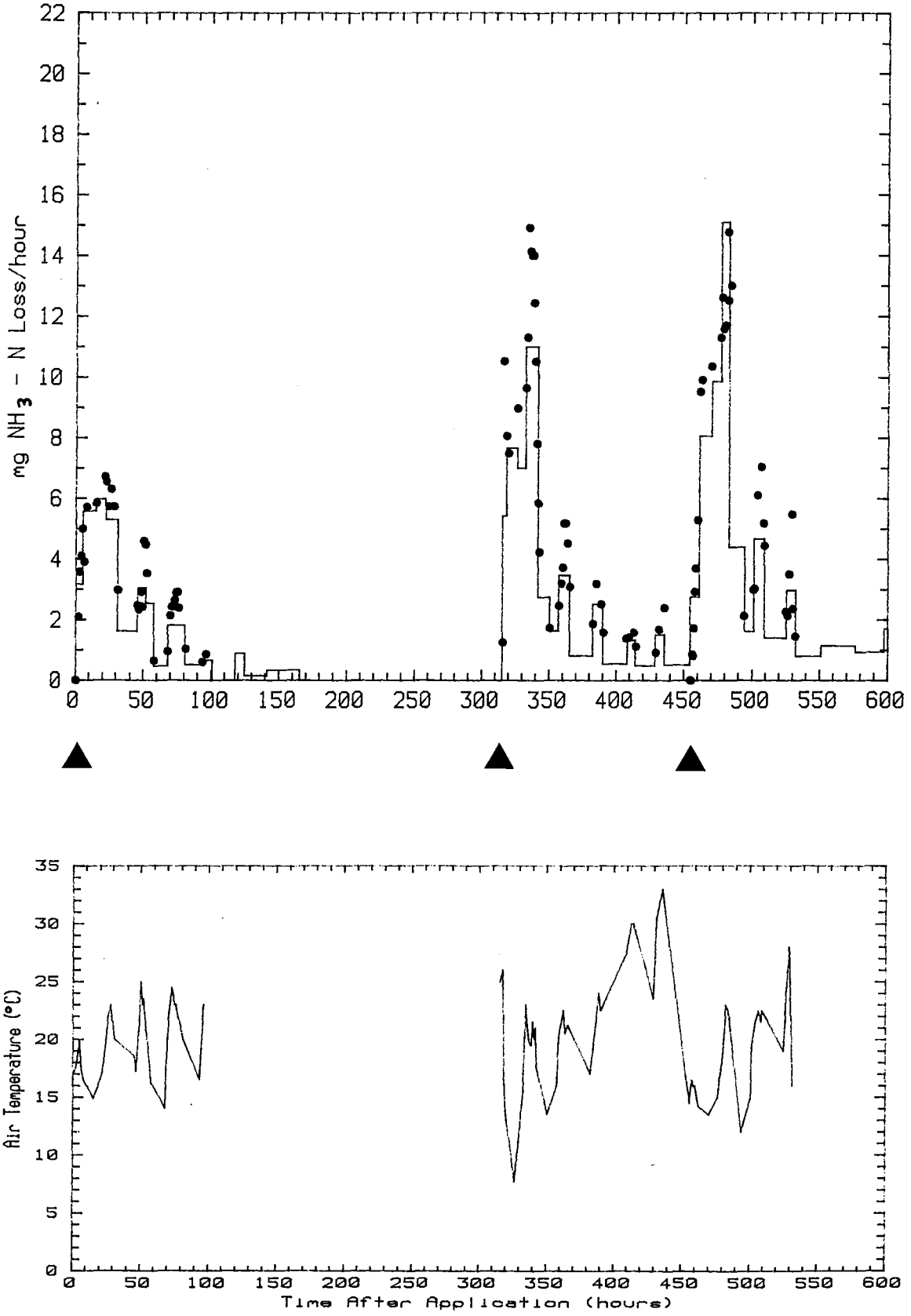

56
28
mg NH_3- N Loss/Hour
0
2
4
6
8
10
12
14
16
18
20
22
0
50
100
150
200
250
300
350
400
450
500
550
600
Air Temperature (°C)
0
5
10
15
20
25
30
35
Time After Application (hours)

Figure 2.6 Rate of ammonia volatilization after 3 sequential (1.5 g N) applications of aqueous urea during summer 1982 and whirling-sling dry-bulb air temperatures 1.5 metres above soil surface.

Histogram = low resolution sampling
(●) = high resolution sampling (mean of 2 replicates)
(▲) = time of urea application

Figure 2.6


mg NH3 - N Loss/hour
0
2
4
6
8
10
12
14
16
18
20
22
0
50
100
150
200
250
300
350
400
450
500
550
600
Air Temperature (°C)
0
5
10
15
20
25
30
35
Time After Application (hours)

2.3.2.3 Urea hydrolysis

In both the summer and autumn experiments, urea hydrolysed more rapidly in urine treated plots than in plots treated with urea alone. For example, during the summer experiments mineral - N analyses on samples taken 5 and 24 hours after application showed unhydrolysed urea - N was significantly less in urine plots than in urea treated plots (Table 2.5, 2.6). The rate of urea hydrolysis in the top 0 - 2.5 cm was calculated by considering the urea - N recovered as a fraction of the recovered mineral - N plus accumulated volatilized - N at each sampling time following application. This fraction decreased rapidly with time and obeyed first order kinetics over the 24 hours following application (Table 2.7). Half-lives for urea hydrolysis calculated from the resulting exponential decay curves were: 3.0 and 4.7 hours for urine and urea respectively during summer and 4.7 and 12.0 hours respectively in autumn. Thus, in both summer and autumn, the rate of urea hydrolysis in urine treated plots was significantly greater than in urea treated plots. This difference in hydrolysis rate was also noted by Doak (1952) who attributed it to hippuric acid, a minor urinary component. Doak (1952) found that hippuric acid appeared to accelerate urea hydrolysis when added to a urine solution at about the same concentration as present in urine. It should be noted, however, that the pH values of both urine samples (pH = 8.6, Table 2.3) were also at the optimum for urease activity (Vlek *et al.*, 1980) thus a specific pH effect cannot be discounted. Since urease activity is known to be temperature dependent (Van Slyke and Cullen, 1914) the overall reduction in hydrolysis rate in the autumn was probably due to the lower mean soil temperature compared with that during summer (Table 2.4).

Table 2.5 Distribution of soil mineral - N and cumulative totals of NH_3 - N volatilization following application[a] of urine and urea solutions in summer.

Sampling time	NH_3 - N volatilized kg NH_3-N ha^{-1}		Soil depth	Mineral-N distribution kg ha^{-1} $depth^{-1}$[b]						Mineral-N recovered kg N ha^{-1}[c]	
				NH_4^+-N		UREA-N		$(NO_2^-+NO_3^-)$-N			
(hours)	URINE	UREA	(cm)	URINE	UREA	URINE	UREA	URINE	UREA	URINE	UREA
1	5 **	1	0-2.5	50 **	28	186 ns	273	0	0		
			0-15	94 *	34	269 ns	321	0	0	368	356
5	18 *	6	0-2.5	142 **	64	17 **	151	0	0		
			0-15	243 **	86	40 **	209	0	0	301	301
24	62 *	37	0-2.5	160 ns	135	1.4 *	9.2	0.2 ns	2.3		
			0-15	253 ns	240	6.1 **	25	2.1 ns	6.6	323	309
96	105 ns	84	0-2.5	99 ns	118	2.8 *	0.5	1.2 ns	3.6		
			0-15	147 ns	191	4.1 ns	1.3	5.5 ns	10.3	262	287
165 e	110 ns	90		nd		nd		nd		nd	
268	nd		0-2.5	80 *	115	0	0	3.3 **	6.5		
			0-15	147 ns	188	0	0	9.0 ns	20.6	266d	299d
984	nd		0-2.5	60 *	91	0	0	2.8 *	7.6		
			0-15	107 ns	151	0	0	25.9 ns	45.9	243d	287d

a Application rate = 500 kg N ha^{-1} (see text).

b Mean of 4 replicates.

c Total mineral-N = (NO_3^--N + NO_2^--N + NH_4^+-N + UREA-N + NH_3 volatilized) of N treated plots after subtraction of controls.

d Includes NH_3-N values obtained at 165 hours.

e Volatilization measurements discontinued at 165 hours.

ns = not significant, * = significant ($P \leq 0.05$), ** = highly significant ($P \leq 0.01$)
nd = not determined

Table 2.6 Distribution of soil mineral - N and cumulative totals of NH_3 - N volatilization following application[a] of urine and urea solutions in autumn 1982.

Sampling time	NH_3 - N volatilized kg NH_3-N ha^{-1}		Soil depth	Mineral-N distribution kg ha^{-1} $depth^{-1}$[b]						Mineral-N recovered kg N ha^{-1}[c]	
				NH_4^+-N		UREA-N		$(NO_2^-+NO_3^-)$-N			
(hours)	URINE	UREA	(cm)	URINE	UREA	URINE	UREA	URINE	UREA	URINE	UREA
1	0	0	0-2.5	28 ns	24	174 ns	139	0	0		
			0-25	33 ns	29	321 ns	176	0	0	354	205
25	43 ns	31	0-2.5	189 ns	152	6.9 **	59	0.3 ns	0.1		
			0-25	253 ns	166	10.1 **	78	2.7 ns	1.7	309	277
72	68 ns	78	0-2.5	132 **	181	2.7 ns	3.2	0	0		
			0-25	216 ns	314	4.6 ns	29	1.3 ns	1.0	290	422
192	121 ns	143	0-2.5	103 *	174	0	0	0.8 **	1.7		
			0-25	244 ns	200	0	0	3.2 ns	4.6	368	348
235e	123 ns	145		nd		nd		nd		nd	
2160f	nd		0-2.5	7.2 *	3.3	0	0	3.4 ns	3.5		
			0-25	8.1 ns	4.3	0	0	12.5 ns	5.5	144d	155d

a = Application rate = 500 kg N ha^{-1} (see text).

b = Mean of 5 replicates.

c = Total mineral-N = (NO_3^- - N + NO_2^- - N + NH_4^+ - N + urea - N + NH_3 volatilized) of N treated plots after subtraction of controls.

d = Includes NH_3 - N values obtained at 235 hours.

e = Volatilization measurements discontinued at 235 hours.

f = final sampling at 3 months.

ns = not significant, * = significant ($P \leq 0.05$), ** = highly significant ($P \leq 0.01$)
nd = not determined

Table 2.7 Regression equations describing urea hydrolysis in 0 - 2.5 cm sampling depth during 24 hours following application.

Season	Treatment	Regression Equation #	R^2	Half-life (hours)	
Summer	Urine	ln Y = -0.430 - 0.230t	0.91 ***	3.0	*
	Urea	ln Y = 0.114 - 0.149t	0.89 ***	4.7	
Autumn	Urine	ln Y = -0.041 - 0.149t	0.99 ***	4.7	***
	Urea	ln Y = -0.038 - 0.058t	0.98 ***	12.0	

Y = fraction of mineral - N recovered as urea - N at time 't'

*** very highly significant ($P \leq 0.001$)

* significant ($P \leq 0.05$)

2.3.2.4 Nitrification

The accumulation of NO_3^- - N and NO_2^- - N during the summer experiment for the period of major gaseous ammonia loss was small since it constituted only about 6% of the extractable soil-N after 96 hours and increased only slowly to 20 - 23% after 41 days (Table 2.5). This contrasts with the observations of Vallis *et al.* (1982) which showed that under hot, moist field conditions, nitrification of ammoniacal urine - N can be very rapid with over 50% of the applied N being recovered as NO_3^- - N after 2 weeks. A severe drought prevailed in January and February of 1982 when only 12 mm of rain fell throughout the entire 984 hour summer field experiment. This lack of water would have probably contributed to the slow nitrification rates, the persistence of ammoniacal - N in the soil and possibly the low uptake of N by plants. Droughts are commonly experienced in Canterbury during summer (Garnier, 1958).

Nitrification was also slow during the autumn experiment (Table 2.6) but low soil temperatures were probably responsible during this period as soil moisture conditions were not limiting.

2.3.2.5 Soil pH

In both the summer and autumn experiments significant increases in soil pH occurred only in the top three sampling depths (0 - 0.5, 0.5 - 1.0 and 1.0 - 2.5 cm) with the largest increases appearing in the 0 - 0.5 and 0.5 - 1 cm layers (Figure 2.7 and Appendix III). As might be expected from the $NH_{3(aq)}$ - pH relationship, maximum soil pH coincided with maximum $NH_{3(g)}$ flux and as soil pH declined so did observed $NH_{3(g)}$ fluxes. The urine patch experiments reported by Vallis *et al.* (1982) reveal a similar $NH_{3(g)}$ flux-pH relationship. In both present

Figure 2.7

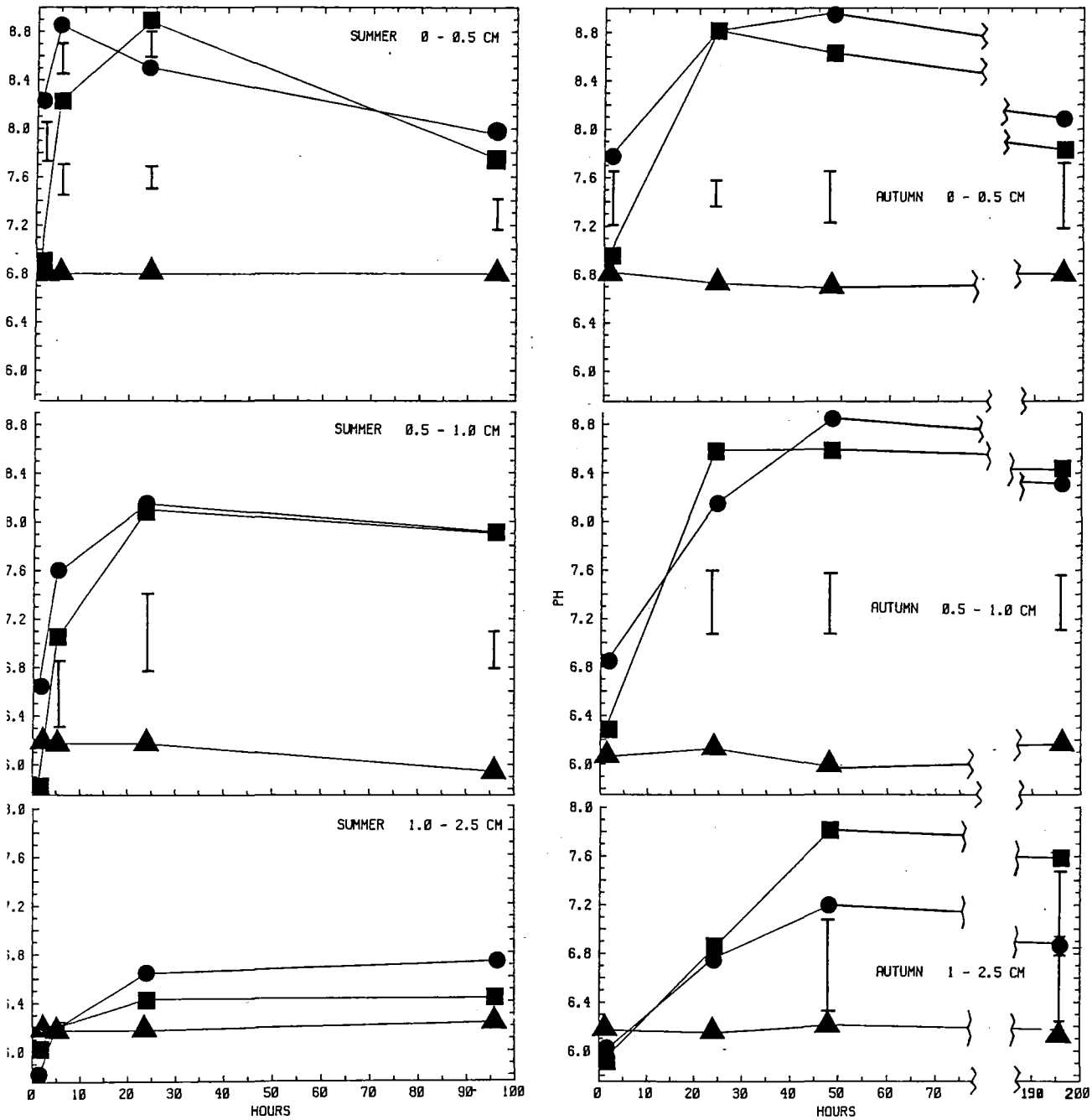


Figure 2.7 Mean soil pH (soil : water = 1 : 2.5) following applications of sheep urine (●), aqueous urea (■) and water (▲) in summer and autumn 1982. (I) = least significant difference.

experiments the periods of ammonia volatilization (0 - 7 days) were accompanied by negligible nitrification in the 0 - 2.5 cm layers (Tables 2.5, 2.6). This suggests that the mechanism of pH decline over this period was the acidification accompanying the volatilization process itself (Avnimelech and Laher, 1977) rather than the nitrification process (Vlek *et al.*, 1981).

Both pH and ammonia fluxes declined more slowly during autumn than summer (Figures 2.4, 2.7) even though total $NH_{3(g)}$ losses were similar. The lower autumn soil temperatures probably slowed the volatilization process by shifting the equilibrium reaction:

$$NH_4^+{}_{(aq)} + H_2O \rightleftharpoons NH_{3(aq)} + H_3O^+$$

towards the left (see section 1.2.1.2). This in turn would have retarded the rate of pH decline.

2.2.3.6 Nitrogen recovery

Estimated total recovery of N as mineral - N during the summer experiment (Table 2.5) showed a large deficit of N immediately after application (1 hour). This is probably due to an artifact of the experimental technique rather than a true loss. The artifact could have arisen from either an edge effect associated with the application area, or a rapid mass flow below the lowest sampling depth or both. Since the N - treated patches were unconfined, lateral movement of N solutions outside the application area (300 cm^2) occurred and this was not determined. This problem can be obviated to some extent by increasing the area of the simulated urine patch (Ball *et al.*, 1979; Vallis *et al.*, 1982) or by basing recovery data on an effective application rate determined as the N present in a defined area at the earliest possible time after lateral movement has ceased.

In the present study it is reasonable to assume that significant lateral movement would have ceased after 1 hour. Using this assumption and based on the effective N application rate after 1 hour the data (Table 2.5) showed that most of the applied N for both the urine and $urea_{(aq)}$ treatments was accounted for as soil mineral - N and volatile $NH_{3(g)}$ up to 41 days after application. Thus little appreciable plant uptake, immobilization, denitrification or leaching could have occurred during this period, probably due to the very dry conditions prevailing.

The deficit in estimated total recovery of mineral - N observed during summer was also observed for the autumn experiment (Table 2.6). Again this was probably due to an experimental artifact since most of the applied N accounted for after 1 hour was also accounted for as soil mineral - N and $NH_{3(g)}$ up to the time when $NH_{3(g)}$ volatilization had virtually ceased (8 days). A final sampling 3 months later showed mineral-N levels only slightly elevated above the controls.

2.3.3 Discussion

The direct ammonia volatilization losses from urine and urea reported here ranged from 7.5 to 37%, depending on the season, and when averaged over the whole year would amount to about 20% of the N from a single application of sheep urine or urea solution of equivalent N content. These losses are comparable in magnitude to results from direct measurements of simulated urine patches or grazed pastures reported by other workers (see section 1.6).

2.3.3.1 Significance of losses

As measurements of N inputs (e.g. biological N fixation) and outputs (e.g. leaching losses) were not made, an accurate assessment of the significance of this loss to the N budget of the pasture is not possible. However, using published N input data reported in studies of comparable situations, relevant calculations can be made. Studies in Canterbury indicate that for non-irrigated pastures receiving no N fertilizers, 120 kg N ha^{-1} yr^{-1} is input from symbiotic N fixation (Crush, 1979; Edmeades and Goh, 1978). Additional background inputs are likely from asymbiotic N fixation by free-living organisms, N dissolved in rainfall, the absorption of atmospheric $NH_{3(g)}$ and N in pollen and dust. Specific data on each of these inputs is unavailable for Canterbury conditions but in a recent review of New Zealand data, Ball (1982) concluded that the original estimate of 15 kg N ha^{-1} yr^{-1} made by Sears *et al.* (1965) fairly approximated background inputs to intensively utilized pastoral systems. If a similar background N input occurs for the extensive dry-land conditions of Canterbury then a total N input of about 135 kg N ha^{-1} yr^{-1} is estimated. Assuming a typical stocking rate of 20 sheep ha^{-1} yr^{-1}, a urination rate of 2900 ml $sheep^{-1}$ day^{-1} at a urine - N concentration of 0.92% (Doak, 1952), about 200 kg N ha^{-1} yr^{-1} is cycled in the pasture as voided urine. Thus on average, 40 kg N ha^{-1} yr^{-1} (i.e. 20% of the urine - N) or 30% of the N input is probably released as $NH_{3(g)}$ from urine patches in a Canterbury pasture. Additional losses are likely particularly if the nitrate that is ultimately formed in the patches (Tables 2.5, 2.6) is subject to leaching and/or denitrification. Losses of N from urine patches as nitrous oxide (N_2O) are considered in Part II of this thesis.

2.3.3.2 Residual volatilization losses

It should be noted that present measurements were discontinued when volatilization rates dropped to < 0.5% of the applied N per day mainly because of the loss of sensitivity in the titration technique. Volatilization almost certainly continued albeit at a much reduced rate. It can be shown theoretically (Avnimelech and Laher, 1977) that given sufficient time and in the absence of competing mechanisms (e.g. nitrification, immobilization) all $NH_4^+{}_{(aq)}$ in soil should ultimately be lost as $NH_{3(g)}$. A slow continuing loss may help to partly explain the lack of agreement often reported between direct measurements and indirect balance estimates (Watson and Lapins, 1969; Simpson, 1968). Usually indirect estimates of losses are higher but they are frequently derived from experiments conducted over much longer time spans and would include 'residual' volatilization. A more sensitive analytical technique would be needed if residual volatilization is to be measured directly.

2.3.3.3 Repeated applications

Repeated applications of urine or urea to the same microplot in the field promoted higher subsequent $NH_{3(g)}$ loss. In a laboratory study Stewart (1970) simulated the fate of urine - N in a cattle feedlot by adding urine to dry soil columns every 4 days for 8 weeks and found that the soil pH approached 10 with about 90% of the applied N lost as ammonia. The results obtained in the present study (Table 2.4) provide the first direct evidence that similar effects could be induced in the field by the spatial and temporal coincidence of urine applications to the soil. These conditions are not normally met in a grazed pasture, however, as the following simple calculation shows. Assuming no overlap

of urine patches, a patch size of 300 cm^2, a stocking rate of 19 sheep ha^{-1} yr^{-1}, and a daily urination volume of 2900 ml $sheep^{-1}$ at 150 ml $urination^{-1}$ (Doak, 1952), the total area that would receive urine in any year is only 40% of the pasture surface. The overlap of patches that would occur with random behaviour would increase their spatial coincidence and decrease the urine affected area accordingly. For example, Jackman (1960) calculated that with the same stocking rate and random urination behaviour, only 30% of a pasture would receive urine in any year. Spatial coincidence of urinations is not high in these hypothetical examples.

However, under certain circumstances (e.g. sheep camps and intensive rotational grazing) both the spatial and temporal coincidence of successive urinations simulated in these current experiments might possibly occur. Estimating the importance of these special conditions to the overall N budget of a pasture is beyond the scope of the present study.

These results do, however, draw attention to the current strategy of applying urea fertilizer to pasture soon after a period of mob stocking (Black, 1983 personal communication). It is reasonable to speculate that the surface application of urea prills to an area affected by recent urine patches might stimulate $NH_{3(g)}$ loss as described above. This possibility is currently being investigated.

2.3.3.4 Enclosure techniques

The use of enclosure techniques for direct field measurements of ammonia volatilization has been questioned by several workers (Beauchamp *et al.*, 1978; Vlek and Craswell, 1981). Their use preceded the more elaborate micrometeorological and aerodynamic methodology now

available, which, although well founded in theory, is limited in application and inappropriate for studying multiple treatment effects. While the continued use of enclosures therefore seems likely their deficiencies must be recognised. These arise mainly from the use of unrealistically low airflow rates which limit the rate of $NH_{3(g)}$ volatilization and lead to an underestimation of the loss (Freney *et al.*, 1981).

Theoretical considerations describing the influence of enclosures on the dynamics of $NH_{3(g)}$ volatilization were reported recently by Vlek and Craswell (1981). Their criterion for minimal influence was when the flushing frequency, F/V (F = headspace flushing rate, V = headspace volume) greatly exceeded the NH_3 evasion constant, k. Substitution of values appropriate to the system used here for the summer experiment showed F/V exceeded k by a factor of 100 - 500 thus suggesting that the volatilization rate was largely unaffected by the rate of flushing (airflow).

As reviewed earlier (section 1.5.1.4) the effect of windspeed on the dynamics of $NH_{3(g)}$ volatilization is important where release occurs from a free water surface (e.g. rice paddies)(Bouwmeester and Vlek, 1981; Denmead *et al.*, 1982). There, turbulent transfer of $NH_{3(aq)}$ to the air-water interface is a precursor to release and is enhanced by increased surface windspeed. The importance of this mechanism in contributing to volatilization from a soil surface is unclear. Using a micrometeorological technique, Denmead *et al.* (1974) showed that windspeed had little effect on the $NH_{3(g)}$ flux from grazed pastures. Similarly, Beauchamp *et al.* (1978, 1982) found no relationship between windspeed and $NH_{3(g)}$ fluxes from surface applied sewage sludge or liquid cattle manure. In situations like these the use of enclosures

would seem appropriate provided the simulated windspeed used was sufficient to realize the maximum volatilization rate or 'volatilization potential' of the system (Vlek and Craswell, 1981).

The criterion above must necessarily be met if the intermittent enclosure technique described by Kissel *et al.* (1977) is used. This method, which was employed during the preliminary experiments (section 2.2) assumes that the rate of $NH_{3(g)}$ release during period of lid closure (typically 10 minutes every few hours) is the same as that when the lid is removed and the microplot is exposed to ambient conditions. In their study of $NH_{3(g)}$ volatilization from liquid swine manure, Hoff *et al.* (1981) showed that the intermittant enclosure technique could greatly underestimate $NH_{3(g)}$ loss when high winds prevailed between periods of lid closure. This may also have occurred in the preliminary experiments reported earlier. The intermittent enclosure technique should therefore only be used when ambient windspeeds are low (e.g. greenhouse experiments) or where windspeed is known to have little effect (see Kissel *et al.*, 1977) or where other suitable precautions are taken. For example, recent chamber designs enable throttling of air flow rates to better simulate natural windspeed (Vallis *et al.*, 1982).

The continuously aspirated enclosure technique used in the present study made no attempt to simulate ambient windspeeds. Although this might be argued to be a major limitation, it does allow direct comparisons between separate field experiments without the possible confounding effects of differing windspeeds or the effects of uncontrollable rainfall. The high resolution data obtained (Figure 2.4) also indicate that the apparatus responded rapidly to temperature induced flux changes which suggests that perturbations induced by the apparatus were minor.

Certainly the recovery of soil mineral - N from non-enclosed microplots taken together with the accumulated $NH_{3(g)}$ released (Tables 2.5, 2.6) indicate that the technique used in the study provided adequate quantitative assessment of the magnitude of each volatilization event.

CHAPTER 3

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CHAPTER 3

THEORETICAL DERIVATION OF A SIMPLIFIED MODEL

3.1 INTRODUCTION

The efficient use of urea fertilizer in arable and pastoral agriculture is often prejudiced by the loss of a portion of the applied nitrogen (N) by ammonia (NH_3) volatilization (Terman, 1979; Freney *et al.*, 1981; Vlek and Craswell, 1981). In grazed pastures, measurements of N transformations following urine and dung return by grazing animals confirm that these systems can also lose a significant fraction of the excreted N by volatilization as NH_3 (Ball *et al.*, 1979; Ball, 1981; Carran *et al.*, 1982; Vallis *et al.*, 1982). The physical, chemical and environmental factors influencing volatilization losses have been investigated in many laboratory experiments and are well documented (see chapter 1). However, little is known about the interaction of these factors and their combined influence on NH_3 volatilization under field conditions.

Attempts have been made to model NH_3 volatilization both from urine patches (Parton *et al.*, 1981) and from flooded soils (Bouwmeester and Vlek, 1981; Denmead *et al.*, 1982). The general nitrogen cycling model of Van Veen and Frissel (1979) also contains an ammonia volatilization submodel. Some of these models have provided a sound theoretical basis for the phenomenon (e.g. Bouwmeester and Vlek, 1981; Denmead *et al.*, 1982), but in others the complexity of the data required has made experimental verification under a variety of field conditions difficult (Parton *et al.*, 1981; Van Veen and Frissel, 1979).

The final usefulness of any model as a predictive tool depends on the nature of the input data it requires. The acquisition of these data must necessarily be easier than a direct measurement for the full value of the model to be realized. A direct measurement of NH_3 volatilization is not simple under field conditions and usually requires frequent monitoring of equipment and intensive gas sampling (Vallis *et al.*, 1982; Beauchamp *et al.*, 1982). Also, many potential experimental sites occur (e.g. hill country) where the use of direct aerodynamic measuring techniques is inappropriate. Similarly, sites occur where the servicing of gas sampling equipment would be difficult. Consequently, a need exists for a volatilization model which is well founded in theory, but which also requires a minimum of input parameters.

This chapter describes the development of a simplified model which aims at predicting NH_3 volatilization losses following urine and aqueous urea applications to pasture. The model is based on the solution chemistry of $NH_{3(aq)}$ (see section 1.2) and has 4 main input parameters:

(i) the rate of urea hydrolysis in the topsoil (0 - 2.5 cm)

(ii) soil surface pH (0 - 0.5 cm)

(iii) soil/air interface temperatures

(iv) the fraction of the applied N present in each of the following compartments:

  (a) the leaf and litter surfaces

  (b) the topsoil (0 - 2.5 cm)

  (c) the subsoil below 2.5 cm.

3.2 GENERAL THEORY

Urea in the form of solid granules, aqueous solution or animal urine is rapidly hydrolysed by urease in soil or on leaf surfaces to produce ammonium carbonate according to the following:

$$CO(NH_2)_2 + 2H_2O \longrightarrow 2NH_4^+ + CO_3^{2-} \qquad [3.1]$$

Subsequent hydrolysis of the carbonate ion causes an increase in soil pH through the generation of hydroxide and bicarbonate ions.

$$CO_3^{2-} + H_2O \rightleftharpoons HCO_3^- + OH^- \qquad [3.2]$$

This results in localized areas with an elevated pH around the fertilizer granule or within the urine patch. The effect of this pH increase on the soil solution chemistry of $NH_4^+{}_{(aq)}$ is one of the principal causes of $NH_{3(g)}$ loss (see section 1.2.1.1).

The chain of events which subsequently determines the extent of NH_3 volatilization from a bare soil surface may be represented by the scheme:

$$\begin{array}{ccccccc} \text{urea}_{(aq)} & \xrightarrow{k_1} & NH_4^+{}_{(aq)} & \overset{D_1}{\rightleftharpoons} & NH_4^+(\text{exchangeable}) & \overset{D_2}{\rightleftharpoons} & NH_4^+(\text{fixed}) \\ & \overset{K_a}{\uparrow\downarrow} & & & & & \\ & & NH_{3(aq)} & \overset{K_h}{\rightleftharpoons} & NH_{3(g)}\text{soil} & \overset{k_2}{\rightleftharpoons} & NH_{3(g)}\text{air} \end{array} \qquad [3.3]$$

Similar equilibria can be written to represent the conditions present in moisture films on leaf or litter surfaces. There, however, the $NH_4^+(\text{exchangeable})$ and the $NH_4^+(\text{fixed})$ terms will be effectively zero. Not included in scheme [3.3] are other mechanisms which can act to deplete ammoniacal-N from the system (e.g. plant uptake, nitrification, denitrification). These processes are incidental to a theoretical description of the equilibrium chemistry of the $NH_4^+{}_{(aq)}$ as such, and are considered separately later.

The magnitude of the rate constants (k_1 and k_2) and the position of the various equilibria are influenced by a number of factors (e.g. soil pH, temperature, soil type, soil moisture and $NH_4^+{}_{(aq)}$ concentration) (see section 1.2).

Since $NH_{3(g)}$ loss occurs from the surface of the soil, of prime importance to any theoretical consideration of the NH_3 volatilization process is an accurate description of the soil solution chemistry at the NH_3 source/air interface (Freney *et al.*, 1981). In particular, the activity (or concentration) of the $NH_{3(aq)}$ at this interface must be characterized. In flooded soils this concentration is effectively that of the bulk solution and is easily measured (Denmead *et al.*, 1982). In unsaturated soil, however, practical characterization of this interface condition is much more difficult and necessitates some simplifying assumptions.

The present consideration is restricted to situations receiving surface applications of aqueous urea or urine. Here, the NH_3 source/air interface is effectively the soil surface together with any leaf or litter surfaces if these are present and intercept a significant proportion of the applied solution (see section 1.3.2). For the purposes of modelling, the instantaneous concentration of ammoniacal-N, ($NH_4^+ + NH_3$), at the soil surface is assumed to be uniform to some chosen depth. Below this depth, any physical, chemical, or biological processes which take place are assumed to have no influence on the soil solution chemistry of the soil surface. Thus, an isolated topsoil compartment is defined within which temporal variations in ammoniacal-N concentration resulting from urea hydrolysis, volatilization, moisture loss or exchange reactions are assumed to be uniformly distributed. The depth of this compartment (2.5 cm) is selected to reflect the principal extent of aqueous fertilizer movement, the effective

distance over which unsaturated diffusive solute movement occurs, and to facilitate experimental verification.

The detailed chemical descriptions and their simplifications which follow, describe conditions relating to $NH_{3(g)}$ loss from a bare soil surface. Modifications introduced in chapter 4 include contributions due to loss from solution films on leaf and litter surfaces.

3.3 DERIVATION OF GENERALIZED CONTROLLING EQUATIONS

3.3.1 Ammoniacal-N Production

The rate of urease catalysed hydrolysis of aqueous urea or urine has been shown to obey normal Michaelis-Menten enzyme kinetics (Nor, 1982). However, few direct field measurements of urea hydrolysis rates in urine patches have been reported to confirm this. Urease activity itself is known to be affected by temperature (Van Slyke and Cullen, 1914), pH (Delaune and Patrick, 1970), soil moisture (Delaune and Patrick, 1970) and urea concentration (Overrein and Moe, 1967). It is located both intracellularly and extracellularly, is most active on the surface of herbage (McGarity and Hoult, 1971), decreases with decreasing organic C, and therefore decreases with soil depth (Zantua and Bremner, 1977). To simulate the complex interaction of all these factors would be difficult.

In laboratory experiments, both first and zeroth-order kinetics have been observed for the initial rate of urea hydrolysis (Vlek *et al.*, 1980; Sahrawat, 1980; Nor, 1982) while in chapter 2 of this thesis field experiments were described in which the rate of urea hydrolysis

following urine or aqueous urea applications to the topsoil (0 - 2.5 cm) of a ryegrass/white clover pasture were adequately described using simple first-order kinetics. Urea hydrolysis occurs rapidly in urine patches (Doak, 1952; Vallis *et al.*, 1982) and consequently the difference between zeroth and first-order behaviour in describing the time taken for "complete" hydrolysis (e.g. 12-24 hours) is minor relative to the duration of a typical volatilization event (e.g. 150-250 hours) (Vallis *et al.*, 1982; and section 2.3.2.1). Therefore, in any simple modelling exercise either zeroth or first-order kinetic behaviour can be used. However, since first-order behaviour better describes enzyme kinetics at low substrate (urea) concentrations, it is assumed here to characterize urea hydrolysis for the full duration of the volatilization event.

Thus the rate of urea hydrolysis will be given by the equation:

$$dU/dt = -k_1.U \qquad [3.4]$$

which on integration with respect to time yields:

$$U_t = U_0 \exp(-k_1.t) \qquad [3.5]$$

where:

U_t = concentration of urea in the soil solution at time = t.

U_0 = initial concentration of urea in the soil solution at time = 0.

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

t = time after urea application.

When written in terms of the production of the hydrolysis product, $NH_{x(aq)}$, (i.e. $NH_4^+{}_{(aq)} + NH_{3(aq)}$) the equation becomes:

$$(NH_x)_t = U_0\{1-\exp(-k_1.t)\} \qquad [3.6]$$

To be used in this volatilization model, the value of k_1 must be determined independently, by either a suitable field experiment or laboratory incubation (e.g. Overrein and Moe, 1967). The latter appears preferable as field determinations are subject to the influence of temperature changes and k_1 is temperature dependent. Within the temperature range 0-55°C urease activity, and hence hydrolysis rate has a Q_{10} of approximately 2 (Van Slyke and Cullen, 1914). This temperature dependence can be included in equation [3.6] by incorporating a suitable temperature scaling factor, 'A'. The production of $NH_{x(aq)}$ during some finite time increment, dt, is then given by:

$$NH_{x(aq)} = U_0\{\exp(-k_1.\ A.t)-\exp(-k_1.A.(t+dt))\} \qquad [3.7]$$

where 'A' is the temperature scaling factor for k_1. For example, if k_1 was obtained from a laboratory incubation experiment at 20°C, 'A' would be given by the equation:

$$A = 0.25\ \exp(0.0693.T) \qquad [3.8]$$

where T is the instantaneous temperature (°C) at time = t.

Values obtained for k_1 by *in situ* field measurements on a pasture site in Canterbury, New Zealand, ranged from 0.230-0.058 per hour with the spread depending mainly on temperature (i.e. season) and the form of substrate (urine or urea) (see section 2.3.2.3). These values correspond to urea half-lives of 3-12 hours respectively. In the situations considered here, the production of NH_x can be very rapid and produce large increases in the total NH_x in the topsoil compartments. These increases will produce corresponding increases in the $NH_{3(aq)}$ concentration at the source/air interface and the volatilized $NH_{3(g)}$ flux.

3.3.2 Ammoniacal-N Volatilization

3.3.2.1 $NH_4^+{}_{(aq)}/NH_{3(aq)}$ equilibrium (K_a)

The generation of $NH_4^+{}_{(aq)}$ by urea hydrolysis is coincident with a rise in soil pH and this affects the equilibrium between $NH_4^+{}_{(aq)}$ and $NH_{3(aq)}$ in the soil solution. The dissociation of $NH_4^+{}_{(aq)}$ can be represented by the equation:

$$NH_4^+{}_{(aq)} + H_2O \rightleftharpoons NH_{3(aq)} + H_3O^+{}_{(aq)} \qquad [3.9]$$

with a temperature dependent equilibrium constant, Ka, where:

$$K_a = [NH_{3(aq)}][H_3O^+{}_{(aq)}]/[NH_4^+{}_{(aq)}] \qquad [3.10]$$

and:

$$\log K_a = -0.09018 - 2729.92/T \qquad [3.11]$$

and T is temperature (°K) (see section 1.2).

Since the interconversion of $NH_4^+{}_{(aq)}$ and $NH_{3(aq)}$ is an extremely rapid first-order equilibrium (Bouwmeester and Vlek, 1981; Moeller and Vlek, 1982) it will not be rate limiting on the volatilization process. The instantaneous $NH_{3(aq)}$ concentration will, however, be directly related to the $NH_{3(g)}$ equilibrium concentration and hence to the rate of $NH_{3(g)}$ volatilization. An expression for this instantaneous $NH_{3(aq)}$ concentration is obtained as follows:

$$\text{let} \quad NH_{x(aq)} = NH_4^+{}_{(aq)} + NH_{3(aq)}$$

$$\text{thus} \quad NH_4^+{}_{(aq)} = NH_{x(aq)} - NH_{3(aq)} \qquad [3.12]$$

From equation [3.10] is obtained:

$$[NH_{3(aq)}][H_3O^+{}_{(aq)}]/K_a = NH_{x(aq)} - NH_{3(aq)} \qquad [3.13]$$

which becomes:

$$NH_{3(aq)} = NH_{x(aq)}/\{1 + H_3O^+_{(aq)}/K_a\} \quad [3.14]$$

Substituting for K_a from equation [3.11] gives:

$$NH_{3(aq)} = NH_{x(aq)}/\{1 + 10^{(0.09018+2729.92/T-pH)}\} \quad [3.15]$$

Thus, the concentration of $NH_{3(aq)}$ depends on pH, temperature, and total ammoniacal-N concentration. An increase in any of these parameters causes an increase in the $NH_{3(aq)}$ concentration which in turn, promotes an increase in $NH_{3(g)}$ loss.

3.3.2.2 $NH_{3(aq)}/NH_{3(g)}$ equilibrium (K_h)

For any solute to be volatilized from the soil solution it must possess an appreciable equilibrium concentration or vapour pressure, in the gas phase, which in turn must exceed the actual vapour pressure of the solute in the air. In the case of $NH_{3(aq)}$ this equilibrium condition is usually described by the expression:

$$NH_{3(aq)} = K\ pNH_{3(g)} \quad [3.16]$$

where 'K' is the Henry's Law equilibrium constant and $pNH_{3(g)}$ is the equilibrium partial pressure of $NH_{3(g)}$ at the surface of the solution (Freney *et al.*, 1981). However, an alternative expression, more useful to the development of this model, was recently reported by Hales and Drewes (1979). This is:

$$NH_{3(aq)} = K_h\ NH_{3(g)soil} \quad [3.17]$$

$$\text{where: } \log K_h = -1.69 + 1477.7/T \quad [3.18]$$

in which K_h is also a Henry's Law equilibrium constant but expressed as the dimensionless ratio of the molar gas phase and liquid phase concentrations. 'T' is temperature in degrees Kelvin.

Thus again an increase in either temperature or $NH_{3(aq)}$ concentration will promote an increase in the equilibirum $NH_{3(g)}$ concentration.

3.3.2.3 $NH_{3(g)soil}/NH_{3(g)air}$ exchange (k_2)

The rate of exchange of $NH_{3(g)}$ between the soil solution and free air is assumed to depend like other soluble gases and vapours on the instantaneous gas concentration gradient above the soil surface, which is given by:

$$R = k_2 \{NH_{3(g)soil} - NH_{3(g)air}\} \quad [3.19]$$

where R is the rate of volatilization (mass/time), $NH_{3(g)air}$ is the bulk air ambient concentration, and k_2 is the exchange coefficient, the value of which depends on the surface aerodynamic roughness and, possibly, wind velocity (Bouwmeester and Vlek, 1981; Denmead *et al.*, 1982; and section 1.2). Whenever $NH_{3(g)air}$ is comparable or greater than $NH_{3(g)soil}$, absorption of atmospheric $NH_{3(g)}$ by the soil solution is a possibility. Where $NH_{3(g)}$ loss occurs (e.g. from urine patches or following fertilizer application) the $NH_{3(g)soil}$ concentration is likely to be many times greater than the ambient $NH_{3(g)air}$ concentration (Vlek and Craswell, 1981), in which case equation [3.19] reduces to:

$$R = k_2 NH_{3(g)soil} \quad [3.20]$$

Substitution for $NH_{3(g)soil}$ from equation [3.15] and [3.17] into equation [3.20] gives:

$$R = \frac{k_2 \quad NH_{x(aq)}}{K_h \{1 + 10^{(0.09018+2729.92/T-pH)}\}} \quad [3.21]$$

In principle therefore, the instantaneous rate of volatilization could be calculated if the soil solution/air interface parameters, pH, T and total ammoniacal-N concentration, were determined, and an accurate evaluation of the exchange coefficient was also available. A series of such determinations could then be integrated over time and an estimate of total NH_3-N loss obtained. Difficulties involved in measuring particularly $NH_{x(aq)}$ would preclude direct application of this equation except possibly for flooded soils (Vlek and Craswell, 1981). Possible dependence of k_2 on windspeed is discussed later (section 3.4.5).

The $NH_{x(aq)}$ concentration in equation [3.21] is formally expressed in mol l^{-1} of soil solution at the soil/air interface. However, any concentration units may be used and the equation should still be valid. $NH_{x(aq)}$ can therefore be expressed as $NH_{x(aq)}/V$ where $NH_{x(aq)}$ is the amount (or weight) of ammoniacal-N in a specified volume of soil solution, V. Alternatively, $NH_{x(aq)}$ can be interpreted as the amount of dissolved NH_x in a volume of soil whose volumetric water content is M_v.

Dissolved NH_x is not normally determined in non-flooded soils as extraction of soil solution at moisture contents below field capacity is difficult. Normally, $NH_{x(exchangeable)} + NH_{x(aq)}$ are determined together by extraction of soil with 2 mol l^{-1} KCl (Bremner, 1965).

3.3.2.4 $NH_{x(aq)}/NH_{x(exchangeable)}$ equilibrium (D_1)

The partitioning of a cation, A^+, between exchange sites and solution is given by:

$$D_1 = A^+_{(\text{exchange sites})}/A^+_{(aq)} \quad [3.22]$$

or:

$$A^+_{(aq)} = A^+_{(total)}/(D_1+1) \quad [3.23]$$

where the concentration terms are either expressed in me/100 g of soil or as me/volume of soil. D_1 is a dimensionless distribution ratio, the magnitude of which is a function of the $A^+_{(aq)}$ soil solution concentration, the CEC of the soil, and the % base saturation and nature of the exchangeable bases present on the exchange sites (Bolt and Bruggenwert, 1976). The partitioning of both $NH_4^+{}_{(aq)}$ and $NH_{3(aq)}$ between exchange sites and solution can be similarly described by the relationship:

$$NH_{x(aq)} = NH_{x(total)}/(D_1+1) \quad [3.24]$$

where $NH_{x(total)} = NH_{x(aq)} + NH_{x(\text{exchange sites})}$

No consideration is given here to changing pH on the ratio of $NH_4^+{}_{(aq)}/NH_{3(aq)}$ and the effect this has on the specificity of the exchange reactions. For example, at high pH, $NH_{3(aq)}$ tends to be adsorbed more strongly on organic matter while at lower pH's, $NH_4^+{}_{(aq)}$ is the species involved, and then mainly with the mineral component of the soil (Freney *et al.*, 1981). Therefore, the value of D_1 may not remain constant but might vary during the course of the volatilization event.

3.3.2.5 $NH_{x(\text{exchangeable})}/NH_{x(\text{fixed})}$ (D_2)

Clay minerals in some soils have the capacity to fix NH_4^+-N in non-exchangeable forms (e.g. Carran *et al.*, 1982). This is normally a slow adsorption process in which the rate of adsorption exceeds the rate of desorption. Unlike cation exchange, a description

of the dynamics of this mechanism based on simple equilibrium chemistry is unlikely to be valid. Fortunately, in many pasture topsoils virtually no fixation occurs and all the mineral-N formed on urea hydrolysis can be accounted for as KCl-extractable N or volatilized $NH_{3(g)}$ up to two weeks following a urine application (Holland and During, 1977; Vallis *et al.*, 1982). This simplified description is therefore restricted to those soils in which fixation of N does not occur. The distribution ratio D_2 is consequently set equal to zero.

Substitution of equation [3.24] into equation [3.21] yields:

$$R = \frac{k_2 \, NH_{x(total)}}{K_h \; M_v \; Q \; (D_1 + 1)} \qquad [3.25]$$

where $NH_{x(total)}$ is now the mass or some other correct measure of the amount of KCl-extractable ammoniacal-N in a specified volume of soil. 'M_v' is the volumetric water content in this volume of soil, and for convenience, Q replaces the term as:

$$Q = \{1 + 10^{(+0.09018+2729.92/T-pH)}\} \qquad [3.26]$$

From equation [3.15] it can be seen that 1/Q represents the mole fraction of the $NH_{x(aq)}$ species present as $NH_{3(aq)}$ which at 298 Kelvin is 0.053, 0.359 and 0.849 for pH's 8.0, 9.0 and 10.0 respectively.

Equation [3.25] is a general description for the instantaneous rate of $NH_{3(g)}$ volatilization from a bare soil surface. The rate of volatilization is shown to be directly proportional to the amount of KCl-extractable ammoniacal-N, and inversely proportional to soil moisture content and the extent of exchange reactions with charged

sites on the soil colloids. Any of the other processes which remove ammoniacal-N (e.g. plant uptake, nitrification) will necessarily lower the rate of volatilization. An increase in either temperature or pH increases the volatilization rate although in a non-linear manner. These simple qualitative predictions have been confirmed in many laboratory investigations, some of which were reviewed in chapter 1.

3.4 DESCRIPTION OF LIMITS OF EACH PARAMETER IN THE VOLATILIZATION EQUATION

The direct application of equation [3.25] for the calculation of volatilization rates is quite impractical since it would require frequent and accurate evaluation of each parameter on the right-hand side of the equation. To facilitate simplification of the equation, the relative effect on 'R' of each parameter in equation [3.25] will now be made. Here, the range of values encountered by each parameter are those which typically accompany the volatilization events following aqueous urea or urine applications to pasture soils as measured in this current study and by other workers (e.g. Doak, 1952; Watson and Lapins, 1969; Holland and During, 1977; Stillwell and Woodmansee, 1981; Vallis *et al.*, 1982).

3.4.1 K_h and Q as Affected by Temperature (T)

The effects of temperature on K_h and Q were calculated using equations [3.18] and [3.26] and are given in Table 3.1. Actual and normalised (20°C) values of each parameter are shown. The data show

that a 10°C increase in T effectively halves the value of Q except at high pH's. The same increase in T also decreases K_h but to a lesser extent. However, since both Q and K_h decrease as T increases they combine to produce about a three-fold increase in R for each 10°C increase in T. Thus for the extreme situation of a diurnal temperature variation of ±10°C, R changes by a factor of about 9. This change will be approximately sinusoidal with a period of 24 hours.

TABLE 3.1

Effect of temperature and pH on the absolute and normalised (20°C) values of parameters 'K_h' and 'Q'

			pH 7		pH 8		pH 9	
Temp. °C	K_h	$\frac{K_{h(T)}}{K_{h(20)}}$	Q	$\frac{Q_{(T)}}{Q_{(20)}}$	Q	$\frac{Q_{(T)}}{Q_{(20)}}$	Q	$\frac{Q_{(T)}}{Q_{(20)}}$
0	5282	2.34	1231	4.81	124	4.66	13.3	3.75
10	3400	1.51	546	2.13	55.5	2.09	6.45	1.82
20	2256	1.00	256	1.00	26.6	1.00	3.55	1.00
30	1538	0.682	127	0.496	12.6	0.474	2.25	0.634
40	1074	0.476	65.9	0.257	6.49	0.244	1.64	0.462

($K_h = NH_{3(aq)}/NH_{3(g)soil}$, $Q = NH_{x(aq)}/NH_{3(aq)}$

3.4.2 Q as Affected by pH

The rapid pH rise which accompanies urea hydrolysis frequently exceeds 2 pH units at the air / soil interface (Doak, 1952; Holland and During, 1977; Vallis *et al.*, 1982). A typical increase from

pH 7 to pH 9 produces a large (60-85 fold) decrease in the value of Q, depending on T (see Table 3.1) resulting in a corresponding large increase in the calculated volatilization rate. Thereafter, pH declines slowly as volatilization proceeds (e.g. see Figure 4 of Holland and During, 1977 or Figure 5 of Vallis *et al.*, 1982). A pH decline or acidification occurs even in the absence of nitrification (Holland and During, 1977; and section 2.3.2.5) and is due to the NH_4^+ ion releasing a proton into solution when an NH_3 molecule is volatilized (Avnimelech and Laher, 1977) accordingly:

$$NH_4^+(aq) \rightleftharpoons H^+(aq) + NH_3(aq) \rightleftharpoons NH_3(g) + H^+(aq) \qquad [3.27]$$

This mechanism is discussed in more detail later. The decline from pH 9 must be about 1.5-2.0 units, to less than pH 7.5, before volatilization effectively ceases (Vlek and Craswell, 1981). This has been shown to occur over a period of about 4-8 days (Watson and Lapins, 1969; Holland and During, 1977; Vallis *et al.*, 1982; and section 2.3.2.1) and during this time it changes Q by a factor of between 20 and 85 (again also depending on temperature).

3.4.3 $NH_{x(total)}$

The $NH_{x(total)}$ term will ultimately be reduced to very low levels because of volatilization and the combined influences of nitrification, plant-uptake, denitrification and immobilization. However, to significantly influence the $NH_{x(total)}$ term during the volatilization event (4-8 days) the rates of these other biological processes must be comparable with the rate of volatilization. Fortunately, it has been shown in many field experiments that the rates of two of these mechanisms, nitrification and plant uptake,

are very much less than the rate of $NH_{3(g)}$ volatilization (Holland and During, 1977; Ball *et al.*, 1979; Carran *et al.*, 1982; Vallis *et al.*, 1982; and section 2.3.2.4). Consequently, in a simple short-term modelling exercise, the influence of these two mechanisms can largely be ignored. Similarly, the magnitude of volatile N losses via biological and chemical denitrification are normally insignificant and typically remove only a tiny fraction of the applied N over the duration of a volatilization event (4-8 days) (Delaune and Patrick, 1970; McKenney *et al.*, 1980; Smith *et al.*, 1982). Rapid immobilization of a fraction of the applied N has been demonstrated (Keeney and Macgregor, 1978; Ball *et al.*, 1979). Often, however, there is an absence of readily available carbon in the topsoils of many intensively grazed pastures. This, together with the high concentrations of mineral-N generated in urine patches could in many cases restrict microbial immobilization during the early volatilization period (Ball and Keeney, 1981). Therefore while this current development is not necessarily restricted to intensively grazed pastures, direct application of the equations derived does assume the effective absence of immobilization during the volatilization event. Thus, the volatilization process can frequently be considered in isolation from these other mechanisms, thereby making the modelling of the $NH_{3(g)}$ loss considerably simpler than it might be otherwise. Large variations in $NH_{x(total)}$ within the topsoil compartment will always be induced through three other mechanisms.

3.4.3.1 Urea hydrolysis

Depending on the rate of urea application, the increase in $NH_{x(total)}$ due to hydrolysis may be very large. For example,

KCl-extractable NH_x concentrations in pasture topsoil are typically 1-10 $\mu g\, ml^{-1}$ of soil whereas in fresh urine patches concentrations can exceed 1000 $\mu g\, ml^{-1}$ of soil (Holland and During, 1977; Vallis *et al.*, 1982).

3.4.3.2 Volatilization of $NH_{3(g)}$

This process decreases $NH_{x(total)}$ in direct proportion to the extent of volatilization. Total volatile $NH_{3(g)}$ losses are typically 10-30% of the applied-N (Denmead *et al.*, 1974; Carran *et al.*, 1982; Beauchamp *et al.*, 1982; Vallis *et al.*, 1982; and section 2.3.2.1). If only half of this applied-N was in the topsoil (0-2.5 cm) compartment in equilibrium with the soil surface, the reduction in the $NH_{x(total)}$ term due to volatilization is only a factor of 20-60%. This is small compared with the large variations in the other terms in equation [3.25] induced by changes in pH and temperature.

3.4.3.3 NH_x movement

Movement of NH_x below the surface soil/air interface will decrease the amount in the topsoil compartment and hence decrease R. Downwards diffusion of $NH_{3(g)}$ may occur but is likely only in alkaline soils in which a significant proportion of the NH_x exists as $NH_{3(aq)}$ (Table 3.1). Leaching of the positively charged NH_4^+ cation is also unlikely to be significant. Hence any NH_4^+ detected below about 2.5 cm under non-saturated conditions probably results from mass flow of solution down large pores immediately after application (e.g. see section 1.2.1.4). Under saturated conditions the rapid movement of unhydrolysed $urea_{(aq)}$ has been demonstrated

(Stillwell and Woodmansee, 1981). Provided an estimate of this initial movement is available, subsequent changes in $NH_{x(total)}$ by leaching or diffusion can probably be ignored.

3.4.4 Soil Moisture (M_v)

Urine continuously returned by grazing animals causes localised increases in soil solution volume. A typical silt-loam pasture soil probably has a topsoil moisture content of 10-30% by weight. The most extreme increase in solution volume in a grazed, non-irrigated sheep pasture therefore occurs when, during a typical urination, 150 ml of urine is voided by a sheep to about 400cm^2 of a dry pasture soil. This effectively doubles the soil moisture content of the top 2.5 cm. Similarly, the most severe drying conditions are met when all this added moisture evaporates. The maximum change in 'M_v' in a non-irrigated pasture is therefore about a factor of 2. In irrigated pastures or where solid urea granules are applied, the change in 'M_v' during any subsequent volatilization event is likely to be much less.

3.4.5 Volatilization Exchange Coefficient (k_2)

As stated earlier (section 3.3.2.3) the value of k_2 depends on the surface aerodynamic roughness. Therefore, the type and height of herbage is important, but since these do not change significantly during a volatilization event, these factors are unlikely to cause k_2 to change. The k_2 may vary as a function of windspeed (see section 1.2.1.5) but this effect is by no means certain. For example, a diffusion based volatilization model by Bouwmeester and Vlek (1981)

predicts an increase in R for increasing windspeed at low pH's, but at high pH's (pH>9) increased windspeed has little effect on R. It was suggested that whereas gas phase resistance was rate limiting on volatilization at pH (7-8), at higher pH's the diffusion of ammoniacal-N to the solution/air interface became rate limiting. Their model was developed to describe volatilization from flooded soils where water movement and diffusion of ions is probably less restricted than in unsaturated soils. This might suggest that the rate of volatilization from non-flooded soils is limited by the rate of diffusion of $NH_{3(aq)}$ or $NH_{3(g)}$ to the soil/air interface rather than on windspeed. Circumstantial evidence to support this is found in the work of Denmead *et al.* (1974) and Beauchamp *et al.* (1978, 1982). In none of these extensive studies on non-flooded systems has a positive relationship between $NH_{3(g)}$ flux and windspeed been reported.

For these reasons, it is assumed here that k_2 is independent of windspeed and essentially constant.

3.4.6 Distribution Ratio (D_1)

Factors influencing the magnitude of D_1 for a particular soil were discussed earlier (section 3.3.2.4). Under "normal" conditions the concentration of a cation in soil solution is many times lower than its concentration on exchange sites (Bolt and Bruggenwert, 1976). However, in urine patches the high added concentrations of both K^+ and NH_4^+ can be expected to be partitioned more evenly. Actual measurements of distribution ratios for NH_4^+ in urine patches remain unreported.

In a similar modelling exercise, Parton *et al.* (1981) used a value of approximately 0.55 for D_1 which remained virtually constant

over a wide $NH_4^+{}_{(aq)}$ concentration range. No particular value for D_1 is assumed here but it is suggested that since the $NH_{x(total)}$ term changes little during most of the volatilizaton event, likewise the distribution ratio, D_1, is unlikely to vary much and may be considered essentially constant. It is also assumed that D_1 is independent of temperature, and that the exchange reactions are reversible and sufficiently rapid so as not to limit the rate of volatilization.

3.5 AMMONIA VOLATILIZATION - A FOUR STAGE PROCESS

The previous evaluation of parameters shows that for the situations considered, the instantaneous value of R depends on the concentration of $NH_{3(aq)}$ at the soil/air interface which in turn is primarily a function of the rate of urea hydrolysis, the pH of the soil/air interface and to a lesser extent, temperature. As mentioned previously (section 3.4), R could in principle be obtained by independent evaluation of each parameter in equation [3.25]. However, this requires a knowledge of k_2 which is unknown, and a precise measurement of D_1 which is difficult.

The simple treatment advanced here recognises the variables k_2, M_v and D_1 to be essentially constant throughout the volatilization event and acknowledges the dominance of the pH term in determining the amount of $NH_{3(aq)}$ present at the soil/air interface and hence $NH_{3(g)soil}$ and R. It is therefore necessary to review more closely the changes in pH which occur within a urine patch and the affect these changes have on the dynamics of $NH_{3(g)}$ loss.

Although the general characteristics of pH change within urine patches have long been recognised (Doak, 1952) there have been only a few studies in which soil surface pH has been measured as a function of time (Doak, 1952; Watson and Lapins, 1969; Vallis *et al.*, 1982). All these studies report similar behaviour from which four sequential stages of pH change may be distinguished. For convenience, they are referred to here as stages 1 through 4.

3.5.1 Definition of Volatilization Stages

Stage 1 begins immediately urine is voided and is characterized by a rapid increase in soil solution pH from native levels to between 8.0 and 9.5. This usually takes between 6 and 48 hours. The increase in pH is consistent with the hydrolysis of urea in the urine to generate NH_4^+ and HCO_3^- (equations [3.1] and [3.2]) and is accompanied by the gaseous release of both NH_3 and some CO_2.

The pH then drops to about 8 over a period of between 2 to 8 days (stage 2), with the bulk of the $NH_{3(g)}$ appearing to volatilize during this time. Then follows an extended period of 1 to 3 weeks (stage 3) in which pH remains constant and the volatilization rate drops considerably.

Finally, residual NH_4^+ nitrifies under the action of *Nitrosomonas* and *Nitrobactor* micro-organisms to yield nitrate according to the equation:

$$NH_4^+ + 2O_2 \longrightarrow NO_3^- + 2H^+ + H_2O \qquad [3.28]$$

During this final fourth stage the generation of protons frequently drops the pH of the surface soil below its original value.

Sometimes there appears to be no clear distinction between stages 3 and 4, particularly where nitrification is rapid (e.g. Vallis *et al.*, 1982). It must be cautioned, therefore, that this classification is made on the basis of a very limited number of reports and may not be a correct description under all conditions. The pH changes and associated volatilization of $NH_{3(g)}$ during stages 2 and 3 especially, are only poorly documented.

3.5.2 pH Changes in Aquatic Systems

Volatilization from aquatic systems and flooded soils has received more intensive study and the dynamics of $NH_{3(g)}$ loss from these systems is now well understood (Vlek and Craswell, 1981). Following urea fertilizer application, aquatic systems undergo the same sort of pH changes described above. It is reasonable to suggest therefore, that the mechanisms now known to promote volatilizaton following urea fertilization of aquatic systems probably also apply to urine patches.

As stated earlier (section 1.5.1.1) Vlek and co-workers (1978, 1981) have stressed the need for the presence of a proton acceptor (or base) to help generate volatilizable $NH_{3(aq)}$ from non-volatile $NH_4^+{}_{(aq)}$ [equation 3.27]. In flooded rice paddies, the hydrolysis of added urea fertilizer leads to the formation of a weak ammonium bicarbonate solution which because of its inherent buffering capacity tends to maintain a pH of about 8. Volatilization proceeds at this constant pH so long as there is sufficient bicarbonate ion (HCO_3^-) present in accordance with the equation:

$$NH_4^+ + HCO_3^- \longrightarrow NH_{3(g)} + CO_{2(g)} + H_2O \qquad [3.29]$$

The simultaneous loss of equimolar amounts of base ($NH_{3(g)}$) and acid (CO_2) maintains the pH. Eventually, the concentration of HCO_3^- becomes so low that buffering no longer occurs and further volatilization drops the pH to values below which the amount of free $NH_{3(aq)}$ is negligible and volatilization effectively ceases. Thus in aquatic systems the ultimate extent of N loss is determined by the amount of bicarbonate available. This bicarbonate buffered system appears entirely consistent with stage 3 volatilization since at pH 8, NH_4^+ and HCO_3^- will also be the dominant ions present in the soil solution of a urine patch. Simultaneous measurement of both $NH_{3(g)}$ and $CO_{2(g)}$ release rates from urine patches would be needed to confirm this.

Vlek and Stumpe (1978) also showed that from aqueous ammonium bicarbonate adjusted to a pH between 8.6 and 9.0 the initial volatilization of $NH_{3(g)}$ was not matched by an equivalent loss of $CO_{2(g)}$. Only when the pH had dropped to about 8 were $NH_{3(g)}$ and $CO_{2(g)}$ lost in equivalent amounts. No mechanism was proposed by them to explain this unpredicted behaviour.

3.5.3 pH Changes in Urine Patches

It is suggested here that the volatilization dynamics reported by Vlek and Stumpe (1978) from ammonium bicarbonate solutions at pH>8 are consistent with the volatilization taking place in urine patches during stage 2. It is further suggested that their proposed volatilization mechanism which requires a proton acceptor still operates between pH 8 and 9.

Between these pH limits the concentrations of both CO_3^{2-} and OH^- are very low and consequently neither of these species can act

as efficient proton acceptors. However, present in approximately equal proportions (at 298K and pH 9.0) are the two bases $HCO_3^-(aq)$ and $NH_{3(aq)}$, the pK_b's of which are 7.65 and 4.76 respectively (Strumm and Morgan, 1970). Since $NH_{3(aq)}$ is therefore the stronger base it will preferentially undergo protonation until its concentration is exhausted (Strumm and Morgan, 1970). Thus, during stage 2, volatilization can be described by the equation:

$$\underset{\text{(acid 1)}}{NH_4^+(aq)} + \underset{\text{(base 2)}}{NH_{3(aq)}} \longrightarrow \underset{\text{(conjugate base 1)}}{NH_{3(g)}} + \underset{\text{(conjugate acid 2)}}{NH_4^+(aq)} \qquad [3.30]$$

Since only a base, $NH_{3(g)}$, is lost from the system without an equimolar amount of acid (CO_2) the pH drops accordingly. When the resulting $NH_{3(aq)}$ concentration is finally too low to sustain further proton acceptance its role is taken over by $HCO_3^-(aq)$ and stage 3 begins.

Stage 2 appears therefore as a "pure" first-order $NH_{3(g)}$ volatilization process not confounded by significant loss of CO_2 and is described by the net equation:

$$NH_{3(aq)} \longrightarrow NH_{3(g)} \uparrow \qquad [3.31]$$

Recognising this, the pH drop which occurs during this stage could be used to calculate directly (using equation [3.15]) the decrease in the proportion (or amount) of $NH_{3(aq)}$ in the solution. When applied to urine patches, this decrease in the calculated amount of NH_3 present in the topsoil during stage 2 should be equal to, and manifest itself as, the volatile $NH_{3(g)}$ lost from the soil surface. Similarly, the rate of $NH_{3(g)}$ loss from the soil surface, R, should equal the rate of change in the volatilizable NH_3 (i.e. $NH_{3(aq)} + NH_{3(\text{exchange sites})}$) in the topsoil. The measurement of

topsoil pH during stage 2 should therefore provide the key to establishing the extent of $NH_{3(g)}$ loss from urine patches.

It must be stressed, however, that only during stage 2 are measureable pH changes in the surface soil likely to relate directly to the rate of $NH_{3(g)}$ loss. However, this hypothesis can still be used to simplify and test the general volatilization equation [3.25] which applies throughout all stages.

3.6 SIMPLIFICATION OF THE SOIL VOLATILIZATION EQUATION

3.6.1 Exclusion of Temperature Effects

A satisfactory description of the situation is somewhat confounded by diurnal temperature fluctuations which affect the magnitudes of K_h and Q in equation [3.25]. In the interim, these temperature effects may be specifically excluded by substituting the mean temperature during the volatilization process into both K_h and Q. The dependency of the $NH_{3(g)}$ flux, R, on pH can then be demonstrated by rearranging equation [3.25] as follows:

$$R = -k_3 \{NH_{x(total)}/Q_{(mean)}\} \quad [3.32]$$

where:

$$-k_3 = k_2/\{K_{h(mean)} \cdot M_v (D_1 + 1)\} \quad [3.33]$$

From equations [3.15] and [3.26] the pH dependent term '1/Q' was the fraction of the $NH_{x(aq)}$ present as $NH_{3(aq)}$ within some specified topsoil compartment. The term '$NH_{x(total)}/Q_{(mean)}$' therefore represents the total amount of KCl-extractable NH_x present as NH_3 i.e. $\{NH_{x(total)}/Q_{(mean)}\} = NH_{3(aq)} + NH_{3(exchange\ sites)}$ at the pH of the soil solution in that compartment. Thus, volatilization of $NH_{3(g)}$

is seen as a first-order decay process which depends only on the value of k_3 and the amount of pH dependent NH_x.

3.6.2 Calculation of Volatilization Rate Constant

Equation [3.32] should apply during all stages of $NH_{3(g)}$ volatilization. However, during stage 2, measured soil surface pH and mean temperature values can be used to evaluate '$NH_{x(total)}/Q_{(mean)}$' as a function of time. It was suggested (section 3.5.3) that the rate of change in '$NH_{x(total)}/Q_{(mean)}$' should equal the rate of $NH_{3(g)}$ loss from the soil surface i.e.:

$$R = \frac{d\{NH_{x(total)}/Q_{(mean)}\}}{dt} \qquad [3.34]$$

Substituting for R in equation [3.32] yields:

$$\frac{d\{NH_{x(total)}/Q_{(mean)}\}}{dt} = -k_3.\{NH_{x(total)}/Q_{(mean)}\} \qquad [3.35]$$

which on integration with respect to time gives:

$$\{NH_{x(total)}/Q_{(mean)}\}_t = \{NH_{x(total)}/Q_{(mean)}\}_o \exp(-k_3.t) \qquad [3.36]$$

or:

$$\ln\{NH_{x(total)}/Q_{(mean)}\}_t = -k_3.t + \ln\{NH_{x(total)}/Q_{(mean)}\}_o \qquad [3.37]$$

Thus a plot of the log of the ratio '$NH_{x(total)}/Q_{(mean)}$' versus time, 't', will have a slope equal to $-k_3$. The intercept represents the natural log of a theoretical maximum value of '$NH_{x(total)}/Q_{(mean)}$' at time = 0.

One further simplification is possible which dispenses with the need to measure '$NH_{x(total)}$' as a function of time if the following observations are considered.

Probably half of the total NH_3-N loss occurs in stage 1. If the total loss is assumed to average 20% of the applied N (Carran *et al.*, 1982; Vallis *et al.*, 1982; and section 2.3.2.1) then the total change in '$NH_{X(total)}$' during stage 2 will only be about 10%. On the other hand, a typical decrease in pH during stage 2 is 1-1.5 units, which in turn reduces '$1/Q_{(mean)}$' by at least a factor of 10. Hence, during stage 2, '$NH_{X(total)}$' can be considered to be constant relative to '$1/Q_{(mean)}$' and for convenience, set equal to unity. Therefore, a plot of '$1/Q_{(mean)}$' versus time will also give a line with slope $-k_3$. i.e.

$$\ln\{1/Q_{(mean)}\}_t = -k_3.t + \ln\{1/Q_{(mean)}\}_o \qquad [3.38]$$

Whether the final plot is linear or not depends on the constancy of k_3 which in turn depends on the constancy of M_V, D_1 and k_2 [equation 3.33]. The previous discussion suggested that variations in these factors would be small. Changes which do occur in any or all of these three factors may be reflected in small changes in the slope of equation [3.38]. The precision with which an instantaneous value of k_3 can be estimated is therefore directly related to the frequency of soil surface pH determinations. The minimum number of pH determinations needed to estimate k_3 is two; one at the beginning of stage 2 and one near the end. The method used here to estimate k_3 cannot be directly applied to stages 1, 3 or 4. However, since M_V, D_1 and k_2 are not expected to change substantially during the course of the volatilization event it seems reasonable that the value for k_3 obtained in stage 2 should also apply during the other stages.

3.6.3 Inclusion of Temperature Effects

As derived above, k_3 was made independent of temperature by substituting the mean temperature into the two temperatures dependent terms 'K_h' and 'Q' in equation [3.25]. After k_3 has been evaluated by the procedure just described, temperature dependence can be included if desired by substituting the actual measured soil/air interface temperature into 'Q' equation [3.32]. The temperature dependency of 'K_h' is included by multiplying k_3 by a temperature scaling factor 'H' where: $H = K_{h(T)}/K_{h(mean)}$ and is a measure of the fractional change in 'K_h' as 'T' departs from '$T_{(mean)}$'. 'H' may be calculated using equation [3.18].

3.6.4 Simplified Volatilization Equation

With the above considerations, the instantaneous rate of volatilization during all stages of the volatilization process can therefore be written as:

$$R = -k_3.H.NH_{x(total)}/Q \qquad [3.39]$$

where $NH_{x(total)}$ may have any appropriate units (e.g. mg or moles). Where the ammoniacal-N in the topsoil is derived solely as a result of urea hydrolysis, $NH_{x(total)}$ may also be expressed as a percentage of the applied N and the rate of $NH_{3(g)}$ loss is then calculated directly as % loss per time.

In addition to urea-N, sheep urine usually contains small, variable amounts of amino-N as various heterocyclic N compounds and peptides (e.g. allantoin, creatinine, hippuric acid and heteroauxin) (Doak, 1952; Bathurst, 1952). There have been very few studies of

the degradation of these compounds in soils (Ladd and Jackson, 1982). However, the relative complexity of these compounds would suggest that their rates of deamination and hydrolysis to yield NH_X may be much slower than the rate of urea hydrolysis. If this is so, then for urine patches the $NH_{X(total)}$ term in equation [3.39] could be replaced by:

$$NH_{X(total)} = \alpha \; . \; (\% \text{ Applied N}) \qquad [3.40]$$

where 'α' is the fraction of the applied urine-N initially present as urea-N + NH_4^+-N. The value of 'α' for urine samples used in earlier volatilization experiments was 0.86 - 0.90 (chapter 2, Table 2.3). Irrespective of the urea content of the urine, if the rates of deamination and hydrolysis of these organic-N compounds are sufficiently slow then 'α' is likely to remain constant for the duration of the volatilization event and as such would be included in k_3. Thus, for urine patches:

$$-k_3 = \alpha.k_2/\{K_{h(mean)}.M_v.(D_1 + 1)\} \qquad [3.41]$$

and

$$R = -k_3.H.(\% \text{ Applied N})/Q \qquad [3.42]$$

Nevertheless, if degradation of non-urea components does occur then the fraction of the urine-N present as urea-N is normally sufficiently large that any increase in 'α' during the volatilization event would still be very small (10 - 15%) and of minor importance compared with the large changes (20 - 85 times) associated with variations in the value of 'Q' (section 3.4.2). Thus, the use of equation [3.42] should remain valid.

The k_3 has units of $time^{-1}$, and can also be used to calculate volatilization half-lives as $t_{½} = 0.693/k_3$.

3.6.5 Applications of the Model

The simplest application of this urine patch model is where loss of ammoniacal-N from the topsoil compartment occurs solely as a result of $NH_{3(g)}$ volatilization to the atmosphere. Then, the generation and subsequent volatilization of ammoniacal-N are given directly by equations [3.7] and [3.42] respectively. Provided the initial disposition of the applied-N is known the only other input parameters required are soil surface pH and temperature and the rate of urea hydrolysis; all of which are relatively easy to measure.

Where volatilization if not the only mechanism reducing ammoniacal-N during the volatilization event, this model could still form the gaseous loss component of a wider N-cycling model. An application of this sort would require detailed knowledge of the rates of the other mechanisms and probably involve the use of ^{15}N.

3.7 DISCUSSION

This chapter examined the various chemical equilibria and transport processes known to influence $NH_{3(g)}$ volatilization from urine patches with a view to develop a verifiable $NH_{3(g)}$ volatilization model which could be used to estimate losses in the field.

A simple 2 compartment model (represented diagrammatically in Figure 3.1) was proposed in which the ammoniacal-N generated by enzyme catalysed hydrolysis of urea was partitioned between the topsoil (0 - 2.5 cm) and the subsoil below 2.5 cm. A general equation was then formulated for describing the rate of $NH_{3(g)}$ volatilization from the soil surface. Volatilization rate was calculated to be directly proportional to the total amount of ammoniacal-N in the topsoil, and inversely proportional

Figure 3.1

AMMONIA VOLATILIZATION MODEL

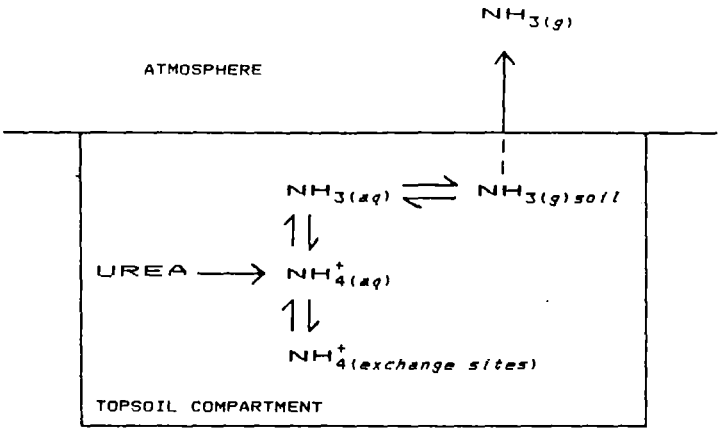

Figure 3.1 Diagrammatical representation of the simplified ammonia volatilization model.

to soil moisture content and the extent of exchange reactions with charged sites on the soil colloids. A critical examination of each term in the volatilization equation revealed that the dominant factors determining relative volatilization rates from urine patches were soil surface pH and temperature.

The dynamics of pH changes at the surface of urine patches and within urea fertilized aquatic systems (e.g. paddy fields) was briefly reviewed. Using data published elsewhere, a semi-empirical approach led to the tentative identification of 4 stages of $NH_{3(g)}$ volatilization, each of which was characterized by its own distinctively changing pH pattern at the soil surface. The pH decline which characterized one of these stages (stage 2) was shown to be consistent with a simple first-order $NH_{3(g)}$ volatilization mechanism, and should therefore be directly related to losses of $NH_{3(g)}$.

It was proposed that a measured pH decline during stage 2 could be used to simplify and solve the general volatilization equation for all stages of a volatilization event. A procedure was outlined to achieve this.

No soil-specific parameters were used in the semi-empirical approach adopted here. The particular behaviour of any individual

pasture soil will depend on the factors already considered and also on a complex interaction of cation exchange capacity and buffering capacity (Avnimelech and Laher, 1977). Their net effect will be manifested in the magnitude of the volatilization constant, k_3, and by the manner in which the soil surface pH changes as a function of time. The model does not attempt to predict pH changes. Instead, the pH values which result from the interaction of all contributing factors are measured to enable the calculation of volatile $NH_{3(g)}$ losses. This apparent limitation of the model may prove useful to its possible application in estimating $NH_{3(g)}$ losses under a wide range of seasonal conditions and a variety of soil types.

Before any application of the model, however, it must be experimentally verified. This is presented in the next chapter.

CHAPTER 4

FIELD VERIFICATIONS OF A SIMPLIFIED MODEL

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CHAPTER 4

FIELD VERIFICATIONS OF A SIMPLIFIED MODEL

4.1 INTRODUCTION

Chapter 3 provided a general theoretical derivation for a mathematical model which described ammonia $NH_{3(g)}$ volatilization from a soil surface. This model was simplified using semi-empirical approximations consistent with the known dynamics of nitrogen transformations in the urine patches of grazing herbivors.

The model consisted of 2 equations which described the generation of ammoniacal-N by urease catalysed hydrolysis of urea and its subsequent volatilization as $NH_{3(g)}$. The implementation of the model necessarily assumes the absence of other mechanisms (e.g. plant uptake and nitrification) during a volatilization event which might also remove ammoniacal-N from the topsoil of a urine patch. As discussed previously (section 3.4.3) this assumption was found to be substantially valid for the limited number of studies on urine patches where these transformations have been measured (Holland and During, 1977; Vallis *et al.*, 1982 and section 2.3.2.6).

Not considered in the original model, however, was a possible contribution to volatile N loss from solution intercepted by leaf and litter surfaces. When urine or aqueous urea is applied to a pasture surface most of it enters the soil but some may be held-up and retained on leaf surfaces and on the litter and residual organic matter of past plant growth (see section 1.3.2). Urease is active under both these conditions but because leaf and litter surfaces have

only a limited cation exchange capacity the hydrolysis products of intercepted solution might be more subject to volatile loss as $NH_{3(g)}$ than if hydrolysis had occurred within the soil itself (Nelson, 1982). On healthy surfaces a proportion of the solution might also be adsorbed directly through the cuticular membrane either as urea or its hydrolysis products and be metabolised by the plant (Yamada *et al.*, 1965; Denmead *et al.*, 1976; Cowling *et al.*, 1981). Although this mechanism would help to reduce volatilization, $NH_{3(g)}$ losses from intercepted solution could still form a significant proportion of the total gas loss (McGarity and Hoult, 1971).

This chapter presents several field verifications of the proposed urine patch volatilization model together with an estimate of the contribution due to 'leaf and litter surface' volatilization. Published data for testing the model are limited because of the specific nature of the model's input parameters. The main data sets used were from the summer and autumn field experiments reported in section 2.3.2 but calculations and comparisons are also made with data reported by Holland and During (1977) and Vallis *et al.* (1982).

4.2 MATERIALS and METHODS

The field site, soil properties, and aspirated enclosure technique used for the detailed field verifications are described in sections 2.2.1 and 2.3.1.

4.2.1 Computer Program

The two controlling equations (section 3.3.1 equation [3.7]) and section 3.6.4 equation [3.42] were used to form the basis of a computer simulation program. This program was written in 'Microsoft Basic' for use on a 48K microcomputer (Appendix I) but a version was also prepared for use under 'Vax Basic'.

4.2.2 Model Input Data

4.2.2.1 Soil surface pH

Monitoring the necessary changes in soil pH was achieved by taking 5 cm diameter soil cores from simulated urine patches applied to non-enclosed plots (5 cores per sampling time) on several occasions during each experiment. These were sectioned to 5 depths, mixed with water in an approximate 1 : 2.5 ratio and the pH was recorded immediately. Measurements taken the following day on these same samples were up to ± 1.8 pH unit different from the initial readings (Appendix III). Changes during the intervening period were consistent with the prior extent of urea hydrolysis in the sample. For example, samples which contained principally unhydrolysed urea-N, increased in pH on standing as hydrolysis continued, while those in which hydrolysis was virtually complete tended to decrease. The immediate readings were considered to better reflect the pH at the sampling time and the 0 - 0.5 cm soil surface readings were used to generate interpolated hourly values as inputs to the computer program.

4.2.2.2 Volatilization rate constant

The measured pH values were also used to independently evaluate the magnitude of the composite first-order volatilization rate constants by the exponential regression procedure described previously (section 3.6.2).

4.2.2.3 Disposition of mineral-N

Mineral-N located within the topsoil (0 - 2.5 cm) compartment and below 2.5 cm was determined by soil sampling and analysis procedures described in section 2.3.1.2.

For the verification exercise, the fraction of the applied N located in the topsoil compartment was required. The model as derived assumed the mineral-N within this compartment was only subject to loss as $NH_{3(g)}$ and that no significant leaching occurred once any initial mass flow had ceased. Consequently, any $NH_{3(g)}$ lost prior to soil sampling must be accounted for and included as part of this topsoil mineral-N fraction. This was achieved by adding the mean $NH_{3(g)}$ loss (kg N ha^{-1}, measured at the time of soil sampling) to the mineral-N located in the topsoil compartment of each unconfined core sample analysed. This value was then expressed as a percentage of the total mineral-N and volatilized-N accounted for in each individual core sample (Appendix II). This was done in an attempt to recognise samples in which substantial mass flow of solution occurred down cracks and worm holes and also to overcome any sampling artifacts associated with unconfined lateral movement of solution described earlier (section 2.3.1.6).

4.2.2.4 Soil surface temperature

For the summer experiment, soil surface air temperatures were recorded continuously on a shaded thermohygrograph. Discrete hourly readings from this record were used to calculate interpolated values for the temperature dependent terms in the model. Continuous soil temperature (0 - 2.5 cm) data were also available and have been used here for model predictions during autumn.

4.2.2.5 Urea hydrolysis rate

The rate of urea hydrolysis, within the top 2.5 cm soil layer was determined by soil sampling and analysis procedures as described in section 2.3.2.3.

4.2.3 Leaf and Litter Surface Volatilization

To estimate the extent of 'leaf and litter surface' volatilization a laboratory experiment was conducted to measure the rate of $NH_{3(g)}$ loss from a free water surface. This was based on the assumption that the exchange coefficient characterizing volatilization from moisture films or droplets on leaf or litter surface, k_2' (equation [4.1]) is the same as that for $NH_{3(g)}$ release from a free water surface.

A cylindrical enclosure of identical construction to those used in the collection of the field data (410 cm^2 x 2.5 cm), was sealed to a dish of similar surface area containing 500 ml of 50 $\mu g\ N\ ml^{-1}$ ammonium sulphate solution. For convenience, the solution was adjusted to pH > 12 by the addition of 10 ml of 50% NaOH solution at which stage virtually all the $NH_{x(aq)}$ was present as $NH_{3(aq)}$ (Vlek and Stumpe, 1978). The system was then aspirated with NH_3 free air

at the same flowrate used for the field experiments (21 l/minute). Volatilized $NH_{3(g)}$ was collected in 2% boric acid and determined by titration with 0.005N H_2SO_4.

Under these conditions k_2' (72.8 h^{-1}) was calculated from the equation:

$$R_{(aq)} = k_2' . NH_{3(aq)} / K_h \qquad [4.1]$$

where $R_{(aq)}$ is the initial rate of volatilization of $NH_{3(g)}$ from the surface of the solution (6.33% h^{-1} per litre of solution) and K_h is the dimensionless Henry's law constant for ammonia (K_h = 2256 at 20°C) (Hales and Drewes, 1979).

For use in the simplified volatilization model a composite 'leaf and litter surface' volatilization constant, k_3', appropriate to each field experiment is defined by:

$$-k_3' = k_2' / (K_{h(mean)} M_v') \qquad [4.2]$$

In equation [4.2], $K_{h(mean)}$ is the value of the Henry's law constant at the mean temperature during the volatilization event. M_v' represents the volume of the solution on the leaf and litter surfaces expressed as a fraction of the total volume of the soil plus herbage assumed to be in equilibrium with the soil/air interface. For example, the volume of soil normally assumed to be in equilibrium with the soil surface in this volatilization model forms a cylinder 400 cm^2 x 2.5 cm deep and occupies 1000 cm^3. If the herbage and litter (negligible volume) intercepted and held up 7 cm^3 of ammoniacal-N solution, then M_v' = 0.007. Substituting this value into equation [4.2] reveals that the effective half-life for loss of $NH_{3(g)}$ from the 7 cm^3 solution (i.e. 0.693 / k_3') is only 9 minutes; a very rapid process indeed.

Table 4.1: Comparison between measured ammonia volatilization losses following urine and aqueous urea applications with values predicted by the simplified volatilization model.

Treatment	Mineral-N Distribution (% of N applied)		Soil volatilization decay constant (h^{-1})	Urea Hydrolysis constant (h^{-1})	Mean temperature (°C)	Duration of simulation (h)	N Volatilized (% of N applied)		Reference
	Surface compartment	Leaf and litter compartment					measured b	predicted c	
Urine	65.2	4.0	0.026 a	0.230	20.4	100	21.5(±1.5)	20.7(±3)	Summer experiment (Sherlock & Goh, 1983b)
Urea (aq)	57.1	2.7	0.030	0.149	20.4	100	16.8(±1.5)	17.4(±3)	
Urine	88.2	6.0	0.0146	0.149	8.3	200	24.4(±5.8)	22.4(±5)	Autumn experiment (Sherlock & Goh, 1983b)
Urea (aq)	88.2	6.0	0.0155	0.058	8.3	200	28.4(±6.4)	19.3[22.5]	
Urine	100	0	0.0258	0.230	23.2	150	28.4	17.2	Simulated from data of Vallis et al. (1982)
Synthetic urine	100	0	0.0183	0.230	16.0	240	20→40d	9.8 [26.2]	Simulated from data of Holland & During (1977)

a actual values : 0→23 h, k_3 = 0.055; 24→60 h, k_3 = 0.026; 60→100 h, k_3 = 0.0175.

b uncertainties are standard errors.

c uncertainties based on standard deviations of pH measurements (see text).

d loss not measured directly but estimated from N recovered (see text).

[ ] value obtained using modified soil surface pH (see text).

4.3 RESULTS

4.3.1 Comparisons Between Measured and Predicted Ammonia Losses

4.3.1.1 Summer experiments

The results obtained in the summer experiments (Table 4.1) show excellent agreement between measured $NH_{3(g)}$ losses in summer and those predicted by the model. At 100 hours after application when volatilization was virtually complete, the measured cumulative loss from the urine patches was 21.1% (20.7% predicted) and 16.8% from the urea solution treatment (17.4% predicted). The measured cumulative NH_3-N loss values for the 10 low resolution sampling times spanning this period were very highly correlated with predicted values ($r = 0.998$ *** for both treatments).

These predictions were obtained using air temperatures recorded hourly with interpolations appropriate to the computer program iteration time (6 minutes). Using only the mean soil surface air temperature (20.4°C) made little difference to the total losses predicted (i.e. 21.9% from urine and 17.6% from urea). Actual temperatures are useful, however, in providing a more rigorous test for the model since they permit the calculation of instantaneous $NH_{3(g)}$ fluxes (Figures [4.1] and [4.2]).

Correlations between measured and predicted fluxes for the 33 high resolution sampling times were again very highly significant ($r = 0.951$ *** for urine and $r = 0.885$ *** for urea solution). More importantly, the mean measured high resolution fluxes were not significantly different from those predicted ($P \leqslant 0.05$). Measured and predicted means were respectively 0.310% per hour and 0.302% per

Figure 4.1 Verification of the simplified volatilization model using "summer" urine patch data.

A. Points = measured high resolution $NH_{3(g)}$ fluxes (3 replicates).

Solid line = predicted $NH_{3(g)}$ flux.

B. Points = measured pH (0 - 0.5 cm, soil : water = 1 : 2.5).

Solid line = interpolation used in model.

(I) = standard deviation (n = 5).

C. Soil surface air temperatures used in model.

Figure 4.1

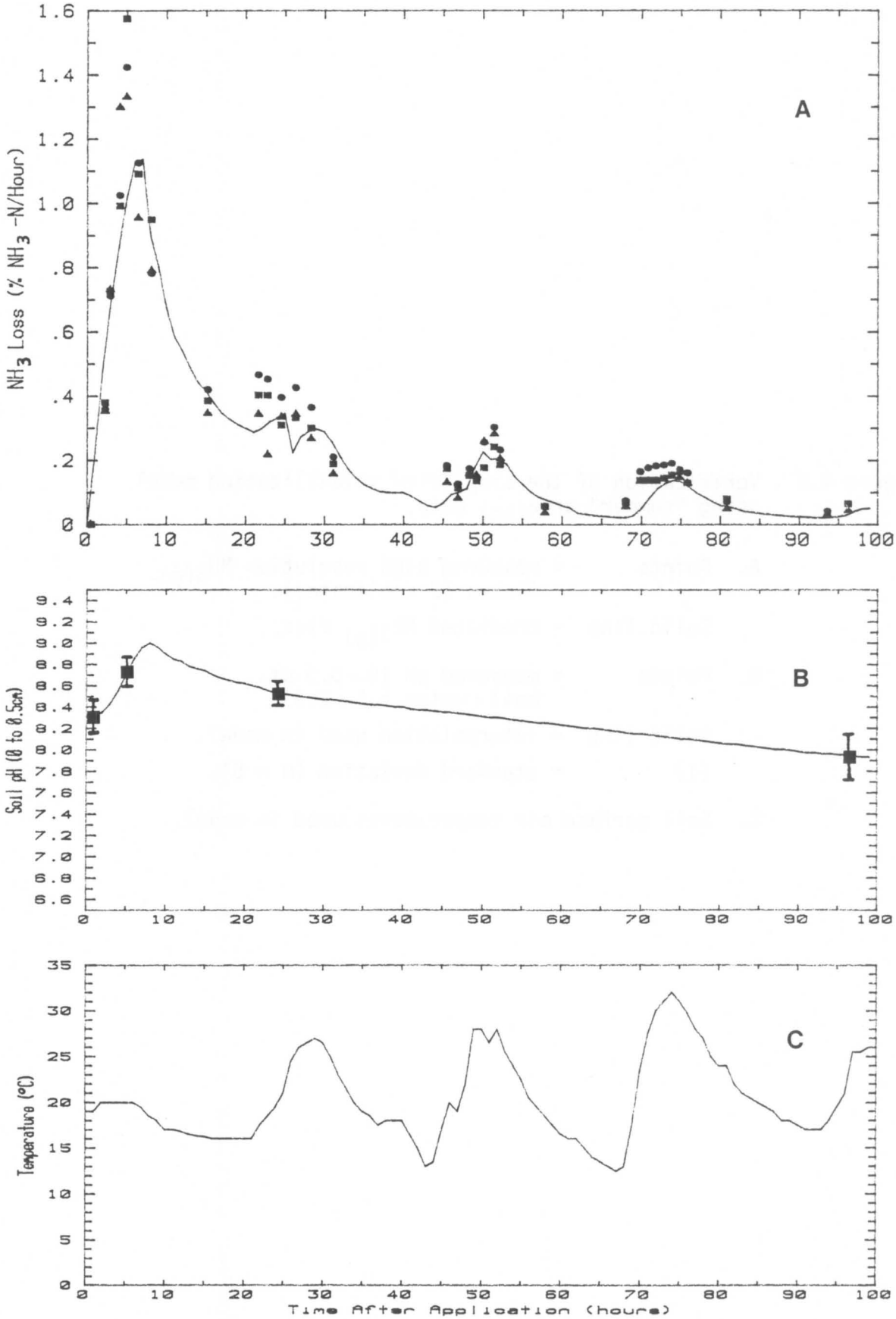

A
NH_3 Loss (% NH_3 -N/Hour)
1.6
1.4
1.2
1.0
.8
.6
.4
.2
0
0 10 20 30 40 50 60 70 80 90 100
B
Soil pH (0 to 0.5cm)
9.4
9.2
9.0
8.8
8.6
8.4
8.2
8.0
7.8
7.6
7.4
7.2
7.0
6.8
6.6
0 10 20 30 40 50 60 70 80 90 100
C
Temperature (°C)
35
30
25
20
15
10
5
0
0 10 20 30 40 50 60 70 80 90 100
Time After Application (hours)

Figure 4.2 Verification of the simplified volatilization model using "summer" $urea_{(aq)}$ data.

A. Points = measured high resolution $NH_{3(g)}$ fluxes (2 replicates).

Solid line = predicted $NH_{3(g)}$ flux.

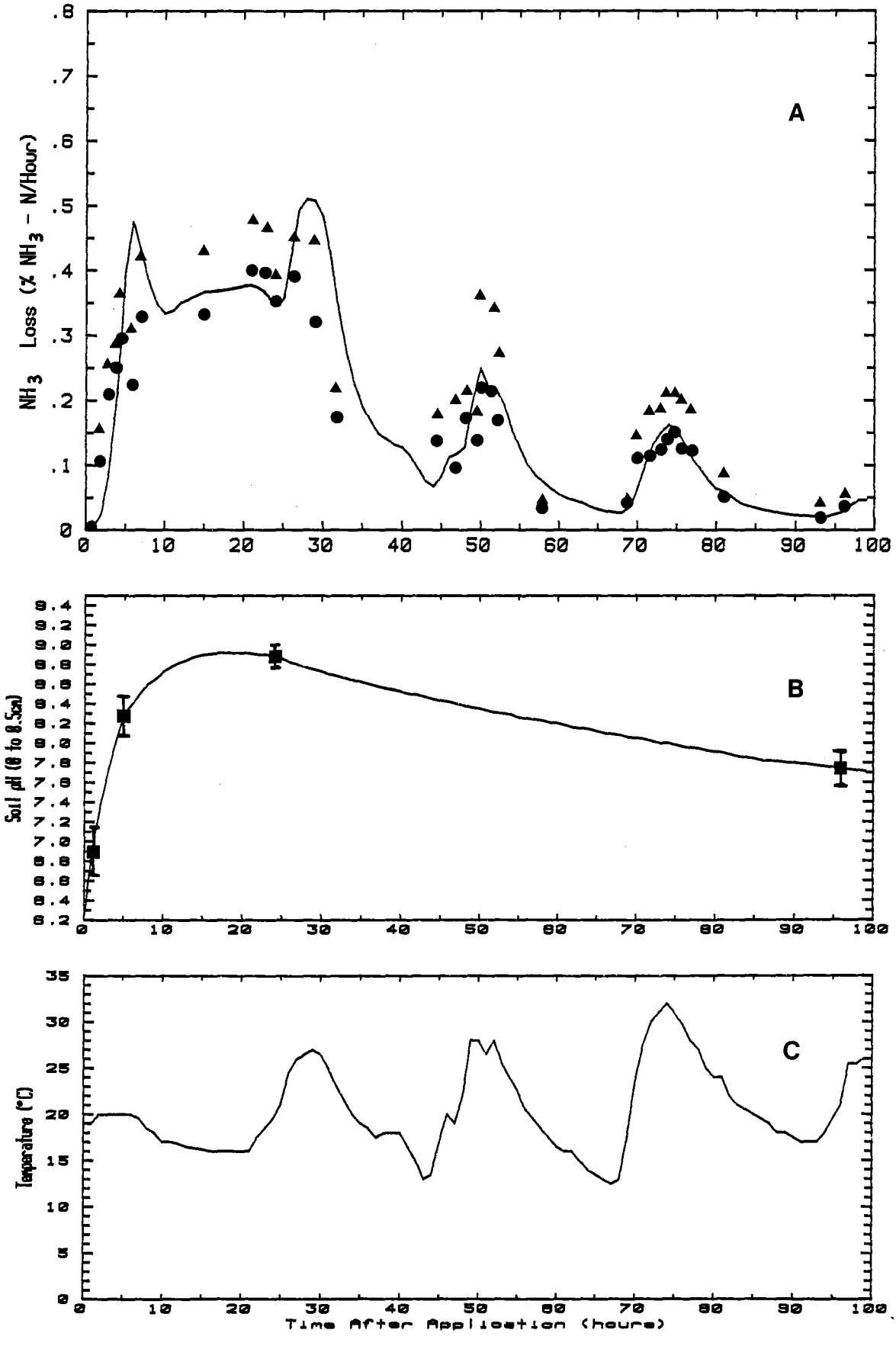
B. Points = measured pH (0 - 0.5 cm, soil : water = 1 : 2.5).

Solid line = interpolation used in model.

(I) = standard deviation (n = 5).

C. Soil surface air temperatures used in model.

Figure 4.2



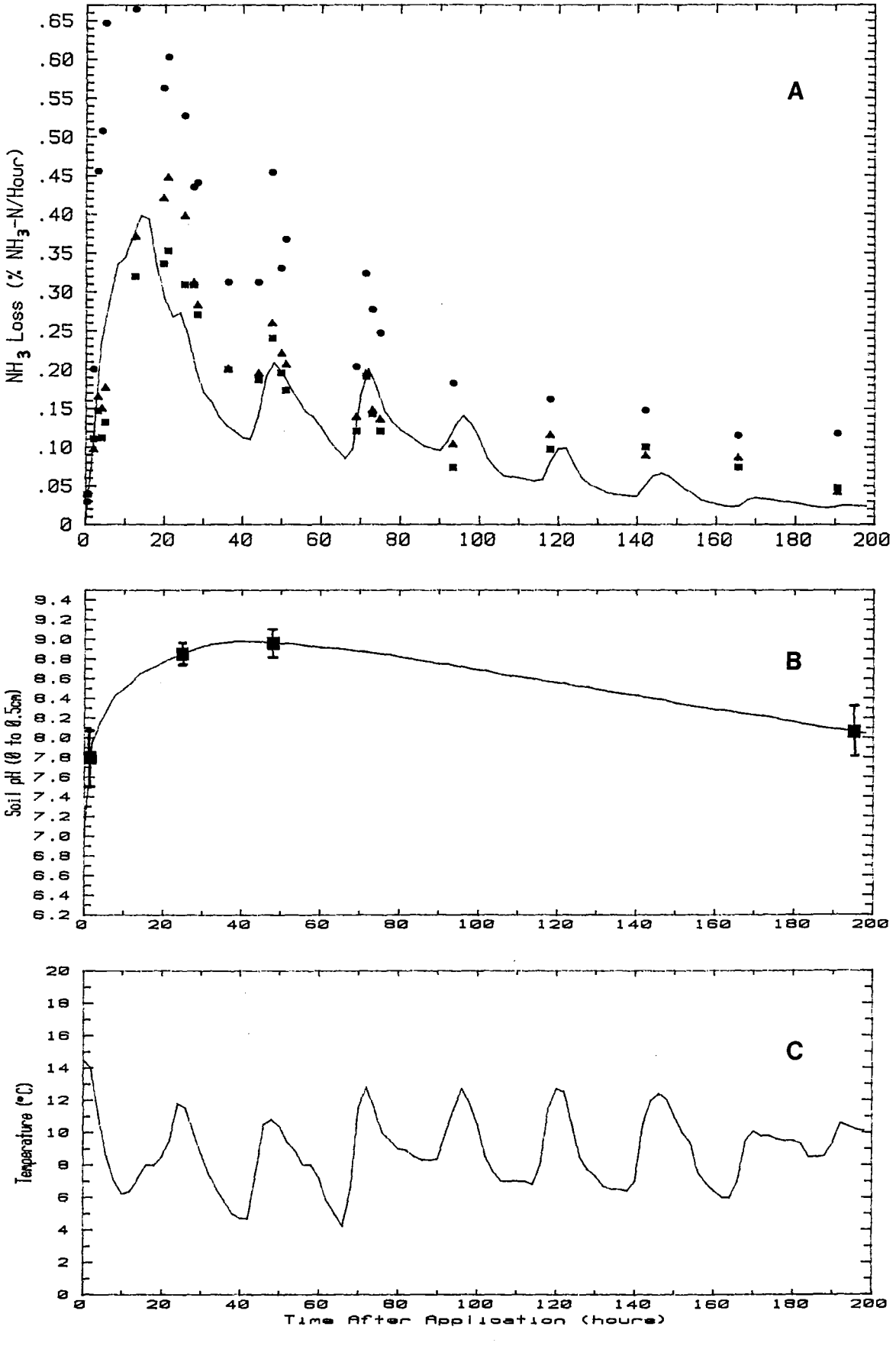
hour from the urine patches and 0.220% per hour and 0.214% per hour from the urea solution treatment.

4.3.1.2 Autumn experiments

Results from the autumn experiments (Table 4.1) also show reasonable agreement between predicted (22.4%) and measured (24.4%) losses for the urine treatment but somewhat poorer agreement between predicted (19.3%) and measured (28.4%) losses for the urea solution treatment. The poorer agreement for the $urea_{(aq)}$ treatment might be partially explained by reference to the measured pH values for the layer immediately below the soil surface (see Figure 2.7). The soil pH at 0.5 - 1.0 cm was uncharacteristically higher (pH = 8.4) than the soil surface (pH = 7.8) at the 192 hour sampling time. Predictions based on interpolated 0.5 - 1.0 cm pH's during the 50 - 200 hour period boosted the calculated losses to 22.5% (Table 4.1). This approach is, however, inconsistent with the derivation of the simplified model which assumes losses occur only from the soil surface and therefore are a function only of soil surface (0 - 0.5 cm) pH.

It must be noted, however, that the non-enclosed plots used for mineral-N and pH analyses were unshielded from rain. Although no rain fell during the summer experiment, 12.4 mm fell on the fourth day of the autumn experiment. This would not have directly affected the $NH_{3(g)}$ losses from the enclosed plots but it may have leached some $NH_{3(aq)}$ below the soil surface in the non-enclosed plots. Thus, the 0 - 0.5 cm pH values used as the 192 hour predictors in the simulation model may have been lower than the actual soil surface pH within the aspirated enclosures. When this is considered, the use of the 192 hour 0.5 - 1.0 cm value appears justified.

Figure 4.3


A
NH_3 Loss (% NH_3-N/Hour)
.65
.60
.55
.50
.45
.40
.35
.30
.25
.20
.15
.10
.05
0
0 20 40 60 80 100 120 140 160 180 200
B
Soil pH (0 to 0.5cm)
9.4
9.2
9.0
8.8
8.6
8.4
8.2
8.0
7.8
7.6
7.4
7.2
7.0
6.8
6.6
6.4
6.2
0 20 40 60 80 100 120 140 160 180 200
C
Temperature (°C)
20
18
16
14
12
10
8
6
4
2
0
0 20 40 60 80 100 120 140 160 180 200
Time After Application (hours)

The greater overall variability between measured losses from replicate plots of both treatments as well as between replicate soil surface pH measurements (Figure [4.3]) used for the predictions renders the autumn data sets less valuable as tests for the model than the summer sets.

4.3.1.3 Predictions from simulation using published data set of Vallis *et al.* (1982)

The published "February" data set of Vallis *et al.* (1982) did not include continuous soil surface air temperatures. Nevertheless, predictions using the mean air temperature recorded 10 cm above the plots were still possible. Using these published data the simulation model predicted a 17.2% N-loss after 6 days compared with 28.4% estimated by the authors. The apparent discrepancy may be due partly to volatilization from the urine intercepted by leaf surfaces. Since no estimate was available for the fraction of the applied urine intercepted by herbage, it was assumed in this simulation that all volatilization occurred from the soil surface. This assumption is almost certainly incorrect. The nature of the pasture *(Nandi setaria)* was morphologically different from the predominantly ryegrass *(Lolium perenne)* pasture on which predicted hold up was based. Also its height (10 - 12 cm) was considerably greater than that in the field experiments described here. These factors would probably combine to intercept more of the applied solution and may thus account for the 11.2% difference between prediction and measured results above.

4.3.1.4 Predictions from simulation using published data set of Holland and During (1977)

Using the pH and mean temperature values from the "October" field experiment of Holland and During (1977), the simulation model predicted a loss of 9.8% of the applied-N as $NH_{3(g)}$ 10 days after urine application. The authors did not directly measure $NH_{3(g)}$ loss but estimated it at between 20 - 40%. Here, leaf and litter surface volatilization information was again unavailable and therefore in the simulation, losses by this mechanism were assumed to be zero. This (probably invalid) assumption may explain some of the apparent discrepancy between observations and predictions. However, the discrepancy is more likely due to the pH values used. These were obtained from 0 - 1.5 cm cores and may therefore not correctly characterize the soil surface pH as required by the simulation model. For example, in this current study it was shown that pH values were between 0.3 - 1.2 units higher in the 0 - 0.5 cm layer compared with the 0.5 - 1.0 cm layer in simulated urine patches on a silt-loam soil in summer (see Figure [2.7]). Similarly, Vallis *et al.* (1982) reported pH's in the surface 0 - 0.5 cm layer of urine patches on a yellow podzolic soil 0.3 - 0.7 pH units greater than those of the 0.5 - 1.5 cm layer.

On the assumption that the 0 - 1.5 cm measurements underestimated surface pH, the data of Holland and During were adjusted by uniformly adding 0.5 to the pH values used in the initial simulation. After the program was re-run, a predicted loss of 26.2% was obtained. This is almost three times that originally calculated and more in keeping with their original estimates. This exercise clearly illustrates the sensitivity of the volatilization model to pH.

4.3.2 Disposition of Mineral-N in Soil and Volatilized $NH_{3(g)}$

4.3.2.1 Topsoil compartment

Substantial movement of applied solutions below 2.5 cm soil depth occurred only during the summer experiment and was attributed to rapid mass flow down large soil pores present because of the dry conditions prevailing (Table 4.1). During summer, approximately 30% of the urine and 40% of the urea solution recovered (i.e. mineral-N + volatilized $NH_{3(g)}$) was located below 2.5 cm after mass flow had ceased (24 hours) (Appendix II).

In autumn, the higher soil moisture content restricted mass flow although in several core samples substantial mineral-N was detected below 2.5 cm (Appendix II). However, 60% of the urine and urea treated plots had more than 90% of their mineral-N in the top 2.5 cm or accounted for as $NH_{3(g)}$, 25 hours after application. Therefore, to characterize the disposition of mineral-N within the topsoil compartment for the simulation model, the modal value of 94% was used for both treatments (Table 4.1).

In both summer and autumn, the fraction of the N below the topsoil (0 - 2.5 cm) compartment remained almost constant during the periods of $NH_{3(g)}$ loss.

The mineral-N recovery data reported by Holland and During (1977) and Vallis *et al.* (1982) also indicate little movement of the applied urine beneath the soil surface layer. In the computer simulations using their data it was therefore assumed that 100% of the N remained in effective chemical equilibrium with the soil surface and was subject to possible volatilization as $NH_{3(g)}$ (Table 4.1).

4.3.2.2 Leaf and litter surfaces

The volume of urine retained on the leaf and litter surfaces (6 ml) was not directly measured. It was estimated by comparing the measured high resolution $NH_{3(g)}$ fluxes from the summer urine treatment with values predicted by the volatilization model. There was excellent agreement when predictions were made using the soil only volatilization model for all sampling times except the 15 hours immediately following application, during which, measured fluxes greatly exceeded predictions. This early discrepancy effectively disappeared, however, when the leaf and litter surface subroutine was included in the computer simulation. For optimal agreement the intercepted volume was set at 6 ml (i.e. 4% of the 150 ml applied). Similar discrepancies for the summer urea solution treatment and both autumn treatments also virtually disappeared when the leaf and litter surface subroutine was used. A 6 ml intercepted volume was again assumed for the autumn experiments, but during summer, the dry herbage was visually hydrophobic and appeared less wetted by aqueous urea than by urine. Consequently, for the summer $urea_{(aq)}$ treatment only, an intercepted volume of 4 ml was used in the computer simulation (Table 4.1).

Mineral-N analyses of the topsoil (0 - 2.5 cm) compartment included solution held on the leaf and litter surfaces. For use in the computer simulations this fraction of the applied-N (e.g. 70% and 94% for summer and autumn urine treatments respectively) was partitioned between the soil only model and the leaf and litter surface subroutine as described above.

As stated previously, interception of applied urine on leaf surfaces was not reported in the other work used here (Holland and During, 1977; Vallis *et al.*, 1982). Therefore, the computer simulations using these data sets assume no hold up of solution. Discrepancies between predicted and measured $NH_{3(g)}$ losses in these cases (Table 4.1) are probably due in part to unaccounted for leaf and litter surface volatilization.

4.3.3 Soil Surface Volatilization Constants (k_3)

Values for k_3 were calculated using the exponential regression technique described previously (section 3.6.2) and are shown in Table 4.1. The theoretical minimum number of soil surface pH determinations required to evaluate a k_3 is two (i.e. at the beginning and end of stage 2 volatilization). However, it could be difficult to distinguish the end of stage 2 volatilization if only 2 pH measurements were used. In that case, a linear interpolation between the 2 measured values of soil surface pH may tend to underestimate k_3 and hence underestimate the resulting $NH_{3(g)}$ flux. However, if this happened, the actual pH values used within the computer simulation would tend to overestimate the resulting $NH_{3(g)}$ flux. These two effects would to some extent compensate for each other. Except for the summer experiment with urine (Figure [4.1]), and the "February" experiment reported by Vallis *et al.* (1982), only two pH measurements were available for evaluating a k_3 from each of the remaining data sets.

4.3.4 Rates of Urea Hydrolysis

It was shown previously (Table 2.7) that for the summer and autumn experiments, urea hydrolysis in the topsoil could be adequately described by first-order kinetics. Rate constants ranged from 0.230 - 0.058 h^{-1}, corresponding to urea half-lives of 3.0 - 12.0 hours respectively (Table 4.1). Urea in urine tended to hydrolyse more rapidly than pure urea and for both solutions hydrolysis was more rapid during summer due to the warmer air temperatures (Table 4.1).

For the experiments of Holland and During (1977) and Vallis *et al.* (1982), urea hydrolysis was reported to have proceeded rapidly. Since no formal rate constants were given, the summer urine treatment value of 0.230 h^{-1} was used in both cases. This approximation is valid since computer simulations show the model is relatively insensitive to the rate of urea hydrolysis when hydrolysis is rapid.

4.3.5 Estimation of Uncertainties

Uncertainties associated with the predicted total % loss values are difficult to quantify since most of the factors contributing do so in a complex non-linear manner. The fraction of the applied solution in effective equilibrium with the soil surface within the topsoil compartment is clearly an important factor and may be difficult to estimate. Also, the fraction of the applied N on the leaf and litter surfaces is important since computer simulations show loss of N as $NH_{3(g)}$ from this compartment is rapid and complete. If the fraction of N assumed intercepted is greater than actually occurs then predicted losses will be correspondingly greater. The influence of uncertainties in this term will decrease as applied

volume increases and as the pasture height and density decreases.

The other main contributors are the hourly pH values used in the simulation. These are obtained by interpolation between the means of measured pH (0 - 0.5 cm) values (e.g. Figure [4.1]). The uncertainties assigned to the total predicted % loss values from both the summer and autumn data sets are based entirely on the standard deviations (S.D.) of these measured pH values. To obtain an estimate of the net uncertainty due to this factor, the computer simulation was performed 3 times for each set of input data. Firstly, using mean interpolated pH values and then using mean (± S.D.) interpolated pH values. The predictions obtained showing the limits of these uncertainties are presented in Table 4.1.

Similar calculations were not possible for the other data sets. However, the uncertainties due to pH variation were probably comparable to those calculated above.

4.4 DISCUSSION

The field experiments used for this current verification exercise were not set up to specifically test this model but considering the many assumptions and approximations on which the model was based, and the limited data available, the general agreement between predictions and measurements is very encouraging. Where discrepancies occurred, they generally resulted in underestimations of loss and highlighted certain factors which clearly need further independent study.

For example, the role of herbage is ambiguous in that it provides an essentially exchange free surface for the rapid volatilization of $NH_{3(g)}$ from retained moisture films, while simultaneously allowing

stomatal uptake of N by the plant. Volk (1959) determined that 20 - 30% of the aqueous urea applied directly to pasture grass leaves was lost as $NH_{3(g)}$ with the remainder presumably taken up by the plants. These values were subsequently confirmed by Simpson and Melsted (1962) using labelled urea. Doak (1952) found that fresh ryegrass plants when immersed in urine and allowed to drain retained a surface coating equivalent to 36% of the fresh herbage weight. Based on this, and herbage weights covering a 300 cm^2 urine patch (e.g. 26 g in autumn) over 9 ml of urine would be expected to be intercepted. However, the fraction of an applied solution obstructed from reaching the soil surface is likely to depend on not only the nature, height and density of the herbage but also seasonal considerations, particularly as these influence litter density, together with possible direct stomatal uptake and the mode of application and hence droplet size and distribution. To accurately evaluate the influence of all these factors on intercepted volume would be difficult and no published estimates are available. The 4 - 6 ml used here is, however, not inconsistent with the net effect of these mechanisms.

To calculate volatilization rates from this intercepted solution the same factors described previously (e.g. urea hydrolysis rate, pH, temperature) must be characterized. An independent measurement of these factors would be very difficult and was not attempted in this current study. Instead, several simplifying assumptions and approximations were adopted. For example, it was assumed that urease activity and hence urea hydrolysis rates on leaf and litter surfaces were the same as those measured for the topsoil compartment. Although this was probably not the case (McGarity and Hoult, 1971),

computer simulations indicate that the model is relatively insensitive to changes in the rate of urea hydrolysis and the approximation is therefore valid. Similarly, the pH of the soil surface (0 - 0.5 cm) was assumed to also adequately characterize the pH of the solution on these other surfaces. Temperature was treated similarly.

It was also assumed that M_V' [equation 4.2] remained constant throughout a volatilization event. This is obviously incorrect as evaporation of surface droplets occurs quite readily under most daytime field conditions. However, the short half-life for $NH_{3(g)}$ loss from this compartment means the rate of loss will depend mainly on the rate of urea hydrolysis and will be little affected by changes in M_V'

Finally, it was assumed that volatilization occurs simultaneously but independently to the atmospheric sink from both the topsoil (0 - 2.5 cm) compartment and the surface moisture films. Again, this was probably incorrect in reality since, for example, it has been shown by Denmead *et al.* (1976) that morning dew formation on leaf surfaces can act as a sink for $NH_{3(g)}$ lost from the soil surface. However, that study involved tall dense plants. For the short pasture considered here, the closeness of the atmospheric sink means substantial interaction between compartments is probably unlikely.

While the influence of plants may be ambiguous, by contrast the pivotal role of surface soil pH is now abundantly clear. What is less clear is the best method for measuring it under the dynamic regime imposed by rapid urea hydrolysis and subsequent volatilization. In this current work it was shown that a soil / water slurry prepared and measured within minutes of sampling was adequate in formulating input data for the model. Large changes in the measured pH values occurred when these same slurries were allowed to stand. When these later

values were used in computer simulations, they resulted in poorer predictions of $NH_{3(g)}$ loss. The pH values used in the simulations of the work of Holland and During (1977) and Vallis *et al.* (1982) might also have suffered in this way. It may be more appropriate therefore to use the technique employed by Doak (1952) and attempt direct *in situ* measurements using a portable pH meter. This would almost certainly be the technique needed should the model be employed to assess volatile losses following surface applications of urea prills.

In the past, many investigators have attempted to correlate the extent of $NH_{3(g)}$ volatilization with native soil pH and these attempts have met with only limited success (e.g. Wahhab *et al.*, 1956; Volk, 1959; Ernst and Massey, 1960; and section 1.2.1.1). There have been comparatively fewer reports of the temporal pH changes which accompany both urea hydrolysis and subsequent $NH_{3(g)}$ volatilization. More recently, Lyster *et al.* (1980) showed $NH_{3(g)}$ loss from urea was correlated with maximal pH values generated following fertilizer addition. This current study has demonstrated that the full course of these pH changes must be characterized before realistic estimates of the extent of $NH_{3(g)}$ loss are possible.

The use of enclosures to directly measure $NH_{3(g)}$ losses was discussed in section 2.3.3.4. Several investigators have questioned this technique and their well founded criticisms relate mainly to the perturbing influence that some enclosure designs have on the dynamics of $NH_{3(g)}$ loss (e.g. Beauchamp *et al.*, 1978; Freney *et al.*, 1981; Vlek and Craswell, 1981). Where air flowrate is either absent or just restricted, the 'volatilization potential' of the system is seldom realised and the extent of the measured loss might be greatly underestimated

(Vlek and Craswell, 1981). In these current experiments no attempt was made to simulate ambient wind-speed, as for example was done by Vallis *et al.* (1982), and it might be argued that this imparts tight limitations on any comparisons between predictions based on the model and the direct measurements. This would be true if the pH and temperature readings used as inputs to the model were obtained from enclosed aspirated micro-plots. They were not. They were instead obtained from similarly treated plots fully exposed to the changing influences of ambient conditions. The observation that predictions made using actual ambient measurements so reliably predicted the detailed pattern of $NH_{3(g)}$ loss in enclosed plots (Figure [4.1]) lends strong circumstantial support to previous comments (section 2.3.3.4) that any perturbing influence the enclosures had was minimal.

The model was conceived in an attempt to better understand the factors driving $NH_{3(g)}$ loss from urine patches under field conditions and in that regard it has largely succeeded. The simple nature of the input data and the fact that it requires no soil-specific parameters suggest that the model could also be utilized as a predictive (or retrodictive) tool. An intriguing potential application stems from the fact that the actual amount of nitrogen and the volume of solution applied to the pasture surface are not required inputs. Both volatilization rates and the final loss may be expressed as percentages of N applied. If the assumption is made that all the applied nitrogen remains in effective equilibrium with the soil surface then *in situ* pH measurements of actual and non-simulated urine patches as occur in normally grazed pastures should, in theory, provide an estimate of the potential loss.

Before that, however, the model requires further testing under a greater variety of circumstances and its limitations must be reiterated. It is a very simplified description of the dynamics of a complex system. Further, it must be appreciated that the assumptions and approximations needed for its development (see Chapter 3) may not hold in situations other than short pasture receiving aqueous urine or urea, within essentially non-leaching, non-nitrifying environments. However, these are the very conditions existing in extensive arid and semi-arid pastoral ecosystems, and in this context it may provide a useful tool in the development of a more complete understanding of an important aspect of the nitrogen cycle.

CHAPTER 5

GENERAL DISCUSSION AND CONCLUSION

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CHAPTER 5

GENERAL DISCUSSION AND CONCLUSION

5.1 PRELIMINARY EXPERIMENTS

The primary objective of a series of preliminary field experiments carried out in 1978 was to develop a field sampling procedure for trapping and quantifying $NH_{3(g)}$ and $NO_{2(g)}$ emissions from urine patches on pasture soils. This was completed successfully and the apparatus was then employed to examine more closely the dynamics of volatilization and to quantify the losses under different seasonal conditions. A previous study had shown volatilization from urine patches to be a rapid process and essentially complete after several days (McGarity and Rajaratnam, 1973). This was confirmed in the preliminary field experiments which also showed that instantaneous $NH_{3(g)}$ fluxes were closely related to diurnal temperature fluctuations. The early estimates of $NH_{3(g)}$ losses from urine patches made in 1978 were, however, somewhat lower than when a similar technique was used at the same site several years later. The reasons for this are unclear and in the absence of soil mineral-N data for the 1978 experiments it would be unwise to speculate.

The preliminary experiments also established that nitrogen dioxide emissions were negligible during the period of principal $NH_{3(g)}$ loss immediately after urine application. These findings have since been confirmed by independent experiments in Southland (Carran *et al.*, 1982). Nitrite + nitrate levels in the topsoil of simulated urine patches in the summer and autumn field experiments

of 1982 were only slightly elevated above the untreated controls (Tables 2.5 and 2.6). Thus, the formation and loss of $NO_{(g)}$ and $NO_{2(g)}$ would have been unlikely at that time also and largely vindicates the decision not to pursue further measurements of these gases.

5.2 FIELD EXPERIMENTS

A consideration of the direct field measurements made during 1982 in this present study supports the established view (Ball *et al.*, 1979; Ball and Keeney, 1981) that volatilization of ammonia from sheep urine patches constitutes an important pathway for N loss from a grazed pasture system. The magnitude of this loss was estimated at about 20% of urine-N or about 30% of the total N inputs for a typical ryegrass / white clover pasture in Canterbury which had received no artificial N fertilizers and was non-irrigated. These values are in substantial agreement with measured and estimated gaseous losses from urine patches in intensively farmed pastoral systems in other areas of New Zealand (Holland and During, 1977; Ball, 1982; Carran *et al.*, 1982).

5.3 SIGNIFICANCE OF $NH_{3(g)}$ LOSSES FROM URINE PATCHES

The relevance of these losses to the overall N budget for New Zealand can be estimated from the following simple considerations. Assuming a mean 20% N loss from all sheep urine patches throughout New Zealand, a urine-N concentration of 0.95% and a daily urine

volume of 2900 ml $sheep^{-1}$ (Doak, 1952), then the total annual N loss through volatilization from the urine patches of the 70 million sheep in New Zealand is about 0.14 T g (i.e. 140 thousand tonnes). However, it is highly unlikely that this value constitutes a net loss from the national N budget since it has been established from overseas studies (e.g. Hutchinson *et al.*, 1982) that only a small fraction of volatilized $NH_{3(g)}$ is transported through the atmosphere to any appreciable distance. Considering the geographical isolation of New Zealand it is reasonable to assume, therefore, that the bulk of this NH_3-N re-enters the ecosystem as "background-N". It can be calculated that if all of this NH_3-N was evenly distributed across the total area of New Zealand then each hectare would receive an annual input of 5.3 kg N. Thus, about a third of the accepted "background-N" input (15 kg N ha^{-1} yr^{-1}, see section 2.3.3.1) is accounted for as being derived from sheep urine patches. Asymbiotic N fixation, N in pollen and dust, NH_3 derived from the decomposition of plant material and NH_3-N derived from bovine urine patches probably account for the bulk of the rest. Thus, the volatilization of $NH_{3(g)}$ from sheep urine patches viewed from within the New Zealand context constitutes an important mechanism not only for N loss from intensively-managed pastures but also for the input of N to areas of low N status.

5.4 STRATEGIES FOR REDUCING $NH_{3(g)}$ LOSSES FROM URINE PATCHES

It is in the interests of the pastoral farmer to attempt to minimise volatilization losses if at all possible since it would appear from the calculations above and in section 2.3.3.1 that $NH_{3(g)}$

losses will exceed gains in the majority of intensively-managed pastoral ecosystems. Unfortunately, in a free grazing situation it would be difficult to tailor conditions to reduce losses as might be possible with an application of artificial fertilizer, since limited control is only possible over one or two important factors. The farmer can control the stocking rate and through the use of fencing can implement an intensive rotational grazing regime to help reduce the effects of camping and achieve a more even return of cycled urine-N. Whether this would also reduce volatilization losses is unclear and no studies comparing the effects of grazing regimes on volatile N losses have been reported.

Another factor over which limited control can be exercised is soil moisture. Ball and Keeney (1981) reported $NH_{3(g)}$ losses of 66% from urine applied to pasture in Manawatu, New Zealand under warm dry conditions while only 16% was lost under warm moist conditions. Similarly, recent studies in Southland (Carran *et al.*, 1982) indicate that losses from urine patches on soil at field capacity were half of the losses measured near wilting point (i.e. 17% and 36% respectively). While this result confirms the earlier reports of Ball and Keeney (1981) both results remain at variance with data obtained under similar conditions in Queensland, Australia. There, Vallis *et al.* (1982) found losses under warm moist conditions were about twice those measured under warm dry conditions at the same grazed pasture site (i.e. 28.8% and 14.4% respectively). These apparently conflicting results may have resulted from channelling of applied urine down large soil pores and worm holes present in the Australian study under dry conditions but absent in the two New Zealand studies. Data to support this suggestion are unavailable. It would appear, however,

that under some conditions the efficacious use of irrigation prior to grazing may help to dilute the ammoniacal-N generated at the soil surface within urine patches which in turn could help to reduce $NH_{3(g)}$ losses.

Quin (1981) has made several novel suggestions to increase the efficiency of urine-N recycling in flat or rolling free draining pastures which, by implication, might also influence the extent of volatilization. These include: the use of catheters or the breeding of animals with small bladders to increase urination frequency, the fitting of suitable devices to the animals to spread the urine over a larger area and the use of salt to increase thirst and thereby increase urine output and decrease N concentration in the urine. Whether any of these techniques are feasible remains to be seen.

5.5 SCOPE FOR FUTURE RESEARCH

5.5.1 The Effects of Soil Moisture

The field experiments in this present study failed to examine several areas of concern while at the same time they have highlighted other areas of interest and several previously unforeseen factors which could be important in refining current knowledge. The effect of soil moisture through a comparison of volatilization losses under several moisture regimes was not examined in the present study. In view of the conflicting results obtained in the other studies discussed earlier, more information is required on the effects of soil moisture in so far as it directly affects $NH_{3(aq)}$ concentrations at the soil surface and as it indirectly affects volatilization by influencing the depth of urine infiltration.

5.5.2 The Effects of Plants and Surface Litter

A hitherto largely unrecognised passive influence by plant leaves and litter surfaces was implicated by the results of this present study. The measured $NH_{3(g)}$ fluxes were consistent with a small fraction of the applied N being volatilized rapidly and completely from a free liquid surface. Free liquid could exist on leaf and litter surfaces which were present on the plots and would therefore have intercepted a portion of the applied solution. The volume of solution involved was not measured directly in the present study but was quantified on the basis of discrepancies between high resolution $NH_{3(g)}$ flux measurements and the predictions of a simplified soil volatilization model. While consistent with previous estimates of intercepted volumes (Doak, 1952), further research is required to develop methods by which intercepted volumes can be estimated directly as it would appear from this current work that the major portion of the N within the intercepted volume undergoes volatilization. This is likely to be a formidable task since as was stated earlier (see section 4.4) the fraction of the applied solution obstructed from reaching the soil depends on a large number of factors.

5.5.3 Fertilizer Application Practices

The effects of the superposition of recent and relict urine patches in simulated sheep camps and under mob-stocking situations (see section 2.3.3.3) has drawn attention to a potential problem of more immediate economic concern to the New Zealand farmer. This is the established practice of applying prilled urea fertilizer to pasture soon after mob-stocking in early spring and autumn (Black, 1983 personal

communication). Recent field experiments carried out at Lincoln College have attempted to assess the implications of this practice. Preliminary results indicate that 7.4% NH_3-N loss followed surface applications of urea prills at 30 kg N ha^{-1} but losses were considerably higher (e.g. 24.7%) when applied at the same rate to week old urine patches (Black, 1983 unpublished data). It is too early at this stage to assess the agricultural and economic significance of these results.

5.5.4 Ammonia Volatilization Predictions

Ammonia volatilization models produced by other workers have attempted to present a description of volatilization from unsaturated soils using well established chemico-physical principles and diffusion theory (Van Veen and Frissel, 1979; Parton *et al.*, 1981). Unfortunately, these models require accurate values for, and a knowledge of temporal variations in many specific input parameters. For example, the model of Parton *et al.* (1981) requires values for more than 14 input parameters which the authors themselves have recognised makes an experimental verification in its present form difficult. The application of these models as predictive tools appears unlikely unless they are simplified considerably.

The development of a simplified $NH_{3(g)}$ volatilization model must be seen as the most important outcome of this present work. It would appear to be the first simple predictive model to be formulated and it is hoped that it will go some way towards satisfying the call for "a relatively simple measurement technique ... that can be used for extensive measurements under a wide range of conditions" (Vlek and Craswell, 1981). The recent field experiments at Lincoln College

discussed earlier also provided a test of the ability of the model to predict losses from surface applied urea prills. Initial results were very encouraging with measured losses in close agreement with predictions (Black, 1983 personal communication). These experiments, however, fall outside the scope of this current work but will be reported elsewhere.

PART II

NITROUS OXIDE PRODUCTION FROM SIMULATED URINE PATCHES AND NITROGENOUS FERTILIZERS APPLIED TO PASTURE

CHAPTER 6

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CHAPTER 6

REVIEW OF LITERATURE

6.1 INTRODUCTION

The interconversion between the principal forms of soil mineral-N (NO_3^- and NH_4^+) is a multi-step bi-directional process initiated by soil micro-organisms and catalysed at each step by specific enzymes. Under certain conditions incomplete interconversion is achieved and gaseous nitrogen compounds may form and be released from the soil surface to the atmosphere. This release constitutes a net loss of "fixed-N" from the soil-plant system and from an agronomic perspective is generally undesirable. Compounds which have been identified include nitric oxide (NO), nitrogen dioxide (NO_2), nitrous oxide (N_2O) and dinitrogen (N_2). The loss of ammonia (NH_3) may also occur but since this is primarily a physico-chemical process and not enzyme catalysed, it was considered separately (see Part I).

An upsurge of interest in gaseous N loss from soil has occurred during the last decade. This has transpired not only out of concern for maximum efficiency of use in N fertilizers but also out of concern that their projected increased use might lead to increases in atmospheric N_2O concentrations and hence to a depletion of the ozonosphere (Crutzen, 1974). The photochemical breakdown of N_2O in the stratosphere yields NO which has a principal role in catalysing the breakdown of stratospheric ozone. The research funding made available has prompted many studies which have led to a greatly improved appreciation of the importance of this aspect of the nitrogen cycle.

The extent of gaseous N loss from soils had been inferred indirectly from N balance studies which generally showed unexplained 10-30% losses of applied mineral-N fertilizers (Allison, 1955). Recent advances in methodology have enabled direct measurements of NO, N_2O, and N_2 under field conditions and have generally confirmed the above estimates.

In this chapter the three principal mechanisms (i.e. denitrification, nitrification and chemo-denitrification) responsible for the production of these gases are discussed together with the factors which influence each of them. A brief discussion of the methods used to measure the release of these gases under field conditions is also included. It is not intended as a comprehensive review of the subject. For that, the reader should consult Delwiche (1981); Payne (1981a); Firestone (1982) and Nelson (1982).

6.2 DENITRIFICATION

6.2.1 Definition

Denitrification is classically defined as the biological reduction of nitrate (NO_3^-) to gaseous products (Payne, 1973). These products are principally N_2 and N_2O although NO has been detected on occasions. Microbiologists now recognise denitrification as a specific respiratory process carried out under anaerobic conditions by a limited number of bacterial genera in which NO_3^- or oxides derived from NO_3^- take the place of O_2 for the metabolization of organic matter and the generation of adenosine triphosphate (A.T.P.). In other words, nitrate and each

of the oxides derived from it serves in turn as an electron acceptor for the oxidation of an organic substrate with the nitrogen ultimately appearing as N_2. Collectively, this sequence is referred to as the pathway of denitrification (Payne, 1981a) and is often represented as:

$$NO_3^- \xrightarrow[\text{reductase}]{\text{nitrate}} NO_2^- \xrightarrow[\text{reductase}]{\text{nitrite}} NO \xrightarrow[\text{reductase}]{\text{nitric oxide}} N_2O \xrightarrow[\text{reductase}]{\text{nitrous oxide}} N_2$$

6.2.2 Enzymes and Micro-Organisms Involved

Specific enzymes catalyse each step in the pathway although not all denitrifying bacteria are capable of synthesising each of the enzymes necessary for complete reduction. Ingraham (1981) distinguished four groups of organisms which lack one or more of the reductases but which could still be regarded as partial denitrifiers. These are:

(a) Organisms that lack nitrite, nitric oxide and nitrous oxide reductases and are capable of only the limited reduction of nitrate to nitrite.

(b) Organisms that lack nitrous oxide reductase and are capable of reducing nitrate only to nitrous oxide.

(c) Organisms that only lack nitrate reductase and therefore reduce nitrite to dinitrogen.

(d) Organisms lacking nitrite reductase and nitrous oxide reductase and can therefore reduce nitrate to nitrite and nitric oxide to nitrous oxide.

The ability to carry out nitrate respiration (group 'a' above) is apparently widely distributed amongst bacteria and although these organisms themselves fail to generate nitrogenous gases their inclusion

as partial denitrifiers was justified on the basis that under anaerobosis they generate an electron acceptor (NO_2^-) which is directly utilizable by other denitrifiers (Ingraham, 1981). This "dissimilatory" reduction of nitrate is therefore distinguishable from the more common "assimilatory" nitrate reduction by virtue of the function that the reaction serves (Tiedje *et al.*, 1981). Assimilatory nitrate reduction occurs both aerobically and anaerobically, does not generate A.T.P. and involves the complete reduction of NO_3^- through to NH_4^+ which is then incorporated as amino acid-N into the tissue of the organism. It is common in many micro-organisms and most plants (Alexander, 1977). In contrast, the denitrification "dissimilatory" pathway occurs only under anaerobic conditions to generate A.T.P. with the products of each successive stage being excreted rather than assimilated by the micro-organism.

Payne (1981a) has preferred a different definition of denitrification and has listed 25 genera of bacteria that fulfil the particular task of reducing NO_2^- to NO. These include the 146 denitrifiers isolated in an extensive survey of 19 soils conducted by Gamble *et al.* (1977). In that major study, the largest group identified was *Pseudomonas fluorescens* which comprised 35% of all the strains isolated. Also identified were representatives of *Alcaligenes* as well as other *Pseudomonas* species and members of the *Flavobacterium* and *Corynebacterium*. The criterion used for classification as denitrifiers was, as in most previous studies of this sort, the ability of the culture to produce N_2 from NO_3^-. Consequently, denitrifiers lacking nitrous oxide reductase or nitrate reductase probably escaped identification. Ingraham (1981) has further pointed out that although *Pseudomonas fluorescens* "must constitute an

important fraction of denitrifiers in soil ... the necessary biases of such a study (the medium used to isolate strains, temperature of incubation, definition of denitrification) suggest that caution should be applied before lesser ecological roles are assigned to other denitrifiers". It is also necessary to remember that the most abundant organisms are not necessarily the most physiologically active.

It is also worth noting that most laboratory research has been carried out on *Paracoccus denitrificans*, *Pseudomonas denitrificans* and *Pseudomonas perfectomarinus*, none of which were isolated in the soil survey of Gamble *et al.* (1977). Therefore, the generalizations about denitrification based on *in vitro* studies of what appear to be relatively minor species must be viewed with caution.

Nevertheless, most workers agree that denitrifiers show a number of physiological and biochemical characteristics in common. For example, the great majority of denitrifiers studied are free-living aerobes and only begin using nitrogenous oxides as electron acceptors when O_2 availability is limiting. Only *Propionibacterium acidi-propionici* (a fermentative anaerobe) has no capability to respire O_2 (Bryan, 1981). There are reports of denitrifiers capable of respiring NO_3^- and NO_2^- under aerobic conditions via "oxydenitrification" (e.g. Vagnai and Klein, 1974; Voets *et al.*, 1975). However, "oxydenitrification" has only been observed where cell densities and organic matter levels are very high and it has been suggested that under these conditions rapidly respiring micro-organisms may limit O_2 availability and trigger denitrification (Bryan, 1981).

While the majority of the denitrifiers studied are free-living, several strains of the N-fixing micro-organism, *Rhizobium*, have been shown to denitrify NO_2^- and NO_3^- *in vitro*. Known *Rhizobium* denitrifiers

include examples of both free-living (Daniel *et al.*, 1980) and extracted symbiotic strains (e.g. Zablotowicz and Focht, 1979). Whether the symbiotic strains retain this ability under field conditions has yet to be demonstrated.

Other characteristics common to denitrifiers include the micronutrients needed for the synthesis or maintenance of activity of the nitrate and nitrite reductase enzymes. Molybdenum has been shown to be present in all isolates of nitrate reductase (Alexander, 1977) and copper is either contained in or required for the synthesis of nitrite reductase (Bryan, 1981). In addition, sulphur and iron appear necessary for enzyme activity and magnesium for the growth of the micro-organisms (Bryan, 1981). For a review of the characteristics of individual isolates see Payne (1981a) or Knowles (1982).

Much less is known about nitric oxide reductase and nitrous oxide reductase. Indeed, until recently the case for nitrous oxide as an obligatory intermediate in the denitrification pathway was still in dispute. Acceptance came with the discovery that in the presence of acetylene (C_2H_2) all denitrifiers that terminate dissimilatory reduction at N_2 undergo selective and reversible inhibition of the final $N_2O \rightarrow N_2$ step (Federova *et al.*, 1973; Balderston *et al.*, 1976; Yoshinari and Knowles, 1976; Klemedtsson *et al.*, 1977). Thus, nitrogen that normally would appear as N_2 appears as N_2O. This "acetylene block" is now widely used in the laboratory as a technique for estimating denitrification and several researchers have also used it under field conditions (see section 6.5.2).

Whereas the role of nitrous oxide as an obligatory intermediate is now universally accepted, the existence of a specific nitric oxide reductase and the role of NO as an obligatory intermediate in the

denitrification pathway is still in doubt. Recent reports by Garber and Hollocher (1981) would appear to rule out involvement of free NO as an obligatory intermediate for 5 common denitrifiers although enzyme-bound NO remained a possibility. More recently these same workers provided evidence for nitroxyl (NOH) as a possible intermediate (Garber and Hollocher, 1982). However, other workers maintain that the case for nitric oxide reductase and the role of NO as an obligatory intermediate is proven (e.g. Payne, 1981b). For a recent summary of the state of the debate see Bryan (1981) or Knowles (1982). Supporters of both these opposing views agree that with the greater understanding of the denitrification mechanism that is now slowly developing, it may be possible ultimately to promote the dissimilatory reduction of nitrogen oxides to NH_4^+ rather than to gaseous products which are not directly plant-available.

Unfortunately, this expressed optimism may be misplaced since in a recent study of non-denitrifying NO_3^- reducers, Smith and Zimmerman (1981) found that the vast majority of the strains isolated were also capable of generating N_2O. Their work indicated that non-denitrifying NO_3^- reducers were more numerous than denitrifiers in soil and could produce N_2O under a wide variety of conditions. The significance of this hitherto unrecognised mechanism to gaseous N loss under field conditions requires urgent attention.

6.2.3 Major Factors Affecting Denitrification from Soils

Populations of denitrifying micro-organisms in arable soils frequently exceed a million per gram of soil (e.g. Jacobson and Alexander, 1980) with higher concentrations generally present in the rhizosphere of plant roots (Alexander, 1977). Consequently, the

presence of denitrifiers in surface soils may be regarded as ubiquitous (Payne, 1981a) and given conditions conducive to the onset of anaerobosis a nitrogenous oxide and an oxidizable carbon source, denitrification would seem inevitable. Each of these factors and their interrelationships are examined below.

6.2.3.1 Moisture content and aeration

Moisture affects denitrification in two ways. Firstly, it is necessary to support normal microbial growth. In the absence of adequate moisture, growth of all micro-organisms (including denitrifiers) is greatly retarded. More important to denitrifiers in particular is the indirect influence of moisture on the aeration status of the soil. As soil pores fill with water following rainfall or irrigation, so the soil air is displaced. If this also coincides with high O_2 consumption (e.g. high microbial activity and high root respiration) the rate of O_2 diffusion through the soil water is unlikely to be adequate to sustain an aerobic environment. Arable soil is normally only saturated with water at the surface for brief periods following irrigation or rainfall. Recent direct field measurements have shown that during these periods, short bursts of the denitrification products N_2O and N_2 were produced from applied NO_3^- fertilizers and released from the soil surface (Ryden *et al.*, 1979b; Ryden and Lund, 1980). Peak losses of 0.05 - 0.4 kg N_2O-N ha^{-1} day^{-1} were recorded in each of these studies and were sustained only while the surface soil was effectively saturated. These workers also used the acetylene inhibition technique to estimate denitrification losses as N_2. Similar release patterns were noted but peak N_2 fluxes were about 4 times the magnitude of the N_2O peaks.

Complete saturation of the surface soil is not mandatory for denitrification. Anoxic zones and microsites may develop whenever biological O_2 demand exceeds the supply. Clearly, factors such as O_2 consumption rate, O_2 diffusion rate and structural factors such as pore geometry and degree of compaction are important (Rolston, 1981; Smith, 1977). In the two examples quoted earlier (Ryden *et al.*, 1979b; Ryden and Lund, 1980) small but measurable N_2O and N_2 losses were still recorded several days after each irrigation when the soil had dried out appreciably. These losses presumably arose from within anoxic microsites.

Gilliam *et al.* (1978) concluded from a study of the effects of soil profile characteristics on denitrification that any soil condition which impedes water flow will be positively related to denitrification. Consequently, they suggested that spatial variability in denitrification under field conditions is likely to be as great as observed variability in water movement. Climatic factors also influence soil aeration and may have more effect on the development of anoxic microsites than either cultivation or compaction (Smith, 1977).

6.2.3.2 Availability of organic matter

Denitrification is a respiratory process and therefore requires an oxidizable substrate. The availability of oxidizable organic matter is therefore an important factor moderating both the rate and total extent of denitrification. This has been recognised since late last century when the mixing of farmyard manure with nitrate fertilizer was discovered to be poor agricultural practice which could lead to substantial N losses through denitrification (e.g. Warmington, 1897, as reported by Payne, 1981a). It has only been in recent times that similar effects have been demonstrated by direct field measurements of

denitrification products. For example, Rolston *et al.* (1982) showed that denitrification losses from NO_3^- fertilizer were between 3 and 6 times higher when additional organic matter, supplied as chopped barley straw, was incorporated into the top 10 cm of soil 2 months prior to the fertilizer application.

The supply of readily decomposable organic matter may in some cases be the rate-limiting parameter in the kinetics of denitrification. In laboratory experiments, Burford and Bremner (1975) demonstrated very highly significant correlations ($r = 0.99$, $P \leq 0.001$) between denitrification potentials and both the water soluble and mineralizable C present in 17 surface soils which differed widely in pH, texture and total organic matter content. The correlation between the total organic carbon content and denitrification potentials of the soils, while still significant ($P \leq 0.05$) was lower ($r = 0.77$). These workers concluded that the water-soluble and mineralizable fractions of the native soil organic matter were particularly susceptible to decomposition and provided most of the substrate necessary for denitrification.

The supply of readily decomposable organic matter and mineralized-N can be particularly high in freshly drained organic soils and can lead to very high rates of denitrification. In a recent study of drained organic soils in the Florida Everglades, Terry *et al.* (1981) measured annual N_2O emission rates under field conditions of up to 165 kg N_2O-N ha^{-1} yr^{-1}. This rate exceeds by almost 2 orders of magnitude, typical N_2O emission rates from mineral soils (e.g. Denmead *et al.*, 1979; Bremner *et al.*, 1980; Mosier *et al.*, 1982).

The fraction of the total organic matter available for use by denitrifiers may also be increased by repeated wetting and drying cycles (Birch, 1958). Although this has yet to be unambiguously

demonstrated in the field, the drying of a soil, particularly at elevated temperatures, has been shown to increase its capacity to denitrify added nitrate under anaerobic conditions (Patten *et al.*, 1980).

High levels of readily decomposable organic matter can also affect denitrification indirectly through a general stimulation of microbial respiration and thereby accelerate the onset of anaerobosis. This effect may help explain the reports of "oxydenitrification" described earlier. Conditions such as this can also occur in the immediate environment of plant roots. When nitrate supply is non-limiting, the presence of plant roots accelerating denitrification is well known (e.g. Woldendorp, 1962; Volz *et al.*, 1976). Not only do dead roots and root exudates provide a ready source of oxidizable organic matter, but root respiration helps to decrease soil O_2 concentrations in the rhizosphere. It is not surprising therefore that denitrification activity is high in the immediate vicinity of roots but decreases rapidly only a few millimetres away (Smith and Tiedje, 1979). However, when NO_3^- concentrations are low, denitrification may be considerably reduced by the presence of plant roots. Smith and Tiedje (1979) have suggested that under these conditions the competition for NO_3^- between denitrifiers and plant uptake may lower nitrate concentrations and thereby reduce denitrification.

6.2.3.3 Nitrate concentration and pH

Denitrification rates in anaerobic soils have been shown to be proportional to the concentrations of NO_3^- and available C (Reddy *et al.*, 1982). At high NO_3^- levels, however, denitrification rates are frequently independent of NO_3^- concentration (e.g. Blackmer and Bremner, 1978).

This pseudo zero-order behaviour under laboratory conditions can be taken to mean that the overall denitrification reaction rate is controlled by the concentration of oxidizable organic matter. Following NO_3^- fertilizer applications under field conditions, zero-order kinetics may be expected also since the rate of C mineralization is likely to be the major rate determining factor. On the other hand, the situation may be complicated by the rate of diffusion of NO_3^- to anaerobic microsites. Since this process is concentration dependent it could render the denitrification kinetics under field conditions first-order with respect to nitrate (Rolston, 1981).

It is well established that an increase in soil NO_3^- concentration causes an increase in the ratio of N_2O/N_2 in the product gases (e.g. Nommik, 1956). This is of great significance from an environmental perspective since N_2O is known to affect the stability of the stratospheric ozone layer. Any factor which could effectively increase N_2O emissions is therefore important. Blackmer and Bremner (1978) made a detailed study of this reaction and concluded that NO_3^- inhibits the reduction of N_2O to N_2 by the denitrifying micro-organisms. The inhibitory effect of NO_3^- was also pH dependent and increased markedly with a decrease in soil pH. This effect of pH on the product ratio had been recognised previously (e.g. Nommik, 1956) although its association with high NO_3^- concentrations had not been made. Denitrification rates are small at low pH and increase as pH increases with the optimum in the range of 7.0 to 8.0 (Knowles, 1982). Therefore, in laboratory incubation experiments the generation of measurable amounts of N_2 and N_2O at low pH's normally required the use of high NO_3^- additions with the result that the product gases were normally dominated by N_2O. Firestone *et al.* (1980) used the short-lived radioisotope ^{13}N to

measure denitrification rates as a function of pH in the effective absence of added NO_3^-. They substantially verified the earlier findings of Blackmer and Bremner (1978) and also found that pH *per se* had very little influence on the N_2O/N_2 ratio which remained constant at about 1 : 20 between pH 4.9 and 6.5. The addition of 10 ppm NO_3^- increased the ratio from about 1 : 6 at pH 6.5 to about 1 : 0.4 at pH 4.9. Firestone *et al.* (1980) concluded that the influence of soil acidity appeared to be exerted through or was interactive with the effect of NO_3^- or NO_2^- concentration.

The interpretation of the results of denitrification experiments at low pH are further confounded by the simultaneous occurrence of chemical reactions involving NO_2^-. These "chemo-denitrification" processes are discussed later.

6.2.3.4 Temperature

As would be expected for a microbially mediated process the rate of denitrification is markedly affected by temperature. Reported rates are low below 10°C but increase rapidly reaching an optimum at 60 to 65°C (Nommik, 1956; Bremner and Shaw, 1958; Keeney *et al.*, 1979). Above this temperature rates decrease again and gas production effectively ceases at 75°C (Keeney *et al.*, 1979). The unusually high optimum temperature may be due in part to a combination of biological and chemical reduction reactions, although the presence of thermophilic species of *Bacillus* have also been implicated (Keeney *et al.*, 1979). Temperature also affects the N_2O/N_2 ratio of the product gases, with higher ratios generally being observed at lower temperatures together with small amounts of NO (Rolston, 1981). These observations are

consistent with a general slowing of each reduction step in the denitrification reaction sequence at low temperatures.

Few direct field measurements of the effects of temperature are available. Rolston *et al.* (1978) determined denitrification rates by directly measuring evolved N_2O and N_2 under field conditions during winter (8°C) and summer (23°C). Total losses from ^{15}N labelled NO_3^- fertilizer applied to manure amended Yolo loam soil were 11% and 73% for the winter and summer experiments respectively. Apart from influencing the total N loss, the lower winter temperature also protracted the period over which labelled gaseous products were released.

6.3 NITRIFICATION

6.3.1 Definition

Nitrification as defined by Alexander (1977) is the biological formation of NO_2^- and NO_3^- from compounds containing reduced nitrogen (e.g. NH_4^+). It is an oxidative aerobic process and is mediated by representatives of the autotrophic micro-organisms, *Nitrosomonas* and *Nitrobactor*. *Nitrosomonas* utilizes NH_4^+ as an oxidizable substrate in an exothermic reaction to generate NO_2^-. This reaction may be represented as:

$$NH_4^+ + 1.5\ O_2 \longrightarrow NO_2^- + H_2O + 2H^+$$

The NO_2^- formed can be oxidized further by *Nitrobactor* in another energy yielding reaction:

$$NO_2^- + 0.5\ O_2 \longrightarrow NO_3^-$$

Both species of micro-organism occur together in soils with the result that NO_2^- rarely appears in any quantity. When it does accumulate, it is usually because of high soil pH, a condition that tends to inhibit *Nitrobactor*.

6.3.2 Mechanism of Nitrification

There exists good evidence that the oxidation of NH_4^+ is a multistep process. The initial product appears to be enzyme-bound hydroxylamine (NH_2OH) which is converted to another and possibly a third intermediate (NO) before forming NO_2^- (Alexander, 1977; Freney *et al.*, 1979). The role of NO as a possible intermediate is, however, by no means certain. This simple description is further complicated by the observation that pure cultures of *Nitrosomonas europaea* may generate traces of N_2O when grown with NH_4^+ or NH_2OH (e.g. Yoshida and Alexander, 1970, 1971). The N_2O itself does not appear to be an intermediate in the nitrification pathway since the micro-organisms are incapable of metabolizing it to NO_2^-. It has been suggested by Alexander (1977) that N_2O might form nonenzymatically from the unknown intermediate by a side reaction:

$$NH_4^+ \longrightarrow NH_2OH \longrightarrow (HNO\ ?) \longrightarrow NO \longrightarrow NO_2^-$$
$$\searrow \quad N_2O + H_2O$$

The release of N_2O from soils during the nitrification of ammoniacal-N under aerobic conditions was first described by Bremner and Blackmer (1978). They showed that significantly larger amounts of N_2O were released from soils treated with urea and $(NH_4)_2SO_4$ than from soils treated with KNO_3 and no release of N_2O was detected from similarly treated sterile soils. In addition, the presence of added

nitrapyrin (a compound which inhibits the oxidation of NH_4^+ to NO_2^-) greatly reduced the N_2O loss from the ammoniacal-N sources. Subsequent work by Freney *et al.* (1978; 1979) showed that N_2O was released from 10 soils with widely different properties over a range of moisture contents. The rate of emission increased with increasing moisture content and with increasing temperature up to 37°C. They also demonstrated N_2O release from a fresh field soil which had not received added water for 6 weeks. These workers concluded that microbial production of N_2O in soil was continuous and that a considerable part of it was produced by the oxidation of ammoniacal-N. There now appears to be little doubt that N_2O may be released from soil as a by-product of the nitrification pathway. For a complete review of available evidence in support of this see Bremner and Blackmer (1981). What is less certain is the significance of these N_2O emissions on the global cycling of N_2O-N and their effects on the stability of the ozonosphere.

6.3.3 Major Factors Affecting N_2O Emissions During Nitrification

Factors which influence nitrification *per se* are likely to also affect N_2O release during nitrification. Increases in temperature, pH, nitrifiable-N concentrations and soil moisture all stimulate nitrification (Alexander, 1977) and should therefore lead to increases in N_2O emissions. Data in support of this are limited although some evidence can be found in recent laboratory studies (Bremner and Blackmer, 1978; 1980; 1981; Freney *et al.*, 1979) and in several field experiments (e.g. Denmead *et al.*, 1979; Breitenbeck *et al.*, 1980; Mosier *et al.*, 1982).

6.3.3.1 Moisture content

As outlined earlier, the addition of increasing amounts of water to air dried and field moist soils incubated under aerobic conditions led to an increase in the initial rate of N_2O release from a suite of different soils (Freney *et al.*, 1979). A more surprising observation was that even when air dried soils were incubated without any added water, measurable amounts of N_2O accumulated in the headspace of the incubation flasks. The addition of microbial inhibitors slowed down the rate of N_2O production while autoclaving or treating the soils with formaldehyde completely prevented evolution of N_2O. Treatment with the nitrification inhibitor, carbon disulphide (CS_2), did not completely prevent N_2O release but reduced it considerably. The authors interpreted these results as evidence that micro-organisms were activated by the addition of water and that much of the N_2O produced came from the oxidation of native NH_4^+. Similar observations were reported by Bremner and Blackmer (1981).

Under field conditions, losses of N_2O through the denitrification and nitrification mechanisms probably occur simultaneously (Smith *et al.*, 1982; Mosier *et al.*, 1981, 1982). This could confound interpretation of the effects of moisture on nitrification losses. For example, Mosier and Hutchinson (1981) found a significant ($r = 0.53$) correlation between N_2O flux and surface soil moisture content following an anhydrous NH_3 application to an irrigated corn crop. However, they were unable to unambiguously assign this to a direct effect on nitrification since some simultaneous denitrification was suspected.

Breitenbeck *et al.* (1980) measured N_2O losses from urea, ammonium sulphate, and calcium nitrate in an attempt to resolve the relative importance of these two mechanisms in the field. They found that

while losses of N_2O from the ammoniacal-N sources were low during the 96 days following application (i.e. 0.11 - 0.18%), losses of N_2O from calcium nitrate were much less (0.01 - 0.04%). This was in spite of soil moisture levels remaining close to field capacity which would have favoured denitrification from NO_3^-. These results provided a field verification of the earlier findings of Bremner and Blackmer (1978) in which N_2O release from ammoniacal-N sources were shown to exceed release from NO_3^- even at quite high soil moisture levels.

More experiments are required to unambiguously determine the direct influence of soil moisture (and other factors) on N_2O losses in the field.

6.3.3.2 Nitrifiable-N

In laboratory incubation experiments, soils amended with nitrifiable-N (i.e. ammonium sulphate, urea or alanine) yielded more N_2O than similar non-amended soils (Bremner and Blackmer, 1978, 1980, 1981). In many of these experiments N_2O production increased linearly with increasing nitrifiable-N as would be expected on the basis of the proposed mechanism (Alexander, 1977).

Field evidence in tentative support of these findings is available from several studies (Breitenbeck *et al.*, 1980; Cochran *et al.*, 1981; Mosier *et al.*, 1982). In each case, cumulative N_2O-N losses attributable to the applied fertilizer (ammonium nitrate, sewage sludge, anhydrous ammonia, ammonium sulphate or urea) increased as the rate of applied N increased. It should be pointed out, however, that these measured losses were very small, amounting to at most 1% of the applied fertilizer and more frequently to less than 0.2%.

The highest losses of N_2O recorded from direct field measurements were by Bremner *et al.* (1981) following the injection of anhydrous ammonia at 250 kg N ha^{-1} into 3 Iowa soils. After 139 days cumulative release amounted to between 4.0 and 6.8% of the applied N. How much of this was due to nitrification was uncertain.

The expected relationship between soil NH_4^+ concentrations and instantaneous N_2O fluxes again appears to be frequently complicated by simultaneous denitrification. For example, Mosier *et al.* (1982) reported a relationship between extractable soil NH_4^+ and N_2O efflux following ammonium nitrate applications to barley plots in Colorado. They interpreted this as evidence for the operation of the oxidative nitrification mechanism. However, in an earlier field experiment in which urea was applied to shortgrass prairie, the same workers found that N_2O fluxes were not correlated with either soil NH_4^+ or NO_3^- levels. To further confound the issue, Smith *et al.* (1982) found N_2O emissions following urea applications to wetland rice were correlated with both the exchangeable NH_4^+ content of the soil and the NO_2^- + NO_3^- concentration of the floodwater. These correlations were explained by NH_4^+ oxidation to NO_3^- in the aerobic surface soil and floodwater followed by the NO_3^- diffusing to moderately anaerobic zones where it was denitrified. Total N_2O-N loss was low, averaging 0.03% and only just exceeded losses from the untreated controls.

6.3.3.3 Soil pH

The rate of nitrification is significantly correlated with pH (Alexander, 1977); increasing as pH increases. In acid environments, nitrification proceeds slowly even in the presence of adequate nitrifiable-N while at high pH, inhibition of NO_2^- oxidation to NO_3^- may occur. While

this can lead to an accumulation of NO_2^-, the rates of the preceding oxidation steps (section 6.3) are unlikely to be affected. Consequently, the rate of N_2O release by the non-enzymatic side reaction should also increase with increasing soil pH. Evidence in support of this is very limited although Bremner and Blackmer (1981) have reported a laboratory incubation experiment with appears to illustrate the effect. Three soils (pH = 5.9, 7.1 and 8.3) were amended with alfalfa as a nitrifiable-N source (10 mg C per gram of soil), moistened to 50% water holding capacity and incubated aerobically at 30°C. After 20 days, accumulated N_2O-N amounted to 313, 853 and 6280 ng g^{-1} soil respectively (Bremner and Blackmer, 1981). A demonstration of the proposed pH relationship under field conditions has yet to be achieved.

6.3.3.4 Temperature

As expected, an increase in temperature led to an increase in N_2O release from soils incubated under aerobic conditions (Freney *et al.*, 1979). These results were discussed earlier (section 6.3) and have since been supported by laboratory data from Bremner and Blackmer (1980). But an increase in temperature should result in an increase in N_2O loss by each of the three possible loss mechanisms (nitrification, denitrification or chemo-denitrification). Consequently, under field conditions where it may be much more difficult to distinguish the actual mechanism of loss, it could be correspondingly difficult to unambiguously recognise the influence of temperature.

Diurnal fluctuations in N_2O fluxes measured in field experiments appear to relate to diurnal temperature fluctuations (Ryden *et al.*, 1978; Denmead, 1979; Denmead *et al.*, 1979). But again, the actual mode of N_2O production may have been by a mechanism other than nitrification. On the

other hand, in a field experiment reported by Cochran *et al.* (1981), the evidence for N_2O loss by nitrification was considered to outweigh that for loss by the other two mechanisms. The direct influence of temperature changes on the nitrification mechanism was evident during the 24 days immediately following applications of anhydrous ammonia to a fallow soil when fluctuations in mean daily air temperatures coincided with fluctuations in daily N_2O-N release.

6.4 CHEMO-DENITRIFICATION

6.4.1 Definition

Chemo-denitrification is the term commonly used to describe various chemical reactions of NO_2^- ion within soils to produce NO, NO_2, N_2O and N_2. That these gases are of non-biological origin is evidenced by their production from sterilized soils amended with added NO_2^-. Under anaerobic laboratory conditions, acidic and mildly acidic soils incubated with NO_2^- generally produce NO and N_2 (Nelson and Bremner, 1969, 1970; Bollag *et al.*, 1973). Aerobic incubations also produce N_2 as well as some NO_2, presumably through the oxidation of NO by O_2. Traces of N_2O are sometimes detected. Several studies have demonstrated an inverse relationship between the amount of gaseous NO or NO_2 and soil pH (Nelson and Bremner, 1969, 1970; Bollag *et al.*, 1973). For mildly acidic soils the amount of gaseous products formed at any particular pH increases with increasing organic matter content, while in soils with pH less than 5 the amount of gaseous products decreases with increasing organic matter (Nelson and Bremner, 1969). A number of reactions have been proposed to account for these observations.

6.4.2 Mechanisms of Chemo-denitrification

6.4.2.1 Nitrous acid decomposition

The reaction most often implicated for generating NO and NO_2 is the self decomposition of nitrous acid (HNO_2). Nelson and Bremner (1970) determined that the stoichiometry of this reaction was consistent with the equation:

$$2\ HNO_2 \longrightarrow NO + NO_2 + H_2O$$

In the closed incubation vessels often used to study these reactions in the laboratory, the products actually obtained depend on a number of additional factors. In an aerobic system, NO is usually oxidised to NO_2 and both gases may then be absorbed by the moist soil. The overall reaction then becomes:

$$2\ HNO_2 + O_2 \longrightarrow 2\ HNO_3$$

(Nelson, 1982). In an anaerobic system, NO_2 will normally be absorbed as before but NO should appear in the enclosed headspace. Under these conditions, the overall equation would be:

$$3\ HNO_2 \longrightarrow 2\ NO + HNO_3 + H_2O$$

(Nelson, 1982).

Under field conditions, the extent to which any of these decomposition reactions takes place is not well documented. Nitrite *per se* is never used as a fertilizer and generally only accumulates in soil at high pH in the presence of ammonia which at high concentrations is toxic to *Nitrobactor*. Ammonia toxicity to *Nitrobactor* might therefore occur after heavy applications of anhydrous ammonia, ammonia solutions or in urine patches. However, direct measurements of simulated sheep urine patches in the field indicated losses of NO and NO_2 were low; amounting

from less than 2% in one study (Barlow, 1974) to zero in another (Carran *et al.*, 1982). On the other hand, the recent application of a very sensitive chemiluminescent technique (Galbally and Roy, 1978) has shown that NO can be released slowly but continuously from soils including unfertilized and ungrazed grassland.

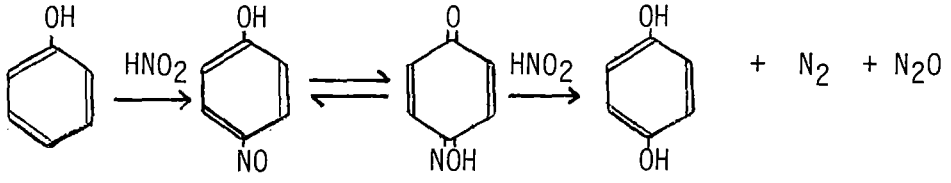
As indicated earlier it had generally been assumed that under aerobic conditions, NO would be oxidized to NO_2 and either absorbed by the soil or soil moisture or released as gas. Galbally and Roy (1978) pointed out that the oxidation of NO by O_2 is a true termolecular reaction whose half-life is, therefore, highly dependent on the NO concentration. At concentrations of 100 ppm or greater the half-life for oxidation is one hour or less, whereas at low concentrations (0.01 ppm) the half-life for its oxidation is in the order of 10,000 hours. This variation in oxidation rate explains why NO at low concentrations can pass unoxidized from the soil to the atmosphere and also why in closed laboratory incubations under aerobic conditions, NO_2 is the major product. It must be emphasised, however, that the exhalation rates measured by Galbally and Roy (1978) were very low (0.2 - 2.3 kg N ha^{-1} yr^{-1}) with measurements for a grazed pasture of 1.2 kg N ha^{-1} yr^{-1}. The exact source of these emissions, whether HNO_2 decomposition, denitrification, or the reaction of NO_2^- with organic constituents in the soil was not known.

6.4.2.2 Reactions of nitrous acid with organic matter

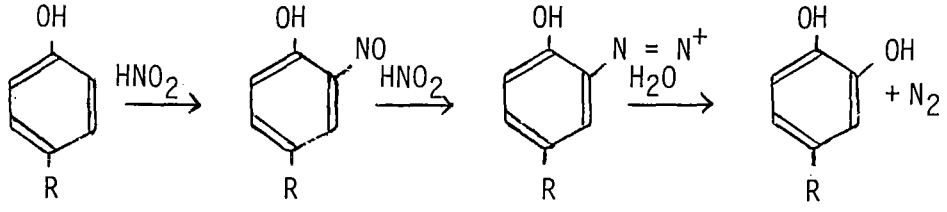
Nelson and Bremner (1970) showed that when the organic matter in soil was removed by ignition at 700°C or by chemical oxidation with basic hypobromite (KOBr - KOH), no N_2 or N_2O was produced from added

NO_2^- while release of NO was unaffected. These workers concluded that the principal gaseous product formed by the reaction between NO_2^- and soil organic matter was molecular nitrogen (N_2) although small emissions of N_2O can also be produced. The effects of various organic materials on NO_2^- decomposition at pH 5 implicated phenols and polyphenols as the soil constituents largely, if not entirely responsible for the formation of N_2 and N_2O (Bremner and Nelson, 1968).

Nelson (1982) suggested two possible mechanisms. The first involves the reaction of phenol with HNO_2 to form para-nitrosophenol, tautomerization of this product to quinone monoxime and the formation of N_2 and N_2O by reaction of the oxime with HNO_2. The equation is given as:



The second mechanism applies to para-substituted phenols only and proceeds through the formation and subsequent decomposition of an ortho-diazonium intermediate:



Stevenson *et al.* (1970) tested a wide range of organic matter fractions for their ability to decompose NO_2^-. Along with N_2O and N_2 they also identified NO as a product and suggested a series of nitrosation reactions can take place when NO_2^- accumulates in soil. These workers concluded that desiccation of the soil following the

partial nitrification of ammoniacal fertilizers would be particularly favourable for conversion of NO_2^- to gaseous products and a slow evolution of N gases through this mechanism could result in significant losses of fertilizer N. However, the extent to which these reactions promote N loss under field conditions is still largely unknown.

6.4.2.3 Reactions of nitrous acid with amines

The reaction between HNO_2 and compounds containing free amino groups (e.g. amino acids, urea and amines) has long been suggested as a possible mechanism for gaseous N loss from soil. This "Van Slyke" reaction only takes place at low pH and the N_2 gas evolved is derived in equal quantities from the two reactants.

$$R\text{-}NH_2 + HNO_2 \longrightarrow R\text{-}OH + H_2O + N_2$$

Good evidence for the occurrence of this reaction under conditions likely to be met in the field was obtained recently by Christianson *et al.* (1979). These workers studied the denitrification of ^{15}N labelled urea applied to an Orthic Black soil (organic matter = 4.6%, pH = 6.1) in the laboratory. They found that 8% of the added urea-N was accounted for as N_2 which had an isotopic ratio consistent with the Van Slyke reaction. Further studies of this sort are needed to better understand the full agricultural significance of this mechanism.

6.4.2.4 Reactions of nitrite with ammonium

Solid ammonium nitrite (NH_4NO_2) explodes on heating to 60-70°C to produce N_2 gas (Weast, 1977). The same reaction proceeds much more

slowly from concentrated solutions of NH_4NO_2 at low pH (pH < 5.2) (Smith and Clark, 1960). Bremner and Nelson (1968) investigated NH_4NO_2 decomposition and found that it did not occur during incubation of acidic soils amended with high concentrations of NH_4^+ and NO_2^- but that some decomposition occurred when similarly treated light-textured, neutral and alkaline soils were air-dried. However, in a recent review, Nelson (1982) observed that there was no evidence that chemo-denitrification occurs to any extent under these conditions. The findings of Christianson *et al.* (1979) cited earlier would tend to contradict this. Clearly some chemo-denitrification can occur at high pH's, albeit by a different mechanism. High concentrations of both NH_4^+ and NO_2^- together with drying conditions might also be found in the surface of urine patches undergoing nitrification. As yet, no direct measurements of possible NH_4NO_2 composition in urine patches have been reported.

6.4.2.5 Reactions of nitrite or nitrous acid with hydroxylamine

Hydroxylamine is a known intermediate in the oxidation of NH_4^+ to NO_3^- (section 6.3) and has been postulated as an intermediate in the reduction of NO_3^- to NH_4^+ (Alexander, 1977). A number of workers (e.g. Arnold, 1954; Wijler and Delwiche, 1954) have speculated that the chemical reaction of NH_2OH with HNO_2 produced by micro-organisms in soils might generate N_2O e.g.:

$$NH_2OH + HNO_2 \longrightarrow N_2O + 2\,H_2O$$

Bremner *et al.* (1980) investigated this possibility and found that the extent of N_2O production by NH_2OH decomposition was highly correlated with pH, exchangeable Ca^{2+}, and oxidised Mn. The production of N_2O in sterilized soils treated with NH_2OH was not greatly increased

by addition of NO_2^-. The workers concluded that if N_2O is formed in soils through nonbiological transformations of NH_2OH produced by soil micro-organisms, very little is generated by the reaction of NH_2OH with NO_2^-. Since free NH_2OH has yet to be detected in soils (Nelson, 1982) the importance of its decomposition under field conditions remains speculative.

6.5 FIELD METHODS FOR MEASURING NO, N_2O AND N_2 LOSSES FROM SOIL

6.5.1 Difference Methods

Evolution of gaseous nitrogen and nitrogen oxides following fertilizer applications has usually been calculated by indirect methods based on measured differences between the known amount of N applied and the amount accounted for in the soil and crop. The efficacy of this procedure is enhanced if ^{15}N enriched fertilizers are used since the extent of N immobilization into the soil organic fraction is then more easily determined. However, it is not possible to unambiguously relegate "missing-N" to gaseous loss without accounting for losses by all other feasible routes (e.g. leaching). This is not always attempted. Also, use of the difference method does not enable the investigator to unambiguously identify the form in which the N was lost (i.e. NH_3, N_2O, NO or N_2). Added to this is the complication that all measurement errors accumulate in the difference value which may diminish its potential usefulness. Direct measurements of gaseous losses are preferable and it is fortunate that over the last decade several methods have been developed and exploited.

6.5.2 Chamber Methods

Most researchers wishing to measure these gases now employ some form of chamber placed over the soil surface. Gases evolved from the soil surface collect beneath the chamber within the confined headspace. Several different procedures have been used to quantify this entrapped gas. In one approach the chamber is completely sealed and small discrete samples are removed to monitor the increase in headspace concentration with time. From this, the flux of gas into the chamber may be calculated. Galbally and Roy (1978) used a variation of this procedure to measure NO exhalation rates from grazed and ungrazed pastures (section 6.4). A necessary precaution is that the chamber should only remain in place for short periods otherwise the build-up of gas within the headspace may retard the rate of loss from the soil surface (Jury *et al.*, 1982).

The other common procedure is to draw ambient air through the enclosed headspace to sweep the evolved gases through suitable external traps. The continuous removal of headspace gases obviates the requirement for short sampling times.

The sealed chamber method can measure N_2O evolution reasonably well since the background N_2O concentration in air is sufficiently low (300 - 350 ppbv) that "normal" rates of evolution quickly result in measurable increases in N_2O headspace concentration (Matthias *et al.*, 1979, 1980; McKenney *et al.*, 1980; Hutchinson and Mosier, 1981; Burford *et al.*, 1981). The N_2O content of gas samples removed for later analysis is usually determined by gas chromatographic techniques using a ^{63}Ni electron-capture detector (e.g. Cicerone *et al*, 1978; Mosier and Mack, 1980) or an ultra-sonic detector (Blackmer and Bremner, 1977). Detection of N_2O emission rates as low as 0.1 kg N_2O-N ha^{-1} yr^{-1}

has been claimed (Matthias *et al.*, 1980). Denmead (1979) reported a procedure which coupled a chamber to a sensitive infrared gas analyser and could detect rates of emission as low as 0.6 kg N_2O-N ha^{-1} yr^{-1}.

Unfortunately, the amount of N_2 evolved during denitrification is difficult to measure directly in sealed chambers because the resulting small increase above the normal 78% N_2 atmospheric concentration cannot be measured. This problem can be obviated to some extent by the use of ^{15}N enriched fertilizers. The content of the N_2O and N_2 released into the enclosed headspace is then determined by periodic sampling and analysis using a mass spectrometer (e.g. Rolston *et al.*, 1978). Detection limits for N_2 fluxes measured by this technique are generally much higher than for N_2O alone. For example, Rolston *et al.* (1978) found that N_2 fluxes lower than 365 kg N_2-N ha^{-1} yr^{-1} were undetectable even when 20 - 40% ^{15}N enriched KNO_3 was applied at 300 kg N ha^{-1}. In a subsequent report, detection limits of 40 - 70 kg N_2-N ha^{-1} yr^{-1} were achieved (Rolston *et al.*, 1982). This method also suffers because of the high cost of the ^{15}N required and is therefore unlikely to be used on a routine basis.

Limmer *et al.* (1982) have described a chamber method which also uses ^{15}N but in an entirely different and novel way. Their small (6 cm diameter) field gas lysimeter was flushed with an N_2 free He / O_2 gas mixture to reduce N_2 levels in the enclosed soil core and headspace to approximately 5000 ppmv. A small sample of ^{15}N labelled N_2 gas was then introduced into the headspace while a flow of He / O_2 was maintained at the base of the lysimeter to prevent back-diffusion of N_2 from the surrounding soil. By monitoring the changes in the ^{15}N content of the headspace gas the rate of N_2 evolution from the soil surface could be determined. These researchers reported an *in situ* rate of N_2 evolution from a silt loam equivalent to 260 kg N_2-N ha^{-1} yr^{-1}.

A procedure which appears to offer greater scope for the routine measurement of denitrified N_2 under field conditions utilizes the ability of acetylene to block the reduction of N_2O to N_2 (see section 6.2). Thus nitrogen that would normally appear as N_2 is evolved as N_2O which is much more readily quantified. This procedure was first used under field conditions by Ryden *et al.* (1979b) and has subsequently been used by others (e.g. Rolston *et al.*, 1982). Some workers have employed the sealed chamber system described earlier and achieved inhibition of nitrous oxide reductase by replacing approximately 10% of the headspace gas with acetylene (e.g. Lensi and Chalamet, 1982). Most workers, however, have used a continuous flow of ambient air through the chamber to sweep the evolved N_2O into molecular sieve traps (Ryden *et al.*, 1978). In these flow-through systems, acetylene is injected through several small tubes into the soil around the sampling area. After the acetylene reaches concentrations of 0.1 - 1% in the soil atmosphere, the chamber is secured over the soil surface and aspiration is initiated. At the completion of the sampling period (typically 3 hours) the molecular sieve trap is sealed and transferred to the laboratory where the trapped N_2O is displaced by adding water and then analysed by gas chromatography. By measuring N_2O release from sites not treated with acetylene both N_2O and total denitrification losses can be determined.

While acetylene inhibition is possibly the best method currently available for the direct measurement of denitrification losses it does suffer from two major drawbacks. Walter *et al.* (1979) and Mosier (1980) found that acetylene also inhibits nitrification by soil micro-organisms. The field use of acetylene inhibition might therefore only provide valid estimates of total denitrification losses where nitrate fertilizers are used or where nitrification during the sampling period is negligible

(Rolston, 1981). Another potential complication is that acetylene was only effective in inhibiting nitrous oxide reductase for a limited time (approximately 160 hours) after which, the slow reduction of N_2O to N_2 resumed (Yoemans and Beauchamp, 1978). These workers subsequently determined that the presence of sulphide (S_2^-) or volatile organic sulphur compounds were implicated in reversing the acetylene induced inhibition of nitrous oxide reductase (Yoemans and Beauchamp, 1982).

6.5.3 Micrometeorological Methods

Several investigators have attempted to use micrometeorological methods to measure N_2O fluxes from the soil surface (e.g. Matthias *et al.*, 1979; Mosier and Hutchinson, 1981). Their efforts have met with varying degrees of success. To utilize this procedure it is necessary to be able to detect significant differences in N_2O concentration in air samples collected at different heights above the soil surface. In a study of this problem, Matthias *et al.* (1979) were able to measure these differences which occurred more frequently in the early morning hours. However, they concluded that the ability to detect concentration differences at different heights was more dependent on micrometeorological conditions than on the amount of N_2O being evolved from the area under study and as such the procedure was of only limited value in assessing N_2O fluxes from soils. Denmead (1979) reached a similar conclusion based on theoretical considerations alone. Nevertheless, Mosier and Hutchinson (1981) appeared to be successful in the use of a micrometeorological procedure to measure N_2O release on at least 4 occasions. Their calculated fluxes were in close agreement with simultaneous measurements made with chambers.

6.5.4 Gaseous Diffusion Method

There are many reports of the application of diffusion theory for the calculation of N_2O fluxes emanating from the surface of soil (e.g. Burford and Millington, 1968; Burford and Stefanson, 1973; Rolston *et al.*, 1976). The method has also been used to measure denitrification of N_2 after the addition of ^{15}N enriched fertilizers (Rolston *et al.*, 1976). The procedure uses Fick's First Law of Diffusion and requires the measurement of the N_2O or N_2 concentration profile within the soil atmosphere as close to the soil surface as possible. It also requires an independent measurement of the soil gaseous diffusion coefficient. Both measurements are subject to considerable error because of the natural variability in most soils. In particular, where the gas is being generated close to the soil surface the concentration profile is very difficult to measure (Rolston, 1981). Also, in the case of N_2O, the development of a pronounced concentration gradient within the soil may not necessarily lead to enhanced emissions since the upwards N_2O flux may be consumed by soil micro-organisms at or close to the soil surface (Blackmer and Bremner, 1976; Seller and Conrad, 1981). For these reasons the gaseous diffusion method has generally lost favour and most researchers now employ chamber methods.

6.6 RELEASE OF N_2O AND N_2 FROM URINE PATCHES AND N FERTILIZERS IN GRAZED PASTURES

With the exception of the publication arising from the current work (Sherlock and Goh, 1983a), there are no reports of measurements of N_2O production following urine applications to pasture soil.

Concentrated urea solutions have been used to simulate urine patches on native shortgrass prairie (Mosier *et al.*, 1981), and several workers have reported field measurements of N_2O from unfertilized grass and grass swards which have received various inorganic or organic N fertilizers (Table 6.1). While aqueous urea and other inorganic N fertilizers may behave to some extent like urine when applied to soil, there are several reasons for presuming that they may not.

Doak (1952) examined in detail the chemical changes which occur in the nitrogenous constituents of urine applied to soil. Apart from urea, urine contains several heterocyclic-N compounds (hippuric acid, heteroauxin and allantoin) which appear to influence the dynamics of urea hydrolysis and subsequent nitrification. Urine hydrolyses more rapidly than a urea solution of equivalent N content (Doak, 1952; section 2.3.2.3). Doak (1952) attributed this difference to the presence of hippuric acid, which, when added to aqueous urea accelerated the rate of hydrolysis. In addition to this, heteroauxin and allantoin were found to be largely responsible for the higher rate of nitrification in urine compared with urea alone. Thus, the generation of a nitrifiable N source and its nitrification is more rapid for urine than for urea alone and this might influence any subsequent generation of N_2O via the nitrification mechanism.

It is reasonable to speculate further that these minor urinary components might also become involved in chemo-denitrification reactions with the possible generation of NO, N_2O and N_2. Whether the heterocyclic components in urine also form an easily metabolizable C source for denitrifying micro-organisms is again open to speculation. If they do, then rapid N_2 losses might be anticipated. While no data are

Table 6.1 Field Measurements of N_2O Emission Rates from Bare Soil and Soil Cropped to Grass.

Daily N_2O Flux (mg N m^{-2} day^{-1})	Annual N_2O Flux (kg N ha^{-1} yr^{-1})	Reference	
	Untreated Soil Cropped to Grass		
0.1 - 0.8		Burford and Hall	(1977)
0.6 - 2.5		Denmead *et al.*	(1979)
0.02 - 1.2		Dowdell *et al.*	(1980)
0 - 1.0		Mosier *et al.*	(1981)
0 - 23	1.3	Duxbury *et al.*	(1982)
0.1 - 0.8	0.8 - 1.0	Webster and Dowdell	(1982)
0.5 - 1.4		Christensen	(1983b)
7.4		Limmer and Steele	(1982)
0 - 2.1	1.7	This Work	
	Untreated Bare Soil		
0 - 4.4	1.2	Bremner *et al.*	(1980)
-0.2 - 0.2		Cochran *et al.*	(1981)
	Soil Cropped to Grass Treated with Inorganic N Fertilizer		
0.2 - 2		Burford and Hall	(1977)
0 - 90 a		Rolston *et al.*	(1978)
0 - 40 b		Rolston *et al.*	(1978)
0.2 - 4		Mosier *et al.*	(1981)
-0.5 - 21	3.3	Ryden	(1981)
0 - 30		Rolston *et al.*	(1982)
0.2 - 24	4 - 8	Webster and Dowdell	(1982)
1 - 4.5		Christensen	(1983b)
0 - 17		This Work	
	Soil Cropped to Grass Treated with Manure or Crop Residues		
0 - 200		Rolston *et al.*	(1982)
1 - 50		Christensen	(1983b)

a 2 kPa soil - water pressure
b 8 kPa soil - water pressure

available to answer these questions, the addition of cow urine was found to have no influence on the denitrification activity of pasture soil measured using a short term incubation technique (Limmer and Steele, 1983). Certainly, the limited field data available in which simultaneous N_2O and N_2 measurements have been made following fertilizer applications to soil cropped to grass, indicate that large losses of N_2 are possible (Table 6.2).

Table 6.2 Field Measurements of N_2 Emission Rates from Bare Soil and Soil Cropped to Grass.

Daily N_2 Flux (mg N m^{-2} day^{-1})	Reference
Untreated Soil Cropped to Grass	
71.2	Limmer and Steele (1982)
Soil Cropped to Grass and Treated with Nitrate-N Fertilizer	
0 - 400 a	Rolston *et al.* (1978)
0 - 180 b	Rolston *et al.* (1978)
0 - 50	Rolston *et al.* (1982)
Soil Cropped to Grass and Treated with Crop Residues	
0 - 1100	Rolston *et al.* (1982)
Bare Soil Treated with Nitrate-N	
0.08 - 0.9	Lensi and Chalamet (1977)
Bare Soil Treated with Manure	
0 - 6000 a	Rolston *et al.* (1978)
0 - 1000 b	Rolston *et al.* (1978)

a 2 kPa soil - water pressure
b 8 kPa soil - water pressure

CHAPTER 7

MEASUREMENTS OF NITROUS OXIDE PRODUCTION

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CHAPTER 7

MEASUREMENTS OF NITROUS OXIDE PRODUCTION

7.1 INTRODUCTION

The increasing demand for food to feed the world's growing population has, amongst other things, prompted the widespread planting of leguminous crops and the use in agriculture of industrially fixed nitrogen. These practices have accelerated dramatically during the twentieth century and have reached a stage where cultivated legumes and industrial N fixation are estimated to account for over half of the total amount of N fixed globally per annum (Table 7.1).

Table 7.1 Comparison of "natural" and human sources of fixed N. *

Source	Rate (Tg per year) #
"Natural" (historic) biological	60
Atmospheric processes	7.4
Grain legumes	40.6
Hay and pasture legumes	28.4
Fossil fuel and other combustion	19.8
Industrial fixation	40

* from Delwiche (1977). # 1 Tg = 10^{12} grams = 10^{6} tonnes

It would appear, therefore, that the nitrogen cycle is no longer operating under the pseudo steady-state condition characteristic of the time prior to the development of modern agriculture. The immediate consequence of this is a likely increase in the N content of the more labile N pools such as the organic and inorganic N of rivers and lakes and the nitrate concentrations of groundwater (Delwiche, 1981). In the longer term, it appears axiomatic that a new steady-state condition will

only be achieved by an increase in the rates of those processes which return fixed nitrogen to the atmosphere (principally, denitrification and nitrification). A product of both of these processes is N_2O which has a principal role in catalysing the breakdown of stratospheric ozone. It has been widely speculated that the increased use of N fertilizers and cultivated legumes might therefore lead to an increase in the atmospheric N_2O concentration which might in turn cause a partial depletion of ozone (O_3) in the stratosphere (CAST, 1976; Crutzen and Ehhalt, 1977; McElroy *et al.*, 1977). To adequately assess this potential threat requires field measurements of the rate of N_2O production.

In modern pastoral agriculture, the aggregation of urine-N in isolated patches provides ideal conditions for $NH_{3(g)}$ volatilization (section 1.6) and may also provide conditions conducive to the loss of fixed N as N_2O (section 6.6). The contribution of N_2O fluxes from urine patches has not previously been extensively studied. This chapter describes experiments which measured and compared the rates of N_2O release from simulated sheep urine patches using sheep urine and solutions of other nitrogenous fertilizers applied to pasture. A field experiment attempted to measure N_2O emission rates under temperature and moisture conditions conducive to both denitrification and nitrification, while growth cabinet and laboratory experiments examined the effects of water addition and repeated applications of aqueous N solutions under simulated field conditions.

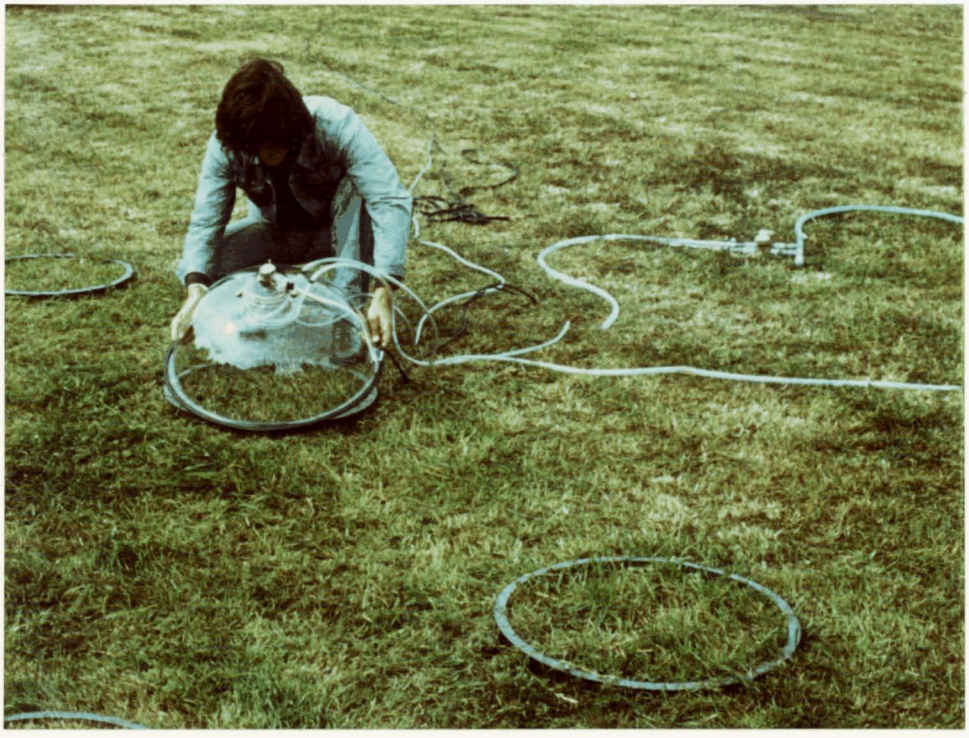
7.2 EXPERIMENT 1 - FIELD MEASUREMENT OF NITROUS OXIDE PRODUCTION

7.2.1 Materials and Methods

7.2.1.1 Field chamber design

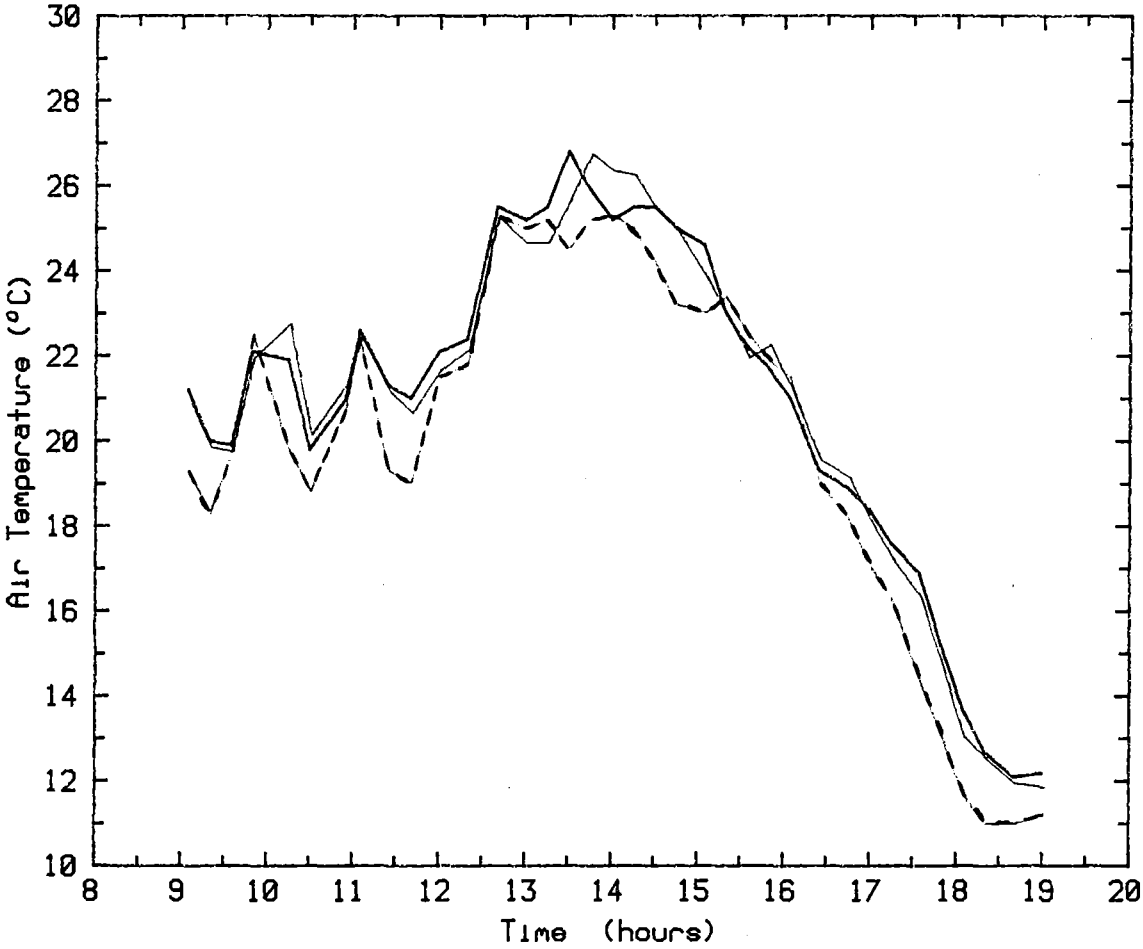
The sealed chambers used for the direct field measurements of N_2O evolution were modelled on those originally employed by Hoult *et al.* (1974) for $NH_{3(g)}$ volatilization measurements. A single chamber consisted of two main parts: a cylindrical steel base section and a transparent hemispherical top (photograph 1). The steel cylinder (20 cm height, 51 cm diameter) was driven into the soil with the top 3 cm exposed and during periods of gas sampling the transparent perspex hemisphere (51 cm diameter, 40 litre internal volume) was clamped to it by 6 symmetrically placed "Bulldog" clips. A neoprene rubber tube was glued to a flange on the top of the cylinder and formed an effective air-tight seal between the two sections.

A 3 volt D.C. motor was fitted external to the centre of each perspex hemisphere with the motor shaft passing through a small hole into the interior. A hairdryer impeller was connected to the motor shaft and when operating provided the necessary turbulence to stir the air thus preventing air temperature and gas concentration gradients. To prevent a greenhouse effect and to help maintain ambient air temperatures during gas sampling, the hemispherical chambers were fitted with copper cooling coils. These were coils of 9 mm O.D. copper tubing which surrounded the impeller and through which artesian water (12-14°C) was slowly passed (1 litre per minute). During periods of bright sunlight, additional cooling was provided by carefully positioned sunscreen cloth. Electronic temperature sensors were placed 4 cm above the enclosed pasture surface and were compared directly with an identical



Photograph 1: Chamber used for direct field measurements of N_2O emissions

Figure 7.1



Internal air temperature (chamber 1)

Internal air temperature (chamber 2)

External air temperature

Figure 7.1 Comparison of air temperatures measured inside and external to field gas sampling chambers. The graduations on the abcissa represent time after midnight on 5/10/78.

sensor mounted in a similar position external to the chambers. Temperature sensors were also positioned at 5 cm and 10 cm depths in the soil. All temperature sensors were scanned manually every 5 minutes while the chambers were in position. The air temperature within the chambers was always within 3°C of the external ambient temperature (Figure 7.1).

7.2.1.2 Gas sampling

After sealing a chamber to its base, samples of the enclosed gas volume were withdrawn via a fine PVC capillary tube (2 mm I.D.) which connected each chamber to a 100 ml syringe located in a field laboratory some 20 metres away. At each sampling time (i.e. 0, 10, 20, 40 and 60 minutes after sealing the chamber) the syringe was pumped several times to purge the connecting capillary and a 20 ml sample was transferred to a previously evacuated blood sample container (vacutainer) using a 3 way plastic tap. These samples were then transferred to the laboratory as soon as possible after acquisition for N_2O analysis.

7.2.1.3 Gas sample analysis

The N_2O analysis method used was similar to that described by Rasmussen *et al.* (1976). A measured volume of sample gas (approximately 5 ± 0.2 ml) was removed from each vacutainer using a well-greased 10 ml gas-tight syringe and injected into a Varian 2800 gas chromatograph fitted with a Pye-Unicam ^{63}Ni electron-capture detector (340°C) and a stainless steel column (0.8 m long, 6 mm O.D.) of Porapak N maintained at room temperature (20°C).

The carrier gas was O_2-free dry N_2 (O.F.N.) which was cleaned by passage through a molecular sieve 5A trap, then a heated "oxytrap" and finally through another molecular sieve 5A trap before entering the instrument at a flow-rate of 40 ml per minute. The O_2 in a sample eluted first followed at about 160 seconds by the N_2O peak. The area under the N_2O peak was calculated automatically by a Varian Aerograph Model 485 integrator.

Calibration was performed frequently using 5 ml samples of compressed air from a cylinder and samples prepared from a standard calibration gas (104 ppmv N_2O in N_2, Matheson USA) diluted with compressed air. Using 5 ml samples, the detector response was linear from 0.35 ppmv (the normal "background" N_2O concentration) to around 10 ppmv.

After 15 samples had been injected, the column oven door was shut and the column was heated to 130°C and maintained at this temperature for 30 minutes. This was done to release and flush from the column, compounds with long retention times which would otherwise interfere with subsequent analyses. The door was then opened and the column was allowed to cool to room temperature before sample analysis was resumed. With this analytical procedure about 60 samples could be analysed in a normal working day.

7.2.1.4 Site, soil and fertilizers used

A permanent ryegrass - white clover pasture at the Lincoln College Research Farm was used for the N_2O release field experiment. It was situated several hundred metres from the site used for the $NH_{3(g)}$ volatilization measurements (chapter 2) on Templeton silt loam soil (Table 2.1, section 2.2.1.3).

Four cylindrical steel base sections were inserted into the soil 6 months prior to the commencement of the experiment. On 2/10/78, applications of either sheep urine, ammonium sulphate, calcium nitrate or distilled water were applied to each of the confined plots. The herbage had previously been cut to 20 mm height. The N treated plots received 4 spot applications of N solution (1.8 g N per 300 cm^2 spot) for a total of 7.2 g N beneath each chamber. The single control plot received 400 ml of distilled water applied as 4 spot applications, each covering 300 cm^2. Two chambers were used for gas sampling and these were placed alternately over the urine and water treated plots and then over the ammonium sulphate and calcium nitrate treated plots several times each day for the following 10 days with a final sampling on 14/11/78 (Appendix IV).

The surface (0 - 50 mm) soil moisture content was determined gravimetrically on cores taken from similarly treated but unconfined control plots, and was found to remain close to field capacity (33%) throughout October and November. Rainfall amounted to 2.7 mm during the 10 day sampling period and occurred on only one occasion; approximately 2000 - 2400 hours on the evening of 6/10/78. A further 24.5 mm was applied to each plot at 1130 hours on the morning of 9/10/78 in an attempt to stimulate denitrification. In the intervening month prior to the final gas sampling on 14/11/78, 65.3 mm of rain fell on the uncovered plots.

7.2.1.5 Calculation of N_2O release rates

The rate of N_2O production was calculated according to Sherlock and Goh (1983a) using the equation:

$$R = k.D.V.\ dC/dT$$

where: R = rate of N_2O production (μg N_2O - N per hour)

dC/dT = rate of change in the concentration of N_2O within the chamber (ppmv per hour)

D = density of $N_2O_{(g)}$ at the sampling temperature (g per litre)

V = volume of the enclosed air space (litres)

k = 0.636 (i.e. the weight fraction of N in N_2O)

Nitrous oxide fluxes (kg N_2O - N ha^{-1} yr^{-1}) were obtained from the expression:

$$F = 0.0876.R/A$$

where: A = the area of the soil confined by the chamber (0.21 m^2)

0.0876 = a units conversion factor

7.2.2 Results

Total amounts of N_2O released in the 10 days following N application were estimated by integrating the rate of loss curves for each plot (Figure 7.2). Losses from the N treated plots were similar at about 7 mg of N_2O - N, with the control plot releasing about 1 mg N_2O - N during the same period (Table 7.2). Measured fluxes were highest on the day of application for both the urine and calcium nitrate treatments while for the ammonium sulphate treated plot the highest measured N_2O flux occurred on the following day (Figure 7.2). Generally, daily N_2O release decreased with time and after 10 days measured fluxes from the N treated plots were only slightly higher than those from the control plot. At the final sampling 1 month later, fluxes from all plots were essentially indistinguishable from the control (Figure 7.2 and Appendix IV).

Figure 7.2

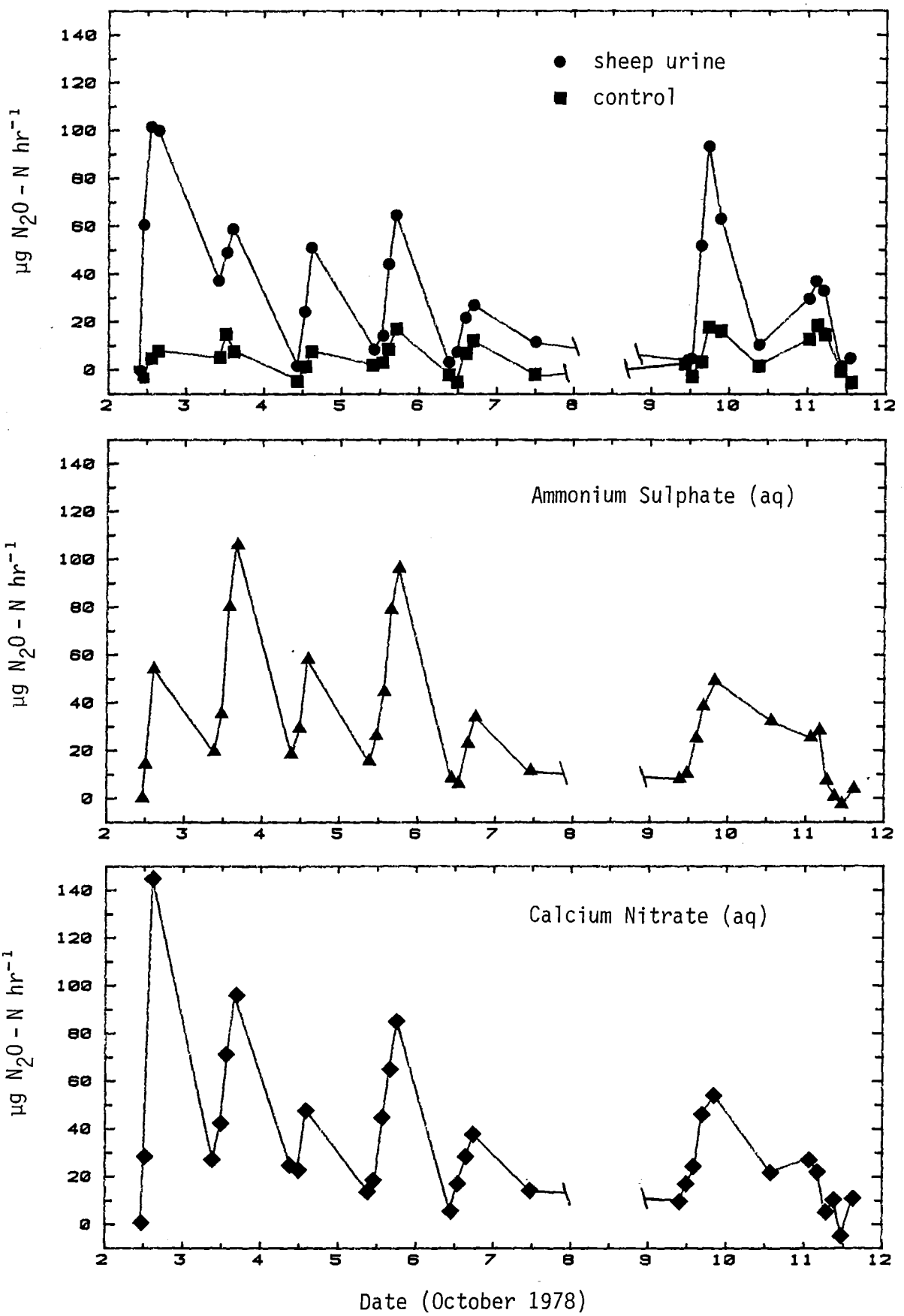

sheep urine
control
Ammonium Sulphate (aq)
Calcium Nitrate (aq)
µg N2O - N hr-1
Date (October 1978)

Table 7.2 Nitrous oxide release from field pasture plots, during 10 day period (2/10/78 - 11/10/78).

Treatment ≠	Mean Estimated N_2O - N Release (mg N_2O - N)	(% of N Applied)
Control	1.1	-
Sheep Urine	6.4	0.07
Ammonium Sulphate	6.8	0.08
Calcium Nitrate	7.7	0.09

≠ 7.2 g N in 400 ml of solution applied in 4 equal patches of 1.8 g N/300 cm^2 in all treatments except the control which received 4 x 100 ml of distilled water.

Only a very small fraction of the applied N (approximately 0.1%) was lost as N_2O from each of the N treated plots (Table 7.2). However, it was possible that total losses were slightly underestimated since the rates of N_2O release were often still increasing in the early evening when daily sampling was usually discontinued (Figure 7.2). Generally the diurnal fluctuations in N_2O release rates during the 10 day monitoring period tended to coincide with similar fluctuations in soil temperature measured at 10 cm depth. For example, on 5/10/78, correlation coefficients between hourly temperatures and N_2O release rates from the ammonium sulphate treated plot were: soil (10 cm depth, $r = 0.995$), soil (5 cm depth, $r = 0.711$) and chamber air ($r = -0.653$). The other N-treated and control plots behaved similarly (Table 7.3.).

Table 7.3 Correlation coefficients relating mean measured N_2O release rates on 5/10/78 to mean soil temperatures and chamber air temperatures.

	Treatment			
	Urine	Ammonium Sulphate	Calcium Nitrate	Control
Soil Temperature (10 cm depth)	0.980	0.995	0.980	0.992
Soil Temperature (5 cm depth)	0.846	0.711	0.702	0.761
Internal Chamber Temperature	-0.781	-0.653	-0.633	-0.860

Several workers (Denmead, 1979; Jury *et al.*, 1982) have cautioned that the true rate of emission of N_2O from soil may be underestimated if the concentration of N_2O in the air within a chamber becomes sufficiently high to significantly reduce the diffusion of N_2O from the soil. If this had occurred, the rate of increase in N_2O with time within the chamber would have slowed. At almost every sampling occasion the N_2O concentration increased linearly with time indicating that the effect of the chamber itself was minimal (e.g. see Figure 7.3). Departure from linearity was sometimes observed but only when release rates were around 5 μg N_2O - N per hour (equivalent to 0.5 mg N_2O - N m^{-2} day^{-1}). These departures were attributed to analytical and sampling uncertainties and effectively limit this method to the reliable estimation of instantaneous fluxes greater than the equivalent of 2 kg N_2O - N ha^{-1} yr^{-1}.

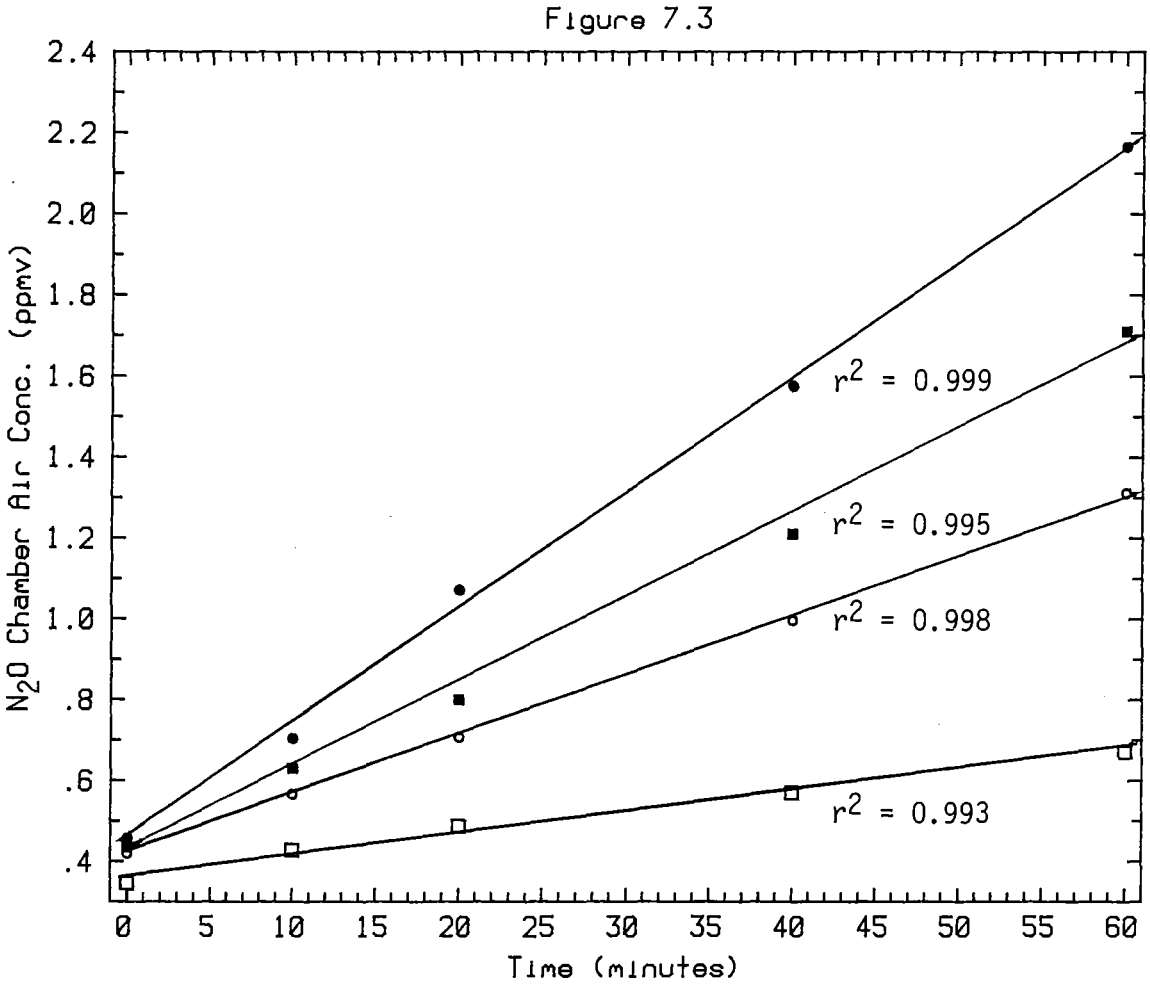


Figure 7.3 The linear relationship between time and N_2O concentration within the field chamber from each plot at several sampling times on 3/10/78.

□ = control plot, 1230 - 1330 hours

○ = calcium nitrate plot, 1125 - 1225 hours

■ = urine plot, 1445 - 1545 hours

● = ammonium sulphate plot, 1340 - 1440 hours

7.2.3 Discussion

The amount of N_2O - N released in the 10 days following the application of N fertilizers and urine as simulated urine patches represented only a very small fraction of the total amount of N applied. This finding is in substantial agreement with the results of field measurements reported by others. For example, Mosier *et al.* (1981) used a chamber method to measure N_2O emissions from simulated urine patches applied as aqueous urea to a native shortgrass prairie. Total N_2O - N losses after 3 months amounted to only 0.6% of the added N, with most of this release occurring after irrigation or rainfall events (Mosier *et al.* 1981). In another field study, measured losses of N_2O - N 13 days after 250 kg N ha^{-1} applications of calcium nitrate, urea and ammonium sulphate fertilizer amounted to 0.01%, 0.08% and 0.1% respectively (Breitenbeck *et al.*, 1980).

Throughout the sampling period, the soil moisture content was close to field capacity (33%) and would therefore have favoured N_2O loss from applied NO_3^- via denitrification (section 6.2.3.1) while also stimulating nitrification losses from ammoniacal-N sources (section 6.3.3.1). The measured N_2O emissions from all three N sources suggest that both mechanisms were occurring simultaneously in the soil. While the unreplicated nature of the experiment precludes a direct statistical comparison between the treatments, losses from the 3 N sources were similar and support the contention that nitrification of ammoniacal-N may be an important source of N_2O emissions from soils (Bremner *et al.*, 1978).

The loss of N_2O from the untreated control plot was about 1 mg N_2O - N in the 10 day period. This corresponded to a mean daily rate of 0.48 mg N_2O - N m^{-2} day^{-1} or an annual rate of 1.7 kg N_2O - N ha^{-1} yr^{-1}

with peak fluxes equivalent to about 2.1 mg N_2O - N m^{-2} day^{-1}. These values were consistent with similar measurements made elsewhere (Table 6.1, section 6.6).

On several occasions, negative fluxes were recorded in the untreated plot with the soil appearing to act as a sink for atmospheric N_2O. Transient sink behaviour has been noted in other studies (e.g. Ryden, 1981) and is usually associated with conditions conducive to microbial reduction of N_2O (i.e. high soil moisture content, lack of available NO_3^- and low soil temperatures). In the present experiment, negative fluxes were always close to the sensitivity limit for this technique and therefore it was not possible to unequivocally distinguish sink behaviour from sampling and analytical uncertainties. Increased sensitivity would be possible by decreasing the internal volume of the transparent hemispherical gas chamber.

7.3 EXPERIMENT 2 - THE EFFECT OF N SOURCE AND MOISTURE CONTENT ON N_2O PRODUCTION

7.3.1 Materials and Methods

7.3.1.1 Pasture block preparation and growth cabinet conditions

Blocks of soil complete with undisturbed pasture herbage were cut from the site used in Experiment 1 (section 7.2.1.4) and trimmed to fit neatly into 5 litre polypropylene containers (liver-pails). The containers and their contents were then divided randomly into 2 groups and adjusted to either 14.0% or 27.5% average soil moisture

content. The following day, all pasture blocks, except controls, received 0.5 g N applied as either calcium nitrate, ammonium sulphate or sheep urine in 100 ml of solution equivalent approximately to 200 kg N ha^{-1}. Control pasture blocks received 100 ml of distilled water. Duplicates of each treatment were placed in a growth cabinet at 70% relative humidity and subjected to a diurnal cycle which simulated 12 hours of daylight at 25°C and 12 hours of darkness at 15°C. The pasture blocks were watered to the required average soil moisture content (i.e. 14.0% or 27.5%) on 3 occasions during the ensuing 10 days.

7.3.1.2 Gas sampling and analysis

When the containers were fitted with an airtight lid, an enclosed air volume of about 1 litre was formed above the soil surface. The surface area directly exposed to the enclosed air volume was 290 cm^2. To monitor N_2O release rates, lids were sealed to the 5 litre containers for 1 hour approximately twice daily. Samples of the enclosed air were removed by syringe immediately after lid closure and again after 1 hour and stored in vacutainers for N_2O analysis using the gas chromatographic procedure described earlier (section 7.2.1.3). Samples containing N_2O concentrations greater than 10 ppmv were generally outside the linear response range of the detector and were re-analysed after diluting 1 : 10 with compressed air. Allowance was made for the N_2O content of the compressed air in subsequent calculations. The rate of N_2O release from the pasture blocks at each sampling time was then calculated from the change in N_2O concentration in the enclosed air volume during the period of lid closure (section 7.2.1.5).

7.3.2 Results

Total N_2O losses released after 7 days were again obtained by integrating the rate of loss curves for each pasture block (Figure 7.4 and Table 7.4).

Table 7.4 Nitrous oxide release from blocks of pasture soil, 165 hours after 100 ml applications of: sheep urine, ammonium sulphate$_{(aq)}$ and calcium nitrate$_{(aq)}$ (0.5 g N/100 ml) or distilled water (0 g N/100 ml).

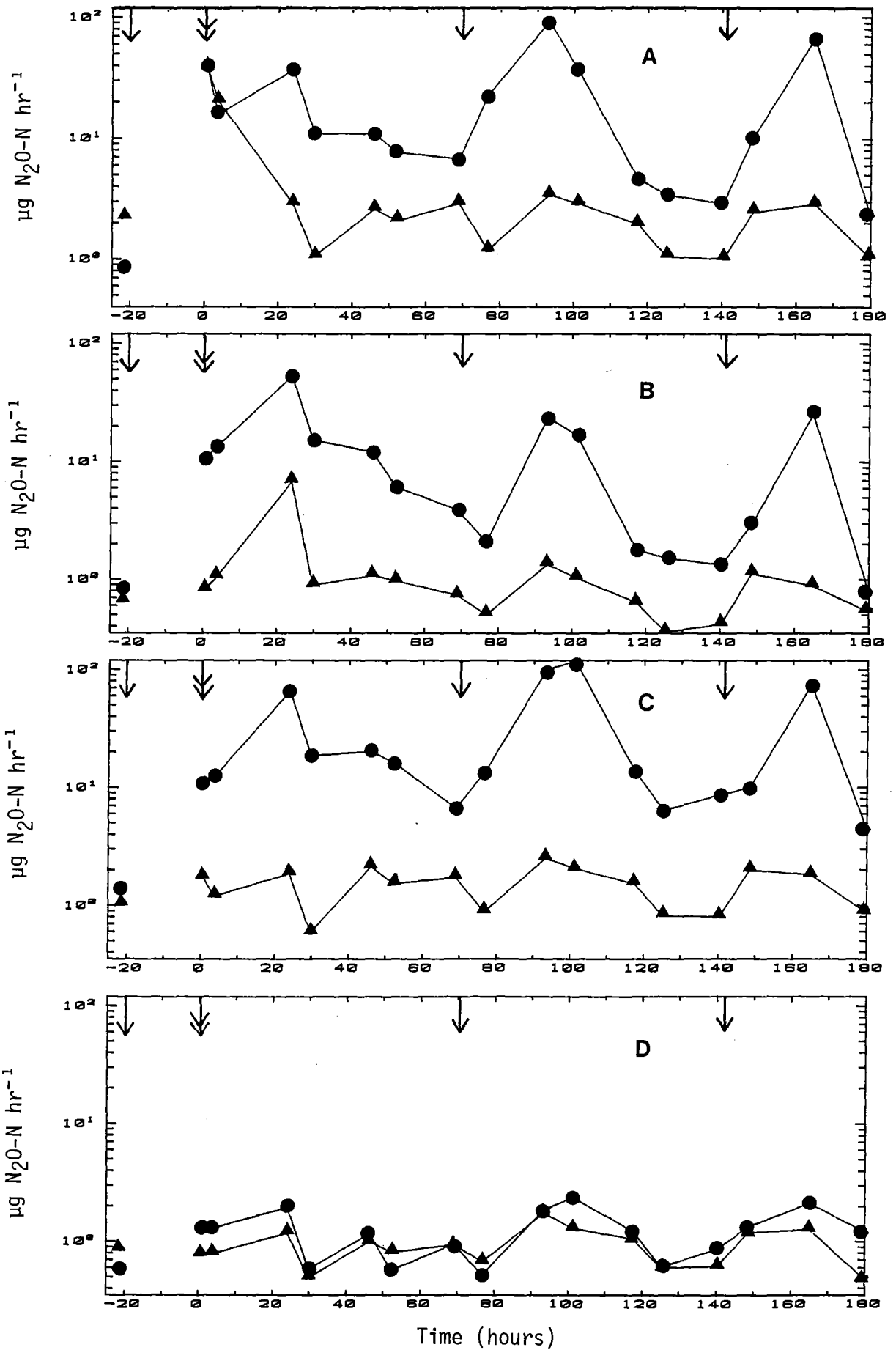
Maximum Moisture Content (%)	Treatment	Mean Estimated N_2O - N Release (mg N_2O - N)	(% of N Applied)
27.5	Control	0.20	-
"	Sheep Urine	3.81	0.72
"	Ammonium Sulphate	5.63	1.09
"	Calcium Nitrate	2.10	0.38
14.0	Control	0.16	-
"	Sheep Urine	0.64	0.10
"	Ammonium Sulphate	0.25	0.02
"	Calcium Nitrate	0.22	0.01

Analysis of variance showed that the pasture blocks watered to 27.5% average soil moisture content lost significantly more N_2O ($P \leqslant 0.05$) than pasture blocks maintained at 14.0% average soil moisture content. Within each moisture regime, differences in total N_2O losses between N treatments were not significant. Differences between the two moisture treatments were particularly apparent the day following the application of water (Figure 7.4, Appendix V) and this was confirmed by analysis of variance of individual release rates at each sampling time. Emission rates from the high moisture

Figure 7.4 Rate of N_2O production from pasture blocks at soil moisture contents of 27.5% (●) and 14.0% (▲) following applications of nitrogen (0.5 g N/100 ml) as:

A, sheep urine; B, calcium nitrate; C, ammonium sulphate; or D, control (0 g N/100 ml). ↡ = time of N application ↓ = time of water applications.

Figure 7.4



treatments were significantly greater ($P \leqslant 0.05$) on each of the days following watering and the initial application of aqueous N solution.

A single highly significant ($P \leqslant 0.01$) and unexpected difference in N_2O emission rates between the 3 N sources occurred immediately (0.6 hours) following aqueous N application when substantial N_2O release was measured from urine treated pasture blocks at both moisture regimes. No analogous emissions were observed from either of the other N treatments. While amounting to only a small fraction of the urine-N, this initial loss appeared unrelated to the soil moisture content and accounted for an estimated 66% and 17% of the total N_2O loss over 165 hours from the low and high moisture treatments respectively.

No clear diurnal fluctuations in N_2O emissions were apparent.

7.3.3 Discussion

The pasture blocks were fitted tightly into the polypropylene containers and it is reasonable to assume, therefore, that N_2O emissions occurred only from the soil surface. The small continuous emissions of N_2O measured on each sampling occasion from the control pasture blocks were equivalent to mean daily fluxes of 0.8 - 1.0 mg N_2O - N m^{-2} day^{-1}. Fluxes of this magnitude are again consistent with the values obtained during the earlier field experiment and with values reported by other workers (Table 6.1, section 6.6).

While similar small continuous emissions were measured from the N-treated blocks, it was obvious from the shape of the rate of loss curves (Figure 7.4) that N_2O release was greatly stimulated by the application of water. This effect was particularly apparent for the higher moisture treatment and is consistent with the findings of a

number of other workers (e.g. Ryden *et al.*, 1979b; Freney *et al.*, 1979; Denmead *et al.*, 1979). Maximum release rates were not detected immediately after water addition but were delayed until the following day. A similar effect has also been noted by Rolston *et al.* (1982). These workers measured both N_2 and N_2O fluxes after NO_3^- additions to soil followed by regular irrigations and found that N_2 fluxes were highest immediately after irrigation with maximum N_2O fluxes occurring 1 to 2 days later. It was suggested that the redistribution of water with time would make the soil profile less anoxic and favours the partial reduction of NO_3^- to N_2O rather than to N_2 (Rolston *et al.*, 1982). Whether this also applies to systems receiving ammoniacal-N treatments is unclear, since nitrification to NO_3^- would be a necessary precursor. Soil NO_3^- and NH_4^+ concentrations were not measured during this current experiment.

The rapid initial production of N_2O which followed the addition of sheep urine to soil had not previously been documented. It occurred only when urine itself was applied and not at a subsequent watering at which time the usual 24 hour delay was noted. Several mechanisms might account for these observations. The CO_2 generated upon the hydrolysis of urea in the urine might produce the rapid onset of anaerobosis in microsites within the soil and so initiate denitrification (Smith and Tiedje, 1979). The N_2O produced would then presumably result from NO_3^- already present in the soil. It is also possible that the N_2O was produced from a chemical reaction between small amounts of NO_2^- or NO_3^- contaminants present in the urine with other constituents of the urine or compounds present in the soil. Alternatively, the N_2O may have resulted from the reaction of minor urine components (e.g. amino acids or heterocyclic amino compounds) with soil constituents. These, and other possible mechanisms were briefly discussed earlier (section 6.6).

Unfortunately, it was not possible to discount the possibility that at least some of the initial N_2O production from urine was an artifact of the analytical technique used. The Porapak N analytical column (section 7.2.1.3) was later found to incompletely resolve CO_2 from N_2O. The presence of CO_2 concentrations greater than about 0.5% exerted a synergistic influence on the E.C.D. response to N_2O. This effect was subsequently described in detail by Hall and Dowdell (1981). It would appear from their findings and those of others (Bremner, 1978, personal communication) that similar problems of this sort may have affected N_2O analyses reported by other workers who have based their analyses on the early method of Rasmussen *et al.* (1976). An enhanced CO_2 flux from the soil surface might be expected upon urea hydrolysis and could result in elevated CO_2 concentrations in the headspace of the plastic containers. This in turn may have led to erroneously high N_2O results. The rapid initial emission of N_2O from urine clearly required further investigation.

7.4 EXPERIMENT 3 - THE EFFECT OF REPEATED APPLICATIONS OF SEVERAL NITROGEN SOURCES ON N_2O PRODUCTION

7.4.1 Materials and Methods

7.4.1.1 Pasture block preparation and sampling

Eight pasture blocks complete with undisturbed pasture herbage were prepared and inserted into polypropylene containers as described previously (section 7.3.1.1). These were transferred to a laboratory window box and maintained there under ambient lighting at a constant

temperature (20°C) for 47 days. During this period the blocks were watered on 8 occasions to field capacity (33% w/w average soil moisture content, Figure 7.5). Duplicate pasture blocks received on each of 3 occasions (i.e. on days 7, 19, and 40) 0.5 g N as either ammonium sulphate, urea or sheep urine in 100 ml of solution: equivalent to approximately 200 kg N ha^{-1}, giving a total application of about 600 kg N ha^{-1}. Control pasture blocks received 100 ml of distilled water. At the completion of the experiment (47 days) the pasture blocks were sectioned to 4 depths (0 - 3, 3 - 6, 6 - 10 and 10 - 14 cm) and subsamples were extracted with 2 mol l^{-1} KCl / phenyl mercuric acetate and analysed for NH_4^+, NO_3^- and NO_2^- (section 2.3.1.2).

7.4.1.2 Urine collection and analysis

For the previous experiments, (sections 7.2 and 7.3) urine was collected from sheep housed in metabolism cages and may have suffered from contamination by faecal material. The urine used in this and subsequent experiments was collected from a cannulated ewe and was free of faecal contamination. Subsamples of the urine analysed immediately after collection contained 13.7 g N per litre, of which 92.5% was urea-N, 0.6% NH_4^+ - N and 6.9% attributed to organic-N. The bulk of the urine was frozen as several separate samples. They were thawed and diluted as required with distilled water just prior to use. The NO_3^- and NO_2^- concentrations were each < 0.2 µg ml^{-1} and did not increase when stored frozen samples were thawed at room temperature. The pH of the urine was 7.1.

7.4.1.3 Gas sampling and analysis

In an attempt to minimize potential sampling problems, the enclosed pasture blocks were themselves transferred for sampling to the gas chromatograph. Samples for analysis were removed using a gas-sampling valve (Carle 8 port fitted with a 1 ml sample loop) and injected directly into the instrument. The analytical column was also changed to effect a more complete separation of CO_2 and N_2O. It consisted of a 3 m x 3 mm O.D. stainless steel column of Porapak Q maintained at 20°C. Carrier gas and flow rates were unaltered (section 7.2.1.3) but adequate separation of CO_2 and N_2O was achieved; their retention times being 195 and 242 seconds respectively. The decreased sample volume also increased the linear response range of the detector to 50 ppmv.

7.4.2 Results

The total amount of N_2O released from the pasture blocks in 45 days was very small, amounting to 9.3, 5.9, 2.6 and 2.0 mg from the urine, urea, ammonium sulphate and control treatments respectively which corresponds to 0.48%, 0.26% and 0.04% of the applied N for the 3 N treatments (Table 7.5). The total mean loss from the urine treated pasture blocks was significantly greater ($P \leq 0.05$) than from the ammonium sulphate and control blocks but not significantly different from the blocks treated with urea alone (Table 7.5).

The pattern of N_2O release from all the pasture blocks, including the controls, was very similar. Emissions of N_2O occurred continuously from all blocks but were greatly enhanced following water additions (Figure 7.5). Generally, the more water required to bring the average soil moisture content back to 33% the greater the magnitude of the subsequent N_2O pulse.

Figure 7.5 Mean soil moisture content (%) and rate of N_2O production from pasture blocks following repeated applications of nitrogen (0.5 g N/100 ml) as:

sheep urine, A (●); urea, B (■); ammonium sulphate, C (▲); or control, A (◆) (0 g N/100 ml). ↡ indicates time of N application.

Figure 7.5

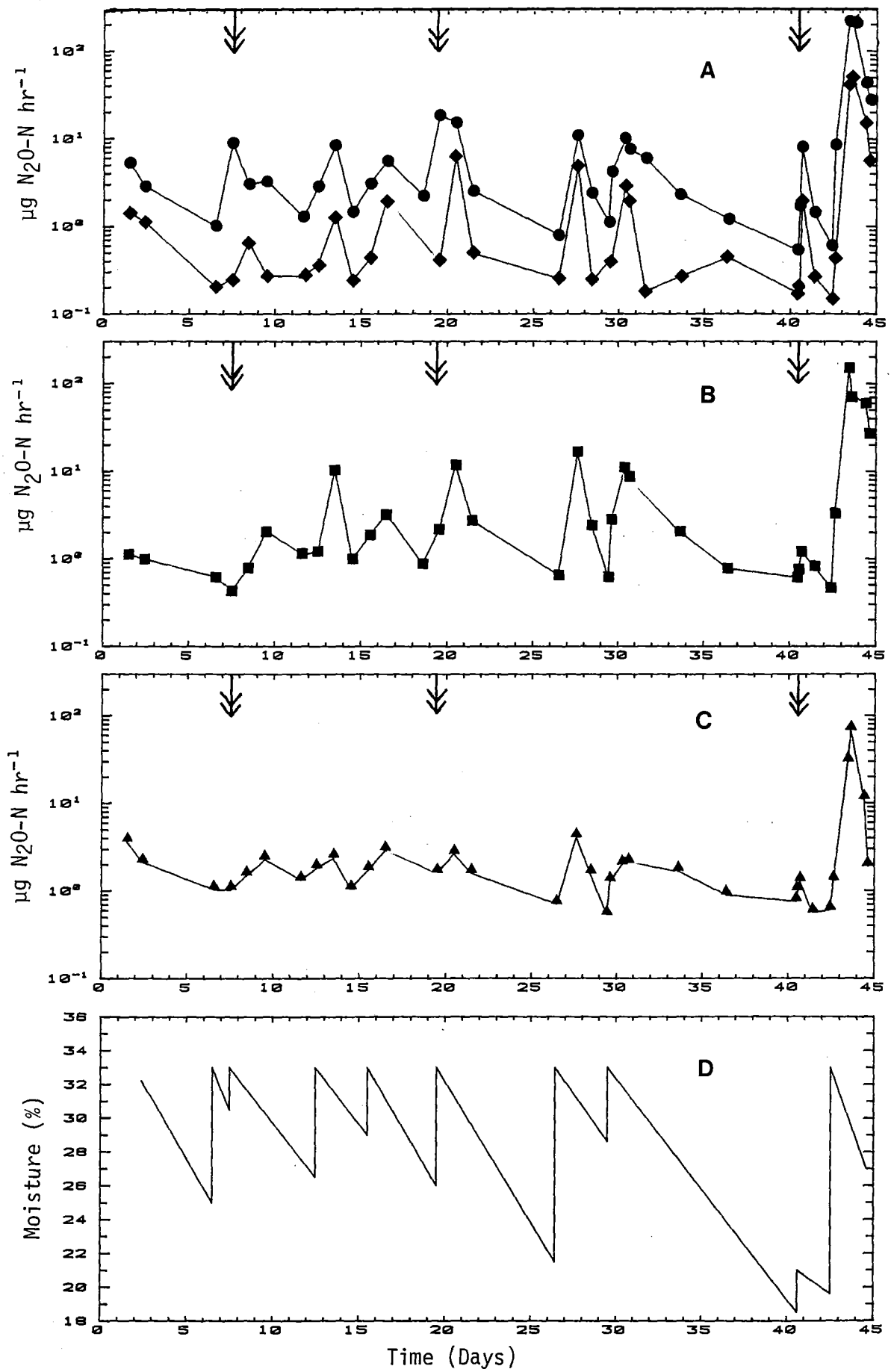


Table 7.5 N_2O release from blocks of pasture soil after the addition of 1.5 g N as sheep urine, $urea_{(aq)}$ or $ammonium\ sulphate_{(aq)}$ in 3 split applications (0.5 g N / 100 ml). Control treatments received 100 ml of distilled water. #

Treatment	Mean Estimated N_2O - N Release					
	Days 6 - 42		Days 42 - 45		Days 6 - 45	
	(mg)	(%)	(mg)	(%)	(mg)	(%)
Control	0.7 a	-	1.3 b	-	2.0 b	-
Urine	3.4 a	0.18	5.9 a	0.30	9.3 a	0.48
Urea	2.4 a	0.12	3.5 ab	0.14	5.9 ab	0.26
Ammonium Sulphate	1.3 a	0.04	1.3 b	0.00	2.6 b	0.04

#Column means followed by the same letter are not significantly different at the 5% level of probability.

The same rapid initial production of N_2O followed urine addition as noted previously (section 7.3.2). Immediately following each addition of aqueous N the N_2O emission rates from the urine treated blocks were significantly ($P \leq 0.05$) greater than from either of the other N treatments (Table 7.6).

The magnitude of the initial N_2O pulses following the first and third urine applications were similar (i.e. 9.1 and 8.2 μg N_2O - N per hour respectively). The second urine application coincided with watering and resulted in a larger N_2O pulse (i.e. 18.6 μg N_2O - N per hour or the equivalent of 15.6 mg N_2O - N m^{-2} day^{-1}). The total amount of N_2O emitted in the pulse immediately following the first urine application on day 7 was about 0.09% of the 0.5 g N applied. Assuming each of the 3 pulses lasted about 24 hours then they collectively accounted for about 30% of the N_2O released up to day 42.

Table 7.6 Mean N_2O release rates from pasture blocks immediately following repeated applications of aqueous-N or water. #

Treatment	Rate of N_2O Release (μg N_2O - N/hour) — Sampling Time (Days)		
	7.53	19.54	40.69
Control	0.25 b	0.40 b	2.08 b
Urine	9.14 a	18.56 a	8.22 a
Urea	0.43 b	2.17 b	1.22 b
Ammonium Sulphate	1.02 b	1.62 b	1.28 b

#Sheep urine, $urea_{(aq)}$, $ammonium\ sulphate_{(aq)}$ or water applied at 7.5, 19.5 and 40.6 days. Column means followed by the same letter are not significantly different at the 5% level of probability.

Of greater overall effect on the total amount of N_2O released from all pasture blocks was the single water addition on day 42 which returned the average moisture content from its driest condition (about 20%) to field capacity (Figure 7.5). From each pasture block, more than half of the total amount of N_2O released during the 45 day period was stimulated by the single water addition (Table 7.5).

Mineral-N analyses on day 47 established that high concentrations of KCl extractable NH_4^+ and NO_3^- existed throughout the N treated pasture blocks together with smaller amounts of NO_2^- (Table 7.7).

7.4.3 Discussion

Repeated additions of urine and aqueous urea was shown previously (section 2.3.2.2) to stimulate $NH_{3(g)}$ volatilization. Recently, Fleisher and Hagin (1981) demonstrated that the nitrification mechanism could be similarly stimulated and proposed this as a strategy to help reduce $NH_{3(g)}$

losses from surface applied urea (section 1.2.1.3). Therefore, it might be anticipated that a series of repeated ammoniacal-N applications would similarly stimulate nitrification and lead to increasing losses of N_2O via the nitrification pathway. While nitrification occurred readily in the N-treated blocks (Table 7.7) it would appear from this experiment that the repeated addition of aqueous ammoniacal-N was not a major factor influencing the extent of N_2O emissions. The major influence was rather the amount and frequency of successive water additions.

Table 7.7 Mineral-N content of dissected pasture blocks on day 47.

	Treatment											
	Urine			Urea			Ammonium Sulphate			Control		
	Mineral-N ($\mu g\ N\ g^{-1}$)											
Depth (cm)	NH_4^+	NO_3^-	NO_2^-	NH_4^+	NO_3^-	NO_2^-	NH_4^+	NO_3^-	NO_2^-	NH_4^+	NO_3^-	NO_2^-
0 -3	94	475	39	107	700	7	292	761	28	39	81	5
3 -6	22	218	8	77	232	29	221	134	21	5	18	3
6-10	56	133	20	32	132	16	170	108	3	5	20	3
10-14	176	118	6	145	208	16	263	139	12	12	29	0

The rapid initial N_2O release from urine treated pasture blocks was not observed when aqueous urea was used. This supports the speculations expressed earlier (section 6.6) regarding the possible differences in behaviour between urine and aqueous urea. The reasons for this difference remain unclear except that NO_3^- or NO_2^- contamination in the urine can probably be discounted. Assuming NO_2^- was present at the detection limit (0.2 $\mu g\ ml^{-1}$), a 100 ml application of a diluted sample would contain about 8 $\mu g\ NO_2^-$ - N

which is insufficient to account for the magnitude (about 100 - 200 μg N_2O - N) of each initial N_2O pulse. The speed of the initial release would tend to favour the suggestion of a chemical reaction, possibly between minor urine components and soil constituents. However, experiments using sterile soil and synthetic urine mixtures with ^{15}N labelling would probably be necessary to elucidate the exact mechanism. Fortunately, the modified gas chromatograph analytical procedure effectively eliminated the possibility of an experimental artifact and essentially confirmed the validity of the previous measurements (section 7.3.2).

7.5 EXPERIMENT 4 - THE EFFECT OF NITROGEN SOURCE ON THE INITIAL RATE OF N_2O RELEASE FROM SOIL

7.5.1 Materials and Methods

7.5.1.1 Soil preparation

In a preliminary study of initial N_2O release rates under nonsaturated aerobic conditions, small scale incubations were performed. Air dried samples of 0 - 10 cm Templeton silt loam soil (10 g, < 2 mm) were placed in 5 x 155 ml serum bottles fitted with gas tight neoprene rubber septa. The headspace gas was flushed with compressed air for 5 minutes and the bottles incubated at 20°C. To three of the bottles a 2.5 ml solution containing 25 mg N as sheep urine, urea or ammonium sulphate was added by syringe. Distilled water (2.5 ml) was added to the fourth serum bottle while the fifth received no amendments. Urine (2.5 ml) was added to a sixth serum bottle in the absence of soil.

7.5.1.2 Gas sampling and analysis

Gas sampling of the enclosed headspace for N_2O was initiated immediately after the addition of solution and continued for the following 2 hours. To overcome the earlier need to frequently flush and purge the analytical column (section 7.2.1.3), the sampling valve was operated in a backflushing mode. While this almost doubled the analysis time for an individual sample to about 9 minutes, it enabled the instrument to be used continuously. The sample volume was also decreased to 0.1 ml to prevent the removal of significant amounts of the headspace gas. This had the added advantage of further reducing possible interferences due to CO_2. A CO_2 concentration of at least 30% was required before tailing of the CO_2 peak influenced the following N_2O peak.

7.5.2 Results

The experiment was repeated 2 more times and the accumulated results plotted in Figure 7.6. From each individual headspace measurement a value for the rate of production of N_2O within the headspace was obtained. Analysis of variance of these values for all treatments showed that the mean rate of production from the urine treated soil samples (6.0 $\mu g\ N_2O\text{-}N\ kg^{-1}\ hr^{-1}$) was significantly greater ($P \leq 0.05$) than from samples treated with ammonium sulphate, urea or water (i.e. 1.0, 3.1 and 2.7 $\mu g\ N_2O\text{-}N\ kg^{-1}\ hr^{-1}$ respectively). Differences between initial rates produced from urea, ammonium sulphate and water were not significant. No N_2O was produced from the unamended soil or from urine in the absence of soil.

Figure 7.6

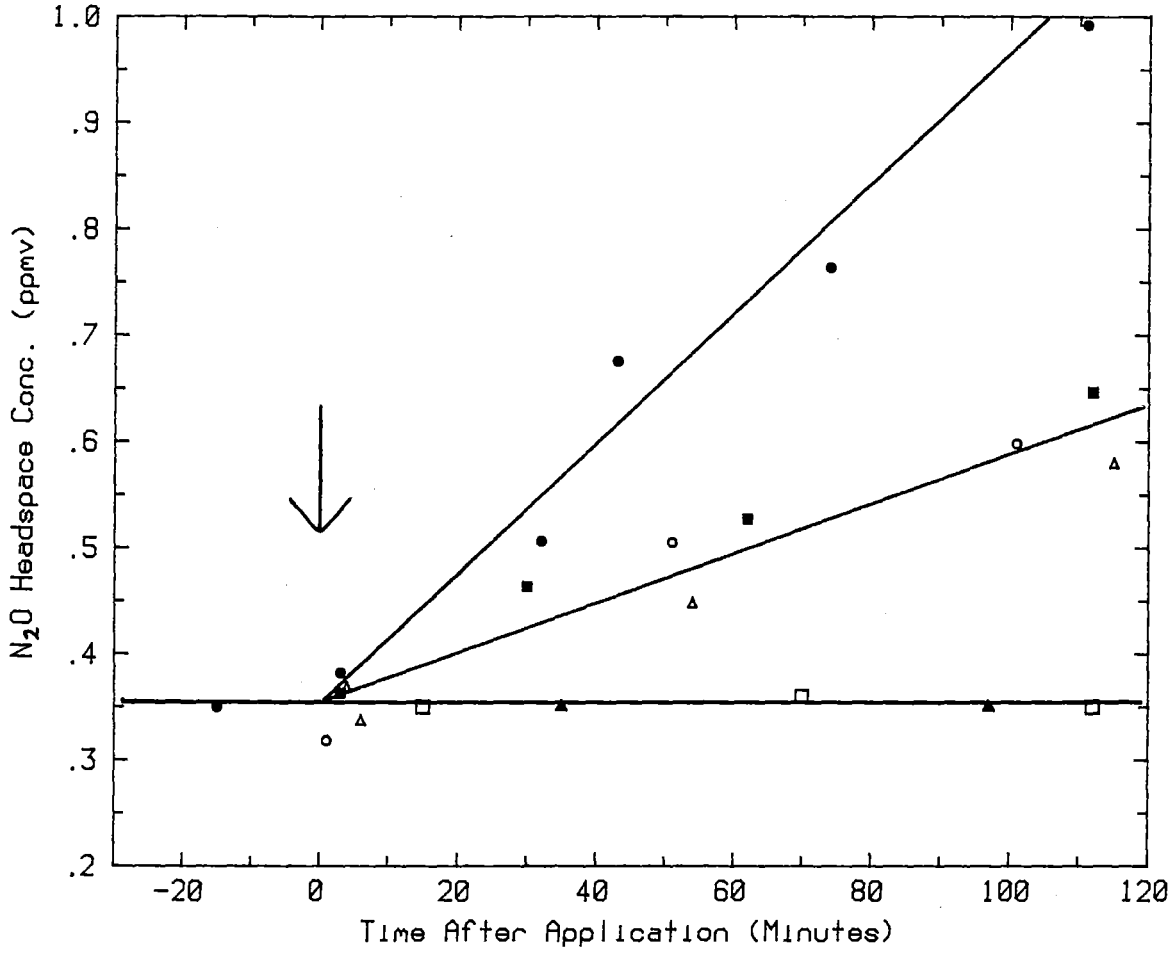


Figure 7.6 Change in N_2O headspace concentration with time immediately following applications of ammonium sulphate, urea, sheep urine and water.

▲ = soil (10 g)
○ = soil (10 g) + H_2O (2.5 ml)
△ = soil (10 g) + 25 mg NH_4^+ - N + H_2O (2.5 ml)
■ = soil (10 g) + 25 mg urea - N + H_2O (2.5 ml)
● = soil (10 g) + 25 mg urine - N + H_2O (2.5 ml)
□ = no soil + 25 mg urine - N + H_2O (2.5 ml)
↓ = application

7.5.3 Discussion

This experiment showed that the addition of aqueous solutions, with and without added N, immediately stimulated the production of N_2O from the Templeton silt loam soil. Sheep urine further stimulated initial N_2O production but the presence of dissolved N as ammonium sulphate or urea had no additional measurable influence. These results agree with the previous findings (sections 7.3.2 and 7.4.2) that urine addition produces an immediate emission of N_2O. The results also confirm the earlier findings of Freney *et al.* (1979) in which the addition of water to air-dry soil was shown to immediately stimulate N_2O production. Short-term incubation experiments of this sort could be useful in elucidating the mechanism responsible for the initial N_2O release from urine.

CHAPTER 8

GENERAL DISCUSSION AND CONCLUSION

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CHAPTER 8

GENERAL DISCUSSION AND CONCLUSION

8.1 FIELD MEASUREMENTS

8.1.1 Chamber Design

The principal objective of the field experiment was to obtain estimates of N_2O emission rates from N-treated pasture under temperature and moisture conditions conducive to both denitrification or nitrification. A desire to ensure the continuation of photosynthesis and to maintain conditions above and within the field plots as close as possible to ambient, dictated the use of a transparent chamber. This in turn imposed a need for active cooling of the chamber air to prevent a greenhouse effect and consequently limited its use to a site supplied with electricity and a water supply. It also imposed severe limitations on the number of chambers deployed simultaneously and therefore restricted the replication of measurements. Most other workers have opted for simpler chamber designs which allow greater portability, and are more easily fabricated but which are usually opaque and have only a limited ability to maintain ambient air temperatures. Whether the need to sustain photosynthesis and near ambient air temperatures is worth the encumbrances outlined above is debatable, and with hindsight a simpler design may have been more worthwhile.

8.1.2 Initial Rate of N_2O Emission

The N_2O emission rate during the first sampling occasion immediately following urine application was twice the initial rate

from the calcium nitrate treated plot and over 4 times the initial rate from the ammonium sulphate plot (Table 8.1). Thus, the rapid initial emission of N_2O from urine that was identified during experiments 2 - 4 also appeared to take place during the field experiment. However, the lack of plot replication precluded a statistical comparison as was carried out for the subsequent experiments.

Table 8.1 Mean rate of N_2O production immediately following aqueous-N or water applications to field pasture plot (1040 - 1155 hours, 2/10/78).

Rate of N_2O Release (μg N_2O - N per hour)			
Treatment			
Sheep Urine	Calcium Nitrate	Ammonium Sulphate	Control
61	28	14	-3

8.1.3 Diurnal Effects

Where N_2O production from soil appears to occur as a product of nitrification, diurnal N_2O fluctuations correspond with fluctuations in topsoil temperature (Denmead *et al.*, 1979). Maximum emission rates generally occur in the afternoon with minimum rates around sunrise. The variations in N_2O emission rates apparent during Experiment 1 also fluctuated diurnally but peak fluxes generally occurred around midnight (Figure 7.2). The fluctuations in emission rate lagged behind the temperature variations in both the surface air and the 5 cm soil depth but appeared to correspond with temperature fluctuations at 10 cm depth

(Table 7.3). This could mean that N_2O production was sited closer to 10 cm rather than at the soil surface. However, the magnitude of the temperature fluctuations at 10 cm (approx. $\pm$ 2°C) were probably insufficient by themselves to produce such large variations (e.g. a factor of 10) in N_2O release rates. Diurnal variations in N_2O fluxes, which were also too large to be explained by temperature fluctuations alone, have been measured in similar field experiments reported by other workers (Denmead *et al.*, 1979; Christensen, 1983b). Christensen (1983b) suggested that diurnal fluctuations in root respiration activity might tend to reduce oxygen concentrations in the rhizosphere and enhance N_2O emissions via denitrification. This mechanism may also have contributed to the diurnal N_2O variations measured during Experiment 1.

If the N_2O released in Experiment 1 had resulted principally as a product of a denitrification reaction then the rate of N_2O release would depend on both the overall rate of denitrification and the $N_2O / N_2O + N_2$ mole ratio. Variations in temperature affect both of these quantities but in opposite respects (Rolston, 1981). Therefore, while the rate of denitrification would be expected to decrease as temperature decreases, the mole fraction of N_2O in the product gases might be expected to increase. Daily variations in soil moisture due to evapotranspiration and dew formation might also affect the overall denitrification rate and N_2O mole ratio. Thus, under field conditions, N_2O emission rates might continue to increase as soil temperature decreases diurnally. Direct measurements of N_2 emission rates were not attempted during Experiment 1, and consequently this additional suggestion must remain highly speculative. The results of Experiment 1 do, however, point out the need to examine diurnal effects

in greater detail and illustrate the potential for both the underestimation or overestimation of N_2O emissions based only on single daily measurements.

8.2 GROWTH CABINET AND LABORATORY MEASUREMENTS

8.2.1 Spatial and Temporal Variability in N_2O Emissions

The structurally intact blocks of freshly cut pasture soil used in the growth cabinet and laboratory experiments served as a useful compromise between small scale incubation experiments which are difficult to relate back to field situations and the more technically demanding field measurements. However, the use of field fresh substrate brings with it the associated problem of high spatial field variability which was reflected in the N_2O emission rates from the pasture blocks. For example, emission rates measured from pasture blocks cut from several square metres of an apparently uniform site gave coefficients of variation of about 80% prior to N application (see Appendices V and VI). High spatial variability in N_2O emission rates has led several investigators to adopt highly replicated experimental designs to distinguish treatment effects or effects associated with soil type (e.g. Breitenbeck *et al.*, 1980; Bremner *et al.*, 1980). Others have examined the temporal variability of individual field plots (e.g. Denmead *et al.*, 1979; Christensen, 1983b). These studies have indicated that individual sites exhibit both short and long term temporal variations in N_2O emission rates associated with factors such as temperature changes or rainfall events, which are at least as large as those associated with spatial variations.

The use of duplicate pasture blocks and a sampling frequency of 1 - 2 samples per day was a compromise adopted in an attempt to accommodate the comparison of treatment effects associated with different N sources as well as the short term effects of watering. The conclusions and extrapolations to the field situation which are based on these measurements attempt to recognise the inherent uncertainties associated with this less than ideal experimental design.

8.3 SIGNIFICANCE OF N_2O EMISSIONS FROM SHEEP URINE AND FERTILIZER NITROGEN APPLIED TO PASTURE SOIL

8.3.1 Agronomical Significance

8.3.1.1 Estimation of maximum annual $N_2O_{(g)}$ loss

Unlike an $NH_{3(g)}$ volatilization event which is essentially complete within a limited time span (e.g. 4 - 8 days, Chapter 2), the pasture block experiments showed that N_2O release was able to be repeatedly stimulated by successive applications of water. The influence of added water was particularly apparent when the average moisture content of the soil after addition approached field capacity (Figures 7.4 and 7.5). The magnitude of the N_2O pulses increased as the amount of water added increased. While emissions of N_2O from the ammoniacal-N sources probably resulted from a side reaction to the nitrification reaction (section 6.3.2) subsequent emissions upon re-watering would have included contributions due to the denitrification pathway (section 6.2.1). Irrespective of the actual mechanism of production, under field conditions successive pulses would be expected to diminish in magnitude as soil mineral-N levels decreased due to plant uptake, $NH_{3(g)}$

volatilization, immobilization, leaching and denitrification as N_2. Soil mineral-N concentrations within urine patches have been shown to approach background levels after 2 - 3 months (Ball *et al.*, 1979; Carran *et al.*, 1982; and section 2.2.3.6). Therefore, the ultimate extent of N_2O loss following a single fertilizer or sheep urine application to pasture soil should depend not only upon the amount and persistence of the mineral-N within the soil but also on the amount and frequency of successive water additions.

Extrapolation of the pasture block experiments to the field situation should be approached with caution. Circumstantial evidence providing some justification for doing this was obtained from the close agreement between N_2O emission rates from unamended soil (Experiment 2), the value obtained in the earlier field experiment (Experiment 1) and values from similar field experiments reported elsewhere (e.g. Denmead *et al.*, 1979; Burford *et al.*, 1981; Webster and Dowdell, 1982; Christensen, 1983b). This agreement encouraged further extrapolations as described below, in an attempt to estimate the maximum likely annual N_2O loss from sheep urine deposition to a grazed pasture in Canterbury.

From Experiment 3, the greatest mean daily loss from all treatments, including controls, followed the application of water (equivalent to about 25 mm of rainfall) on Day 42 (Figure 7.5). The water was added 13 days after the previous watering and stimulated a total mean N_2O - N loss from the urine treatments of 5.9 mg N_2O - N (Table 7.4). After subtracting the control, the mean rate of loss during the 13 day drying and rewetting event was 0.35 mg per day (i.e. 0.023% per day, or about 8.6% per year). A repeated addition of 25 mm of water every 13 days would be equivalent to 700 mm yr^{-1}, and closely approximates the annual rainfall of many areas of the Canterbury Plains (Crush, 1979). From the

shape of the rate of loss curves (Figure 7.4 and 7.5), it is reasonable to assume that successive drying and rewetting cycles at 13 day intervals would stimulate further N_2O pulses. Assuming mineral-N levels persisted above the background levels for 3 months, then extrapolation of these results to the field situation suggests that probably less than 2% of the urine-N would be released as N_2O under the conditions described above. This would amount to about 4 kg N_2O - N ha^{-1} yr^{-1} directly attributable to sheep urine patches in a typical, grazed, ryegrass white-clover pasture in Canterbury (section 2.3.3.1). This in turn is the equivalent of about 3% of the estimated total annual N inputs (135 kg N, section 2.3.3.1) and therefore consitutes an agronomically insignificant amount of the N cycled annually in the urine of grazing animals.

While recognising the inherent uncertainties involved in the pasture block measurements (section 8.2.1), this estimation was based on the drying rewetting event which registered the maximum daily N_2O loss, and from pasture blocks in which added sheep urine had undergone transformations to both ammoniacal and nitrate-N (Table 7.7). Under varying annual field conditions, actual N_2O losses would probably be less than this, since low soil moisture levels are common for protracted periods during summer and prolonged waterlogging is rare in the silt-loam soils of Canterbury (Crush, 1979).

An estimated maximum loss of 2% of the applied urine-N is also consistent with the results of field experiments in which concentrated urea solutions were used to simulate ungulate urine deposition on a native shortgrass prairie in Colorado (Mosier *et al.*, 1981). Total N_2O - N losses after 3 months amounted to 0.6% of the applied urea-N. No other estimates from simulated urine patches have been reported.

8.3.1.2 The $N_2O / N_2O + N_2$ ratio and N_2 emissions

The production and release of N_2O via the denitrification pathway is almost invariably accompanied by simultaneous emissions of N_2 (section 6.2). The instantaneous ratio of these two gases is often highly variable. Published values range from 0 - 1 (e.g. Rolston *et al.*, 1982) and depend upon the interaction of many factors. These include: soil type, soil NO_3^- concentration, soil temperature, soil pH and degree of anoxia as influenced by moisture content and microbial activity (Rolston, 1981 and section 6.2). However, it would appear from the very limited field data available that the ratio of the total amounts of each gas produced over an extended time period may be considerably less variable. For example, Rolston *et al.* (1982) measured the emission rates of both gases from a Yolo loam treated with 285 kg N ha^{-1} as KNO_3 under 3 different irrigation regimes. The same amount of water was applied at frequencies of 3 irrigations per week, 1 irrigation per week and 1 irrigation every 2 weeks, to areas cropped with perennial ryegrass. Total denitrification losses were measured using both the ^{15}N and C_2H_2 inhibition method for 52 days and amounted to 4.2, 3.3 and 2.3 kg N_2O - N ha^{-1} respectively for the 3 irrigation regimes. While the N_2O mole ratios determined under the widely differing irrigation and soil moisture conditions also varied widely between sampling times, the time-averaged N_2O mole ratios for the various irrigation treatments were similar (0.25 $\pm$ 0.05) (i.e. 20 - 30% of the denitrified N from each treatment appeared as N_2O). This close agreement would appear to provide tentative evidence that field measurements of total integrated N_2O losses, which have been suitably calibrated using ^{15}N or C_2H_2 inhibition techniques, may also provide

worthwhile estimates of denitrification losses as N_2. Similar findings have recently been reported by Lensi and Chalamet (1982).

Unfortunately, this potential application may be inadequate for the assessment of N_2 losses following applications of ammoniacal fertilizers, urea, or urine. Urine-N is principally urea-N and readily hydrolyses to NH_4^+ on contact with soil (section 2.3.2.3). Therefore, within a sheep urine patch, some initial N_2O production probably results from nitrification of ammoniacal-N with both the nitrification and denitrification pathways contributing subsequently. The C_2H_2 inhibition technique is known to inhibit nitrification (section 6.5.2). Therefore, its field use to measure N_2 losses from urine patches would fail to include any N_2O loss resulting from the oxidative pathway. Conversely, in the absence of C_2H_2, N_2O emissions could include losses arising from both the oxidative and reductive pathways and the values obtained may, therefore, be inappropriate for the calculation of valid $N_2O / N_2O + N_2$ mole ratios. These potential problems have yet to be checked by direct field measurements.

High concentrations of ^{15}N label could also be used (e.g. Rolston *et al.*, 1982), but only as a synthetic urine mixture. To adequately account for all possible mechanisms of loss, ^{15}N labelling of each potentially active nitrogenous compound within the urine would be required and this could be both difficult and expensive. Nevertheless, the use of synthetic urine containing high concentrations of ^{15}N labelled urea-N could provide useful information about N_2 and N_2O release from pasture soils.

The direct gas lysimetric technique described by Limmer *et al.* (1982) also appears to offer the potential for measuring both N_2 and N_2O emissions from urine patches in grazed pastures (see section 6.5.2).

The single *in situ* measurement reported by these workers gave calculated emissions rates of 71.2 mg N_2 - N m^{-2} day^{-1} and 7.4 mg N_2O - N m^{-2} day^{-1}, equivalent to 260 kg N_2 ha^{-1} yr^{-1} and 27 kg N_2O ha^{-1} yr^{-1} respectively. The crop and site history of the Horotiu silt loam soil used in the study were not stated. A possible drawback with this method is the overestimation of N_2 fluxes due to the desorption of N_2 dissolved in the soil solution. The contribution of this dissolved N_2 to the measured N_2 flux from the soil surface is unknown.

Given the limited amount of field data currently available it is quite premature to use published $N_2O / N_2O + N_2$ mole ratios for estimating total denitrification losses from urine patches. Many more field experiments are needed before such ratios are likely to be used with any confidence. However, the small fractions of applied-N generally reported lost following ammoniacal fertilizer and simulated urine applications (e.g. Mosier *et al.*, 1981) together with the large fractions often unaccounted for in the soil, plants, leachate, or as volatilized $NH_{3(g)}$, (e.g. Ball *et al.*, 1979; Carran *et al.*, 1982) indicates that substantial amounts of N_2 may be lost from urine patches by denitrification.

8.3.1 Global Significance

To place the contribution of N_2O released from urine patches in a global context it is necessary to briefly review current understanding of N_2O cycling. The original theoretical predictions of Crutzen (1974) were that a doubling of the atmospheric N_2O concentration would lead to a 20% decrease in total ozone (O_3) in the stratosphere. Since stratospheric O_3 is responsible for absorbing potentially harmful ultra-violet radiation,

a perturbation of such magnitude would lead to an increase in ultra-violet intensity at ground level with potentially dangerous consequences to life (Bolin and Arrhenius, 1977). The effects of an increase in N_2O concentration have recently been substantially revised by the discovery of a hitherto unrecognised series of reactions which lead to the formation of O_3 within the troposphere. These are represented generally by the equations:

$$RO_2 + NO \longrightarrow RO + NO_2$$

$$NO_2 + h\nu \longrightarrow NO + O$$

$$O + O_2 + M \longrightarrow O_3 + M$$

$$\text{net} \quad RO_2 + O_2 \longrightarrow RO + O_3$$

where R = CH_3, CH_3CO and H (Crutzen, 1981). Thus, N_2O (which decomposes photochemically to NO) is now implicated in both the destruction of stratospheric O_3 and the formation of tropospheric O_3. The net result of an increase in atmospheric N_2O concentration now appears to be a lowering of the centre of mass of the O_3 to altitudes below 25 km as well as a possible overall increase in global O_3 concentrations (Crutzen, 1981). Thus, the original scenario is now largely discounted. However, both O_3 and N_2O absorb infra-red radiation and are therefore important to the thermal stability of the atmosphere. Increases in the concentrations of both of these compounds may add significantly to the Earth's "greenhouse" effect by trapping outgoing terrestrial radiation, thereby causing an increase in surface temperatures (Wang *et al.*, 1976). The long-term consequences of this may be just as severe as O_3 depletion.

A recent estimate of the effect of the increased usage of fertilizer-N indicated that a doubling of the N_2O content of the

atmosphere could occur at the earliest by the end of the next century (Crutzen, 1981). This estimate was based on a N_2O / N_2 production ratio of 20% for both terrestrial and aquatic denitrification, together with an anticipated increase in N-fixation to 200 Tg N yr^{-1} by early next century. However, the estimate only attempted to quantify the contributions due to the increasing use of artificially fixed fertilizer-N and did not include possible increases in global N_2O production rates due to nitrification losses (Bremner and Blackmer, 1978), or from the burning of biomass (Crutzen *et al.*, 1979). It also failed to include possible increased emissions from land receiving no artificially fixed N but planted with N fixing legumes, and from the excreta of animals grazing on such land. Each of these latter sources is clearly of recent anthroprogenic origin and has probably stimulated N_2O emissions above those of earlier geological times (Delwiche, 1977).

With regular inputs of fertilizer-N in a cropping situation, annual N_2O emissions would be expected to be related to the total amount of N applied. However, in a grazed pasture, the grazing animal is likely to have an additional major influence. Not only would the application of N fertilizers result in some direct N_2O production, but N_2O release would also be expected from each urine patch. To give some scale to the effects of free grazing, it was estimated previously (section 2.3.3.1) that a typical grazed pasture in Canterbury would support 20 sheep ha^{-1} yr^{-1} and receive 200 kg N ha^{-1} yr^{-1} as cycled urine in addition to 120 kg N from symbiotic N fixation. If the same pasture had been cropped for seed or hay, it would presumably not suffer the N_2O emissions of up to 4 kg N_2O - N ha^{-1} yr^{-1} (section 8.3.1.1) from the 200 kg N deposited as urine. This simple comparison should not, however, be interpreted as implying a difference in the ultimate fate of the 120 kg N fixed in either system.

In a cropped system, the crop is removed, processed, and often consumed elsewhere either by humans or animals, whereupon it is excreted, with the fixed N only then undergoing possible denitrification (Delwiche, 1981). On the other hand, in the pasture system a portion of the fixed N is continuously cycled through the urine and dung of the animals and therefore subject to possible denitrification *in situ*. Thus, the urine patch in a grazed pasture system is seen not only as the focus for the loss of fixed N via leaching and $NH_{3(g)}$ volatilization (Ball *et al.*, 1979) but also as the focus for the production of N_2O.

The measurements made in the present study also indicated an additional initial N_2O loss each time urine was applied to pasture soil but not when aqueous solutions of ammonium sulphate, calcium nitrate or urea were supplied. The magnitude of this initial loss was unrelated to the moisture content of the soil and was estimated at about 30% of the total N_2O loss from each simulated urine patch (section 7.4.2). While forming only a small and agronomically insignificant fraction of the N estimated as fixed annually, this initial loss (approximately 0.09% of the urine-N) was comparable to the total N_2O losses sustained following applications of ammoniacal fertilizers to cropping soils in several overseas studies (Breitenbeck *et al.*, 1980; Cochran *et al.*, 1981). Whatever the origin of this N_2O, it would need to be considered in any global N_2O model which included contributions from grazing animals.

8.4 SCOPE FOR FUTURE RESEARCH

8.4.1 Initial N_2O Release from Urine Patches

A sustained effort is required to elucidate the mechanism responsible for the observed initial release of N_2O which follows urine addition to pasture soils (sections 7.3 - 7.5). Also, in the absence of contrary evidence, it must be presumed that these initial N_2O emissions are accompanied by simultaneous emissions of other nitrogenous gases, especially N_2. If such emissions occur, they may be of agronomical significance. Short-term incubation experiments (e.g. section 7.5) carried out in atmospheres free of N_2 would be useful in demonstrating the existence of possible initial emissions of other nitrogenous gases.

8.4.2 Long Term Field Measurements

It appears from the present work that N_2O losses from urine patches in grazed pasture soil are of little agronomical significance. Future research should therefore be directed towards quantifying possible losses of N_2 by denitrification. Laboratory assays of the denitrification potentials of soil can yield valuable information about the factors which influence denitrification (Limmer and Steele, 1982). However, the interaction of these factors in the field is difficult to simulate in the laboratory and even the use of intact blocks of pasture soil in controlled growth cabinet experiments is only a poor substitute for sustained, direct, long-term field measurements. Unfortunately, the methodological problems that have plagued field measurements of N_2 emissions (section 6.5 and 8.3.1.2) continue to be the greatest single obstacle to the realization of this goal.

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GENERAL SUMMARY

The general physico-chemical and biological factors which are known to influence ammonia volatilization are reviewed in chapter 1. Specific reference is also made to the effects of plants and volatilization from calcareous soils and from urine patches.

Chapter 2 describes experiments in which ammonia volatilization losses from simulated sheep urine patches in a perennial ryegrass (*Lolium perenne* L.) / white clover (*Trifolium repens* L.) pasture in Canterbury, New Zealand were measured in the field during the summer, autumn and winter periods. An enclosure technique was used with microplots (23 cm diameter) receiving either sheep urine or aqueous urea at rates equivalent to 500 kg N ha^{-1} and monitored continuously until measured losses decreased to 0.5% per day. Mean volatilization losses from urine treated plots were 22.2% of the applied N in summer, 24.6% in autumn and 12.2% in winter. Corresponding losses from the urea treated plots were 17.9%, 28.9% and 8.5%. Differences between these two N sources were not significant although the seasonal differences were significant ($P \leqslant 0.05$). Changes in $NH_{3(g)}$ fluxes were found to be related to measured changes in soil pH and air temperature. Two repeated applications of urine or aqueous urea to the same microplot resulted in significantly greater subsequent volatilization losses averaging 29.6% from the second and 37.5% from the third application.

Most of the applied N was accounted for as either soil mineral N ($NH_4^+ + NO_3^-$) or $NH_{3(g)}$. Preliminary experiments under similar conditions showed no measureable $NO_{2(g)}$ was released. Urea hydrolysis was rapid and obeyed first order kinetics during the 24 hours following

application. Calculated half-lives of urea in urine and aqueous urea were significantly different and were 3.0 and 4.7 hours respectively during the summer and 4.7 and 12.0 hours during the autumn.

Implications of the results obtained to practical field situations together with the efficacy of the enclosure technique for measuring volatilization losses are discussed.

Theoretical considerations for the development of a simplified model for predicting volatilization losses of ammonia gas ($NH_{3(g)}$) from the urine patches of grazing herbivors in a pasture ecosystem are presented in chapter 3. The volatilization of $NH_{3(g)}$ is treated as a physico-chemical phenomenon based on the soil solution chemistry of urine patches to develop a general equation to describe the rate of volatilization from a pasture surface. A semi-empirical approach was then used in which published data define typical limits for the parameters appearing in the volatilization equation. This led to the simplification of the general volatilization equation into a more usable and more readily verifiable form.

The dominant factor in determining the rate of volatilization of $NH_{3(g)}$ was shown to be the soil surface pH. To better understand the dynamics of pH changes within urine patches, the more extensive literature dealing with volatilization losses from flooded soils was reviewed. From the apparent similarities between the two systems a procedure was described by which a careful monitoring of soil surface pH as a function of time could be used to solve the simplified equation.

To calculate $NH_{3(g)}$ fluxes this model requires the following as input data: a knowledge of the disposition of the applied-N within the soil profile; the rate of urea hydrolysis in the topsoil; and soil surface pH and temperature measurements throughout the duration of a volatilization event.

Published field experimental data together with the field experimental data from this present study were used in chapter 4 to compare measured $NH_{3(g)}$ losses following applications of urine or aqueous urea to pasture soils with values predicted by the simplified ammonia volatilization model. Total measured losses were generally in close agreement with predications. For example, predicted losses following applications of urine to a ryegrass - white clover pasture in the present study were 20.7% in summer and 22.4% in autumn and were highly correlated with measured losses of 21.5% and 24.4% respectively ($r = 0.998$).

The model was also tested for instantaneous rate of ammonia gas loss at 33 discrete sampling times for the summer experiment. Correlations were again highly significant ($r = 0.951$ for urine and $r = 0.885$ for urea).

The interception of urine solution by herbage and litter on the pasture surface is discussed and was shown to account for some of the discrepancies between measurements and predictions. Soil surface pH was confirmed as an important factor in determining the extent of ammonia gas loss, and the practicalities of measuring this parameter under field conditions are presented. It was concluded that the model offers the potential for predicting ammonia volatilization losses following urine or aqueous urea applications to short pasture in non-leaching, non-nitrifying environments.

Chapter 6 provided a general review of the mechanisms by which other nitrogenous gases (N_2O, N_2 and NO) are released from soil. Particular reference was made throughout to field measurements and the factors which influence the rate of release of these gases under field conditions.

Field, growth cabinet and laboratory measurements of N_2O emissions from simulated urine patches are reported in chapter 7. A sensitive electron-capture / gas chromatographic analytical procedure was combined with a short duration enclosure method to monitor the build-up of N_2O in the enclosed headspace above the pasture surface. Measured N_2O losses from sheep urine and other inorganic N fertilizers were small, with maximum losses estimated at < 2% of the applied N. Fluxes of N_2O from untreated soil were similar for all experiments. Values ranged from 0 - 2.1 mg N_2O - N m^{-2} day^{-1} and agreed with values reported in the literature. It was concluded that direct gaseous N_2O losses from typical silt-loam pasture soils in Canterbury were of little agronomical significance.

Whereas N_2O release following applications of aqueous urea, ammonium sulphate or calcium nitrate took 12 - 24 hours to peak, significantly greater ($P \leq 0.05$) N_2O fluxes were measureable immediately after the application of urine. This immediate release of N_2O occurred only when urine itself was applied to soil and not at subsequent waterings. Then the usual 12 - 24 hour delay was noted. The initial N_2O pulse from urine was unrelated to soil moisture content and amounted to about 30% of the N_2O lost from each urine patch or about 0.09% of the applied urine-N.

In chapter 8 the origin and significance of the initial N_2O from urine was discussed and it was concluded that any global N_2O model would need to include this hitherto unrecognised source of the gas.

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APPENDIX I

```
10 REM                AMMONIA VOLATILIZATION
12 REM                  SIMULATION PROGRAM
14 REM
16 REM       'NN' = N volatilizable at beginning of cycle for
18 REM              soil-N pool.
20 REM       'NM' = As for 'NN' but for leaf-surface N pool.
22 REM       'FI' = N volatilizable at the end of the cycle
24 REM              for soil-N pool.
26 REM       'FM' = As for 'FI' but for leaf-surface N pool.
28 REM       'DN' = Additional N input during cycle for
30 REM              soil-N pool.
32 REM       'DM' = As for 'DN' but for leaf-surface N pool.
34 REM       'TI' = Time increment for cycling model ( hours )
36 REM       'NH3'= Ammonia flux ( mg NH3-N/hr ) released at the
38 REM              end of the cycle (soil-N pool only).
40 REM       'NZ3'= As for 'NH3' but for leaf-surface N pool.
46 REM       'T'  = Actual real time for finish of cycle
48 REM              measured relative to initiation = 0.
54 REM       'U0' = Percentage of N added present in soil-N pool
56 REM       'U1' = As for 'U0' but for leaf-surface pool.
62 REM       'A'  = Urea ( or urine ) 1st order decay constant
64 REM              (soil-N pool only).
66 REM       'A1' = As for 'A' but for leaf-surface N pool.
68 REM       'K'  = Volatilization decay constant.( hours -1)
70 REM       'K1' = As for 'K' but for leaf surface N pool.
72 REM       'AV' = Variable used in averaging calulation for
74 REM              NH3 flux per hour.
76 REM       'AZ' = As for 'AV' but for leaf-surface N pool.
78 REM       'HR' = Henry's Law temperature scaling ratio
80 REM              (dimensionless).
86 REM       'H'  = Henry's Law constant (dimensionless ratio of
88 REM              mol/l concentrations).
90 REM       'HA' = Henry's Law constant for average temperature
92 REM              during post NH4 production phase.
94 REM       'TV' = Average temperature ('C) during post NH4
96 REM             production phase (8.9'C).
```

```
98 DIM TE(220):DIM PH(200):DIM TX(220)
100 FOR I%=0 TO 215 :READ TE(I%):TX(I%)=TE(I%)+273:NEXT I%
102 FOR I%=0 TO 200 :READ PH(I%):NEXT I%
104 A$="###.#":B$="#.####":C$="##.###":D$="##.##":E$="#.###"
106 REM
108 REM       The variable set below contains the necessary
110 REM       values to simulate the NH3 gaseous loss from a
112 REM       URINE application on 11/5/82 at Lincoln College.
114 REM
116 U0=88.2:K=0.0146:A=0.149
118 U1=6.0:K1=3.337:A1=0.149
120 REM
122 REM      Assume a total of 94.20% of N remains in top
124 REM      2.5 cm.(i.e. 88.2% + 6.0% in two compartments)
126 REM
128 REM      This version does not require the actual wt
130 REM      of urea-N as an input, but considers instead
132 REM      urea-N as 100 parts and everything is calculated
134 REM      as %loss/hour etc.
136 REM
138 NN=0:NM=0:T=0:TI=0.1:NH3=0:NZ3=0:FI=0:FM=0:TV=8.9
139 Y%=0
140 HA=10[(-1.69+(1477.7/(TV+273))):    'I' symbol = exponential
142 REM
144 REM        In line 300 '199' is the duration of the
146 REM        simulation in hours.
148 REM
150 REM
152 REM        Main timing loop begins here
154 REM
300 FOR I%=0 TO 199 STEP 1
302 DPH = PH(I%+1)-PH(I%)
304 DTX = TX(I%+1)-TX(I%)
305 REM
306 REM        Incremental timing loop begins here
307 REM
308 FOR II%=0 TO (1/TI)-1
320 GOSUB 1700
330 GOSUB 1100
350 GOSUB 1300
360 IF ABS(AA-(1/TI))<0.001  THEN GOSUB 1400
370 T=T+TI:AA=AA+1
375 NEXT II%
380 NEXT I%
400 STOP
```

```
1100 REM
1101 REM          Subroutine to input to N pools due to UREA
1102 REM          hydrolysis.
1103 REM
1110 DN=UO*(EXP(-A*T)-EXP(-A*(T+TI)))
1115 DM=U1*(EXP(-A1*T)-EXP(-A1*(T+TI)))
1120 FI=(NN+DN):NN=FI-(NH3*TI)
1125 FM=(NM+DM):NM=FM-(NZ3*TI)
1130 RETURN
1300 REM
1301 REM          Subroutine to calculate combined pH and
1302 REM          temperature dependence of NH3(g).
1303 REM
1320 NH3=K*HR*FI/(1+10[(.09018+Q))
1325 NZ3=K1*HR*FM/(1+10[(.09018+Q))
1330 AV=AV+NH3
1335 AZ=AZ+NZ3
1340 RETURN
1400 REM
1401 REM          Subroutine to PRINT output to screen.
1402 REM          CMD"JKL" dumps screen output to printer
1403 REM          every 15 lines.
1404 REM
1405 Y%=Y%+1
1406 IF Y%=15 THEN GOTO 1408 ELSE GOTO 1410
1408 CMD"JKL"
1409 Y%=0
1410 FLUX = (AV + AZ)*TI:AV=0:AZ=0:TZ=TZ+FLUX
1420 PRINT USING A$;T;:PRINT TAB(7);
1425 PRINT USING B$;FLUX;:PRINT TAB(15);
1430 PRINT USING C$;FM;:PRINT TAB(24);
1432 PRINT USING C$;FI;:PRINT TAB(32);
1435 PRINT USING C$;TZ;:PRINT TAB(39);
1440 PRINT USING D$;PH;:PRINT TAB(46);
1445 PRINT USING D$;TX-273;:PRINT TAB(52);
1450 PRINT USING E$;HR;:PRINT TAB(57);I%
1455 AA=0
1460 RETURN
1600 REM
1700 REM        Subroutine to establish interpolated values of
1701 REM        pH and TX at specific times defined by the time
1702 REM        increment 'TI'
1704 REM
1710 PH = PH(I%) + (DPH*II%*TI)
1720 TX = TX(I%) + (DTX*II%*TI)
1730 Q = (2729.92/TX)-PH
1740 H = 10[(-1.69 + (1477.7/TX))
1750 HR=HA/H
1760 RETURN
```

```
2000 REM
2001 REM      Data below are AIR/SOIL interface temperatures from
2002 REM      a thermometer placed 1.5cm below ground level for
2003 REM      duration of the experiment.
2004 REM
2010 DATA 15.0,14.5,14.0,13.0,11.0,9.50,8.50,7.80,7.00,6.70,6.20,6.10
2020 DATA 6.40,6.50,7.20,7.50,8.00,8.00,8.00,8.20,8.50,9.00,9.50,10.8
2030 DATA 11.8,12.0,11.5,10.8,10.0,9.00,8.70,8.50,7.50,7.00,6.50,6.00
2040 DATA 5.80,5.50,5.00,4.80,4.70,4.60,4.70,5.80,7.50,9.00,10.5,10.7
2050 DATA 10.8,10.5,10.4,9.80,9.40,9.00,8.90,8.50,8.00,8.00,8.00,7.50
2060 DATA 7.20,6.50,5.80,5.50,5.00,4.70,4.20,5.00,6.50,9.50,11.6,12.5
2070 DATA 12.8,12.0,11.5,10.6,10.0,9.50,9.50,9.30,9.00,9.00,8.90,8.80
2080 DATA 8.50,8.30,8.30,8.30,8.30,8.30,8.40,9.00,10.0,11.5,11.4,12.0
2090 DATA 12.7,12.3,11.8,11.5,10.5,9.50,8.50,8.20,7.60,7.00,7.00,7.00
2100 DATA 7.00,7.00,7.00,7.00,7.00,7.00,6.80,7.00,8.00,9.30,11.5,12.0
2110 DATA 12.7,12.9,12.5,11.6,10.5,9.40,8.50,8.00,7.70,7.60,7.30,6.90
2120 DATA 6.70,6.60,6.50,6.50,6.50,6.50,6.40,6.30,7.00,8.50,10.5,11.5
2130 DATA 12.0,12.5,12.4,12.3,12.0,11.7,11.0,10.5,10.0,9.60,9.40,8.50
2140 DATA 7.50,7.30,6.90,6.50,6.40,6.00,6.00,6.00,6.00,6.00,7.00,8.50
2150 DATA 9.50,10.2,10.1,9.90,9.80,9.80,9.80,9.70,9.60,9.50,9.50,9.50
2160 DATA 9.50,9.50,9.30,9.00,8.50,8.50,8.50,8.60,8.60,8.80,9.40,10.0
2170 DATA 10.6,10.7,10.4,10.3,10.2,10.1,10.1,10.1,10.1,10.2,10.2,10.2
2180 DATA 10.2,10.3,10.3,10.1,10.0,10.0,10.0,10.0,10.4,10.5,11.0,11.8
3000 REM
3001 REM       The data below are pH's 0-0.5cm obtained by
3002 REM       interpolation from measured values.
3003 REM
3010 DATA 7.8,7.82,7.95,8.05,8.15,8.22,8.30,8.35,8.44,8.45
3011 DATA 8.50
3020 DATA 8.55,8.57,8.60,8.65,8.67,8.69,8.70,8.73,8.75,8.77
3030 DATA 8.80,8.81,8.83,8.84,8.86,8.87,8.89,8.90,8.91,8.93
3040 DATA 8.94,8.95,8.95,8.96,8.97,8.97,8.98,8.98,8.98,8.98
3050 DATA 8.98,8.98,8.98,8.98,8.97,8.97,8.97,8.97,8.96,8.96
3060 DATA 8.96,8.96,8.95,8.95,8.94,8.94,8.93,8.93,8.92,8.92
3070 DATA 8.92,8.92,8.91,8.91,8.90,8.90,8.89,8.89,8.88,8.88
3080 DATA 8.87,8.87,8.86,8.86,8.85,8.85,8.84,8.84,8.83,8.82
3090 DATA 8.81,8.81,8.80,8.79,8.79,8.78,8.77,8.77,8.76,8.75
3100 DATA 8.75,8.75,8.74,8.73,8.73,8.72,8.71,8.70,8.70,8.69
3110 DATA 8.68,8.68,8.67,8.66,8.65,8.64,8.64,8.63,8.63,8.62
3120 DATA 8.61,8.61,8.60,8.60,8.59,8.58,8.58,8.57,8.57,8.56
3130 DATA 8.55,8.55,8.54,8.53,8.53,8.52,8.51,8.51,8.50,8.49
3140 DATA 8.48,8.48,8.47,8.46,8.46,8.45,8.44,8.44,8.43,8.43
3150 DATA 8.42,8.41,8.40,8.40,8.39,8.39,8.38,8.37,8.36,8.35
3160 DATA 8.35,8.34,8.33,8.32,8.31,8.31,8.30,8.30,8.29,8.28
3170 DATA 8.28,8.28,8.27,8.27,8.26,8.25,8.24,8.24,8.23,8.23
3180 DATA 8.22,8.22,8.21,8.21,8.20,8.19,8.18,8.17,8.17,8.16
3190 DATA 8.15,8.14,8.14,8.13,8.12,8.11,8.11,8.10,8.09,8.09
3200 DATA 8.08,8.08,8.07,8.07,8.06,8.05,8.04,8.04,8.03,8.03
```

APPENDIX II

Mineral-N Distribution Following Sheep Urine Applications (Summer 1982)

(Sampling Time = 1 hour)

Mineral-N (kg N/ha/Sampling Depth) corrected for controls

Sampling Depth (cm)

Replicate	0-2.5			2.5-5			5-10			10-15			Min-N		Ratio (0-2.5)/(0-15)
Number	UREA	NH4	NOx	UREA	NH4	NOx	UREA	NH4	NOx	UREA	NH4	NOx	Total	NH3(g)	(%)
1	206	51	0	43	11	0	30	16	0	10	4	0	369	5	70
2	119	45	0	3	1	0	10	4	0	5	2	0	188	5	88
3	202	63	0	61	28	0	76	63	0	29	17	0	539	5	50
4	218	40	0	7	6	0	46	17	0	12	12	0	357	5	72
mean	186	50	0	28	11	0	41	25	0	14	9	0	363	5	65

(Sampling Time = 5 hour)

Mineral-N (kg N/ha/Sampling Depth) corrected for controls

Sampling Depth (cm)

Replicate	0-2.5			2.5-5			5-10			10-15			Min-N		Ratio (0-2.5)/(0-15)
Number	UREA	NH4	NOx	UREA	NH4	NOx	UREA	NH4	NOx	UREA	NH4	NOx	Total	NH3(g)	(%)
1	16	133	0	4	10	0	7	49	0	10	91	0	320	18	49
2	9	151	0	3	6	0	5	15	0	5	24	0	217	18	76
3	21	193	0	6	10	0	8	38	0	6	27	0	309	18	71
4	23	90	0	6	10	0	9	23	0	23	100	0	286	18	43
mean	17	142	0	5	9	0	7	31	0	11	61	0	283	18	59

(Sampling Time = 24 hour)

Mineral-N (kg N/ha/Sampling Depth) corrected for controls

Sampling Depth (cm)

Replicate	0-2.5			2.5-5			5-10			10-15			Min-N		Ratio (0-2.5)/(0-15)
Number	UREA	NH4	NOx	UREA	NH4	NOx	UREA	NH4	NOx	UREA	NH4	NOx	Total	NH3(g)	(%)
1	2	173	0	1	17	0	1	81	0	1	39	0	314	62	63
2	1	159	0	2	6	0	1	57	0	1	51	0	278	62	65
3	1	156	0	1	13	0	2	22	0	1	39	0	235	62	74
4	2	151	0	2	8	0	2	24	0	3	20	0	212	62	78
mean	1	160	0	1	11	0	2	46	0	2	37	0	260	62	69

Mineral-N Distribution Following Sheep Urine Applications (Summer 1982)

(Sampling Time = 96 hour)

Mineral-N (kg N/ha/Sampling Depth) corrected for controls

Sampling Depth (cm)

	0-2.5			2.5-5			5-10			10-15					Ratio
Replicate Number	UREA	NH4	NOx	UREA	NH4	NOx	UREA	NH4	NOx	UREA	NH4	NOx	Min-N Total	NH3(g)	(0-2.5)/(0-15) (%)
1	3	107	3	0	3	1	0	25	0	0	22	7	170	105	79
2	2	107	0	0	3	1	5	42	0	0	20	5	185	105	74
3	2	116	1	0	6	1	0	24	3	0	16	2	170	105	81
4	4	66	2	0	1	0	0	20	0	0	12	1	107	105	83
mean	3	99	1	0	3	1	1	28	1	0	17	4	158	105	79

(Sampling Time =264 hour)

Mineral-N (kg N/ha/Sampling Depth) corrected for controls

Sampling Depth (cm)

	0-2.5			2.5-5			5-10			10-15					Ratio
Replicate Number	UREA	NH4	NOx	UREA	NH4	NOx	UREA	NH4	NOx	UREA	NH4	NOx	Min-N Total	NH3(g)	(0-2.5)/(0-15) (%)
1	0	63	4	0	1	1	0	13	3	0	12	2	99	110	85
2	0	75	4	0	3	0	0	18	1	0	13	0	114	110	85
3	0	109	3	0	7	3	0	45	4	0	29	3	203	110	71
4	0	74	2	0	5	1	0	21	2	0	100	6	211	110	58
mean	0	80	3	0	4	1	0	24	2	0	39	3	157	110	73

(Sampling Time =984 hour)

Mineral-N (kg N/ha/Sampling Depth) corrected for controls

Sampling Depth (cm)

	0-2.5			2.5-5			5-10			10-15					Ratio
Replicate Number	UREA	NH4	NOx	UREA	NH4	NOx	UREA	NH4	NOx	UREA	NH4	NOx	Min-N Total	NH3(g)	(0-2.5)/(0-15) (%)
1	0	76	3	0	12	3	0	3	2	0	8	2	108	110	87
2	0	41	3	0	4	0	0	40	14	0	40	0	142	110	61
3	0	73	5	0	17	9	0	17	9	0	14	3	147	110	73
4	0	49	1	0	4	1	0	7	1	0	20	6	90	110	80
mean	0	60	3	0	9	3	0	17	7	0	21	3	122	110	74

Mineral-N Distribution Following Aqueous Urea Applications Summer (1982)

(Sampling Time = 1 hour)

Mineral-N (kg N/ha/Sampling Depth) corrected for controls

Sampling Depth (cm)

	0-2.5			2.5-5			5-10			10-15					Ratio
Replicate Number	UREA	NH4	NOx	UREA	NH4	NOx	UREA	NH4	NOx	UREA	NH4	NOx	Min-N Total	NH3(g)	(0-2.5)/(0-15) (%)
1	175	19	0	7	3	0	7	1	0	36	3	2	252	1	77
2	266	28	0	5	0	0	22	4	0	18	3	0	346	1	85
3	244	37	0	3	0	0	11	3	0	18	2	3	322	1	87
4	406	27	0	4	0	0	23	5	0	38	4	6	513	1	84
mean	273	28	0	5	1	0	16	3	0	28	3	3	358	1	84

(Sampling Time = 5 hour)

Mineral-N (kg N/ha/Sampling Depth) corrected for controls

Sampling Depth (cm)

	0-2.5			2.5-5			5-10			10-15					Ratio
Replicate Number	UREA	NH4	NOx	UREA	NH4	NOx	UREA	NH4	NOx	UREA	NH4	NOx	Min-N Total	NH3(g)	(0-2.5)/(0-15) (%)
1	91	50	0	12	3	0	12	2	0	20	14	2	207	6	69
2	153	67	0	12	8	0	27	15	0	24	4	0	310	6	72
3	168	72	0	6	4	0	16	8	0	26	9	3	313	6	77
4	190	66	0	6	4	0	43	7	0	30	10	6	361	6	71
mean	151	64	0	9	5	0	25	8	0	25	9	3	298	6	72

(Sampling Time = 24 hour)

Mineral-N (kg N/ha/Sampling Depth) corrected for controls

Sampling Depth (cm)

	0-2.5			2.5-5			5-10			10-15					Ratio
Replicate Number	UREA	NH4	NOx	UREA	NH4	NOx	UREA	NH4	NOx	UREA	NH4	NOx	Min-N Total	NH3(g)	(0-2.5)/(0-15) (%)
1	17	157	3	4	16	0	11	38	5	5	30	0	286	37	66
2	16	155	4	4	15	0	3	25	2	3	28	0	256	37	73
3	2	87	3	1	7	0	1	20	1	1	13	5	140	37	73
4	2	140	0	1	13	0	12	108	9	17	110	4	418	37	39
mean	9	135	3	3	13	0	7	48	4	6	46	2	275	37	59

Mineral-N Distribution Following Aqueous Urea Applications Summer (1982)

(Sampling Time = 96 hour)

Mineral-N (kg N/ha/Sampling Depth) corrected for controls

Sampling Depth (cm)

Replicate	0-2.5			2.5-5			5-10			10-15			Min-N		Ratio (0-2.5)/(0-15)
Number	UREA	NH4	NOx	UREA	NH4	NOx	UREA	NH4	NOx	UREA	NH4	NOx	Total	NH3(g)	(%)
1	0	106	3	3	13	2	0	56	0	0	24	4	211	84	65
2	0	142	1	0	21	7	0	52	4	0	39	5	270	84	64
3	0	104	5	0	1	3	0	18	1	0	13	7	151	84	82
4	2	120	6	0	4	0	0	25	0	0	23	3	183	84	79
mean	1	118	4	1	9	3	0	38	1	0	24	5	204	84	72

(Sampling Time =268 hour)

Mineral-N (kg N/ha/Sampling Depth) corrected for controls

Sampling Depth (cm)

Replicate	0-2.5			2.5-5			5-10			10-15			Min-N		Ratio (0-2.5)/(0-15)
Number	UREA	NH4	NOx	UREA	NH4	NOx	UREA	NH4	NOx	UREA	NH4	NOx	Total	NH3(g)	(%)
1	0	85	6	0	7	0	0	28	0	0	9	11	146	90	77
2	0	145	7	0	22	1	0	37	0	0	20	4	237	90	74
3	0	103	8	0	10	2	0	53	10	0	62	19	266	90	56
4	0	125	5	0	10	8	0	41	4	0	0	2	196	90	77
mean	0	115	6	0	12	3	0	40	4	0	23	9	211	90	70

(Sampling Time =984 hour)

Mineral-N (kg N/ha/Sampling Depth) corrected for controls

Sampling Depth (cm)

Replicate	0-2.5			2.5-5			5-10			10-15			Min-N		Ratio (0-2.5)/(0-15)
Number	UREA	NH4	NOx	UREA	NH4	NOx	UREA	NH4	NOx	UREA	NH4	NOx	Total	NH3(g)	(%)
1	0	85	2	0	13	0	0	14	5	0	22	6	147	90	75
2	0	90	8	0	11	4	0	13	12	0	9	4	151	90	78
3	0	96	13	0	17	5	0	75	37	0	46	40	327	90	48
4	0	92	8	0	4	3	0	7	2	0	10	3	129	90	87
mean	0	91	8	0	11	3	0	27	14	0	22	13	189	90	68

Mineral-N Distribution Following Sheep Urine Applications (Autumn 1982)

(Sampling Time = 1 hour)

Mineral-N (kg N/ha/Sampling Depth) corrected for controls

Sampling Depth (cm)

Replicate	0-2.5			2.5-5			5-10			10-15			15-25			Min-N		Ratio (0-2.5)/(0-25)
Number	UREA	NH4	NOx	UREA	NH4	NOx	UREA	NH4	NOx	UREA	NH4	NOx	UREA	NH4	NOx	Total	NH3(g)	(%)
1	181	23	0	4	2	0	124	3	0	212	6	0	157	3	0	715	0	29
2	133	18	0	20	1	0	48	0	0	31	0	0	54	0	0	306	0	49
3	161	26	0	7	1	0	19	0	0	8	1	0	15	3	0	241	0	77
4	171	31	0	2	0	0	2	0	0	0	0	0	10	3	0	218	0	93
5	222	41	0	8	1	0	10	0	0	4	0	0	4	0	0			
mean	174	28	0	8	1	0	40	1	0	51	1	0	48	2	0	370	0	55

(Sampling Time = 25 hours)

Mineral-N (kg N/ha/Sampling Depth) corrected for controls

Sampling Depth (cm)

Replicate	0-2.5			2.5-5			5-10			10-15			15-25			Min-N		Ratio (0-2.5)/(0-25)
Number	UREA	NH4	NOx	UREA	NH4	NOx	UREA	NH4	NOx	UREA	NH4	NOx	UREA	NH4	NOx	Total	NH3(g)	(%)
1	6	216	0	2	20	1	1	0	0	2	72	1	2	31	1	355	43	67
2	7	158	0	0	1	0	0	0	1	0	0	1	0	16	1	184	43	92
3	6	166	0	1	24	0	0	0	1	0	0	1	0	0	1	200	43	89
4	3	115	0	0	0	0	0	0	0	0	0	1	0	1	0	120	43	99
5	12	291	0	2	33	0	3	54	0	4	58	1	0	11	0	471	43	67
mean	7	189	0	1	16	0	1	11	0	1	26	1	0	12	1	266	43	77

(Sampling Time = 48 hours)

Mineral-N (kg N/ha/Sampling Depth) corrected for controls

Sampling Depth (cm)

Replicate	0-2.5			2.5-5			5-10			10-15			15-25			Min-N		Ratio (0-2.5)/(0-25)
Number	UREA	NH4	NOx	UREA	NH4	NOx	UREA	NH4	NOx	UREA	NH4	NOx	UREA	NH4	NOx	Total	NH3(g)	(%)
1	2	118	0	1	51	0	1	59	1	1	8	1	1	19	1	262	68	57
2	7	133	0	1	6	0	0	0	0	0	3	0	0	6	0	158	68	92
3	2	150	0	1	144	0	0	64	0	0	3	0	0	4	0	367	68	51
4	2	119	0	0	7	0	0	0	0	0	0	0	4	6	2	140	68	91
5	1	141	0	1	21	0	0	16	0	0	1	0	0	0	0	181	68	84
mean	3	132	0	1	46	0	0	28	0	0	3	0	1	7	1	222	68	70

Mineral-N Distribution Following Sheep Urine Applications (Autumn 1982)

(Sampling Time =192 hours)

Mineral-N (kg N/ha/Sampling Depth) corrected for controls

Sampling Depth (cm)

	0-2.5			2.5-5			5-10			10-15			15-25					Ratio
Replicate																Min-N		(0-2.5)/(0-25)
Number	UREA	NH4	NOx	UREA	NH4	NOx	UREA	NH4	NOx	UREA	NH4	NOx	UREA	NH4	NOx	Total	NH3(g)	(%)
1	0	92	0	0	27	0	0	9	0	0	13	1	0	12	1	155	121	77
2	0	125	0	0	29	0	0	3	0	0	1	0	0	1	0	159	121	88
3	0	133	1	0	14	1	0	18	1	0	0	0	0	1	0	169	121	88
4	0	92	2	0	35	1	0	76	2	0	213	2	0	243	3	669	121	27
5	0	73	0	0	9	0	0	2	0	0	0	0	0	0	0	85	121	94
mean	0	103	1	0	23	0	0	21	1	0	45	1	0	51	1	247	121	61

(Sampling Time = 3 Months)

Mineral-N (kg N/ha/Sampling Depth) corrected for controls

Sampling Depth (cm)

	0-2.5			2.5-5			5-10			10-15			15-25					Ratio
Replicate																Min-N		(0-2.5)/(0-25)
Number	UREA	NH4	NOx	UREA	NH4	NOx	UREA	NH4	NOx	UREA	NH4	NOx	UREA	NH4	NOx	Total	NH3(g)	(%)
1	0	9	4	0	0	0	0	1	1	0	0	1	0	0	1	17	123	97
2	0	10	3	0	0	0	0	0	1	0	0	0	0	0	0	15	123	99
3	0	5	4	0	0	0	0	0	1	0	0	10	0	0	20	41	123	80
4	0	5	3	0	0	0	0	0	0	0	0	0	0	2	0	10	123	98
5																		
mean	0	7	3	0	0	0	0	0	1	0	0	3	0	0	5	21	123	93

Mineral-N Distribution Following Aqueous Urea Applications Autumn (1982)

(Sampling Time = 1 hour)

Mineral-N (kg N/ha/Sampling Depth) corrected for controls

Sampling Depth (cm)

Replicate	0-2.5			2.5-5			5-10			10-15			15-25			Min-N		Ratio (0-2.5)/(0-25)
Number	UREA	NH4	NOx	UREA	NH4	NOx	UREA	NH4	NOx	UREA	NH4	NOx	UREA	NH4	NOx	Total	NH3(g)	(%)
1																		
2	119	16	0	0	0	0	0	0	0	0	1	0	4	0	0	141	0	96
3				20	1	0	49	0	0	0	1	0	2	0	0			
4	185	41	0	19	5	1	29	4	0	6	0	1	0	0	0	291	0	78
5	112	16	0	3	2	0	4	0	0	4	1	1	7	2	0	153	0	84
mean	139	24	0	11	2	0	21	1	0	3	1	1	3	1	0	195	0	84

(Sampling Time = 24 hour)

Mineral-N (kg N/ha/Sampling Depth) corrected for controls

Sampling Depth (cm)

Replicate	0-2.5			2.5-5			5-10			10-15			15-25			Min-N		Ratio (0-2.5)/(0-25)
Number	UREA	NH4	NOx	UREA	NH4	NOx	UREA	NH4	NOx	UREA	NH4	NOx	UREA	NH4	NOx	Total	NH3(g)	(%)
1	56	121	0	1	0	0	1	0	0	4	0	0	6	4	0	194	31	92
2	69	147	0	1	0	0	2	0	1	2	3	1	2	0	1	229	31	95
3	69	157	0	1	1	0	8	8	1	0	0	1	0	0	0	246	31	93
4	43	146	0	16	20	0	1	1	1	0	0	0	0	2	0	231	31	84
5	59	192	0	14	13	0	30	11	1	2	1	0	4	0	0	327	31	79
mean	59	152	0	7	7	0	8	4	1	2	1	1	3	1	0	245	31	88

(Sampling Time = 48 hour)

Mineral-N (kg N/ha/Sampling Depth) corrected for controls

Sampling Depth (cm)

Replicate	0-2.5			2.5-5			5-10			10-15			15-25			Min-N		Ratio (0-2.5)/(0-25)
Number	UREA	NH4	NOx	UREA	NH4	NOx	UREA	NH4	NOx	UREA	NH4	NOx	UREA	NH4	NOx	Total	NH3(g)	(%)
1	4	179	0	1	10	0	2	1	0	17	14	0	11	23	0	263	78	77
2	2	235	0	7	178	1	28	81	0	31	96	1	23	160	1	845	78	34
3	3	157	0	1	14	0	0	0	0	0	3	0	0	2	0	180	78	92
4	5	178	0	1	12	0	0	0	0	0	0	0	0	0	1	197	78	95
5	2	154	0	2	26	0	1	10	0	4	33	0	2	2	0	235	78	75
mean	3	181	0	2	48	0	6	18	0	10	29	0	7	37	1	344	78	62

Mineral-N Distribution Following Aqueous Urea Applications Autumn (1982)

(Sampling Time =192 hour)

Mineral-N (kg N/ha/Sampling Depth) corrected for controls

Sampling Depth (cm)

Replicate	0-2.5			2.5-5			5-10			10-15			15-25			Min-N		Ratio (0-2.5)/(0-25)
Number	UREA	NH4	NOx	UREA	NH4	NOx	UREA	NH4	NOx	UREA	NH4	NOx	UREA	NH4	NOx	Total	NH3(g)	(%)
1	0	119	1	0	6	0	0	0	0	0	0	0	0	5	0	131	143	96
2	0	267	1	0	42	1	0	6	0	0	3	0	0	1	0	321	143	89
3	0	137	2	0	16	1	0	0	0	0	3	0	0	1	0	159	143	93
4	0	150	3	0	17	4	0	2	2	0	0	2	0	2	1	181	143	91
5	0	198	2	0	19	1	0	4	0	0	5	0	0	3	2	233	143	91
mean	0	174	2	0	20	1	0	2	1	0	2	0	0	2	0	205	143	92

(Sampling Time = 3 Months)

Mineral-N (kg N/ha/Sampling Depth) corrected for controls

Sampling Depth (cm)

Replicate	0-2.5			2.5-5			5-10			10-15			15-25			Min-N		Ratio (0-2.5)/(0-25)
Number	UREA	NH4	NOx	UREA	NH4	NOx	UREA	NH4	NOx	UREA	NH4	NOx	UREA	NH4	NOx	Total	NH3(g)	(%)
1	0	7	6	0	1	0	0	0	0	0	0	0	0	1	1	16	145	98
2	0	5	4	0	0	0	0	0	0	0	0	1	0	1	1	13	145	98
3	0	1	3	0	0	0	0	0	1	0	0	0	0	1	1	6	145	98
4	0	0	2	0	0	0	0	0	1	0	0	0	0	0	0	4	145	99
5																		
mean	0	3	4	0	0	0	0	0	1	0	0	0	0	0	1	10	145	98

SOIL pH (SUMMER EXPERIMENT)

Sampling Time = 1 Hour Treatment = Urine

SOIL DEPTH (mm)

Replicate Number	0-5		5-10		10-25		25-50		50-100	
	initial	24 hour	initial	24 hour	initial	24 hour	initial	24 hour	initial	24 hour
1	8.25	8.20	6.10	6.65	5.60	5.70	5.50	5.75	5.40	6.00
2	8.20	7.90	6.25	6.80	7.95	7.15	7.85	7.20	8.00	7.45
3	8.30	7.90	6.95	7.30	6.05	6.20	6.10	6.05	6.05	6.15
4	7.85	7.55	6.45	6.80	5.50	5.80	5.90	5.95	5.95	5.95
5	8.55	8.45	7.40	7.55	5.90	6.05	6.45	6.35	6.95	6.55
mean	8.23	8.00	6.63	7.02	6.20	6.18	6.36	6.26	6.47	6.42

Sampling Time = 5 Hours Treatment = Urine

SOIL DEPTH (mm)

Replicate Number	0-5		5-10		10-25		25-50		50-100	
	initial	24 hour	initial	24 hour	initial	24 hour	initial	24 hour	initial	24 hour
1	8.65	8.05	7.45	6.50	7.05	6.85	7.25	6.95	7.25	6.95
2	8.65	7.90	7.50	6.85	5.70	5.70	5.75	5.85	5.85	5.95
3	8.95	8.55	8.15	7.35	6.05	6.20	6.00	6.15	5.95	6.20
4	8.80	8.20	7.35	6.70	5.60	5.80	5.65	5.85	5.70	5.95
5	8.80	8.10	7.45	6.90	6.55	6.15	5.70	6.05	5.85	6.00
mean	8.77	8.16	7.58	6.86	6.19	6.14	6.07	6.17	6.12	6.21

Sampling Time = 24 Hours Treatment = Urine

SOIL DEPTH (mm)

Replicate Number	0-5		5-10		10-25		25-50		50-100	
	initial	24 hour	initial	24 hour	initial	24 hour	initial	24 hour	initial	24 hour
1	8.35	7.65	7.90	6.95	5.90	5.90	6.05	5.90	6.15	6.15
2	8.50	7.75	8.30	7.40	6.20	6.05	5.65	5.80	5.85	6.05
3	8.50	7.95	7.60	6.95	6.00	6.05	6.30	6.15	7.50	7.05
4	8.70	7.85	8.65	8.00	6.75	6.55	6.20	6.10	6.50	6.40
5	8.45	8.10	8.30	7.75	7.30	6.85	7.05	6.70	7.45	7.15
mean	8.50	7.86	8.15	7.41	6.43	6.28	6.25	6.13	6.69	6.56

SOIL pH (SUMMER EXPERIMENT)

Sampling Time = 96 Hours Treatment = Urine

SOIL DEPTH (mm)

Replicate Number	0-5		5-10		10-25		25-50		50-100	
	initial	24 hour	initial	24 hour	initial	24 hour	initial	24 hour	initial	24 hour
1	7.95	7.55	7.85	7.25	6.60	6.35	6.45	6.10	6.55	6.25
2	8.20	7.65	8.05	7.50	6.70	6.20	6.50	6.30	5.95	5.70
3	8.05	7.75	8.15	7.55	7.55	7.00	6.45	6.35	5.80	5.65
4	7.65	7.35	7.65	6.95	6.15	5.70	5.95	5.50	7.15	6.85
5	7.90	7.45	7.85	7.30	6.65	5.90	6.05	5.90	6.15	5.95
mean	7.95	7.55	7.91	7.31	6.73	6.23	6.28	6.03	6.32	6.08

Sampling Time =264 Hours Treatment = Urine

SOIL DEPTH (mm) (n.d. = not determined)

Replicate Number	0-5		5-10		10-25		25-50		50-100	
	initial	24 hour	initial	24 hour	initial	24 hour	initial	24 hour	initial	24 hour
1	7.95	n.d.	7.95	n.d.	6.40	n.d.	5.10	n.d.	5.65	n.d.
2	8.25	n.d.	8.05	n.d.	7.05	n.d.	5.10	n.d.	5.45	n.d.
3	8.10	n.d.	7.85	n.d.	6.25	n.d.	5.15	n.d.	5.60	n.d.
4	8.15	n.d.	7.85	n.d.	5.80	n.d.	5.10	n.d.	5.15	n.d.
mean	8.11		7.93		6.38		5.11		5.46	

SOIL pH (SUMMER EXPERIMENT)

Sampling Time = 1 Hour Treatment = Urea

SOIL DEPTH (mm)

Replicate Number	0-5		5-10		10-25		25-50		50-100	
	initial	24 hour	initial	24 hour	initial	24 hour	initial	24 hour	initial	24 hour
1	7.20	7.80	5.70	6.55	5.80	5.20	6.05	5.90	6.15	5.95
2	6.70	7.55	5.55	6.55	6.10	5.80	6.05	6.05	6.25	5.95
3	6.85	7.65	6.05	7.10	5.90	6.30	6.00	6.00	6.10	6.00
4	7.10	7.90	6.15	7.10	6.25	6.05	6.00	5.90	6.40	6.55
5	6.60	7.25	5.50	6.50	6.10	6.30	6.10	6.30	6.10	6.35
mean	6.89	7.63	5.79	6.76	6.03	5.93	6.04	6.03	6.20	6.16

Sampling Time = 5 Hours Treatment = Urea

SOIL DEPTH (mm)

Replicate Number	0-5		5-10		10-25		25-50		50-100	
	initial	24 hour	initial	24 hour	initial	24 hour	initial	24 hour	initial	24 hour
1	8.20	8.20	7.45	7.30	6.60	6.75	6.30	6.45	6.55	6.80
2	8.45	8.25	7.05	7.05	6.05	6.10	6.10	6.10	6.30	6.30
3	7.90	7.95	6.25	6.60	5.80	5.85	6.10	6.20	6.20	6.20
4	8.55	8.35	7.45	7.40	6.45	6.25	6.05	6.05	5.80	5.75
5	8.05	7.90	7.00	6.90	6.10	6.10	6.15	6.15	6.30	6.05
mean	8.23	8.13	7.04	7.05	6.20	6.21	6.14	6.19	6.23	6.22

Sampling Time = 24 Hours Treatment = Urine

SOIL DEPTH (mm)

Replicate Number	0-5		5-10		10-25		25-50		50-100	
	initial	24 hour	initial	24 hour	initial	24 hour	initial	24 hour	initial	24 hour
1	8.35	7.65	7.90	6.95	5.90	5.90	6.05	5.90	6.15	6.15
2	8.50	7.75	8.30	7.40	6.20	6.05	5.65	5.80	5.85	6.05
3	8.50	7.95	7.60	6.95	6.00	6.05	6.30	6.15	7.50	7.05
4	8.70	7.85	8.65	8.00	6.75	6.55	6.20	6.10	6.50	6.40
5	8.45	8.10	8.30	7.75	7.30	6.85	7.05	6.70	7.45	7.15
mean	8.50	7.86	8.15	7.41	6.43	6.28	6.25	6.13	6.69	6.56

SOIL pH (SUMMER EXPERIMENT)

Sampling Time = 96 Hours Treatment = Urea

SOIL DEPTH (mm)

Replicate Number	0-5		5-10		10-25		25-50		50-100	
	initial	24 hour	initial	24 hour	initial	24 hour	initial	24 hour	initial	24 hour
1	7.95	7.60	7.85	7.25	6.25	6.15	5.80	5.45	5.90	5.85
2	7.60	8.15	8.00	7.55	6.70	6.55	5.85	5.60	5.95	5.75
3	7.85	7.50	8.15	7.45	6.65	6.20	6.20	5.85	6.15	5.60
4	7.85	7.70	7.85	7.15	6.05	5.85	5.85	5.25	5.80	5.85
5	7.50	7.45	7.65	7.25	6.50	6.20	6.05	5.85	6.65	6.30
mean	7.75	7.68	7.90	7.33	6.43	6.19	5.95	5.60	6.09	5.87

Sampling Time =264 Hours Treatment = Urea

SOIL DEPTH (mm) n.d. = not determined

Replicate Number	0-5		5-10		10-25		25-50		50-100	
	initial	24 hour	initial	24 hour	initial	24 hour	initial	24 hour	initial	24 hour
1	7.95	n.d.	7.75	n.d.	6.80	n.d.	5.35	n.d.	5.30	n.d.
2	8.15	n.d.	7.95	n.d.	7.50	n.d.	5.70	n.d.	5.40	n.d.
3	7.95	n.d.	8.05	n.d.	7.20	n.d.	4.80	n.d.	5.10	n.d.
4	7.95	n.d.	7.80	n.d.	6.15	n.d.	5.05	n.d.	5.70	n.d.
5	8.10	n.d.	8.20	n.d.	6.70	n.d.	4.75	n.d.	5.15	n.d.
mean	8.02		7.95		6.87		5.13		5.33	

SOIL pH (AUTUMN EXPERIMENT)

Sampling Time = 1 Hour Treatment = Urine

SOIL DEPTH (mm)

Replicate Number	0-5		5-10		10-25		25-50		50-100	
	initial	24 hour	initial	24 hour	initial	24 hour	initial	24 hour	initial	24 hour
1	7.60	7.05	6.10	6.00	5.90	5.50	5.80	5.50	5.80	5.60
2	7.55	6.85	7.10	6.75	6.00	6.00	5.80	5.70	5.70	5.60
3	8.10	7.30	7.35	7.30	6.10	5.90	6.00	5.70	5.90	5.60
4	8.00	7.20	6.60	6.50	6.00	5.80	5.80	5.60	5.70	5.70
5										
mean	7.81	7.10	6.79	6.64	6.00	5.80	5.85	5.63	5.78	5.63

Sampling Time = 25 Hours Treatment = Urine

SOIL DEPTH (mm)

Replicate Number	0-5		5-10		10-25		25-50		50-100	
	initial	24 hour	initial	24 hour	initial	24 hour	initial	24 hour	initial	24 hour
1	8.80	7.10	8.25	7.30	7.00	6.55	6.40	6.50	7.60	6.95
2	8.70	7.10	7.20	6.80	5.80	5.80	6.00	5.80	6.10	5.90
3	8.70	6.90	8.00	7.00	5.90	5.80	6.00	6.30	5.60	5.60
4	8.80	7.50	8.50	7.85	7.20	6.80	6.80	6.10	6.00	6.00
5	9.10	7.70	8.75	7.40	7.90	6.90	6.70	5.70	5.60	5.50
mean	8.82	7.26	8.14	7.27	6.76	6.37	6.38	6.08	6.18	5.99

Sampling Time = 48 Hours Treatment = Urine

SOIL DEPTH (mm)

Replicate Number	0-5		5-10		10-25		25-50		50-100	
	initial	24 hour	initial	24 hour	initial	24 hour	initial	24 hour	initial	24 hour
1	9.00	7.35	8.75	8.10	6.85	6.50	5.90	5.70	5.90	5.60
2	9.00	7.20	8.90	7.40	7.45	6.90	6.20	6.00	5.90	5.70
3	9.10	7.70	8.95	8.00	7.90	6.95	6.30	6.05	6.00	5.60
4	8.70	6.90	8.85	7.50	6.55	6.20	6.20	5.90	6.10	5.85
5	9.00	7.40	8.75	7.70	7.20	6.60	6.50	6.25	6.00	5.55
mean	8.96	7.31	8.84	7.74	7.19	6.63	6.22	5.98	5.98	5.66

SOIL pH (AUTUMN EXPERIMENT)

Sampling Time = 192 Hours Treatment = Urine

SOIL DEPTH (mm)

Replicate Number	0-5		5-10		10-25		25-50		50-100	
	initial	24 hour	initial	24 hour	initial	24 hour	initial	24 hour	initial	24 hour
1	7.80	6.65	8.20	7.10	7.00	6.60	5.65	5.55	5.95	5.85
2	8.20	6.80	8.60	7.40	6.90	6.60	5.30	5.20	5.65	5.65
3	8.00	6.75	8.40	7.60	6.50	6.20	5.55	5.50	5.90	6.00
4	7.80	6.60	8.35	7.40	7.65	7.10	5.95	5.95	5.80	5.65
5	8.50	7.40	8.00	7.15	6.25	6.20	5.60	5.60	5.45	5.45
mean	8.06	6.84	8.31	7.33	6.86	6.54	5.61	5.56	5.75	5.72

Sampling Time = 3 Months Treatment = Urine n.d. = not determined

SOIL DEPTH (mm)

Replicate Number	0-5		5-10		10-25		25-50		50-100	
	initial	24 hour	initial	24 hour	initial	24 hour	initial	24 hour	initial	24 hour
1	6.50	n.d.	6.45	n.d.	6.45	n.d.	6.25	n.d.	5.85	n.d.
2	6.65	n.d.	6.95	n.d.	6.70	n.d.	6.05	n.d.	5.85	n.d.
3	6.60	n.d.	6.55	n.d.	6.35	n.d.	5.85	n.d.	5.95	n.d.
4	6.55	n.d.	6.00	n.d.	6.23	n.d.	5.90	n.d.	5.75	n.d.
mean	6.58		6.49		6.43		6.01		5.85	

SOIL pH (AUTUMN EXPERIMENT)

Sampling Time = 1 Hour Treatment = Urea

SOIL DEPTH (mm)

Replicate Number	0-5		5-10		10-25		25-50		50-100	
	initial	24 hour	initial	24 hour	initial	24 hour	initial	24 hour	initial	24 hour
1	7.20	7.00	6.00	6.05	5.80	5.70	5.80	5.80	5.80	5.60
2	7.10	7.20	6.60	6.65	5.80	5.60	5.90	5.80	5.70	5.60
3	6.70	6.55	6.20	6.00	5.90	5.70	5.90	5.80	5.80	5.50
4	7.30	7.60	6.40	6.70	6.20	6.10	6.00	5.90	5.80	5.70
5	6.50	6.15	6.20	5.80	5.90	5.60	5.90	5.70	5.80	5.60
mean	6.96	6.90	6.28	6.24	5.92	5.74	5.90	5.80	5.78	5.60

Sampling Time = 25 Hour Treatment = Urea

SOIL DEPTH (mm)

Replicate Number	0-5		5-10		10-25		25-50		50-100	
	initial	24 hour	initial	24 hour	initial	24 hour	initial	24 hour	initial	24 hour
1	8.60	7.00	8.60	7.50	7.05	6.40	5.80	5.70	5.70	5.50
2	8.80	7.00	8.45	7.70	6.90	6.60	6.00	5.85	5.70	5.70
3	8.90	7.60	8.80	8.00	7.50	7.00	7.10	6.90	7.05	6.65
4	8.90	7.50	8.60	7.80	6.45	6.90	5.75	5.70	5.60	5.50
5	8.90	7.05	8.50	7.40	6.30	6.10	5.80	5.70	5.60	5.50
mean	8.82	7.23	8.59	7.68	6.84	6.60	6.09	5.97	5.93	5.77

Sampling Time = 48 Hours Treatment = Urea

SOIL DEPTH (mm)

Replicate Number	0-5		5-10		10-25		25-50		50-100	
	initial	24 hour	initial	24 hour	initial	24 hour	initial	24 hour	initial	24 hour
1	8.85	7.70	8.90	8.20	7.60	7.05	7.00	6.60	7.30	6.95
2	7.80	6.75	7.70	6.65	6.95	6.40	6.10	5.75	6.15	5.95
3	8.80	7.30	8.85	7.75	7.70	7.05	6.60	6.30	6.40	6.30
4	8.80	6.95	8.65	7.60	8.15	7.20	6.80	6.50	6.35	6.35
5	8.90	7.55	8.90	8.00	8.60	7.70	6.80	6.50	6.90	6.60
mean	8.63	7.25	8.60	7.64	7.80	7.08	6.66	6.33	6.62	6.43

SOIL pH (AUTUMN EXPERIMENT)

Sampling Time = 192 Hours Treatment = Urea

SOIL DEPTH (mm)

Replicate Number	0-5		5-10		10-25		25-50		50-100	
	initial	24 hour	initial	24 hour	initial	24 hour	initial	24 hour	initial	24 hour
1	7.90	6.55	8.35	7.10	7.85	6.95	6.20	6.20	5.90	5.80
2	7.00	6.25	8.20	7.10	7.20	6.85	6.20	6.00	5.90	5.80
3	7.80	7.00	8.15	7.45	6.95	6.70	6.45	6.40	6.10	6.10
4	8.10	6.95	8.65	8.10	8.20	8.00	8.00	7.65	6.90	6.65
5	8.30	7.10	8.75	8.10	7.65	6.80	5.70	5.60	5.60	5.25
mean	7.82	6.77	8.42	7.57	7.57	7.06	6.51	6.37	6.08	5.92

Sampling Time = 3 Months Treatment = Urea n.d. = not determined

SOIL DEPTH (mm)

Replicate Number	0-5		5-10		10-25		25-50		50-100	
	initial	24 hour	initial	24 hour	initial	24 hour	initial	24 hour	initial	24 hour
1	6.26	n.d.	6.00	n.d.	5.65	n.d.	6.00	n.d.	6.10	n.d.
2	6.30	n.d.	6.45	n.d.	5.90	n.d.	5.80	n.d.	6.00	n.d.
3	6.30	n.d.	6.20	n.d.	5.75	n.d.	5.95	n.d.	6.20	n.d.
4	6.26	n.d.	6.13	n.d.	5.80	n.d.	5.93	n.d.	6.03	n.d.
mean	6.28		6.20		5.78		5.92		6.08	

APPENDIX IV

EXPERIMENT 1.

Fertilizer applied at 1100 hours on 2/10/78.
Sampling period = 1 hour from times indicated.
Chamber gas samples taken at 0,10,20,40 and 60 minutes.

Regression coefficient is for a linear rate of N2O increase within the chamber.

		Temperature (°C)				Treatment: Ammonium sulphate		Treatment: Calcium Nitrate	
Date	Time (hours)	Chamber Air	External Air	Soil 5cm	Soil 10cm	N2O-N flux (ug N2O-N/hr)	Regression Coefficient	N2O-N flux (ug N2O-N/hr)	Regression Coefficient
2/10/78	1155	23.5	24.5	13.1	10.3	14	.997	28	.992
"	1420	24.2	23.3	15.8	11.8	54	.982	145	.991
3/10/78	0910	21.2	21.4	10.7	11.1	19	.996	27	.997
"	1125	23.8	24.1	13.1	11.4	35	.993	42	.998
"	1340	24.8	23.6	14.9	12.1	80	.999	71	.997
"	1555	21.1	19.2	15.1	12.7	106	.995	96	.974
4/10/78	0910	18.5	17.5	11.5	11.8	18	.991	25	.995
"	1135	21.1	20.7	13.1	11.9	29	.999	22	.999
"	1355	22.9	21.1	14.7	12.2	58	.999	48	.999
5/10/78	0900	21.9	21.9	12.3	12.1	15	.992	14	.981
"	1120	21.7	21.9	14.1	12.6	26	.989	19	.923
"	1335	26.4	25.2	15.9	12.9	45	.984	44	.944
"	1545	21.3	21.5	16.7	13.8	79	.998	65	.998
"	1800	12.3	11.1	15.1	14.2	96	.994	85	.996
6/10/78	1025	17.3	14.3	11.5	11.9	8	.786	6	.872
"	1245	19.4	18.9	13.1	12.2	6	.558	17	.944
"	1525	17.7	17.5	13.4	12.8	23	.986	28	.955
"	1740	8.8	5.8	13.1	13.1	34	.997	38	.988
7/10/78	1105	20.2	19.6	12.9	12.5	11	.967	14	.954
9/10/78	0925	16.6	17.6	10.8	11.2	8	.991	10	.984
"	1140	21.1	21.3	13.1	11.8	10	.771	17	.906
"	1410	22.4	22.9	15.4	12.7	25	.975	24	.981
"	1620	16.2	15.1	15.5	13.9	38	.995	46	.996
"	2015	10.8	9.5	13.3	13.5	49	.998	54	.996
10/10/78	1330	24.9	23.8	16.7	13.7	32	.981	22	.997
11/10/78	0140	9.6	9.6	11.7	12.3	25	.999	28	.997
"	0400	11.5	13.6	11.9	12.4	28	.961	22	.996
"	0620	13.2	12.8	12.6	13.2	7	.911	5	.986
"	0900	21.8	22.3	11.5	12.1	0	.581	10	.889
"	1115	20.2	19.7	12.5	13.6	-3	-.398	-5	-.533
	1435	19.4	17.1	12.8	14.7	4	.760	11	.821
14/11/78	1035	24.4	23.1	14.2	14.2	2	.763	7	.971
"	1345	25.4	23.6	17.8	17.9	2	.521	2	.319

EXPERIMENT 1.

Fertilizer applied at 1030 hours on 2/10/78.
Sampling period = 1 hour from times indicated.
Chamber gas samples taken at 0,10,20,40 and 60 minutes.

Regression coefficient is for a linear rate of N2O increase within the chamber.

						Treatment			
		Temperature (°C)				Urine		Control	
Date	Time (hours)	Chamber Air	External Air	Soil 5cm	Soil 10cm	N2O-N flux (ug N2O-N/hr)	Regression Coefficient	N2O-N flux (ug N2O-N/hr)	Regression Coefficient
2/10/78	1040	23.1	23.5	11.7	10.2	61	.948	-3	-.901
"	1305	26.7	25.8	14.6	11.3	102	.995	5	.883
"	1525	20.4	20.1	15.5	11.5	100	.975	8	.890
3/10/78	1020	22.1	22.3	11.6	11.1	37	.993	5	.924
"	1230	25.4	23.6	14.1	14.1	49	.987	15	.993
"	1445	23.2	22.4	15.1	12.5	59	.995	8	.986
4/10/78	1025	18.8	17.8	11.6	11.2	2	.405	-4	-.748
"	1245	22.5	20.8	13.8	12.1	24	.992	1	.606
"	1500	20.3	18.2	15.6	13.2	51	.984	8	.953
5/10/78	1010	22.5	22.9	12.9	11.9	9	.897	2	.698
"	1230	24.8	24.5	14.6	12.5	14	.990	3	.865
"	1440	23.3	23.5	16.9	13.4	44	.998	9	.959
"	1650	17.3	15.8	16.3	14.9	65	.995	17	.989
6/10/78	0915	14.4	11.3	10.4	11.2	3	.939	-2	-.849
"	1140	17.4	15.2	11.8	11.7	7	.858	-5	-.748
"	1355	15.7	13.1	13.9	12.5	22	.997	7	.973
"	1640	15.2	14.1	14.2	13.8	27	.923	12	.884
7/10/78	1150	19.6	18.5	12.7	12.7	11	.951	-2	-.631
9/10/78	1035	19.9	19.1	11.6	11.4	4	.904	3	.764
"	1245	23.3	23.6	14.8	12.8	5	.883	-2	-.683
"	1515	20.2	18.6	16.3	13.6	52	.799	4	.782
"	1735	13.8	11.3	14.5	13.5	94	.983	17	.997
"	2135	9.7	8.5	11.8	12.6	63	.998	16	.991
10/10/78	0900	20.9	21.6	11.1	11.6	10	.916	2	.527
11/10/78	0030	11.5	11.8	11.5	11.9	30	.989	13	.974
"	0250	10.3	9.1	12.1	12.6	37	.945	18	.986
"	0510	6.8	6.3	11.6	12.2	33	.978	16	.966
"	1010	16.6	16.7	11.8	12.5	1	.003	0	-.017
"	1325	24.2	24.4	12.1	14.2	5	.887	-5	-.997
14/11/78	0930	21.5	20.3	13.1	13.2	7	.984	0	-.01
"	1145	25.5	23.7	16.5	16.1	-1	-.097	-5	-.734
"	1450	26.5	24.6	19.8	20.2	6	.831	-6	-.836

APPENDIX V

EXPERIMENT 2.

Nitrous oxide release from pasture blocks. (ug N2O-N per hour)

Pasture blocks watered at -20, 70.5, and 142 hours. 0.5g N applied at 0 hours. Maximum moisture content = 27.5%

Time	Urine			Calcium Nitrate (aq)			Ammonium Sulphate (aq)			Control		
(Hours)	Rep.1	Rep.2	Mean	Rep.1	Rep.2	Mean	Rep.1	Rep.2	Mean	Rep.1	Rep.2	Mean
-21.5	0.79	0.90	0.85	0.81	0.87	0.84	1.22	1.52	1.37	0.56	0.63	0.60
0.6	27.89	48.84	38.37	15.86	5.55	10.71	5.48	16.68	11.08	1.53	1.05	1.29
3.7	15.33	16.30	15.82	21.14	5.53	13.34	5.95	18.99	12.47	1.19	1.41	1.30
24.0	25.99	47.73	36.86	82.60	23.44	53.02	54.05	77.95	66.00	2.70	1.17	1.94
29.8	4.96	16.85	10.91	28.79	1.52	15.16	9.73	27.41	18.57	0.64	0.52	0.58
46.0	5.73	16.07	10.90	21.21	2.67	11.94	7.59	32.97	20.28	1.26	1.06	1.16
52.2	4.49	10.80	7.65	9.92	2.28	6.10	7.47	24.74	16.11	0.16	0.98	0.57
69.0	4.87	8.47	6.67	3.32	4.38	3.85	3.70	9.60	6.65	1.22	0.68	0.95
76.7	16.29	28.77	22.53	2.84	1.29	2.07	6.48	20.22	13.35	0.57	0.46	0.52
93.3	34.00	152.14	93.07	43.41	3.54	23.48	41.10	156.88	98.99	2.01	1.68	1.85
101.2	24.72	49.03	36.88	31.01	2.71	16.86	48.86	190.44	119.65	2.77	1.94	2.36
117.5	3.26	5.96	4.61	2.16	1.43	1.80	3.57	24.30	13.94	1.49	0.97	1.23
125.3	1.64	5.15	3.40	2.28	0.75	1.52	2.53	10.29	6.41	0.79	0.43	0.61
140.4	2.02	3.69	2.86	1.92	0.73	1.33	3.65	13.72	8.69	0.96	0.77	0.87
148.5	5.67	14.54	10.11	3.35	2.55	2.95	5.97	14.05	10.01	1.63	1.03	1.33
165.0	37.21	97.50	67.36	48.09	2.97	25.53	35.46	115.01	75.24	n.d.	2.13	2.13
238.5	0.03	4.56	2.30	0.97	0.61	0.79	2.36	6.45	4.41	1.35	1.05	1.20

EXPERIMENT 2.

Nitrous oxide release from pasture blocks. (ug N2O-N per hour)

Pasture blocks watered at -20, 70.5, and 142 hours. 0.5 g N applied at 0 hours. Maximum moisture content = 14.0%

Time	Urine			Calcium Nitrate (aq)			Ammonium Sulphate (aq)			Control		
(Hours)	Rep.1	Rep.2	Mean	Rep.1	Rep.2	Mean	Rep.1	Rep.2	Mean	Rep.1	Rep.2	Mean
-21.5	0.88	3.47	2.18	0.76	0.55	0.66	1.02	1.01	1.02	0.99	0.68	0.84
0.6	54.50	24.00	39.25	0.68	0.96	0.82	2.28	1.16	1.72	0.76	0.77	0.77
3.7	32.32	8.20	20.26	0.75	1.33	1.04	1.57	0.83	1.20	0.85	0.72	0.79
24.0	3.47	2.20	2.84	0.91	12.53	6.72	2.14	1.55	1.85	1.28	1.08	1.18
29.8	1.27	0.83	1.05	0.45	1.33	0.89	0.67	0.50	0.59	0.49	0.49	0.49
46.0	3.03	2.14	2.59	1.06	1.10	1.08	2.49	1.75	2.12	0.73	1.27	1.00
52.2	2.45	1.66	2.06	0.65	1.28	0.97	1.87	1.19	1.53	0.83	0.78	0.81
69.0	n.d.	2.87	2.87	0.77	0.69	0.73	2.12	1.33	1.73	0.94	0.94	0.94
76.7	1.38	0.95	1.17	0.50	0.50	0.50	1.06	0.70	0.88	0.74	0.59	0.67
93.3	4.35	2.45	3.40	1.40	1.28	1.34	2.97	2.02	2.50	1.99	1.49	1.74
101.2	3.47	2.28	2.88	1.09	0.97	1.03	2.40	1.67	2.04	1.40	1.17	1.29
117.5	2.45	1.43	1.94	0.63	0.64	0.64	1.72	1.34	1.53	1.18	0.92	1.05
125.3	1.32	0.75	1.04	0.38	0.34	0.36	0.96	0.66	0.81	0.70	0.50	0.60
140.4	1.22	0.75	0.99	0.42	0.42	0.42	0.89	0.70	0.80	0.69	0.54	0.62
148.5	3.37	1.49	2.43	1.19	1.05	1.12	2.28	1.68	1.98	1.44	0.94	1.19
165.0	3.85	1.83	2.84	0.91	0.85	0.88	2.10	1.52	1.81	1.51	1.02	1.27
238.5	1.28	0.73	1.01	0.55	0.50	0.53	1.24	0.48	0.86	0.48	0.45	0.47

APPENDIX VI

EXPERIMENT 3.

Nitrous oxide release from pasture blocks (ug N2O-N per hour)

Pasture blocks watered at: 6.5,12.5,15.5,19.5,26.4,29.5,and 42.5 days. N applied at: 7.5,19.5, and 40.6 days.

Time	Urine			Urea(aq)			Ammonium Sulphate (aq)			Control		
(Days)	Rep.1	Rep.2	Mean	Rep.1	Rep.2	Mean	Rep.1	Rep.2	Mean	Rep.1	Rep.2	Mean
1.51	0.57	10.14	5.36	0.40	1.83	1.12	0.68	6.52	3.60	0.50	2.38	1.44
2.41	0.49	5.28	2.89	0.83	1.15	0.99	0.53	3.71	2.12	0.32	1.92	1.12
6.56	0.06	1.93	1.00	0.23	1.00	0.62	0.21	1.84	1.03	0.21	0.19	0.20
7.53	11.53	6.74	9.14	0.13	0.72	0.43	0.24	1.79	1.02	0.14	0.36	0.25
8.47	4.23	1.88	3.06	0.43	1.15	0.79	0.46	2.54	1.50	0.05	1.27	0.66
9.52	2.66	4.00	3.33	0.51	3.62	2.07	1.32	3.24	2.28	0.16	0.38	0.27
11.65	1.76	0.80	1.28	0.55	1.67	1.11	0.80	1.85	1.33	0.18	0.36	0.27
12.52	3.73	2.07	2.90	0.64	1.77	1.21	1.12	2.51	1.82	0.29	0.44	0.37
13.50	14.50	2.78	8.64	15.51	5.40	10.46	1.07	3.65	2.36	1.88	0.79	1.34
14.51	1.55	1.37	1.46	0.53	1.40	0.97	0.26	1.85	1.06	0.21	0.26	0.24
15.52	3.90	2.34	3.12	1.71	2.03	1.87	0.80	2.68	1.74	0.47	0.40	0.44
16.48	9.11	2.21	5.66	3.62	2.84	3.23	1.13	4.57	2.85	0.56	3.68	2.12
17.58	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	2.50	2.50	n.d.	0.54	0.54
18.58	2.53	1.92	2.23	0.87	n.d.	0.87	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
19.54	23.67	13.44	18.56	2.33	2.01	2.17	0.55	2.72	1.64	0.42	0.37	0.40
20.48	26.07	4.70	15.39	19.19	4.52	11.86	1.12	4.16	2.64	1.99	10.82	6.41
21.48	3.60	1.45	2.53	2.21	3.18	2.70	0.89	2.29	1.59	0.63	0.34	0.49
26.48	0.97	0.60	0.79	0.41	0.88	0.65	0.41	0.98	0.70	0.25	0.25	0.25
27.61	19.29	3.05	11.17	29.78	3.21	16.50	0.62	7.63	4.13	8.10	1.69	4.90
28.45	3.66	1.16	2.41	3.61	1.21	2.41	0.65	2.43	1.54	0.32	0.15	0.24
29.44	1.19	1.03	1.11	0.57	0.64	0.61	0.41	0.65	0.53	0.41	0.39	0.40
29.61	6.77	1.66	4.22	3.75	1.86	2.81	0.53	2.03	1.28	0.50	0.34	0.42
30.41	19.20	1.06	10.13	20.07	2.03	11.05	0.90	3.28	2.09	1.81	4.09	2.95
30.64	13.61	1.59	7.60	15.46	1.94	8.70	0.69	3.48	2.09	1.42	2.57	2.00
31.58	5.97	n.d.	5.97	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.31	0.05	0.18
33.62	3.65	0.96	2.31	3.03	1.02	2.03	0.87	2.45	1.66	0.35	0.18	0.27
36.41	1.95	0.49	1.22	1.14	0.40	0.77	0.61	1.16	0.89	0.48	0.39	0.44
40.48	0.61	0.45	0.53	0.78	0.43	0.61	0.48	1.02	0.75	0.16	0.17	0.17
40.57	1.16	2.27	1.72	1.04	0.45	0.75	0.56	1.42	0.99	0.22	0.19	0.21
40.69	7.32	9.12	8.22	1.69	0.75	1.22	0.72	1.83	1.28	3.98	0.18	2.08
41.41	1.75	1.07	1.41	1.07	0.57	0.82	0.28	0.84	0.56	0.34	0.19	0.27
42.44	0.71	0.47	0.59	0.79	0.12	0.46	0.56	0.63	0.60	0.15	0.15	0.15
42.62	7.56	9.59	8.58	5.08	1.58	3.33	0.90	1.62	1.26	0.49	0.40	0.45
43.43	271.77	178.17	224.97	166.43	136.97	151.70	32.86	25.13	29.00	56.46	31.44	43.95
43.61	216.61	217.72	217.17	19.74	120.54	70.14	39.10	95.66	67.38	61.69	40.78	51.24
44.39	78.29	9.08	43.69	20.91	101.98	61.45	5.07	16.87	10.97	11.67	19.24	15.46
44.63	48.01	8.07	28.04	6.32	49.98	28.15	3.44	0.33	1.89	5.24	5.78	5.51