

**AMMONIA VOLATILIZATION FROM INTENSIVELY
MANAGED DAIRY PASTURES**

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CENTRALE LANDBOUWCATALOGUS



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AMMONIA VOLATILIZATION FROM INTENSIVELY MANAGED DAIRY PASTURES

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STELLINGEN

1. De ammoniakvervluchtiging blijft bij beweiding op kleigrond beperkt tot 8 procent van de uitgescheiden N en wordt vooral gestuurd door de hoogte van de N-gift en de kationenuitwisselingscapaciteit van de grond. (Dit proefschrift)
2. De ammoniakopname en -afgifte door gras is een dynamisch proces met fluctuaties tussen dag en nacht en gedurende het verloop van de hergroeiperiode van een snede gras. (Dit proefschrift)
3. Reabsorptie door gras van geëmitteerde ammoniak uit urine- en mestplekken is een belangrijke oorzaak voor verschillen tussen ammoniakmetingen met de tunnelmethode en de massabalansmethode. (Dit proefschrift)
4. Het aanzuren van runderdrijfmest is een goede methode om de ammoniakemissie gedurende opslag en na uitrijden te beperken. (Dit proefschrift)
5. Vermindering van de ammoniakemissie op rundveebedrijven hoeft niet te leiden tot een verhoging van andere N-verliezen. (Dit proefschrift)
6. Eventuele maatregelen voortkomend uit onderzoek om de hoeveelheid N in faeces te vergroten ten koste van die in urine zal leiden tot een lagere N-werking van drijfmest en het risico op nitraatuitspoeling vergroten.
7. Het uit productie nemen van landbouwgrond voor natuurgebieden bemoeilijkt de realisatie van het mineralenaangifte systeem (MINAS) van de overheid om op landbouwgronden een vermindering van de nutriëntenoverschotten te bereiken.
8. Goed onderzoek dient zo gepresenteerd te worden dat potentiële opdrachtgevers bereid zijn vervolgonderzoek te financieren.
9. Het schrijven van en onderhandelen over onderzoeksvorstellen zijn vaardigheden die aan het einde van de studie gedoceerd zouden moeten worden.
10. Het gebruik van duurzaam geproduceerd tropisch hardhout draagt meer bij aan de instandhouding van het tropisch regenwoud dan het niet meer gebruiken van tropisch hardhout door de westerse wereld.
11. De wetgeving ter beperking van de nutriëntenemissie door landbouwhuisdieren zou ook van toepassing moeten zijn op gezelschapsdieren.
12. Een kind kan meer vragen stellen dan ouders kunnen beantwoorden.
13. De Markerwaard, die komt er wel.

Stellingen behorend bij het proefschrift "Ammonia volatilization from intensively managed dairy pastures".

D.W. Bussink, Wageningen, 11 december 1996

VOORWOORD

Het in dit proefschrift beschreven onderzoek is uitgevoerd bij het Nutriënten Management Instituut (NMI) te Lelystad. Aan de totstandkoming van dit proefschrift hebben veel mensen bijgedragen.

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The objectives of this thesis are (i) to quantify NH_3 volatilization from grassland, (ii) to gain understanding of the NH_3 volatilization processes on grassland and (iii) to study measures how to reduce NH_3 volatilization from grassland as such and on farm scale. Volatilization of NH_3 was studied of N fertilized grassland under grazing by dairy cows, of mown N fertilized grassland during regrowth and of cattle slurry application.

Grazed pastures on a loamy soil showed large variations in NH_3 emissions between individual cuts. Rainfall and sward management affected NH_3 volatilization rate. There was not much difference in NH_3 emissions between years. At a N fertilizer rate of $550 \text{ kg N ha}^{-1} \text{ yr}^{-1}$, NH_3 losses were 8.5%, 7.7% and 6.9% in 1987, 1988 and 1990, respectively, of the N returned to the sward in urine and faeces. At $250 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ they were 3.1% and 3.3% in 1988 and 1990, respectively. Whole season measurements are required to obtain reliable data on NH_3 volatilization. Volatilization of NH_3 was related to N excretion and N application rate. A calculation model was developed to estimate NH_3 volatilization from N application rate. Measurements on the same soil showed that a mown-only sward released NH_3 during a few days after fertilization with calcium nitrate (100 kg N ha^{-1}). Thereafter a net uptake was observed until harvest. On average a net uptake of aerial NH_3 was measured of a few kg N ha^{-1} per regrowth period. The measured NH_3 fluxes were much greater during the day than during the night. The NH_3 compensation point (on average $14 \mu\text{g NH}_3\text{-N m}^{-3}$) could be related to grass N content and soil water content. It is suggested that on grazed swards reabsorption of emitted NH_3 from urine and dung spots is important. Because of this micrometeorological techniques are required to determine NH_3 losses from grazed swards.

Urea (U) fertilizers may emit NH_3 , whereas calcium ammonium nitrate (CAN) fertilizers may emit N_2O or may be susceptible for nitrate leaching. Agronomic trials in the Netherlands (NL) confirmed the superiority of CAN to urea, whereas in the UK and Ireland U was effective as CAN, especially in the first cut. It was proved that especially the higher amount of rainfall in the UK and Ireland compared to NL caused the observed differences. Optimizing herbage yield, thereby minimizing N losses may be the best approach to decide which fertilizer to use. A calculation model was developed to improve decision analysis whether to use U or CAN. Under prevailing NL conditions for the first and second cut, it is only once every 5 and 7 years profitable to use U instead of CAN.

Acidification of cattle slurry with nitric acid resulted in marked reductions in NH_3 emissions. Micrometeorological experiments showed reductions of on average 85, 72 and 55% for acidified slurry with pH values of 4.5, 5.0 and 6.0, respectively. The measured losses could be related to temperature, slurry pH, potential water evaporation and NH_4^+ concentration. It was possible to calculate which pH would be required to obtain a certain reduction in NH_3 emission.

Losses of NH_3 occur during slurry application, housing, slurry storage, grazing, fertilizer application and from crops, in descending order of importance. The main strategies to reduce potential NH_3 loss are lowering the excretion of urea with urine and/or reducing the rate of NH_3 from slurry loss by technical means. However, reducing NH_3 loss may increase other N losses. To prevent this a farm scale approach is required. Modelling showed great scope for reducing NH_3 losses and N budget surpluses on dairy farms by improved management.

Key words: ammonia, volatilization, urine, faeces, grassland, N fertilizer, slurry, application, nitric acid, micrometeorological techniques, ammonia compensation point, dairy cattle, reduction

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CHAPTER 1

GENERAL INTRODUCTION

GENERAL INTRODUCTION

Until the beginning of this century organic manures were the main sources of nitrogen for application on farms. It was known that the handling, storage and application of these manures were all associated with ammonia (NH_3) losses. To maintain the nutrient value of livestock wastes, efforts were undertaken to prevent these losses by using closed manure storages, by adding chemicals to the manures and/or by harrowing immediately after manure application or injection (Heck, 1931). However the costs and technical difficulties made these measures often inapplicable for practice at that time.

With the large scale introduction and use of N fertilizers from the 1950s onwards, research interest in NH_3 losses from livestock wastes faded. Renewed interest emerged after NH_3 volatilization became an environmental issue in the 1980s (Van Breemen et al., 1982). Ammonia volatilization is an environmental issue because (i) high NH_3 concentrations in the air around animal housing can damage vegetation (Van Eerden, 1982; Fangmeier et al., 1994), (ii) it leads to an increased deposition of NH_3 and ammonium, which may contribute to water and soil acidification (Van Breemen et al., 1982) and (iii) emission of NH_3 is one of the main sources of increased N supply to nature areas leading to a change in flora and to eutrophication of terrestrial and aquatic ecosystems (Ellenberg, 1985, Isermann, 1990b).

With the recognition of the problem in the 1980s research was started to quantify NH_3 emissions. This was further stimulated by results of a study of Buisman et al. (1987) in which the NH_3 emissions were estimated for all European countries. According to this study, and others, up to 90% of the total NH_3 burden to the atmosphere originates from agriculture, with fertilizers and especially livestock wastes as major sources. Cattle farming and especially dairy farming is regarded as the largest source within animal husbandry in all countries. Buisman et al. (1987) estimated that two thirds of the total NH_3 emissions from animal husbandry resulted from cattle.

Total NH_3 losses from animal husbandry have increased by about 50% between 1950 and 1980 (Apsimon et al. 1987). In the Netherlands, losses from cattle farming have also increased considerably due to the increased use of N fertilizers on grassland during the last decades and the importation of feed and concentrates. These increased stocking densities and dietary N contents. Emissions peaked between 1985 and 1990 and started to decrease thereafter.

Though the emission sources were quantified, the exact amount of the emission was uncertain due to lack of data and due to extrapolation of results from trials in countries with totally different soil and climatic conditions. Because of the negative effects of NH_3

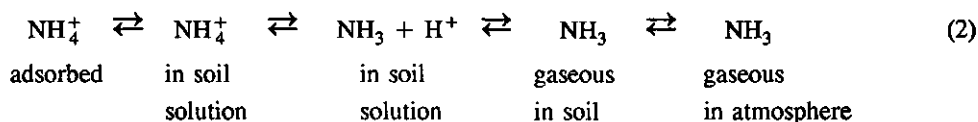
there was an urgent need for additional data in order to quantify NH_3 emissions and more importantly, how NH_3 emissions could be reduced. From 1985 onwards, research on this issue was started in the Netherlands. This thesis deals with NH_3 emission from grasslands in dairy farming systems. Ammonia emissions arise from grazing, application of slurry and fertilizer and the grass crop itself (Plants can release and take up NH_3 via their stomata.). The latter is generally regarded as a minor source. Other major NH_3 losses from dairy farming, are from cattle housing and storage of slurry.

Origin of and factors affecting NH_3 emission

Animal waste is the main source of NH_3 emission in animal husbandry (Buisman et al. 1987), with dairy cows as the major source. Annual N intake with herbage and concentrates by a dairy cow varies between 130-210 kg, depending on N fertilizer rate of grassland and milk yield (Mandersloot, 1992). Only 15-25% of the N intake is retained in milk and beef (Van Vuuren en Meijs, 1987; Mandersloot, 1992). The remainder is voided in urine and faeces. Especially urine contains easily decomposable components, mainly urea. The amount of urea in urine varies between 50-90% (Doak, 1952; Nehring et al. 1965). Urea in animal waste and in urea-containing fertilizers has to hydrolyze to ammonium carbonate before it becomes prone to NH_3 volatilization.



The enzyme urease acts as the catalyst in the hydrolysis. This enzyme is abundant in agricultural soils (Bremner and Mulvaney, 1978) and on stable floors, so that complete hydrolysis occurs usually within a few hours on stable floors and within a few days in soils (Vertregt and Rutgers, 1988). Hydrolysis is affected not only by the amount of enzymes but also by temperature, pH, soil moisture, organic matter content and cation exchange capacity (Freney et al., 1983). Before NH_3 volatilization takes place, the NH_4^+ has to be converted to NH_3 . The various reactions which govern NH_3 loss can be represented as:



The NH_3 volatilization rate is controlled by the rate of removal and of dispersion of NH_3 into the atmosphere. Its rate is affected by (i) environmental factors such as temperature,

windspeed, rainfall and atmospheric NH_3 concentration, by (ii) soil factors such as buffer capacity, infiltration rate, pH, cation exchange capacity and by (iii) agronomic factors such as the amount and N concentration of the applied slurry, fertilizer and voided urine/faeces. Generally, high temperatures, pH, windspeed and N concentration of animal wastes stimulate NH_3 emission, whereas high rainfall, CEC, infiltration rate, buffer capacity and atmospheric NH_3 concentrations reduce NH_3 emission. These factors have been discussed in detail by Freney et al. (1983), Horlacher and Marschner (1990) and Jayaweera and Mikkelsen, 1990). Besides NH_3 volatilization, NH_4^+ is removed from soil solution by uptake by plants and microbes and by nitrification. Nitrification contributes towards reduced NH_3 emissions. If nitrification is inhibited (e.g. by Didin) NH_3 emissions can increase (Amberger, 1990).

The factors involved in NH_3 emission are many fold and often interactions exist between parameters. This may contribute to the great variations in NH_3 emissions reported in the literature. As mentioned, local emission data are required to obtain representative data.

Ammonia losses from grasslands

Grasslands are well fertilized in the Netherlands. Average total N application from fertilizers and organic manures peaked between 1985 and 1990 at around 400 kg N ha^{-1} . At present average N fertilization on specialized dairy farms, e.g. the MDM farms, amounts to 350 kg N ha^{-1} grassland (Beldman and Den Boer, 1995). The daily N intake with herbage by grazing these grasslands amounts to 600 g cow^{-1} , of which less than 25% is retained in milk and beef (Van Vuuren and Meijs, 1987). Grazing-only of such pastures may result in N returns with urine and faeces of up to 400 kg ha^{-1} . This means a high potential for NH_3 losses. Reviewing the literature, Buisman et al. (1987) estimated that NH_3 volatilization from the N contained in urine and faeces was 40% and 5%, respectively. These data were mainly based on experiments under controlled conditions (wind tunnels, laboratory), with urine and or faeces. Under real grazing conditions, the situation is more complex. Emissions result from urine and faeces, but also from decaying grass, applied fertilizer and emission or re-absorption by the grass crop. With micrometeorology techniques the net NH_3 emission can be measured. Besides quantification of NH_3 losses due to grazing it is important to figure out which factors determine NH_3 losses and how NH_3 losses can be reduced.

Most dairy cows are kept in cubicles. The slurry produced during the housing period in cubicles is applied to grassland and arable land. The common way of slurry application till 1992 was surface spreading. It was usually carried out with a tank fitted with a

splash plate. The slurry is pumped through an orifice onto a splash plate and is spread onto the soil or grassland surface. Considerable NH_3 emissions may be expected from this technique due to the large exchange area with the atmosphere and because half of the slurry N is ammoniacal N. From agronomical trials, it was estimated that N efficiency varied between 10-35% compared to mineral fertilizer (Anonymous, 1987). These low efficiencies and the large variation was mainly due to NH_3 emission, which was expected to vary between 10 and 95% of the applied ammoniacal N (Anonymous, 1987). Buisman et al. (1987) assumed in their emission inventory a value of 40% of the applied ammonium N.

In the Netherlands grassland receives considerable amounts of fertilizer as calcium ammonium nitrate (CAN). Worldwide, urea is the main N fertilizer with 40% of total N usage in agriculture (IFA, 1992). Emissions of NH_3 from applied fertilizer come only from N in the ammonium form, or from compounds such as urea which can hydrolyse to ammonium. Ammonia emissions from CAN on grassland are generally considered to be below 5% and mostly less than 2%. (Lightner et al., 1990; Velthof et al., 1990). Only on calcareous soils higher emissions up to 10% could be expected (Hargrove, 1977; Whitehead and Raistrick, 1990). However, these experiments were conducted in the laboratory with bare soils and probably overestimated NH_3 emissions. Velthof et al. (1990) using windtunnels to measure NH_3 emissions from urea and CAN on a heavy clay grassland (pH-KCl 5.5) found mean NH_3 losses over 7 experiments of 22.6 and -1.8 % of the applied N, respectively. This indicates the low potential of NH_3 volatilization from CAN. Field experiments on other soil types are lacking. However, many experimental data are available from agronomic field trials, which indicate a higher N efficiency of CAN than of urea on all grassland soils during the whole growing season, except on peat grassland (Van Burg et al., 1982). This higher efficiency probably results from the lower potential for NH_3 volatilization of CAN. However CAN gives more rise to nitrate leaching, N_2O emission and denitrification. More recent experiments from the British Isles suggests that there is not much difference in efficiency between CAN and urea applied for the first cut (Watson et al., 1990). Ammonia volatilization from urea may be outcompeted by leaching and denitrification from CAN.

Plants can release and take up NH_3 via the stomata, depending on environmental conditions and N status of the plants (Holtan-Hartwig and Bøckman, 1994). The concentration in the air at which no NH_3 is taken up or released is called the NH_3 compensation point. Above this level plants take up and below this level plants emit NH_3 . The compensation point and as a result uptake or release of NH_3 depends among others on crop type, physiological status and fertilizer application rate ((Holtan-Hartwig and Bøckman, 1994, Harper et al., 1987). The release of NH_3 increases with fertilizer application rate (Schjørring, 1989; Maheswari et al., 1992). During senescence/ripening a plant can also

release NH_3 as was shown in an experiment with well fertilized barley, where a loss of 1.3 kg N ha^{-1} was measured (Schjørring, 1991). Published data for NH_3 emissions from crops/plants are many fold but form an incoherent picture (Holtan-Hartwig and Bøckman, 1994). Micrometeorological techniques seem to give the most direct and reliable indications of field emissions. Experiments on well fertilized pastures are sparse. Most of the experiments were done under semi-controlled conditions (wind tunnels) with decaying grass. These experiments showed that cut grass left to dry and which was not subjected to decomposition, released little or no NH_3 , whereas in humid conditions volatilization amounted to 20-47% of herbage N content (Whitehead et al., 1988). Vertregt and Rutgers (1988) estimated a loss of 3 kg N ha^{-1} from decaying grass during the growing season. Holtan-Hartwig and Bøckman (1994) estimated that the net NH_3 emission from agricultural land is $1\text{-}2 \text{ kg N ha}^{-1}$ more than from natural vegetation. In emission inventories the contribution of vegetation is generally lacking. An exception is the ECETOC (1994) estimate.

Reducing NH_3 losses from grasslands

Reducing NH_3 losses from grazing animals should be possible by lowering the N intake or reducing the time spent grazing by keeping the cows indoors during summer and feeding them low N containing feeds. A lower N intake reduces the amount of urinary N voided on the pasture. This may reduce NH_3 emission. A lower N intake is also possible by reducing fertilizer N input to grassland. This reduces herbage production and is thus not always possible. Keeping the cows indoors during summer increases NH_3 loss potential during housing and storage and from slurry application. On farm scale the net effect might be an increase of total NH_3 emissions. This illustrates that reducing NH_3 emissions requires a whole farm approach, because reductions in one part of the system may increase the NH_3 losses in other parts. Moreover, reducing NH_3 losses may increase losses due to nitrate leaching and denitrification. For example injection of slurry is a good technique to reduce NH_3 losses. But when slurry is injected in late autumn, the crop cannot use the not volatilized N. After nitrification this N will leach or denitrify as shown by Thompson et al. (1987). Generally speaking, an increase of other N losses by reducing NH_3 emissions should be avoided. Looking to the N budget of a dairy farm this means that every $\text{kg NH}_3\text{-N}$ emission reduction should lead to a similar or larger reduction on the N budget of the farm. This should be possible because the reductions in NH_3 emission lead to an improvement in the nutrient value of slurry. Savings on the purchase of fertilizers, forage and/or concentrates should therefore be possible.

Three strategies can be followed to reduce NH_3 losses from slurry application on

grassland, (i) reducing the exchange area with the atmosphere, (ii) lowering the pH of the slurry which causes a shift of Eq. 1 to the left and (iii) lowering the concentration of N in slurry by dilution. Much emphasis was put on the first strategy. Besides deep injection, techniques as shallow injection with open slots and narrow bandspreading (trailing hoses and trailing feet) were developed. An advantage of these techniques is that they also reduce the stench associated with surface application. Acidification is possible with all kinds of acid, like nitric and sulfuric acid. In the Netherlands most emphasis was put on nitric acid, because the added N improved the nutrient value of the slurry. Testing was done by application of the acid in the slurry kept in the storage under the slats in cubicles (to reduce also NH_3 losses from housing) and by mixing it through the slurry just before application. Dilution is possible by adding water to the slurry before application or by applying irrigation immediately after application.

Reducing NH_3 losses from fertilizer application is possible by (i) choosing the right fertilizer (generally ammonium nitrate in stead of urea containing fertilizers) and by (ii) reducing the amount of fertilizer applied. The latter is possible by improvement of the nutrient value of slurry by using slurry techniques with reduced NH_3 emission.

Objectives and approach for this thesis

Related to the problems associated with NH_3 emissions from grassland systems as described above, the objectives of this thesis are (i) to quantify NH_3 emission from grassland, (ii) to gain understanding of the emission processes on grassland and (iii) to study measures how to reduce NH_3 emissions from grassland as such and on farm scale.

Quantification of NH_3 losses and analysis of emission processes was generally done through experiments with grazing dairy cattle, with slurry application and fertilized mown grassland. Micrometeorological techniques were used to minimize effects of the measurement equipment on the measurement environment. Statistical modelling was used to determine the effect of fertilizer type on agronomic efficiency and thereby on the risk of NH_3 volatilization.

In Chapter 2 and 3 losses from grazing dairy cattle are quantified. The major factors involved in NH_3 emission from grazing cattle are discussed and the effect of lowering N fertilizer application was tested. A simple model was developed to determine NH_3 emission as function of soil type and fertilizer N application rate. In Chapter 4 and 5 the NH_3 cycling of a well fertilized pasture is investigated during the growing periods of the second and fourth cut. The aim was to quantify the NH_3 losses (per cut and) on a diurnal basis and to relate these losses to management and environmental conditions. In Chapter 6 the application of slurry and the potential of acidified slurry in reducing NH_3 emissions was investigated. A simple model was developed to predict NH_3 losses from surface

applied acidified slurry. In Chapter 7 the agronomic potential of urea and CAN was investigated, based on statistical analysis of field trial data from grasslands in western Europe. A simple model was developed to predict under which circumstances the financial benefits from CAN are exceeding those of urea. As pointed out, a farm scale approach of NH_3 emission is necessary because intervening in one part of the cycle may affect NH_3 emissions in other parts. Also other N losses may be stimulated when NH_3 emissions are reduced. In Chapter 8 the major NH_3 losses are reviewed based on the literature. Strategies are discussed on how to reduce NH_3 emissions. A simple model is presented to demonstrate how a whole farm approach can contribute to reductions in NH_3 losses. Finally, Chapter 9 presents an overview and a general discussion in relation to the objectives of this thesis.

CHAPTER 2

AMMONIA VOLATILIZATION FROM GRASSLAND RECEIVING NITROGEN FERTILIZER AND ROTATIONALLY GRAZED BY DAIRY CATTLE

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AMMONIA VOLATILIZATION FROM GRASSLAND RECEIVING NITROGEN FERTILIZER AND ROTATIONALLY GRAZED BY DAIRY CATTLE

ABSTRACT

The micrometeorological mass balance method was used to measure ammonia (NH_3) volatilization from rotationally grazed swards throughout the 1987 and 1988 growing seasons. In both years the swards were dressed with calcium ammonium nitrate (CAN) split over 7 dressings. In 1987 the sward received a total of 550 kg N ha⁻¹, in 1988 a total of 550 or 250 kg N ha⁻¹. For the 550 kg N ha⁻¹ treatments there were 8 and 9 grazing cycles, respectively, in 1987 and 1988 and 7 for the 250 kg N ha⁻¹ treatment. Losses from the 550N sward were 42.2 and 39.2 kg N ha⁻¹ in 1987 and 1988, respectively; this was equivalent to 8.5 and 7.7% of the N returned to the sward in the excreta of the grazing cattle. The NH_3 loss from the 250N sward was 8.1 kg N ha⁻¹ in 1988, which was equivalent to 3.1% of the N returned to the sward in excreta during the growing season. There was a wide variation in NH_3 volatilization between the individual grazing periods. This indicates the necessity of continued measurements throughout the growing season to obtain reliable data on NH_3 volatilization. Soil humidity is suggested to be a key factor, because emissions were high from wet soil, and low from drier soil. Results of a Monte Carlo simulation study showed that the measured NH_3 loss from the 250N and 550N swards had a standard deviation of 13 and 5% of the mean, respectively.

INTRODUCTION

On grazed swards with a fertilizer N input of 200 kg N ha⁻¹ yr⁻¹ and more - as is common in the Netherlands - only a minor portion of the N from ingested herbage is retained in milk or live weight gain. The remainder, about 75-95%, is excreted in dung and urine (Lantinga et al., 1987; Van Vuuren and Meijs, 1987). Generally, the recovery of excreted N in herbage yield is low on well fertilized swards (Lantinga et al., 1987). The fraction not recovered in herbage yield may be immobilized by the soil microbial biomass or may be lost from the soil-grassland system through a combination of NH_3 volatilization, nitrate leaching and denitrification.

Losses of NH_3 to the atmosphere are of great concern, because of the impact they may have on aerosol chemistry (Ziereis and Arnold, 1986) and acid deposition (Apsimon et al., 1987). The major input of NH_3 into the atmosphere is thought to be the NH_3 volatilized from urine and faeces excreted by farm livestock (Apsimon et al., 1987). Only

limited data exist on NH_3 losses from grazed swards. Losses were found to depend on fertilizer input (Jarvis et al., 1989b); total dressings of 210 and 420 kg N ha⁻¹ yr⁻¹ resulted in NH_3 losses of 10 and 25 kg N ha⁻¹, respectively (Jarvis et al., 1989b). A grass-clover sward gave a loss of 7 kg N ha⁻¹ (Jarvis et al., 1989b). On tropical pastures dressed with 374 kg N ha⁻¹ yr⁻¹, NH_3 losses amounted to 17-34 kg N ha⁻¹ (Harper et al., 1983b).

Losses of NH_3 from grazed pastures are thought to result mainly from urine deposited by cattle (Jarvis et al., 1989b; Lantinga et al., 1987). The main N component in urine is urea, which has a high potential for NH_3 volatilization (Freney et al., 1983). The extent of the NH_3 loss is also affected by soil and environmental factors (Freney et al., 1983) and possibly grassland management. In the present study NH_3 losses from rotationally grazed swards were measured continuously throughout the grazing season. The swards were grazed with dairy cows and supplied with a total of 250 or 550 kg N ha⁻¹ yr⁻¹ as calcium ammonium nitrate (CAN). It was hypothesized that higher N dressings would increase herbage yield and herbage N concentration, and thus N intake and N excretion by the cows. More N excretion increases the potential for NH_3 loss. Measured losses were therefore related to the estimated N returns via dung and urine to the sward.

MATERIALS AND METHODS

Method

A micrometeorological mass balance method, similar to the method described by Denmead (1983), was used to measure NH_3 losses from grazed plots throughout the 1987 and 1988 growing seasons. This method assumes that the vertically integrated product of wind speed and the difference between the centre and boundary of the plot in NH_3 concentration of the air, divided by the fetch is equal to the NH_3 flux from the soil surface. The fetch, which is the distance between upwind boundary and the centre of the plot should be known exactly.

Measurements

Differences in NH_3 concentration between the centre and the boundary of the plot were measured via NH_3 sampling traps in the centre of the plot and at the windward boundary. Eight such traps were fixed to a mast in the centre of the plot, at heights of 0.25, 0.40, 0.55, 0.75, 1.00, 1.30, 2.30 and 3.30 m. At the windward boundary of the plot, a mast was placed with five NH_3 traps, at heights of 0.40, 0.55, 0.75, 1.30 and 2.30 m. Fewer

traps were placed at the boundary because the background concentration was low and essentially uniform with height. Each trap contained 20 ml 0.02 M H_3PO_4 held in 100 ml collection tubes. With Charles Austin pumps (85 SE) air was sucked through the acid via a gas dispersion tube (porosity 2) at a rate of 2.4 l min^{-1} , controlled by a Platon flow meter. A correction of 0.1 to 0.25 l min^{-1} was made for the measured pressure drop between the flow meter and the air inlet of the trap. Sampling and analysis of the 0.02 M H_3PO_4 solution was usually carried out on a 24 h basis. The tubes were transferred to the laboratory and the NH_3 concentration was determined by means of the phenol-hypochlorite method (Weatherburn, 1967).

Wind speed was measured on a mast outside the plot, at eight different heights, varying from 0.40 to 4.30 m. Casella cup anemometers (T16108/2) were used at the lower four positions, while Lambrecht cup anemometers (1469I) were used at the four top positions. Wind direction was measured with a Porton windvane. The wind data were recorded on mechanical counters. Other weather data (rainfall, air temperature, radiation and potential evaporation) were provided by the meteorological station at the experimental site.

Sampling was continuous throughout the period May-October. In a number of cases, the sampling traps were analyzed four times a day to determine the diurnal pattern of the NH_3 emission. In 1988, extra NH_3 traps were fixed at the mast and analyzed in order to determine the accuracy of the NH_3 measurements.

Experimental treatments

The experimental site, with a size of five ha, was situated on a young marine, calcareous loam soil in the Flevopolder in the Netherlands. The sward was more than 7 years old, with ryegrass (*Lolium Perenne* L.) as the dominant grass species. The top 5 cm of the soil had a clay content 19.5%, an organic matter content of 8.3%, a CEC of $0.28 \text{ mol}_c \text{ kg}^{-1}$ and a pH(KCl) of 6.8. The background NH_3 concentration in the atmosphere is relatively low in the Flevopolder, mainly because the polder is predominantly used for arable farming. In 1987, the experiment was carried out on one square test plot of 0.18 ha, heavily fertilized with a total of $550 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ as CAN, split into 7 dressings. In 1988 there were two treatments, receiving totals of 550 and $250 \text{ kg N ha}^{-1} \text{ yr}^{-1}$, split into 7 and 6 dressings, respectively. These plots were circular, with a radius of 23 m, to obtain a constant fetch, and were 80 m apart. After the last fertilizer N dressing in september of 1987 there were another two grazing periods on the 550N plot, because herbage continued to grow until late in autumn. In 1988, the 250N plot was grazed twice and the 550N plot three times after the last fertilization in September.

The plots were rotationally grazed - as is common in the Netherlands - with lactating Holstein Friesian dairy cows (age 2-7 yrs). The cows first grazed on a field with the same N treatment as the test plot to become accustomed to the N concentration of the grass. Grazing on the test plot started at a target herbage yield of 1700 kg DM ha⁻¹. Stocking rates were high, 60 to 120 cows ha⁻¹, in order to have the sward grazed in one or one and a half days and to ensure that the distribution of dung and urine patches over the plot was as uniform as possible. Within two days after grazing the sward was dressed with fertilizer N and then allowed to regrow prior to the next grazing period.

The total N intake by the dairy cows via herbage and concentrates (1 kg per cow per day) and the N retention in milk and live weight gain (PJAG Deenen, pers comm) were used to calculate the N content of the excreta. The distribution of N between faeces and urine per grazing period was calculated as follows (Lantinga et al., 1987):

$$\text{N retention} = 0.0087 \times (\text{number of cow grazing days}) + (\text{milk protein yield})/6.38 \quad (\text{kg N ha}^{-1}) \quad (1)$$

$$\text{N in faeces} = \text{N intake} \times 0.0078 \quad (\text{kg N ha}^{-1}) \quad (2)$$

$$\text{N in urine} = \text{N intake} - \text{N in faeces} - \text{N retention} \quad (\text{kg N ha}^{-1}) \quad (3)$$

where N intake is total N intake via herbage and concentrates in kg ha⁻¹. It is assumed that about 2/24 of the excreta were not returned to the sward immediately, because the cows were in the milking shed twice a day for about 1 h during milking time. So as to verify the N in excreta calculated from equation (3), urine produced during grazing was sampled and analyzed a number of times during the 1988 grazing season. Between 10 to 18 cows were sampled in the morning, in the afternoon and in the evening by collecting urine in 0.5 l pots attached to a beanpole. Sampling was done on the day before grazing started on the test plot. Because of this, cow behaviour was not disturbed on the test plot. The urine was analyzed for total N by a Kjeldahl method (Smit, 1979).

RESULTS

Ammonia emissions

During the 1987 growing season, cumulative NH₃ volatilization was 42.2 kg N ha⁻¹ from the sward supplied with 550 kg N ha⁻¹ yr⁻¹ (Table 1). The amount volatilized varied considerably between grazing periods. The NH₃ volatilization per grazing period was related partly to the amount of N excreted via dung and urine per grazing period (Table 1). Hence, the NH₃ losses were expressed as percentages of the total amount of N excre-

Table 1. Cow grazing days, N retention, N excretion and NH₃ emissions during the 1987 (550N) and 1988 (550N and 250N) grazing seasons.

Period	Cow grazing days	N retention by cows kg ha ⁻¹	N excretion		NH ₃ -N emission		
			faeces kg ha ⁻¹	urine kg ha ⁻¹	kg ha ⁻¹	% of N excreted on plot	g per cow grazing day
1987: 550N							
1. 7/5 - 2/6	149	21.7	16.9	52.2	3.36	5.3	22.6
2. 2/6 - 22/6 ^t	128	18.0	17.7	63.5	9.34	12.5	73.2
3. 22/6 - 6/7 ^t	109	12.8	12.8	56.2	7.05	11.1	64.7
4. 6/7 - 28/7	76	9.7	10.0	39.2	2.78	6.1	36.6
5. 28/7 - 23/8 ^t	136	16.0	12.8	49.7	8.48	14.8	62.3
6. 23/8 - 16/9	124	11.2	17.2	66.8	4.01	5.2	32.3
7. 16/9 - 20/10	97	10.6	13.8	48.0	4.33	7.6	44.4
8. 20/10 - 29/10**	90	0.9	12.4	50.0	2.77	4.8	30.9
total/mean	908	101	114	425	42.2	8.5	46.5
1988: 550N							
1. 4/5 - 20/5	167	22.8	22.5	58.7	2.94	3.9	17.6
2. 20/5 - 9/6	140	19.0	20.1	60.9	5.71	7.7	40.9
3. 9/6 - 7/7 ^t	108	14.8	15.2	54.0	8.24	12.9	76.0
4. 7/7 - 27/7 ^t	100	13.8	17.6	53.6	8.24	12.6	82.2
5. 27/7 - 17/8	101	13.8	14.6	56.5	5.44	8.3	53.8
6. 17/8 - 5/9	143	19.5	14.3	41.2	0.63	1.2	4.4
7. 5/9 - 4/10 ^t	84	11.4	8.6	32.0	3.80	10.2	45.5
8. 4/10 - 31/10**	95	0.7	10.8	51.5	2.15	3.5	26.6
9. 31/10 - 10/11**	36	0.3	3.8	17.9	2.01	9.3	56.0
total/mean	974	116	127	428	39.2	7.7	40.2
1988: 250N							
1. 4/5 - 20/5	111	16.2	13.8	27.0	0.69	1.8	6.2
2. 20/5 - 9/6	106	15.5	16.6	34.9	1.38	2.9	13.0
3. 9/6 - 13/7 ^t	77	11.2	10.5	22.3	1.73	5.7	22.6
4. 13/7 - 4/8 ^t	72	10.5	12.4	28.1	1.13	3.0	15.6
5. 4/8 - 5/9	63	9.3	10.1	24.6	1.77	5.5	27.9
6. 5/9 - 4/10 ^t	74	10.8	11.8	31.4	0.63	1.6	8.5
7. 4/10 - 14/10**	76	0.5	9.0	33.5	0.77	1.8	10.1
total/mean	580	74	84	203	8.1	3.1	14.0

** During this period the sward was grazed by dry cows.

t The sward was topped after grazing.

ted on the pasture in each period. The relative losses varied from 4.8 to 14.8% with a mean of 8.5%. Or, expressed in a different way, the average loss was 47 g N (range 23.6 to 73.2) per cow per grazing day.

In 1988, cumulative NH_3 volatilization was 39.2 kg N ha⁻¹ for the 550N plot and 8.1 kg N ha⁻¹ for the 250N plot. The difference between the two plots was striking throughout the season. On average, 7.7% of the excreted N volatilized from the 550N plot and 3.1% from the 250N plot (Table 1).

Figure 1 shows typical patterns of NH_3 loss, for four consecutive grazing periods. Generally, NH_3 losses were high during the first few days after grazing and decreased to negligible amounts about 10 days after the grazing period. In most cases, a peak emission was measured on the second day. Rainfall appeared to influence this general pattern. The relatively low NH_3 emissions following grazing in the second half of August were associated with high rainfall (Fig. 1). The NH_3 emission rate varied also between day and night. During day-time the emission rate was much higher than during night-time. Maximum emission rates were recorded between 12.00 and 17.00 h (Fig. 2).

N excretion

Mean results of the urine analyses for urine collected during 1988 are shown in Table 2. The mean N concentration of the urine varied during the day, and also between days. Typically, the N concentration was higher in the early morning and lower in the evening. This diurnal variation is probably related to the drinking pattern of the dairy cows during the day. The urine from the 250N plot generally had a lower N content, however the differences were small and inconsistent. This difference is very small in relation to the large difference in NH_3 emission per cow grazing day recorded between the 550N and 250N plot in 1988 (Table 2).

In 1987 there were 908 cow grazing days, and an estimated 101 kg N ha⁻¹ were retained in milk and live weight gain (Table 1). An estimated 539 kg N ha⁻¹ was excreted, 425 kg N in urine and 114 kg N in dung. The estimated N excreted in urine was 3.7 times of that in dung. In 1988 there were 974 cow grazing days per ha on the 550N plot and 580 on the 250N plot. This difference was mainly due to the higher grass production on the 550N plot. Calculated N excretion was 555 and 287 kg ha⁻¹ on the 550N and 250N plots, respectively. The ratio between N excreted via urine and faeces was 3.4 and 2.4 on the 550N and 250N plot, respectively. Expressed per cow grazing day, the ratio of estimated N excretion via urine was 1.26 times higher on the 550N plot than on the 250N plot. The results of the urine analysis (Table 2) did not show a 26% difference in N excretion via urine. Thus far we are unable to interpret this difference. Possibly more urine was excreted on the 550N plot (H Valk, pers comm).

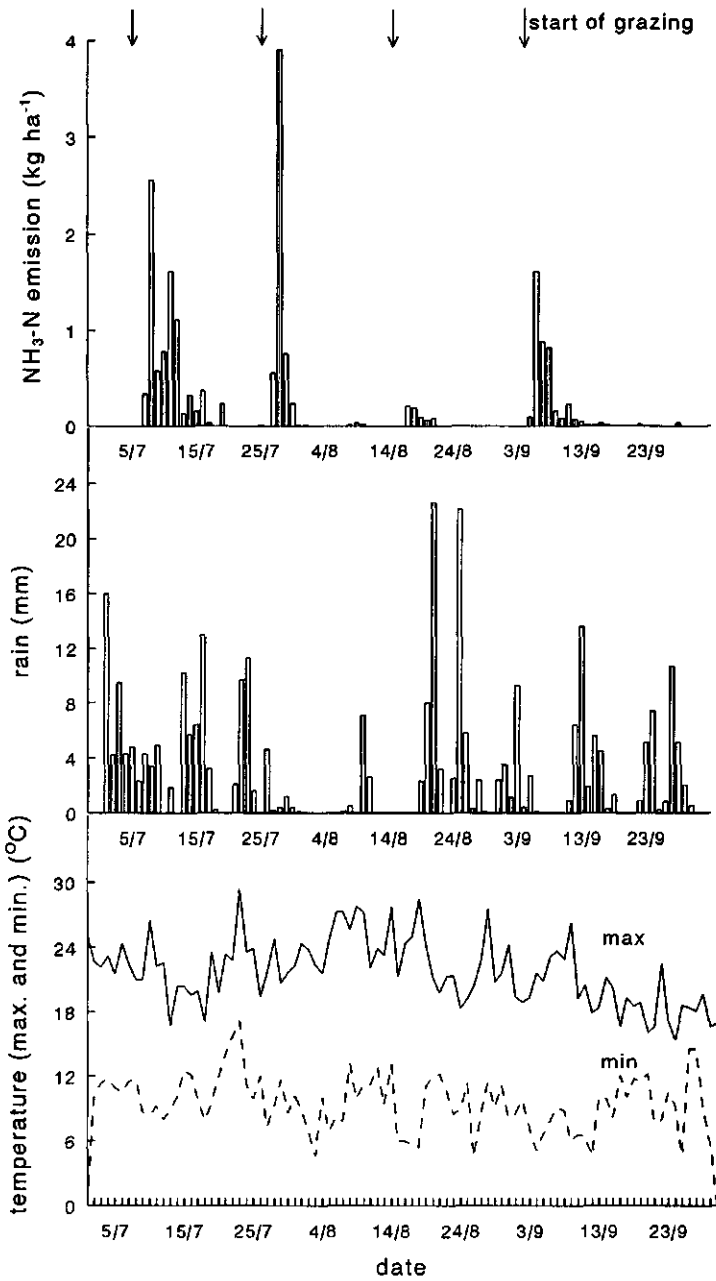


Fig. 1. Daily values for NH₃ emission, global radiation, rainfall and minimum (---) and maximum (—) temperatures at 1.50 m during the 4th, 5th, 6th and 7th grazing period on the 550N plot in 1988.

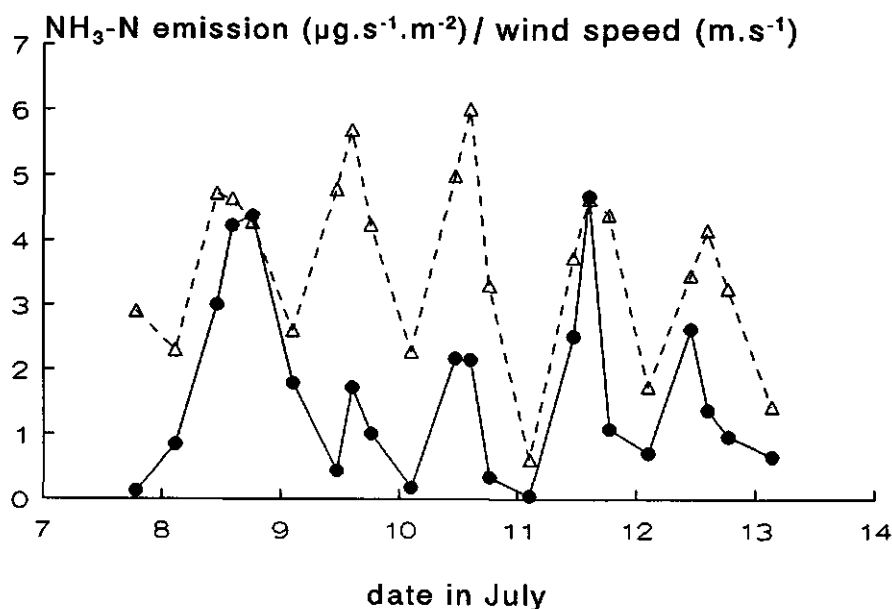


Fig. 2. NH₃ emission pattern (—●—) and wind speed (-△-) during the first five days of the 4th grazing period in 1988 on the 550N plot.

Table 2. N content of urine collected from grazing dairy cows on 9 June, 27 July and 5 September 1988.

Period		Total-N (g l ⁻¹)	
		550N	250N
9 June	morning	11.1	10.0
	afternoon	8.4	9.5
	evening	8.0	7.1
	daily mean	9.1	8.9
27 July	morning	9.1	
	afternoon	6.9	
	evening	5.8	
	daily mean	7.2	
5 September	morning	9.5	9.6
	afternoon	8.2	6.2
	evening	7.7	7.1
	daily mean	8.6	7.5

' between 10 and 18 cows were sampled per period

DISCUSSION

Error Analysis

The overall error in the cumulative NH_3 emission depends on the distribution of urine and dung patches over the plot and on the accuracy of the wind speed and NH_3 concentration measurements. During the season dung patches were counted per quarter section of the plot. The numbers per section were found to be very similar and the patches were evenly distributed. The distribution of urine patches is much more difficult to quantify. However, since dung patches were randomly distributed, the urine patches were assumed to also be evenly distributed. An almost uniform distribution of urine and dung patches provides a relatively regular pattern of NH_3 sources over the plot. A high degree of uniformity of NH_3 source is a prerequisite for the mass balance method (Denmead, 1983). The error of the measured wind profile was small as the log-linear wind profiles generally had a correlation coefficient of 0.95 or more and the anemometers had an error of $\pm 1\%$.

The largest error in the NH_3 emission was found in the accuracy of the NH_3 concentration measurements. The duplicate measurements of NH_3 concentration indicated that the mean coefficient of variation (cv) was 5 to 6% (Table 3). The cv was essentially independent of measuring height and NH_3 concentration.

To estimate the effect of the variations in the concentration measurements on variations in NH_3 emission from the 250N and 550N plots a 'Monte Carlo' simulation (Mihran, 1972) was carried out, using a normal distribution of the logarithmically transformed NH_3 concentrations, with the cv's (Table 3) as standard deviation. For each measuring day in 1988 on the 550N and 250N plot 50 NH_3 emission simulations were run. Statistical analysis of the 50 cumulative seasonal NH_3 emissions for the 550N and 250N plots gave cv's of 5% and 13%, respectively. These results indicated that the concentration measurements were an appreciable source of error in the determination of NH_3 emission, particularly at low emission rates.

Another possible source of error is associated with diurnal variations in wind speed and NH_3 concentration profile (Fig. 2). These possible errors were examined by comparing the calculated NH_3 emission based on means per day and means per quarter day. This comparison was made for 19 days in 1988 (Table 4). The mean total emission calculated on a quarter-day basis was slightly higher than that based on one mean per day. The statistically significant ($p < 0.01$, Student t-test) mean difference was equivalent to about 10% of the mean per 24 hrs. This suggests, that the means given in Table 1 are underestimates of the actual emission. However, the summed experimental error increases by doing quarter day measurements, because of a fourfold increase in the number of samp-

Table 3. The coefficient of variation (cv) and standard error (se) of the NH_3 concentrations based on duplicate measurements from grazed plots receiving two fertilizer N rates.

N rate $\text{kg ha}^{-1} \text{ yr}^{-1}$	Number of duplicates	Mean level $\mu\text{gN m}^{-3}$	Se $\mu\text{gN m}^{-3}$	Cv %
250N	90	10.1	0.535	5.3
550N	175	14.2	0.909	6.4

lings and concentration measurements. Furthermore, the relative error of the NH_3 measurements tend to increase as the NH_3 concentration decreases by a factor 4. Given these arguments and that the estimated cumulative NH_3 emission based on a mean per day was only 10% lower than the summed daily total of means per quarter day and the additional costs associated with extra measurements, we consider that daily measurements are acceptable.

Effects of N fertilization

Losses of NH_3 from grazed plots are the sum of the NH_3 losses from applied fertilizer, dung and urine and from decaying grass after topping (Whitehead and Lockyer, 1989). NH_3 losses from the applied CAN fertilizer are likely to be negligible (Velthof et al., 1990). Little herbage remained after grazing and topping, therefore only a small proportion of total herbage production decayed in the field. Furthermore, the environmental conditions during the growing season of relatively dry air and intermittent rainfall, were not conducive to NH_3 loss from decaying herbage (Whitehead and Lockyer, 1989; N Vertregt, pers comm). Therefore, it is likely that the measured NH_3 losses in our experiments resulted mainly from excreta.

Generally, the volatilization potential of urine is considerably greater than that of faeces due to the very labile nature of urea which in well fertilized temperate grassland constitutes 75% or more (Doak, 1952; Groenwold and Heringa, 1981; Jarvis et al., 1989a) of the total N content of urine. The much higher potential for NH_3 loss from urine compared to dung has been confirmed in enclosure experiments (Lockyer and Whitehead, 1990; MacDiarmid and Watkin, 1972a; Sherlock and Goh, 1984). In our experiments it was calculated that, on the 550N sward, about 78% of the excreted N was contained in urine and 22% in faeces. This estimated partitioning is in agreement with experimental data from well-fertilized pasture (Van Vuuren and Meijjs, 1987), where approximately 70% of the excreted N was present in urine.

It has sometimes been assumed that approximately 40% of the N in urine and 5% of

TABLE 4. $\text{NH}_3\text{-N}$ emission (kg ha^{-1}) based on four measurement periods per 24 h and on one period, for 19 days in 1988 on the 550N plot.

Date	per measuring period ¹				A+B+C+D	24 h period	(A+B+C+D) -24 h
	A	B	C	D			
20-05	0.00	0.61	0.13	0.10	0.84	0.63	0.21
21-05	0.13	0.21	0.21	0.02	0.65	0.68	-0.03
22-05	0.11	0.22	0.12	0.02	0.47	0.55	-0.08
23-05	0.04	0.16	0.06	0.02	0.28	0.18	0.10
24-05	0.09	0.51	0.11	0.14	0.75	0.67	0.08
8-07	0.49	0.67	0.71	0.69	2.56	2.47	0.09
9-07	0.07	0.28	0.16	0.07	0.58	0.46	0.12
10-07	0.36	0.34	0.06	0.02	0.72	0.53	0.19
11-07	0.40	0.77	0.17	0.27	1.61	1.52	0.09
12-07	0.42	0.23	0.15	0.31	1.11	1.04	0.07
27-07	0.00	0.00	0.15	0.41	0.56	0.81	-0.25
28-07	0.69	0.80	0.63	1.78	3.90	3.86	-0.04
29-07	0.30	0.26	0.04	0.06	0.76	0.49	0.27
30-07	0.07	0.04	0.02	0.11	0.24	0.12	0.12
6-09	0.00	0.77	0.41	0.34	1.52	1.32	0.20
7-09	0.22	0.03	0.10	0.33	0.68	0.56	0.12
8-09	0.49	0.21	0.06	0.06	0.82	0.33	0.49
9-09	0.02	0.03	0.04	0.07	0.16	0.14	0.02
10-09	0.00	0.05	0.00	0.03	0.08	0.10	-0.02
total					18.29	16.46	1.83
mean							0.097*
se							0.022

1) A = 7.00 - 12.30 h, B = 12.30 - 17.00 h, C = 17.00 - 21.30 h and D = 21.30 - 7.00 h

* Differs significantly from 0 ($p < 0.01$, Student t-test).

the N in faeces from grazing cattle volatilizes as NH_3 (Buijsman et al., 1987). These percentages suggest that approximately 30% of the excreted N volatilized as $\text{NH}_3\text{-N}$ on well fertilized grassland. Our data indicate much lower NH_3 losses of approximately 8% of the total amount of excreted N. Other recent field experiments in NW Europe indicated similar small losses. In the UK, NH_3 losses of 25 kg N ha^{-1} , corresponding to 9.0% of the excreted N, were determined on a 420N sward (Jarvis et al., 1989b). Under subtropical conditions NH_3 losses may be much larger due to higher temperatures. On a 374N grazed pasture in Queensland, Australia, 14.4 to 28.4% of the urinary N volatilized as NH_3 (Harper et al., 1983b).

There was an effect of fertilizer application rate on the total NH_3 volatilization loss.

The loss from the 550N plot was almost five times higher than that from the 250N plot. Part of this difference can be attributed to the difference in the total amount of excreta returned to the sward due to a lower intensity of grazing. Expressed as a percentage of the estimated excreted N, the total NH_3 volatilization loss from the 550N plot was 2.5 times larger. The difference in emission rates from heavily and moderately fertilized swards was less pronounced in a UK study (Jarvis et al., 1989b). In that study NH_3 losses from rotationally grazed 420N and 210N plots were 9.0% and 6.7% of the excreted N. This corresponded to 12.1% and 11.2% of the total urinary N (Jarvis et al., 1989b). The difference between the UK study and our study regarding the effect of N fertilizer application rate may possibly be attributed to differences in soil type, like the higher clay content of the soil used in this study. Differences in climatic conditions between the UK and the Netherlands are likely to be small.

An increase in N concentration in urine will increase the potential for NH_3 volatilization. This was confirmed in an experiment with yearling steers (Jarvis et al., 1989a). Higher N application rates gave higher N concentrations in urine and a proportional increase in NH_3 losses. In our experiment, higher N concentrations were expected in the urine on the 550N plot than on the 250N plot, but the limited results in Table 2 show only minor differences, despite of the large differences in NH_3 emission for the grazing periods beginning at the 9th of June and the 5th of September in 1988 (Table 1).

Effects of soil and environmental conditions

Numerous soil and environmental conditions affect NH_3 emission (Freney et al., 1983). For instance, temperature generally has a positive effect on volatilization (Freney et al., 1983). However in our experiment, temperature did not have a straightforward effect; warm periods did not coincide with peak emissions (Fig. 1).

There was a tendency for NH_3 volatilization to be higher from wet soil than from dry soil. For example, rain just before and during grazing in the 4th and 5th grazing period (Fig. 1) coincided with high emission rates. In contrast, during and for the first three days after grazing in the 6th grazing period it was relatively dry, and very low NH_3 losses occurred during the 6th grazing period. It is suggested that urine infiltrates more rapidly and deeply into dry soil. This would result in lower NH_4^+ concentrations in the upper layers of dry soil compared to wet soil, and reduce the potential for NH_3 volatilization.

Effects of grassland management

Some of the large differences in NH_3 losses between grazing periods (Table 1) may be due to differences in grassland management. NH_3 losses from the 550N plot were relatively large in the 2nd, 3rd and 5th grazing period of 1987 and in the 3rd, 4th and 7th period of 1988. In all these periods the sward was topped after grazing. The resultant increase in the surface area of dung patches (combined with decaying herbage toppings (Whitehead et al., 1988)) may contribute to the higher NH_3 losses measured from topped swards.

Another important management decision factor is herbage yield. It was difficult to achieve the target yield of about 1700 kg DM ha^{-1} at the start of grazing, in this experiment it ranged from 1500 to 3000 kg ha^{-1} . The inverse relationship between herbage yield and herbage N content influences the N intake of cattle and consequently the N content of excreta and its potential for volatilization. Jarvis et al. (1989b) observed a positive relationship between herbage N concentration and emission percentage. However no clear relationships could be established between herbage yield, N concentration of herbage, N intake of herbage and NH_3 emission for the various grazing periods in our experiment, probably because of the confounding influence of weather conditions.

In conclusion in this experiment, the level of N fertilization had an effect on NH_3 losses. A number of environmental soil and management factors may also have an effect, consequently the nature of the relationship between N application rate and NH_3 emission from grazed swards is difficult to quantify. The data from this study suggest that reducing N application rate may be an effective tool in minimizing NH_3 losses from grazed swards. Further studies over time, on different soil types and with different management regimes are required to develop a clear understanding of the relationship between N fertilizer rates and NH_3 volatilization from grazed swards.

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CHAPTER 3

RELATIONSHIPS BETWEEN AMMONIA VOLATILIZATION AND NITROGEN FERTILIZER APPLICATION RATE, INTAKE AND EXCRETION OF HERBAGE NITROGEN BY CATTLE ON GRAZED SWARDS

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RELATIONSHIPS BETWEEN AMMONIA VOLATILIZATION AND NITROGEN FERTILIZER APPLICATION RATE, INTAKE AND EXCRETION OF HERBAGE NITROGEN BY CATTLE ON GRAZED SWARDS

ABSTRACT

Grazed pastures emit ammonia (NH_3) into the atmosphere; the size of the NH_3 loss appears to be related to nitrogen (N) application rate.

The micrometeorological mass balance method was used to measure NH_3 volatilization from rotationally grazed swards on three plots in the autumn of 1989 and throughout the 1990 growing season. The aim of the research was to derive a mathematical relationship between NH_3 volatilization and N application rate, which would vary between soil type and weather conditions. In both years the plots received a total of 250, 400 or 550 kg N ha⁻¹ as calcium ammonium nitrate (CAN) split over 6 to 8 dressings. The number of grazing cycles ranged from 7 to 9 for the three N plots.

In the last two grazing cycles of 1989, NH_3 losses were 3.8, 12.0 and 14.7 kg N ha⁻¹ for the 250N, 400N and 550N plots, which was equivalent to 5.3%, 13.9% and 14.4% of the amount of N excreted on the sward, respectively. In 1990, NH_3 losses were 9.1, 27.0 and 32.8 kg N ha⁻¹ for the 250N, 400N and 550N plots, which was equivalent to 3.3%, 6.9% and 6.9% of the N excreted, respectively. Differences in urine composition between the plots were relatively small. Rainfall and sward management affected the size of the NH_3 volatilization rate. Volatilization of NH_3 was related to N excretion and N application rate.

A calculation procedure is given to enable the estimation of NH_3 volatilization from N application rate. Adjustments can be made for grazing efficiency, grazing selectivity, N retention in milk and liveweight gain, concentrate N intake and milking duration. Losses of NH_3 increase progressively with an increase in N application rate until herbage yield reaches a maximum at an application rate of about 500 kg N ha⁻¹ yr⁻¹.

INTRODUCTION

Studies on fertilized grazed swards showed that a significant part of the nitrogen (N) excreted on the sward in dung and urine may be lost from the grassland system through ammonia (NH_3) volatilization (Bussink, 1992; Jarvis et al., 1989a). These losses are of concern because of the impact NH_3 may have in aerosol chemistry (Ziereis and Arnold, 1986), eutrophication and acidification (Apsimon et al., 1987).

Losses of NH_3 from grazed swards are thought to originate mainly from the urine

deposited by cattle (Jarvis et al., 1989a; Lockyer and Whitehead, 1990; Sherlock and Goh, 1984). The main N component in urine is urea, which is known to have a high potential for NH_3 volatilization (Freney et al., 1983). Losses of NH_3 were found to depend on fertilizer application rate (Bussink, 1992; Jarvis et al., 1989b). Inputs of 210 and 420 kg N ha^{-1} yr^{-1} resulted in NH_3 losses of 10 and 25 kg N ha^{-1} , respectively, in a study with grazed swards in the UK (Jarvis et al., 1989b). My study (Bussink, 1992) with fertilizer application rates of 250 and 550 kg N ha^{-1} yr^{-1} gave losses of 8 and 41 kg N ha^{-1} yr^{-1} , respectively. Reducing the N application rate may thus be an effective tool in minimizing NH_3 losses from grazed swards, but this would reduce milk production and/or liveweight gain.

Still unknown is the precise relationship between the fertilizer N application rate and NH_3 volatilization from dung and urine of grazing ruminants as a function of soil type and weather conditions. Jarvis et al. (1989b) proposed a more than proportional increase of the NH_3 volatilization at increasing N application rates on grazed swards. Others (Bussink, 1992; Harper et al., 1983b) have done experiments with 1 or 2 N application rates only, or have carried out laboratory experiments using artificial urine (Vertregt and Rutgers, 1991; Whitehead et al., 1989). Such experiments are unsuitable for deriving a relationship between N application rate and NH_3 volatilization on grazed swards.

Generally, herbage yield and N concentration increase together with N application rate (Deenen and Lantinga, 1993; Van der Meer and Van Uum-Van Lohuyzen, 1986). As a consequence, generally speaking, stocking density, N intake per grazing animal and thus N excretion, especially urinary N, also increase with an increase in N application rate (Jarvis et al., 1989a; Van Vuuren and Meijs, 1987). This results subsequently in an increasing potential for NH_3 loss (Bussink, 1992; Jarvis et al., 1989a). Increasing N application rate may also affect the composition of urine. For instance, the ratio of urea N to total N in urine may increase together with N application rate (Jarvis et al., 1989a). In addition, the concentration of hippuric acid, which is a catalyst to urea hydrolysis and therefore a possible cause of changes in NH_3 volatilization (Doak, 1952), may also be altered.

In the present study, NH_3 losses from three rotationally grazed pastures, differing in N application rate, were measured continuously throughout the grazing season. The swards were grazed with dairy cows and fertilized with totals of 250, 400 or 550 kg N ha^{-1} yr^{-1} as calcium ammonium nitrate (CAN). Herbage yield, N intake and N retention in milk and liveweight gain were measured to calculate the N excretion in faeces and urine. These results were supplemented with information from literature sources to derive relationships between N application rate, N intake via herbage and N excretion by cattle, and NH_3 volatilization from the sward.

MATERIALS AND METHODS

Experimental plots

The experimental site, with a size of 8 ha, was situated on a young marine, calcareous loam soil in the Flevopolder in the Netherlands. The background NH₃ concentration in the atmosphere is relatively low (5-15 µg NH₃-N m⁻³), mainly because the polder is predominantly used for arable farming.

The sward was more than 9 years old, with ryegrass (*Lolium perenne* L.) as the predominant grass species. The soil composition is shown in Table 1. Measurements were carried out on three circular plots with a radius of 23 m and were 80 m to 250 m apart. In 1989, the three plots were fertilized with 242, 360 and 559 kg N ha⁻¹ yr⁻¹ as CAN, split into 7, 6 and 7 dressings, respectively. In 1990 fertilizer N applications were 224, 405 and 551 kg N ha⁻¹ y⁻¹, split into 7, 8 and 8 dressings, respectively.

Table 1. Some properties of the 0-5 cm soil layer.

Plot	Organic matter %	Clay (< 2µ) %	CaCO ₃ %	CEC mol _c kg ⁻¹	pH-KCl
250N	8.9	20	7.0	0.280	6.9
400N	4.7	22	8.6	0.247	7.1
550N	8.2	18	6.4	0.281	6.9

The plots were rotationally grazed with lactating Holstein Frisian dairy cows (age 2-7 yrs), except for the last grazing period in 1990 when non-lactating cows grazed the plots. The cows initially grazed for one and a half days on a field with the same N application rate as the test plot to accustom them to the N concentration of the grass. Grazing on the test plot started at a target herbage yield of 1700 kg dry matter (DM) ha⁻¹. Stocking rates were high, 60 to 110 cows, in order to graze the sward within two days and to ensure that the distribution of dung and urine patches over the plot was as uniform as possible. Within two days after grazing the sward was dressed with fertilizer N and then allowed to regrow prior to the next grazing period. The area surrounding the test plots was mown intermittently.

Determination of intake and excretion of N

The total N intake by the dairy cows via herbage and concentrates - 1-3 kg per cow grazing day (cgd⁻¹) - and the N retention in milk and liveweight gain were used to calculate the N

content of the excreta. Herbage yield and N yield just before and after grazing were measured by means of a double sampling procedure as described in detail by Deenen and Lantinga (1993). The difference in yield before and after grazing corrected for regrowth during grazing (Lantinga, 1986) gave the total intake of herbage and herbage N per grazing period. The N retention in milk and liveweight gain was calculated as follows:

$$\text{N retention} = \text{NCGD}(\text{LWNG} + \text{MN}_y)/1000 \quad (\text{kg N ha}^{-1}) \quad (1)$$

with:

NCGD = number of cow grazing days (ha^{-1})

LWNG = liveweight N gain per cow grazing day = $8.7 \text{ (g N cgd}^{-1}\text{)}$ (Bussink, 1992)

MN_y = milk N yield per cow grazing day (g N cgd^{-1})

The partitioning of N in faeces and urine was calculated as follows (Lantinga et al., 1987):

$$\text{N in faeces} = \text{DM intake} * 0.0078 \quad (\text{kg N ha}^{-1}) \quad (2)$$

$$\text{N in urine} = \text{total N intake} - \text{N retention} - \text{N in faeces} \quad (\text{kg N ha}^{-1}) \quad (3)$$

where:

total N intake = the total N intake via herbage and concentrates in kg ha^{-1} .

The amount of N excreted on the sward was corrected for the time that the cows were in the shed for milking, assuming a uniform distribution of urine and faeces excretion during the day. In order to verify the amount of N in urine calculated from Eq. 3, urine was sampled in the shed during milking time two or three times per grazing period. Between 10 to 18 cows were sampled per test plot. The urine was analyzed for hippuric acid (Kubota et al., 1988), urea (Talke and Schubert, 1965) and total N (Smit, 1979).

Determination of NH_3 losses

A micrometeorological mass balance method was used to measure NH_3 losses from the plots. The principles behind this method have been given elsewhere (Denmead, 1983). Differences in NH_3 concentration between the centre and the boundary of the plot were measured via NH_3 sampling traps at different heights in the centre of the plot and on the windward boundary. Each trap contained 20 ml 0.02 M H_3PO_4 held in 100 ml collection tubes. Air was sucked through the acid via a gas dispersion tube at a rate of 2.4 l min^{-1} , controlled by a flow meter. A correction was made for the measured pressure drop between the flow meter and the air inlet of the trap. The NH_3 traps were exchanged every 24 h and were analyzed for ammonium N (Weatherburn, 1967) within a week.

Wind speed was measured on a mast outside the plot, at seven different heights. Vector cup anemometers (A101ML) were used at the lower four positions, while Lambrecht cup anemometers (1469I) were used at the top three positions. Wind direction was measured with a Porton windvane. Air temperature, radiation and rainfall were also measured. The weather data were recorded on a data logger (DT100F). Further details of the measurement procedure are given in my previous paper (Bussink, 1992).

RESULTS

Herbage yield and intake

In the autumn of 1989, herbage intake was higher on the 400N and 550N plots than on the 250N plot (Table 2). In the last two grazing periods there were 171, 221 and 221 cgd on the 250N, 400N and 550N plots, respectively.

In 1990, gross herbage yields were 14.1, 17.2 and 17.2 ton DM ha⁻¹ on the 250N, 400N and 550N plots, respectively. The corresponding N yields were 423, 621 and 666 kg ha⁻¹ yr⁻¹. Net herbage intake is given in Table 3. The pattern of herbage production differed between the three plots. Production was high in the first half of the growing season of 1990 on the 250N and 550N plots and decreased somewhat in the second half of the growing season, whereas the opposite (which was unexpected) happened on the 400N plot. Herbage yield on the 400N plot was particularly low in the first grazing period of 1990. There were 758, 863, and 989 cgd on the 250N, 400N and 550N plots, respectively (Table 3). The calculated average DM intake with grass and concentrates was 17.1, 15.8 and 16.0 kg cgd⁻¹ in 1989 and 17.4, 17.1 and 17.1 kg cgd⁻¹ in 1990 on the 250N, 400N and 550N plots, respectively.

Excretion of N

Herbage N concentration and the composition of the urine responded to N application rate, although the variation between grazing periods was notably large (Table 4). The total N and urea N concentrations of urine increased together with an increase of N application rate, due to the increase in herbage N concentration (Table 4).

In 1989, total N excretions via urine and faeces, calculated in accordance with Eqs. 1-3, were 86, 103 and 121 kg ha⁻¹ for the 250N, 400N and 550N plots, respectively (Table 2). Urinary N represented 75%, 74% and 78% of total N excretion, respectively. Remarkably, the calculated N excretion per cow, i.e. 501, 466 and 549 g cgd⁻¹, showed little variation between the three plots.

Table 2. DM intake, cow grazing days, N retention, N excretion and NH_3 volatilization during the autumn of 1989.

Period	Gras intake kg DM ha^{-1}	Concen- trates kg DM ha^{-1}	Cow grazing days	N re- tention kg ha^{-1}	N excretion faeces, kg ha^{-1}	urine kg ha^{-1}	Fraction of total excreted N on the plot	NH_3 -N volatilization kg ha^{-1}	% of N excre- tion on the plot	g per cow grazing day
250N										
1. 13/9 -17/10	1015	78	60	6.8	8.1	23.8	0.823	0.55	2.1	11.1
2. 17/10-31/10	1693	145	111	11.5	13.6	40.4	0.853	3.3	7.1	34.8
total/mean	2708	223	171	18.3	21.6	64.2	0.842	3.8	5.3	26.4
400N										
1. 13/9 -17/10	1264	113	85	9.3	10.2	35.4	0.823	3.8	10.2	54.4
2. 17/10-31/10	2060	180	136	20.8	16.5	40.8	0.853	8.2	16.7	70.7
total/mean	3323	293	221	30.1	26.7	76.2	0.840	12.0	13.9	64.6
550N										
1. 13/9 -17/10	1447	113	85	10.2	11.5	43.2	0.823	4.4	9.8	62.9
2. 17/10-31/10	1934	180	136	15.1	15.6	51.0	0.853	10.2	18.0	87.9
total/mean	3381	293	221	25.3	27.1	94.3	0.839	14.7	14.4	79.3

Table 3. DM intake, cow grazing days, N retention, N excretion and NH₃ volatilization during 1990.

Period	Gras* intake kg DM ha ⁻¹	Concen- trates kg DM ha ⁻¹	Cow grazing days	N re- tention kg ha ⁻¹	N excretion faeces kg ha ⁻¹	urine kg ha ⁻¹	Fraction of total excreted N on the plot	NH ₃ -N volatilization kg ha ⁻¹	% of N excre- tion on the plot	g per cow grazing day
250N										
1. 3/5 - 21/5	1598	211	150	6.7	13.6	23.1	0.871	0.53	1.6	4.1
2. 21/5 - 20/6 [†]	2482	309	128	17.2	21.0	40.9	0.872	0.83	1.5	7.4
3. 20/6 - 17/7 [†]	2829	317	133	18.1	23.7	42.4	0.874	2.91	5.0	25.0
4. 17/7 - 29/8	1887	135	81	9.4	15.2	26.5	0.92	2.82	7.4	37.8
5. 29/8 - 19/9 [†]	538	228	85	10.3	5.8	9.6	0.92	0.004	0.0	0.0
6. 19/9 - 24/10	1709	106	106	11.5	13.6	39.6	0.92	0.59	1.2	6.1
7. 24/10 - 2/11	1252	0	75	0.7	9.4	35.4	0.795	1.44	4.1	24.2
total/mean	12295	1306	758	83.9	102.2	217.4	0.876	9.1	3.3	13.7
400N										
1. 3/5 - 21/5	950	163	90	13.2	8.4	7.1	0.871	0.66	4.9	8.4
2. 21/5 - 20/6 [†]	2295	333	122	16.8	19.8	46.1	0.875	2.51	4.3	23.5
3. 20/6 - 17/7 [†]	1612	252	119	15.7	14.0	63.4	0.920	5.46	7.7	49.9
4. 17/7 - 29/8	1089	179	107	13.9	9.5	32.1	0.875	5.12	14.0	54.7
5. 29/8 - 19/9 [†]	2527	179	83	12.5	20.3	52.5	0.920	2.27	3.4	29.7
6. 19/9 - 24/10	2320	317	131	17.5	19.8	55.8	0.920	1.76	2.5	14.6
7. 24/10 - 2/11	1564	98	99	9.8	12.5	42.3	0.920	2.34	4.6	25.7
8. 2/11 - 2/11	1399	0	112	1.0	10.5	39.8	0.764	6.85	17.8	80.1
total/mean	13756	1520	863	100.5	114.9	339.0	0.861	27.0	6.9	36.3
550N										
1. 3/5 - 21/5	2936	309	219	24.0	24.4	59.1	0.871	1.56	2.1	8.2
2. 21/5 - 20/6 [†]	2876	414	167	21.0	24.8	71.3	0.873	5.21	6.2	35.7
3. 20/6 - 17/7 [†]	2425	238	98	13.4	20.0	68.8	0.920	4.04	4.9	44.8
4. 17/7 - 29/8	1923	268	125	16.9	16.5	50.7	0.873	9.07	15.5	83.1
5. 29/8 - 19/9 [†]	1763	187	101	12.3	14.7	45.0	0.920	4.37	8.0	48.0
6. 19/9 - 24/10	1409	219	101	8.9	12.3	37.6	0.920	2.24	4.9	24.1
7. 24/10 - 2/11**	1380	106	99	10.6	11.2	38.6	0.920	2.98	6.5	32.7
8. 2/11 - 2/11	1033	0	81	0.7	7.7	36.1	0.774	3.31	9.7	52.7
total/mean	15745	1742	989	107.8	131.5	407.1	0.880	32.8	6.9	37.7

* Intake 4% lower; because 4% of plot area used for determination of herbage yield. ** During this period the sward was grazed by non lactating cows. † The sward was topped after grazing.

Table 4. Mean N concentration in herbage and faeces and concentrations of total N, hippuric acid and urea and the fraction of urea N to total N in urine.

Plot; Grazing period	N in dry herbage g kg ⁻¹	N in faeces g kg ⁻¹	N in urine g l ⁻¹	Hippuric acid g l ⁻¹	Urea in urine g N l ⁻¹	Urea N % of total N in urine
1989:						
250N						
13/9	36.4	3.4	6.5	**	5.85	90
17/10	34.1	3.9	8.5	-	7.39	87
400N						
13/9	34.2	3.5	6.2	-	5.58	90
17/10	34.2	2.5	8.6	-	7.22	84
550N						
13/9	39.3	3.7	8.4	-	7.89	94
17/10	41.4	3.1	9.0	-	8.19	91
1990:						
250N						
1. 3/5	30.9	-	6.14	-	4.00	65
2. 23/5	29.5	4.2	6.84	6.91	4.41	64
3. 21/6	27.6	3.3	5.11	5.48	3.48	68
4. 16/7	26.1	3.6	-	-	-	-
5. 29/8	37.0	3.9	8.20	3.64	6.90	84
6. 21/9	37.6	3.6	8.34	2.39	7.09	85
7. 25/10	37.8	3.1	4.98	2.89	4.56	92
mean	31.0*	3.6	6.60	4.26	5.07	77
400N						
1. 3/5	26.4	-	6.56	-	3.62	55
2. 23/5	34.3	4.6	8.11	7.41	5.80	72
3. 14/6	55.5	4.5	-	-	-	-
4. 6/7	48.3	3.7	7.49	3.74	7.34	83
5. 31/7	33.1	3.8	-	-	-	-
6. 29/8	37.8	3.6	9.50	4.29	8.30	87
7. 20/9	41.2	3.2	6.02	2.38	5.34	89
8. 25/10	38.2	3.4	5.76	2.69	5.01	87
mean	38.7*	3.8	7.24	4.02	5.72	79
550N						
1. 3/5	35.0	-	6.81	-	5.08	75
2. 23/5	38.1	5.0	8.83	5.17	6.83	77
3. 14/6	40.5	4.7	-	-	-	-
4. 6/7	41.4	3.5	7.87	3.60	6.33	80
5. 31/7	39.4	3.9	-	-	-	-
6. 29/8	38.8	3.8	10.76	2.92	9.74	91
7. 20/9	43.3	3.8	9.09	2.60	8.19	90
8. 25/10	44.9	3.7	5.13	2.60	4.67	91
mean	39.5*	4.0	8.08	3.38	6.80	84

* weighted mean ** not determined

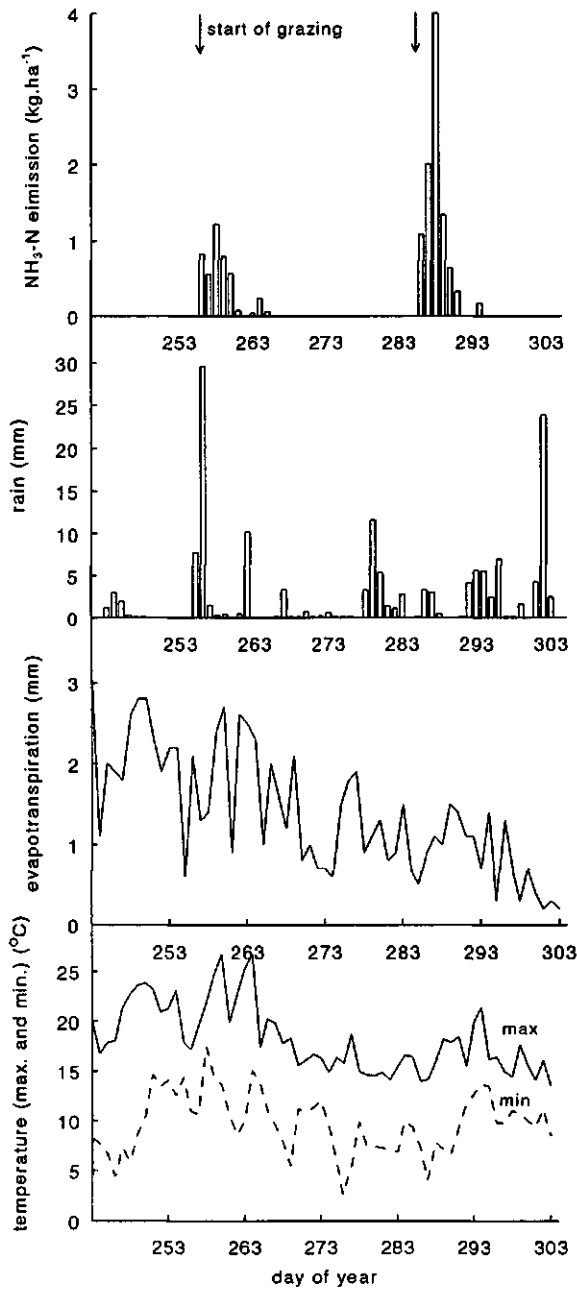


Fig. 1. Daily values for NH₃ volatilization, global radiation, evaporation, rainfall and minimum (---) and maximum (—) temperatures at 1.50 m during the last two grazing periods on the 550N plot in 1989.

In 1990, total N excretion on the 250N, 400N and 550N plots was 320, 454 and 539 kg ha⁻¹, respectively, of which 68%, 75% and 76% was urinary N (Table 3). Again, the calculated N excretion per cow, i.e. 421, 526 and 545 g cgd⁻¹, showed little variation between the 400N and 550N plots.

NH₃ volatilization

In 1989, NH₃ volatilization was 3.8, 12.0 and 14.7 kg N ha⁻¹ for the 250N, 400N and 550N plots, respectively (Table 2). In 1990, total NH₃ volatilization was 9.1, 27.0 and 32.8 kg N ha⁻¹ for the 250N, 400N and 550N plots, respectively (Table 3).

Results of the statistical analysis indicate that the coefficient of variation (cv) of NH₃ concentration measurements ranged from 10 to 11% for the three plots. This was much higher than in the previous experiment (Bussink, 1992). The reason for this increase is not clear. To estimate the effect of variations in concentration measurements on the variations in NH₃ losses, Monte Carlo simulations were performed. The mean cv of the simulated seasonal NH₃ volatilization was 12.4%, 9.4% and 9.0% for the 250N, 400N and 550N plots, respectively.

Losses of NH₃ varied considerably between grazing periods (Tables 2 and 3). Generally, NH₃ losses were high during the first few days after grazing, decreasing to negligible amounts within 10 days after grazing (Fig. 1). A peak volatilization was measured on the second or third day, generally. Rainfall appeared to have a major influence. High rainfall in mid September 1989 at the start of grazing coincided with relatively low NH₃ losses (Fig. 1). In contrast, low rainfall in the second half of October coincided with high NH₃ losses. Comparable patterns were observed in 1990. High rainfall a few days after the start of the sixth grazing period resulted in low NH₃ losses. A slight rain around the start of the fourth and eighth grazing periods on the 400N and 550N plots coincided with high NH₃ losses (data not shown).

DISCUSSION

Effect of the sward N status on NH₃ volatilization

Measured NH₃ losses from grazed plots are predominantly the net result of NH₃ losses from deposited excreta and reabsorption of volatilized NH₃ by the sward. Losses from excreta depend heavily on fertilizer N application and sward management as discussed below. Active absorption of aerial NH₃ up to 0.27 kg N ha⁻¹ day⁻¹ was measured when the sward suffered from N deficiency (Bussink et al., 1996). This suggests that the sward absorbed more NH₃

on the 250N plot than on the 400N and 550N plots, because of the strong fertilizer response between the plots with 250 and 400 kg N ha⁻¹ yr⁻¹ (Fig. 4).

Uptake of excreted N by the sward may also suppress the net NH₃ loss rate on the plot with a low N application rate. Generally, herbage yield and N uptake respond positively to excreted N when N application rates are low. Thus, a positive response to excreted N was measured on a sward supplied with 250 kg N ha⁻¹ yr⁻¹, whereas a zero response was measured on a sward supplied with 400 kg N ha⁻¹ yr⁻¹ (Deenen and Middelkoop, 1992). This suggests that a smaller fraction of the excreted N deposited was subject to NH₃ losses on the 250N than on the 400N and 550N plots. In conclusion, uptake of excreted N together with absorption of NH₃ may have contributed to the much lower NH₃ losses at a N application rate of 250 kg ha⁻¹ yr⁻¹ than at rates of 400 and 550 kg ha⁻¹ yr⁻¹.

Effects of grassland management on NH₃ volatilization

The target yield of about 1700 kg DM ha⁻¹ at the start of grazing appeared difficult to achieve. During the experimental period herbage yield on offer ranged from 650 to 4000 kg ha⁻¹ per cut. With such a wide variation the inverse relationship between herbage yield and herbage N concentration (Meijs, 1981) may affect the relationship between N excretion and NH₃ volatilization. However, no clear relationship was found between herbage yield per cut and measured NH₃ losses, possibly because other factors masked this effect.

Stocking density may also affect the N content in excreta and NH₃ losses, because of its effect on grazing efficiency (Meijs, 1981). Generally, the N concentration in the herbage consumed and thus N excretion is inversely related to grazing efficiency. In 1990, mean grazing efficiency was rather high; 87%, 80% and 91% of gross herbage yield was consumed on the 250N, 400N, and 550N plots, respectively. Values ranging from 75 to 80% are considered to be common (Klapp, 1963). In addition, due to selective grazing, calculated mean N concentration of herbage intake in 1990 was 1.02, 1.07 and 1.04 times higher than gross herbage N concentration on the 250N, 400N and 550N plots, respectively. Higher values have been found in other grazing experiments and in practice (Meijs, 1981; Waite et al., 1950).

Topping may also contribute to NH₃ losses, as was found in the previous experiment (Bussink, 1992), because it increases the surface area of dung patches. However, no stimulating effect of topping was observed in 1990, probably because other factors like weather conditions have masked such effect.

Effect of urine composition on NH₃ volatilization

Urine spots are major sites of NH₃ volatilization on grassland, but the contribution of urine

depends partly on its composition. An increase in urea concentration increases NH_3 volatilization (Jarvis et al., 1989b; Sherlock and Goh, 1984; Whitehead et al., 1989). Our unpublished lab results showed a 1.7 times increase in proportional NH_3 loss as urea concentration increased from 5 to 11 g l^{-1} . Hippuric acid in urine may also promote NH_3 volatilization, because it acts as a catalyst to urea hydrolysis (Doak, 1952; Whitehead et al., 1989). Hippuric acid concentrations ranged between 2.4 and 7.4 g l^{-1} (Table 4), which is above the optimum concentration of about 1 g l^{-1} (Whitehead et al., 1989) for a maximum catalysis effect.

Urea concentrations increased together with N application rate (Table 4), whereas hippuric acid concentrations decreased. Based on our lab results it is suggested that the effect of increasing urea concentrations on NH_3 volatilization is only partly counteracted by the effect of decreasing hippuric acid concentrations if N application rates increase from 250 to 550 $\text{kg ha}^{-1} \text{yr}^{-1}$. In addition, the proportion of the total excreted N in the urine increases with N application rate, which may also increase NH_3 volatilization. The overall effect is that an increase in N application rate is likely to have increased NH_3 loss more than proportionally through its effect on urine composition.

Effect of CEC on NH_3 volatilization

The fraction of excreted N lost as NH_3 was similar on the 400N and 550N plots, in 1989 and 1990 (Table 2 and 3). However, a more than proportional increase in volatilization rate with N application rate was expected, as previously discussed. The similar loss rates on the 400N and 550N plots might be explained by differences in soil properties (Table 1). Recently it was shown that CEC was the soil property most closely related to the extent of NH_3 volatilization (Whitehead and Raistrick, 1993a); the higher the CEC the less NH_3 volatilized. In this experiment, the CEC of the soil of the 400N plot was lower than that of the 250N and 550N plots (Table 1). This would suggest that less NH_4^+ was adsorbed by the soil of the 400N plot than by the 250N and 550N plots, and that relative NH_3 loss was higher from the 400N plot than from the 250N and 550N plots.

Total N excretion and NH_3 volatilization

The relationship between the summed N excretion and summed NH_3 volatilization for the 1990 data is shown in Fig. 2. Also included are the 1987 and 1988 data (Bussink, 1992) and data from a UK study (Jarvis et al., 1989b). The incomplete data of 1989 were omitted. Total NH_3 volatilization (V , $\text{kg N ha}^{-1} \text{yr}^{-1}$) was related to total N excreted in dung and urine (N_{excr} , $\text{kg ha}^{-1} \text{yr}^{-1}$). There was a remarkable consistency in the 1987, 1988 and 1990 data. A power function of the type $V = a N_{\text{excr}}^b$ may adequately describe the relationship between

V and Nexcr (Jarvis and Bussink, 1990). Hence:

$$V = 7.70 \cdot 10^{-6} \text{ Nexcr}^{2.491} \quad (R^2=0.98) \quad (4)$$

The amount of N excreted depends on DM intake and dietary N concentration. The latter affects the fraction of urinary N in Nexcr (Van Vuuren and Meijs, 1987) and hence the NH₃ loss rate. The fraction of excreted N lost as NH₃ (vfrac, kg kg⁻¹) was related to the average dietary N concentration (ND, g kg⁻¹ DM) (see Fig. 3):

$$\text{vfrac} = 2.717 \cdot 10^{-7} \text{ ND}^{3.389} \quad (R^2 = 0.96) \quad (5a)$$

The data of Jarvis et al. (1989b) (Fig. 3) could be described by:

$$\text{vfrac} = 1.267 \cdot 10^{-4} \text{ ND}^{1.853} \quad (R^2 = 0.96) \quad (5b)$$

Two factors may have contributed to the differences between the study of Jarvis et al. (Jarvis et al., 1989b) and this study (Figs. 2 and 3). Firstly, young steers grazed the UK plots, compared with lactating dairy cows in this study. Generally, N retention by non lactating cattle is lower than that of lactating cattle (Coppoolse et al., 1990). The mean N retention by young steers was calculated from Jarvis et al. (1989a) 5 g kg⁻¹ DM intake, compared with 6.5 g for the dairy cows in my 1990 grazing experiment. Thus N excretion and also urinary N concentration will be higher with young steers than with dairy cows, resulting in a higher NH₃ loss rate.

Secondly, there is a slight difference in soil type and CEC. The CEC was 0.20 mol_c kg⁻¹ in the UK study (Jarvis et al., 1989b) compared with 0.28 mol_c kg⁻¹ at this site. This will have contributed to the difference in NH₃ loss (Whitehead and Raistrick, 1993a). Differences in climatic conditions are likely to have been small and will not have contributed much to the difference in NH₃ loss between the UK study and this study. In the UK study, daily variability in NH₃ loss was influenced significantly by wind speed, but this was not observed in this study.

To assess the NH₃ volatilization rate for a grazing season as a function of N application rate, ND and Nexcr should be known. Total NH₃ volatilization V can then be calculated from:

$$V = \text{vfrac} \cdot \text{Nexcr} = \text{vfrac} \cdot f_p \cdot (\text{N intake} - \text{N retention}) \quad (6)$$

with f_p as the fraction of Nexcr that is deposited on the grazed plot and N intake as the sum of N intake with herbage and concentrates. Determination of herbage N intake may be cal-

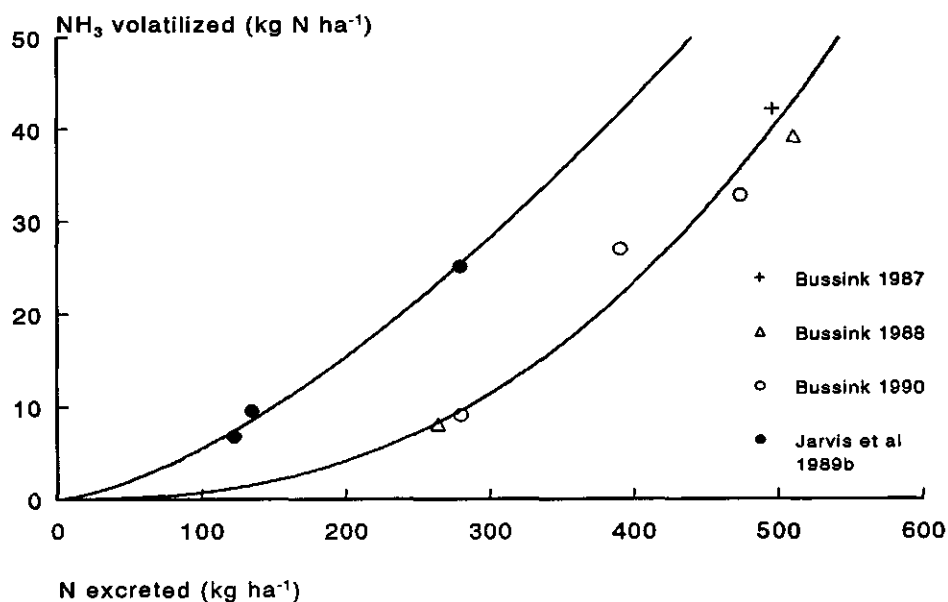


Fig. 2. Relationship between annual N excretion on the sward and annual NH_3 volatilization from my previous study in 1987 and 1988 (Bussink, 1992) and this study in 1990. Data of Jarvis et al. (1989b) are also plotted (average of 1986 and 1987).

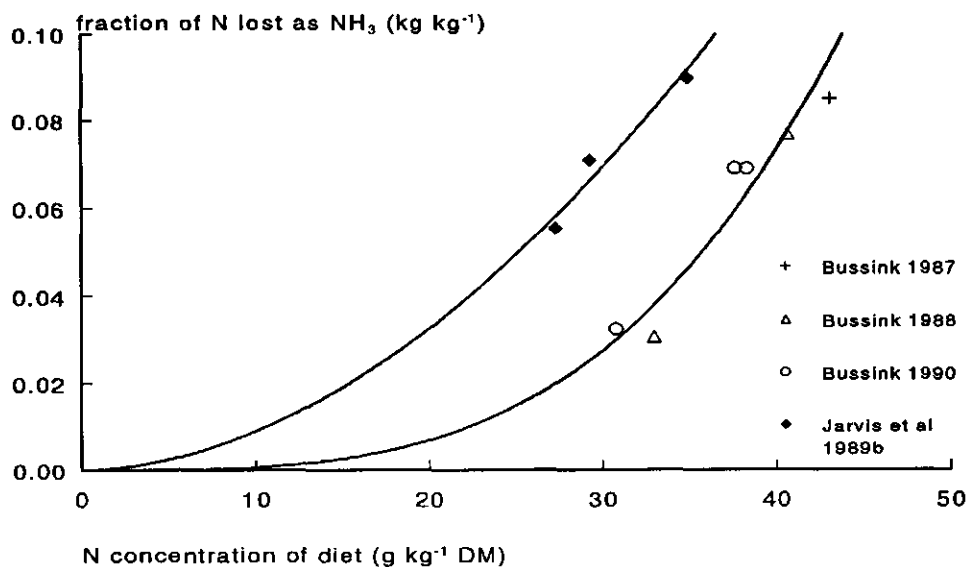


Fig. 3. The effect of the N concentration of the diet on NH_3 losses as fraction of N excreted based on my previous study in 1987 and 1988 (Bussink, 1992) and this study in 1990. Data of Jarvis et al. (1989b) are also plotted (average of 1986 and 1987).

culated from gross herbage DM yield (H_y , $\text{kg ha}^{-1} \text{ yr}^{-1}$) and herbage N concentration (HN_c , $\text{g kg}^{-1} \text{ DM}$) as determined in mowing experiments, if corrections are made for extra herbage growth and N uptake from N in excreta and for grazing efficiency and selectivity. The variables H_y and HN_c depend among others on N application rate, soil type and management (Fig. 4). Total N intake and ND can now be calculated as follows:

$$\text{N intake} = f_g H_y (f_s (f_n + HN_c) + A_c N_c / h_{incow}) / 1000 \quad (\text{kg ha}^{-1}) \quad (7)$$

$$\text{ND} = \frac{\text{N intake}}{\text{DM intake}} = \frac{f_s (f_n + HN_c) + A_c N_c / h_{incow}}{(1 + A_c / h_{incow})} \quad (\text{g N kg}^{-1} \text{ DM}) \quad (8)$$

with:

f_g = grazing efficiency factor [0.86]

f_s = grazing selectivity factor [1.04]

f_n = extra herbage N uptake from excreta [$2.5 \text{ g N kg}^{-1} \text{ DM}$, obtained from curves 1 and 4 in quadrant 1 of Fig. 4]

A_c = the amount of concentrates [1.75 kg cgd^{-1}]

N_c = N content of concentrates [26 g kg^{-1}]

h_{incow} = herbage DM intake per cow [16 kg cgd^{-1}]

$f_g H_y / h_{incow}$ = NCGD

Combining Eqs. 1, 5a, 6, 7 and 8 gives finally:

$$V = 2.717 \cdot 10^{-7} \left[\frac{f_s (f_n + HN_c) + A_c N_c / h_{incow}}{(1 + A_c / h_{incow})} \right]^{3.389} \cdot f_p f_g (f_s H_y (f_n + HN_c) + (A_c N_c - \text{LWNG} - \text{MN}_y) / h_{incow}) =$$

$$= 2.126 \cdot 10^{-10} H_y (HN_c - 1.478) (0.9375 HN_c + 4.907)^{3.389} \quad (9)$$

where: $\text{MN}_y = 103 \text{ g N cgd}^{-1}$ (the average value of the 1990 study), and $f_p = 0.875$

The relationship between annual NH_3 volatilization rate and N application rate from grazed only grassland is now obtained by combining Eq. 9 with the equations that relate H_y and HN_c to N rate as shown in Fig. 4. If the sward is also mown intermittently then H_y and HN_c have to be corrected for these cuts.

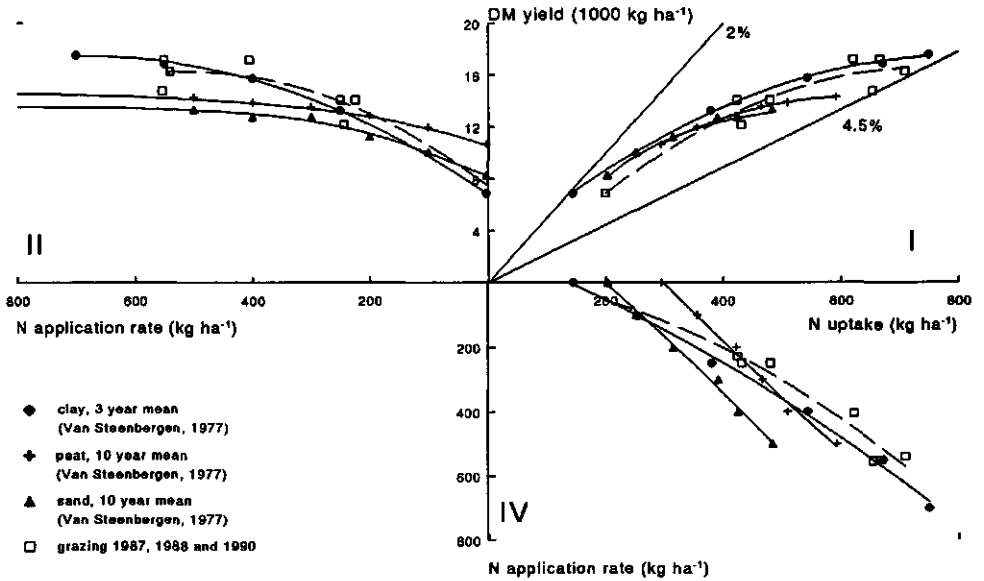


Fig. 4. The effect of rate of fertilizer N application on N uptake and DM yield of herbage under cutting and rotational grazing with dairy cows for different grassland soil types.

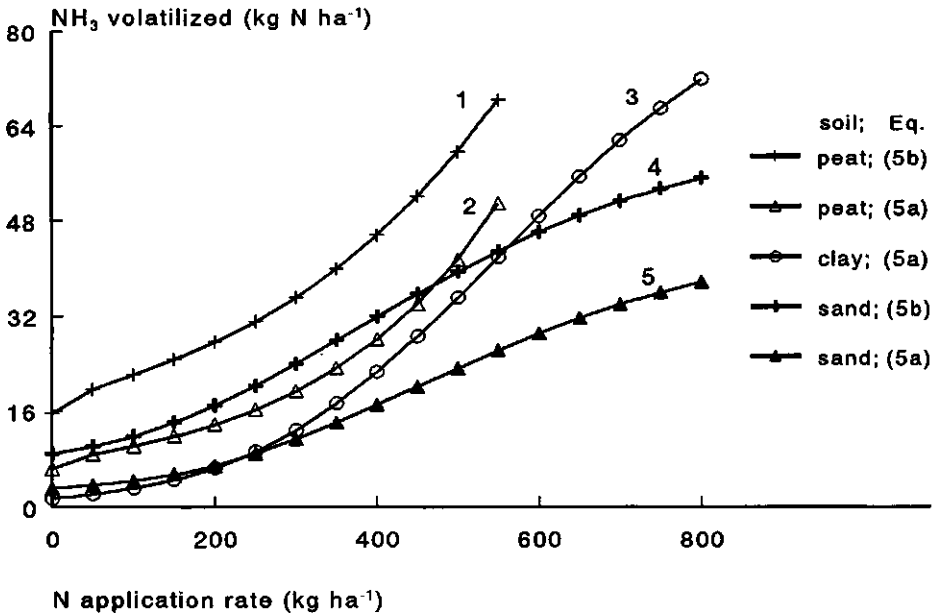


Fig 5. The calculated effect of fertilizer N application rate on NH₃ volatilization for different grassland soil types, using equations (5a) and (5b).

The calculated loss for this site is shown in Fig. 5 (curve 3). For N rates of 250, 400 and 550 kg ha⁻¹ yr⁻¹ NH₃ losses were 9.2, 22.5 and 42.0 kg N ha⁻¹. This is in agreement with the measured NH₃ losses. Up to 500 kg N ha⁻¹ NH₃ losses increase progressively due to increasing H_y and HN_c. Above this N rate the increase in NH₃ loss rate slows down, because H_y tends to reach a maximum (Fig. 4). The variable, HN_y and thus herbage N uptake also reaches a maximum (see e.g. Van der Meer and Van Uum-Van Loohuyzen, 1986), though this maximum does not show up so obvious in Fig. 4. Grazing at high N rates may also cause sward deterioration (Deenen and Lantinga, 1993) which further reduces maximum NH₃ losses.

Calculated NH₃ loss rates for other soil types are shown in Fig. 5. The estimations for sand and peat soil have been made by combining Eq. 9 with the H_y and HN_c data of Fig. 4. The differences between curves 1 and 2 and curves 4 and 5 reflect the differences between Eq. 5a and 5b, which are probably related to differences in CEC of the soil and in grazing animal type, as noted before. Calculated NH₃ losses from the peat soil are high, even when fertilizer N is withheld, because of its high mineralization rate. Curves 1 and 2 may apply to Dutch peat soils since CEC values of 0.20 to 0.28 mol_c kg⁻¹ are common. Estimated losses from the sandy soil (curve 4 and 5) clearly level off at high N rates, due to the diminishing return of H_y and herbage N uptake.

In conclusion, this study showed that N application rate had a strong effect on NH₃ volatilization from grazed swards. Also management factors, N recovery from excreta and aerial NH₃ absorption by the sward, urine composition, CEC and weather conditions affected NH₃ loss rate.

A mathematical relationship between NH₃ volatilization and N application rate was derived, which may be applied to other sites if the CEC is comparable to that in the studies described here. Adjustments can be made for grazing efficiency and selectivity, N retention in milk and liveweight gain, concentrate N intake and milking duration, if necessary.

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CHAPTER 4

AMMONIA TRANSPORT IN A TEMPERATE GRASSLAND: I. SEASONAL TRANSPORT IN RELATION TO SOIL FERTILITY AND CROP MANAGEMENT.

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**AMMONIA TRANSPORT IN A TEMPERATE GRASSLAND: I. SEASONAL
TRANSPORT IN RELATION TO SOIL FERTILITY AND CROP MANAGEMENT**

ABSTRACT

An understanding of N cycling in agricultural systems is necessary to optimize N-use efficiency and reduce N losses to the environment. The objectives of this research were to evaluate N cycling in a highly-fertilized grassland in a humid temperate climate and to observe the effects of N surplus and deficit on NH₃ absorption/desorption by the grass. Soil, plant, and weather measurements were taken concurrently and soil-plant-atmosphere N transport were determined. After N application, soil inorganic N decreased rapidly to background levels due to possible microbial immobilization and plant N demand. Much of the immobilized N was remobilized during the growth period, but at insufficient rates to avoid N stress by the crop, as shown by absorption of NH₃. During spring, 70% of the plant N came from applied fertilizer with the balance obtained from mineralized organic N (27%) and absorption of NH₃ (2.6%). During summer, fertilizer N accounted for 60% of accumulated grass N and NH₃ absorption accounted for 4.5%, with the balance coming from mineralized organic N. The daily NH₃ CP was variable, but the average seasonal NH₃ CP was about 14 $\mu\text{g m}^{-3}$.

INTRODUCTION

Application of N fertilizer to pasture often is required to provide adequate yield and economic return to beef and dairy producers. However, there is increased concern regarding the fate of applied N in relation to NO₃ leaching (Ryden et al., 1984; Garwood and Ryden, 1986) and NH₃ emission (Hutchinson and Viets, 1969; Nihlgard, 1985; Roelofs et al., 1987).

Ammonia is the dominant alkaline N form in the atmosphere and the principal neutralizing agent for airborne acids. It can be released to or absorbed from the atmosphere by soils and plants. Some studies have shown large losses from urea fertilizer applications (Harper et al., 1983c), losses from urine and feces deposited by grazing animals (Vallis et al, 1982; Bussink, 1994), and losses from application of livestock wastes (Terman, 1979; Beauchamp, 1983). Other studies have shown high losses (Harper et al., 1987) or minimal losses (Schjørring and Byskov-Nielsen, 1991; Harper et al., 1995) by plants. Ammonia emissions can also be high from animal holding areas such as feedlots (Hutchinson and Viets, 1969; Oosthoek et al., 1991), dairies, and swine or poultry production facilities.

Consequently, NH_3 emissions are high in areas of concentrated livestock production such as western Europe and western USA. Reported estimates in western Europe range from 2.9 to 3.2 Mt $\text{NH}_3\text{-N yr}^{-1}$ (ECETOC, 1994), with cattle being the major source of NH_3 emissions.

Generally, NH_3 emission estimates neglect the effects of cropping practices on NH_3 emissions or atmospheric absorption. This may generate incorrect estimates, especially in the case of highly fertilized pastures (100-400 kg N $\text{ha}^{-1} \text{yr}^{-1}$), common in large parts of northwestern Europe. For example, Harper et al. (1983a) found more than twice as much NH_3 loss from N application in a dormant pasture than from a pasture with an actively growing canopy. It is generally suggested that agricultural sources represent a large contribution to atmospheric NH_3 content (Langford et al., 1992), but agricultural crops (Harper et al., 1983c, 1987, 1995) and forests (Langford and Fehsenfeld, 1992) can also serve as a sink when exposed to air enriched with NH_3 . Conversely, Langford and Fehsenfeld (1992) showed that forests may act as a source when exposed to air containing low NH_3 concentrations.

Whether plants act as a source or sink depends on the NH_3 compensation point (CP) (i.e., the ambient NH_3 concentration at which no net exchange of NH_3 between plant and atmosphere occurs; Meyer, 1973), which varies depending on plant species (Farquhar et al., 1980; Langford and Fehsenfeld, 1992), plant growth stage and the soil-plant N status (Harper et al., 1983c, 1987), and day-night conditions (Bussink et al., 1996). Some studies (Harper et al. 1989, 1995) suggest that legume species act as an NH_3 sink regardless of the N status of the plant. A report of moorlands (Sutton et al., 1992) suggests there was no NH_3 CP, because the values of "estimates of the mean surface" NH_3 concentrations were approximately zero.

Most of the NH_3 absorption and desorption occurs from the stomata during daytime, but NH_3 can be absorbed by the plant through the cuticle or stomata via dew or rainwater on the leaf (Harper et al., 1987; Van Hove et al., 1989). Based on results of a laboratory study, Van Hove et al. (1989) calculated that NH_3 absorbed in the dew would be small compared to stomatal uptake; however, in-field studies by Harper et al. (1987) showed a large NH_3 partial pressure gradient from the air to dew on the leaf surfaces. A companion study (Bussink et al., 1996) showed that measured NH_x concentration in dew was always less than the maximum NH_x concentration possible in the dew under measured ambient conditions.

These findings suggest that under certain soil and plant N conditions, plants may be an NH_3 sink in regions of large anthropogenic sources (such as Northern Europe and the midwestern USA), but an NH_3 source in other areas. Areas of high emissions of SO_4 and NO_3 aerosols may decrease the partial pressure of NH_3 due to the scavenging effect of neutralizing the acidic aerosols (ApSimon et al., 1987), and thus reduce the sink strength of plants.

The purpose of this research was to evaluate N cycling in the soil-plant-atmosphere continuum in highly N-fertilized grassland in a humid temperate climate and to observe the effects of a N surplus and deficit on NH_3 absorption-desorption by the grass. Little is known about NH_3 cycling in these fertilized grass swards. There may be a substantial risk of NH_3 losses via the plant to the atmosphere. This manuscript will discuss the relation between seasonal crop management (fertilizer input, mowing conditions), soil fertility, and soil water conditions. The effect of environmental conditions on daily fluctuations are discussed in a companion paper (Bussink et al., 1996).

MATERIALS AND METHODS

Nitrogen transport in the soil, plant, and atmosphere continuum was monitored in a temperate humid perennial ryegrass (*Lolium perenne*, L.) forage pasture on a calcareous loam soil located in a polder (reclaimed sea) region of the Netherlands (near Swifterbant, 52°35' N, 5°40' E). The pasture had been intensively managed since 1985 and used rotationally as a silage or grazed pasture system. The pasture had received dairy slurry as well as fertilizer N in previous years. In this study the pasture was mowed rotationally for silage production on Day of Year (DOY) 142 and 212. Nitrogen was applied as 50 m³ ha⁻¹ slurry (approximately 200 kg N ha⁻¹) on DOY 32 and as 43 kg N ha⁻¹ calcium ammonium nitrate on DOY 100. Calcium nitrate was applied a few days after each of four cuttings for silage (applications of 100 kg N ha⁻¹ on DOY 144, 100 kg N ha⁻¹ in split applications on DOY 180 and 186, 80 kg N ha⁻¹ on DOY 215, and 60 kg N ha⁻¹ on DOY 242). At an herbage yield of approximately 3000 kg DM ha⁻¹, the pasture was mowed, and the herbage was allowed to remain for 1 or 2 d in the pasture, where it was turned over to stimulate drying. Soil N data (at depths of 0 to 0.02, 0.02 to 0.05, 0.05 to 0.1, 0.1 to 0.2, 0.2 to 0.4, 0.4 to 0.6, 0.6 to 0.8, and 0.8 to 1.0 m) were taken on 13 dates throughout the summer measurement period. Plant N measurements including leaf and stubble (the plant material between the soil surface and harvester cutting height), were made on 8 days each throughout the spring (Fig. 1) and summer (Fig. 2) growing periods. All soil and plant samples were randomly collected from four locations in the fetch area.

Total plant N was measured using Kjeldahl digestion, and soil N (NH_4 and NO_3) was determined colorimetrically on 2 M KCl soil extracts. Atmospheric concentrations of NH_3 were measured using gas washing techniques (Weier et al., 1980) on 17 dates, before each fertilizer application, and several times after each fertilizer application (see Fig. 1 and 2), throughout the spring and summer cutting periods. Soil mineralization rates were measured using a modification of the soil tube method of Raison et al. (1987), by the use of

nonfertilized plots (10 random locations), by mass balance using N isotopes (^{15}N), and by a laboratory incubation technique on both the fertilized and unfertilized plots (Hassink, 1994). Nitrogen isotopes were used to evaluate fertilizer N uptake in separate plots for each measurement period. The above measurements were used to evaluate the soil N availability rate (SNAR, $\text{kg N ha}^{-1} \text{d}^{-1}$), described by Sharpe et al. (1988), where SNAR equals the sum of the soil N net mineralization rate and the fertilizer uptake rate, less the plant N uptake rate.

The gradient-diffusion technique was used for determination of gaseous NH_3 transport. The usual form of the gradient diffusion relationship is

$$F = -K_g \Delta g / \Delta z \quad (1)$$

where F is the gas flux, g is the density of the gas in question with respect to height z , and K_g is the eddy diffusivity or transport coefficient of the gas. The transport coefficient K_g was obtained by the aerodynamic method (Denmead and Raupach, 1993), with the assumption of equality of exchange coefficients between NH_3 and wind momentum. The relationship for determination of the momentum balance transport coefficient is

$$K_{\text{mb}} = \frac{-k^2(u_2 - u_1)}{\{\ln[(z_2 - z_d)/(z_1 - z_d)]\}^2 \Psi^2} \quad (2)$$

where u is horizontal wind speed, and Ψ is the Dyer-Hicks stability correction factor (Dyer and Hicks, 1970). Harper (1988) and Denmead and Raupach (1993) give discussions of and errors associated with this and other micrometeorological techniques. In a review of several accuracy evaluation studies, Harper (1988) showed a range of estimated and measured errors ranging from 6 to 20%. The gradient-diffusion approach is based on the assumption that, in the unobstructed air layer above the crop surface, NH_3 transport occurs by turbulent diffusion along the gradient of mean concentration. It is further assumed the air has blown over a homogenous exchange surface, so that the concentration profiles in the air are in equilibrium with the local rate of gas exchange and net horizontal concentration gradients are negligible. To ensure that these constraints are met, at least a 100:1 fetch ratio is designed in any direction (upwind distance of uniform canopy divided by the measurement height). Under these conditions, the vertical flux density of the gas will be constant with height in the air layers close to the ground and a one-dimensional (vertical) analysis can be evaluated (Denmead et al., 1978; Harper et al., 1983c). This technique does not disturb the plant-soil system nor the environmental factors' effects on the exchange process (Denmead and

Raupach, 1993). Gradient diffusion also horizontally averages the large spatial variability of NH_3 or other gas fluxes from the soils and plants. The chief disadvantage is the need for a large fetch; consequently, we made measurements in the middle of a 10-ha pasture to assure adequate fetch in all directions. Additional discussion of the technique used in this study is given in a companion paper (Bussink et al., 1996).

Curves were developed as derived smoothing functions (\hat{y}) using the procedure of Harper and Snyder (1987), and are the best-fit mean lines to the data. The integrals of NH_3 flux vs. time were determined from stochastic integration (Snyder and Harper, 1986) of the area under the best-fit mean line, \hat{y} , to the data.

RESULTS AND DISCUSSION

Spring Measurement

Figure 1 shows the results of the spring measurement period from 23 May (DOY 143) through 22 June (DOY 173) and Fig. 2, two summer measurement periods from 31 July (DOY 212) to 4 September (DOY 247). Figure 1C shows plant N production from before application of fertilizer to harvest. Herbage production above the cutting height (defined as grass) accounted for most of the plant growth since the stubble (aboveground live plant below cutting height) and root dry matter did not significantly change throughout both growth periods.

Soil inorganic N as NH_4 and NO_3 (Fig. 1E, F) was very low (about 6 kg N ha^{-1} as $\text{NH}_4 + \text{NO}_3$) prior to fertilizer application and increased only to a maximum of about 45 kg N ha^{-1} on DOY 151, despite a N application of 100 kg N ha^{-1} . A large N (as NO_3) decrease in the soil was observed between DOY 151 and 157 in the 0- to 200-mm layer (about 40 kg N ha^{-1}), which was not explained by plant uptake (about 12 kg N ha^{-1} ; Fig. 1C). Possibly a large part of the applied N was immobilized by the microbial biomass (Hassink et al., 1991) or resulted from leaching of NO_3 by the 40 mm of rain on DOY 154 and 155. Soil NO_3 levels did increase in the 20- to 50-mm and 50- to 100-mm soil layers on DOY 157. After the rain, there was no measurable evidence that the remainder was leached to the deeper soil cores below the root zone, but Dekker and Bouma (1984) have shown NO_3 transport through soil cracks. Denitrification could have caused some of the NO_3 decrease; however, in a simultaneous study (de Klein, personal communication), N loss via denitrification was undetectable during this time period. Although the NH_4 levels were less than NO_3 , they increased after fertilizer application for a brief period, possibly due to mineralization of organic N.

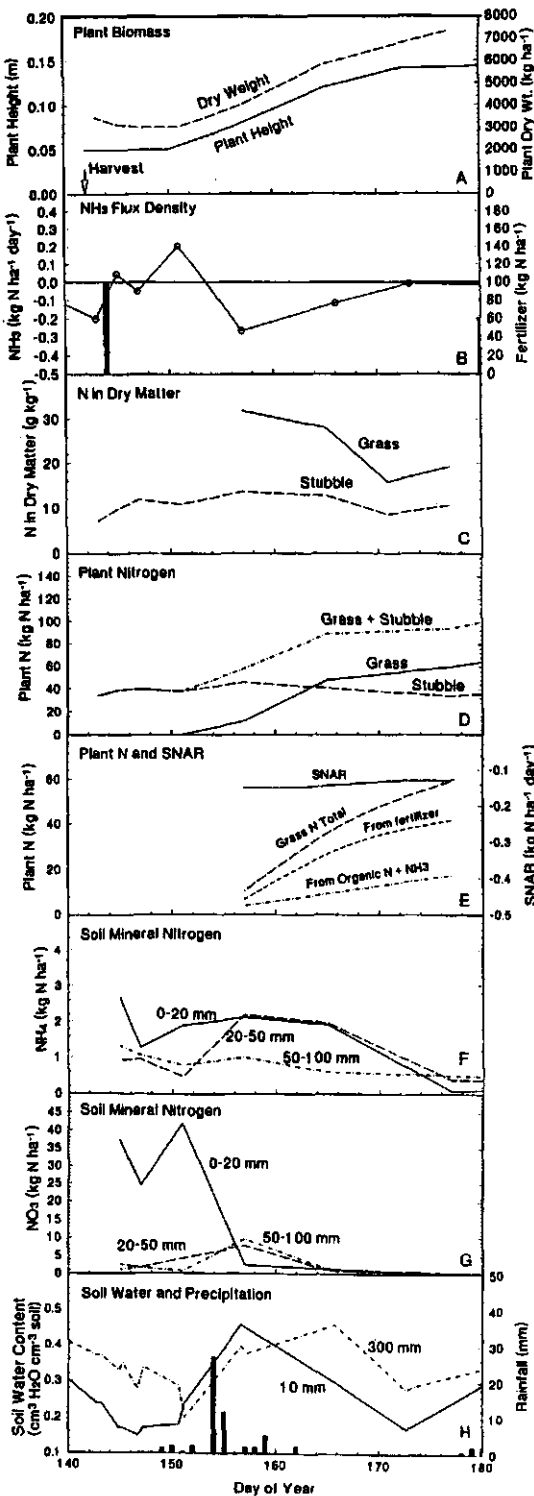


Fig. 1. Soil, plant and atmospheric measurements in a temperate perennial ryegrass pasture during the spring growth period: (A) NH_3 flux density with fertilizer application; (B) plant N concentration; (C) plant N content; (D) plant N and soil N availability rate index (SNAR); (E) soil mineral N content as NH_4 ; (F) soil mineral N content as NO_3 ; (G) soil water content and rainfall and timing.

Grass N (above the stubble) became measurable about DOY 153 and increased until harvest (Fig. 1C). Grass N concentration (Fig. 1B) was highest initially and decreased to a low concentration before harvest, due to increased C content and very low soil inorganic N availability late in the spring measurement period (lower than is normal for perennial ryegrass (Sibma and Alberda, 1980)). Grass N content at harvest was about 65 kg N ha⁻¹, equivalent to 65% of the applied fertilizer N. We found that the net plant N from fertilizer increased during grass regrowth (Fig. 1D), as determined from ¹⁵N studies, and amounted to about 45 kg N ha⁻¹ or 70% of the total accumulated plant N. It should be noted, however, that the actual net fertilizer N was probably larger because isotopes do not account for plant emission of ¹⁵NH₃ to the atmosphere and absorption (replacement) of atmospheric ¹⁴NH₃ (Harper et al., 1983a; Harper and Sharpe, 1995), nor for exchange with unlabeled N in the soil. The balance of harvested N was derived from mineralization of soil organic N, NH₃ absorption, and N deposition.

After fertilizer application, a small efflux of NH₃ was observed (Fig. 1A). An absorption period is observed after the brief efflux period, which might have been caused by lack of rainfall and the condition that only a part of the fertilizer NO₃ penetrated the soil where it was easily immobilized. On DOY 149, there was some rain causing an apparent complete dissolution of the remaining surface residual fertilizer and thus a sharp increase in soil inorganic N. The 45 kg N ha⁻¹ (NO₃ + NH₄) that was available in the 0- to 20-mm layer was sufficient for grass growth and gave also a high N-uptake rate, resulting in high production rates of NH₄ in the plant and thereby NH₃ effluxes. Ammonia is toxic to plant tissues and is released to the atmosphere under these high N conditions (Harper et al., 1987). The increase in soil NO₃-N was brief (Fig. 1F) and the concentration decreased towards zero halfway through the growing period. It is likely that most of the efflux was from the plant, due to luxury uptake and overloading of the plant with N.

The decrease of available soil NO₃ was rapid, and there was only a short period of NH₃ efflux, with the average daily flux becoming negative (i.e., an influx) soon after the first rainfall. Atmospheric NH₃ concentrations varied throughout the spring growing period between 5 and 23 μg m⁻³, with an average of about 13 μg m⁻³. Ammonia influx continued throughout the growing period with the highest influx occurring at the period, when the soil NO₃ content of the 0- to 20-mm layer rapidly approached zero (Fig. 1F). After DOY 157, NH₃ influx began to decrease even though the soil inorganic N content remained quite low. We think the decrease was due to soil water stress (Fig. 1G) and the consequent reduction in stomatal aperture and transport of gases between the leaves and ambient atmosphere. The integral of the NH₃ flux density relationship for the spring measurement period was 2.3 ± 1.7 kg N ha⁻¹, which is about 12% of the harvested N not derived from fertilizer, or 2.6% of the total N harvested. The large standard deviation of the mean was due, we think, to the

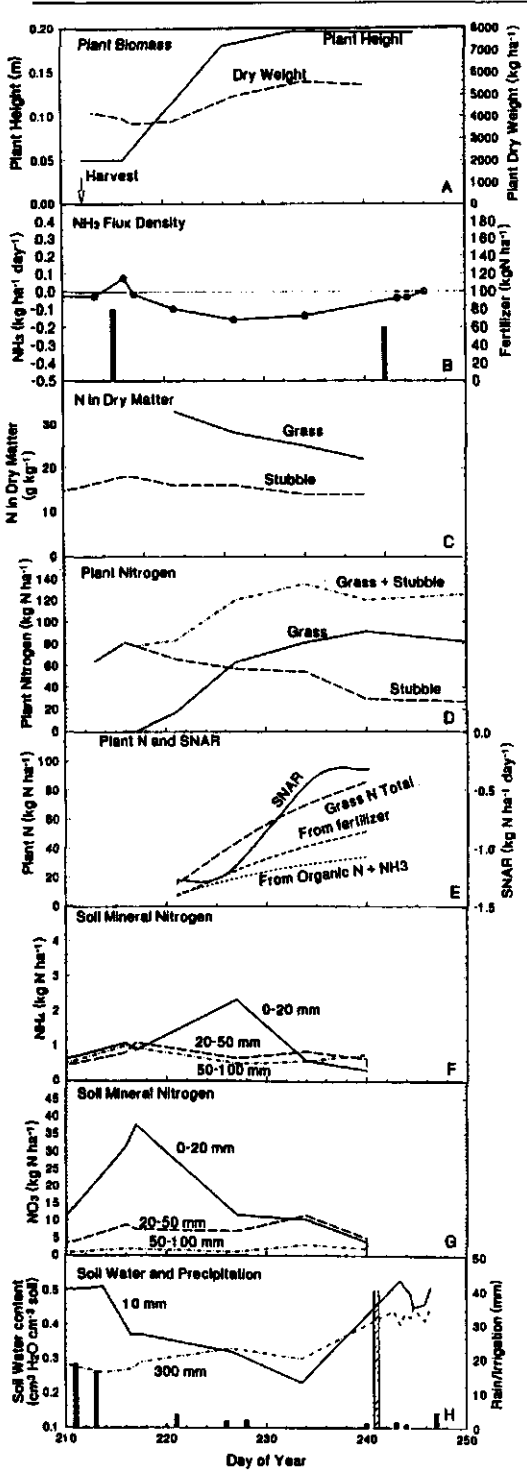


Fig. 2. Soil, plant and atmospheric measurements in a temperate perennial ryegrass pasture during the spring growth period: (A) NH₃ flux density with fertilizer application; (B) plant N concentration; (C) plant N content; (D) plant N and soil N availability rate index (SNAR); (E) soil mineral N content as NH₄; (F) soil mineral N content as NO₃; (G) soil water content and rainfall and timing.

inability of obtaining a close-fitting smoothed curve (Snyder, 1980) to the data. Other studies have shown small but significant seasonal NH_3 influx by tropical grasses (*Setaria* and *Digitaria* spp.; Harper et al. 1983c) and wheat (*Triticum aestivum* L.; Harper et al., 1987) during periods of plant N stress and large short-term NH_3 influxes when background concentrations were high (Harper and Sharpe, 1995).

Summer Measurement

Figure 2 shows the results of measurement series from 31 July through 4 September (DOY 212-247). Although $\text{Ca}(\text{NO}_3)_2$ fertilizer had been applied on DOY 180 and 186 at rates of 60 and 40 kg N ha^{-1} , respectively, soil inorganic N was very low before fertilizer application on DOY 215. After fertilizer application on DOY 215, an efflux of NH_3 similar to the spring measurement was observed. Soil NO_3 content in the 0- to 100-mm layer increased only about 30 kg N ha^{-1} , despite the application of 80 kg N ha^{-1} . The remaining fertilizer was probably immobilized, as in the spring measurement period. The drop in soil NO_3 content of the 0- to 20-mm layer between DOY 217 and 226 (26 kg N ha^{-1}) was about equal to N uptake by the crop (23 kg N ha^{-1}). Soil NH_4 concentrations did increase later in the measurement period, possibly due to increased microbial activity.

Grass herbage became measurable about DOY 218 and increased until the end of the measurement period. Fertilizer was applied at the end of the summer measurement period (Fig. 2A) for another study, but it did not affect grass growth significantly. Grass N concentration was highest initially (Fig. 2B), but the concentration did not drop as much as during the spring measurement period (Fig. 1B), nor did the soil inorganic N content. Grass N content at the end of this measurement period (DOY 240) was about 86 kg N ha^{-1} (Fig. 2D), an equivalent of about 108% of the applied summer fertilizer N. From ^{15}N studies, we determined that N from fertilizer increased in the grass throughout the summer measurement period (Fig. 2D) and amounted to about 52 kg N ha^{-1} , representing about 60% of the total accumulated grass N. Grass N from organic N and NH_3 increased steadily throughout this growing period and at the end of the period was 34 kg N ha^{-1} , or about 40% of the total accumulated grass N. The integral of the NH_3 flux density relationship (Fig. 2A) for the summer measurement period was about $3.9 \pm 0.9 \text{ kg N ha}^{-1}$, or about 11% of the grass N not derived from fertilizer and 4.5% of the total harvested grass N. The amount of N from NH_3 during the summer measurement period was larger than during the spring measurement period. Since soil water content was more favorable during the late summer measurement period, allowing maximum stomatal opening, there was the potential for larger amounts of NH_3 absorption.

Seasonal Ammonia Transport

The major portion of influx into the plant canopy during the first measurement period was delayed until a rainfall event washed the fertilizer into the soil (Fig. 1G). In both measurement periods, NH_3 influx reached its maximum as soil $\text{NO}_3\text{-N}$ decreased. During the spring measurement period, influx began to diminish and was almost zero by the end of the measurement period, but the influx intensity in the summer period continued at a constant rate until fertilizer application for the following measurement period. Ammonia influx slowed down earlier in the spring growing period, probably due to the lower soil water content since the NH_3 CP is sensitive to soil water content (discussed later).

Ammonia efflux began immediately after fertilizer application; however, the efflux (due to N excess above plant requirements) was of short duration during both measurement periods, an indication of the rapidity with which the microbial biomass can immobilize applied N. Much of the immobilized fertilizer in both measurement periods was remobilized and taken up by the crop within 20 d after application (Fig. 1D and 2D). Relative to total uptake during the summer measurement period, the crop absorbed slightly more nonfertilizer N than during the spring period (30 vs. 40%).

Soil Nitrogen Availability Rate

The soil N availability rate (SNAR) index represents the relationship between total plant uptake, fertilizer N uptake, and the net soil organic N mineralization rate (the amount of N produced by the soil in relation to N used by the plant; Sharpe et al., 1988). Sharpe et al. (1983) found that so long as the SNAR index was greater than zero, NH_3 was given off in a wheat cropping system while the crop was in a vegetative state. During a period where they observed a short-term negative SNAR index, the plants showed net absorption of atmospheric NH_3 (Harper et al., 1987). In the studies reported here, plant growth characteristics were different for the two measurement periods, with a denser, shorter canopy in the spring than in the summer. Nitrogen production during the two cutting periods were similar (about 60 kg N ha^{-1} , Fig. 1C and 2C). A larger proportion of the total grass N content was derived from fertilizer in the spring (Fig. 1D and 2D) than in the summer; however, the total uptake of fertilizer N was higher in summer than in spring.

The SNAR was calculated from smoothed data of grass N, isotope, and mineralization measurements, and it showed a N deficiency (SNAR less than zero) for the spring harvest period (the summer SNAR was not calculated, due to incomplete data). Ammonia flux density determinations (Fig. 1A) showed that the spring crop experienced a N deficiency throughout most of the measurement period. Isotope measurements began 13 d after fertilizer application, and the first SNAR calculation showed a negative value, indicating that N was

being obtained from some source or sources in addition to the soil. The SNAR was reasonably constant throughout the measurement period, showing an average N deficiency of about $0.1 \text{ kg N ha}^{-1} \text{ d}^{-1}$. The average NH_3 -N input to the crop for the period was about the same rate, $0.1 \text{ kg N ha}^{-1} \text{ d}^{-1}$.

Ammonia flux density determinations during the summer measurement period showed a similar N-deficiency relationship with NH_3 being absorbed from the atmosphere throughout the growth period, except for the first two d after fertilizer application. Although SNAR was not determined for the entire summer period (due to incomplete stubble yields), there was a decrease in stubble N content, suggesting redistribution of N from the stubble, a N redistribution often neglected. We think the NH_3 absorption was due to more favorable soil water conditions allowing maximum stomatal opening and to rapid immobilization of applied fertilizer.

Ammonia Compensation Point

To evaluate the influences on the NH_3 CP in this study, regression analysis was run on both periods' individual 2-h sample periods on the following data: sample period NH_3 concentrations (at 1.2 m above the canopy surface) with respect to incident radiation, air temperature (0.15 m above the grass surface), soil water content (25- to 45-mm depth), plant leaf N, and soil NH_4 and NO_3 content (0- to 40-mm depth). The NH_3 CP is defined in this study (see also Bussink et al., 1996) as the concentration at which NH_3 flux is zero in the regression relationship. Others (Farquhar et al., 1980; Harper et al., 1987, 1989; Morgan and Parton, 1989) have defined the NH_3 CP somewhat differently, depending on the measurement techniques used, but similar values are obtained.

The average 24-h NH_3 CP was $14.4 \mu\text{g m}^{-3}$ and had little correlation with atmospheric NH_3 concentration ($r^2 = 0.22$). When 'all' environmental variables were included (i.e., incident radiation, leaf N concentration, and soil water content), the correlation improved markedly ($r^2 = 0.67$) with soil water content having the highest individual correlation. It is interesting to note that, even though the NH_3 CP of this crop is higher than that reported by other crops (Harper and Sharpe, 1995), the average background NH_3 concentration of $17 \mu\text{g m}^{-3}$ was higher than the NH_3 CP, resulting in a net absorption of NH_3 by the crop regardless of the environmental variables or time of day. Harper and Sharpe (1995) reported situations, when the background NH_3 was high over a corn (*Zea mays* L.) crop resulting in NH_3 absorption from the atmosphere during periods of senescence and high soil and plant N, which normally have a N efflux. They suggested that atmospheric NH_3 , when significantly higher than the plant NH_3 CP, can override the normal soil-plant and senescence relationships. We believe this is the first study to report that continuously high atmospheric NH_3 can result in a seasonal net uptake of N from the atmosphere regardless of soil and/or plant condition.

A more thorough discussion of diurnal cycling of NH_3 fluxes along with changes in the NH_3 CP in response to soil and plant influence is given in Bussink et al. (1993).

Summary

These studies have shown that on a heavily fertilized grass cropping system, soil inorganic N levels can decrease rapidly following N application to background levels due to microbial immobilization and plant N demand. Much of the immobilized N is remobilized during the growth period, but at insufficient rates to avoid N stress by the crop. Absorption of atmospheric NH_3 by the crop indicated a N stress throughout both measurement periods, except for the first few days after fertilizer applications. The SNAR also indicated N stress (less than 0) throughout the spring growth period and absorption of atmospheric NH_3 was sufficient to satisfy the N deficiency.

During the spring measurement period, grass N harvested represented an equivalent 65% of the applied fertilizer; however, from isotope studies we found that N from fertilizer was only 70% of the total N in the harvested grass (Therefore, only 45% of the applied N was recovered in the grass), with the balance of the harvested N obtained from mineralization of organic N and absorption of atmospheric NH_3 . Atmospheric NH_3 absorption amounted to about 12% of the grass N not derived from fertilizer. During the summer period, grass N was equivalent to 108% of the summer fertilizer application, but isotope studies showed that the summer fertilizer application accounted for only 60% of the accumulated grass N. Fertilizer N accounted for 65% of the grass N harvested, with the balance coming from remobilization of previously immobilized fertilizer applications, mineralization of organic N, redistribution of stubble N, and absorption of atmospheric NH_3 . Atmospheric NH_3 absorption amounted to 11% of the grass N not derived from fertilizer during the summer period. The contribution of atmospheric NH_3 -N to the harvested crop N ranged from 2.6 to 4.5%. Using a regression analysis to calculate an NH_3 concentration at the net flux rate of zero, a seasonal NH_3 CP was determined to be about $14 \mu\text{g m}^{-3}$, a value that compares closely with previously reported values for grasses under field conditions.

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CHAPTER 5

AMMONIA TRANSPORT IN A TEMPERATE GRASSLAND: II. DIURNAL FLUCTUATIONS IN RESPONSE TO WEATHER AND MANAGEMENT CONDITIONS.

**AMMONIA TRANSPORT IN A TEMPERATE GRASSLAND:
II. DIURNAL FLUCTUATIONS IN RESPONSE
TO WEATHER AND MANAGEMENT CONDITIONS.**

ABSTRACT

Ammonia emission into the atmosphere is of concern because of its potential impact on atmospheric aerosol chemistry and fertilizer N use efficiency. The purpose of this study was to evaluate the effects of N surplus and deficit on soil-plant-atmosphere NH_3 exchange in a temperate humid grassland. Plant and soil N measurements were made along with NH_3 fluxes using flux-gradient techniques. Ammonia flux was related to the plant ammonia compensation point (NH_3 CP), which was controlled by plant N concentration and management practices (such as harvest and fertilization). The measured fluxes were generally much larger during daytime than during nighttime. The daily variation in flux was apparently caused by higher diffusive resistance at night. Generally, there were no significant differences between daytime and nighttime NH_3 CP. Ammonia was absorbed in dew and released during dew evaporation; however, nighttime absorption exceeded daytime release, with some of the N apparently being captured by the crop.

INTRODUCTION

Surface-atmosphere exchange of gaseous NH_3 influences aerosol chemistry (Ziereis et al., 1986) and acid deposition (Nihlgard, 1985). The major source of NH_3 is thought to be livestock production systems (principally ruminants) and NH_3 -containing fertilizers (ApSimon et al., 1987). As indicated in a companion paper (Harper et al., 1996), agricultural crops may play an important role in NH_3 cycling by absorbing or releasing varying amounts of NH_3 . Enclosure measurements (Whitehead and Lockyer, 1987; Holtan-Hartwig and Bøckman, 1994) have indicated large variations in NH_3 exchange between plants and the atmosphere, some of which may have been due to perturbation by the enclosures used for measurement (Denmead and Raupach, 1993). Because application of less invasive micrometeorological techniques is labor- and instrumentation-intensive and requires large fields to satisfy fetch requirements, few results have been reported for crop NH_3 cycling (Harper, 1988; Denmead and Raupach, 1993).

Large NH_3 fluctuations have been seen on annual, seasonal, and daily time scales, including large short-term absorption by pastures around sunset and sunrise (Harper et al., 1983a), seasonal loss and absorption by wheat (*Triticum aestivum* L.; Harper et al.,

1987), a small loss in barley (*Hordeum vulgare* L.; Schjørring and Nielsen, 1991), seasonal absorption by legumes (Harper et al., 1989, 1995) and absorption-desorption in a forest (Langford and Fehsenfeld, 1992). Whether a plant acts as a sink or source depends upon its NH_3 compensation point (NH_3 CP), or the ambient concentration at which no net exchange of NH_3 between plant and atmosphere occurs (Meyer, 1973), which is affected by plant type (Farquhar et al., 1980; Harper et al., 1995), plant growth stage (Harper et al., 1983a), and soil-plant N status (Harper et al., 1987).

Worldwide, grasslands and forage production systems are major cropping systems. Ammonia flux measurements have been made on grasslands to determine weather effects on N fertilizer losses (Harper et al., 1983b) and to examine the effect of animals on loss rates (Vallis et al., 1982), but the effects of the grass crop itself and grassland management on NH_3 transport have not been specifically addressed. The purpose of this study was to analyze the daily variability in NH_3 absorption/desorption in a temperate humid grassland.

MATERIALS AND METHODS

This study was conducted in 1989 in a temperate humid perennial ryegrass pasture (*Lolium perenne*, L.) on calcareous loam soil located in a polder region (reclaimed seabed) of The Netherlands (near Swifterbant, $52^\circ 35'N$, $5^\circ 40'E$). The pasture had been intensively managed in previous years and was intermittently mowed for silage production or grazed while receiving about 400 kg N ha^{-1} annually. In this study, the pasture was only used for silage production. The sward was mowed at a herbage yield of approximately $3000 \text{ kg DM ha}^{-1}$. Harvesting at such yield levels is common in the Netherlands. Harvesting and fertilizer application is discussed in Harper et al. (1996).

The pasture was mowed five times during the growing season. Each cut received N fertilizer at rates of 100 (in two applications), 80, and 60 kg ha^{-1} . Fertilizer was applied at the beginning of spring growth (Day of Year (DOY) = 32 and 100), and a few days after the first, second, third, and fourth cut (DOY 144, DOY 180 and 186, DOY 215, and DOY 242). The applied fertilizer was calcium nitrate, except for the first cut where $50 \text{ m}^3 \text{ ha}^{-1}$ slurry (DOY 32) and 43 kg N as calcium ammonium nitrate was applied.

Soil, plant, and aerial measurements for N transport were made on 15, 13, and 17 days, respectively, between DOY 138 and DOY 247. Aerial measurements were integrated for 24- or 48-h periods and took place after cutting for silage on DOY 142 and 212. Aerial measurements were most frequent prior to and immediately after fertilization, because near this period the largest effects were expected. Less frequent measurements were made during grass regrowth. Micrometeorological instrumentation were located in

the center of a square, 10-ha test plot to obtain adequate fetch (upwind canopy distance/measurement height) in all directions for wind profile development. Wind speed (rotating cup anemometers), air temperature (covered, wind-ventilated thermocouples), and NH_3 concentrations were measured 0.1, 0.2, 0.4, 0.8, 1.2, and 1.6 m above the canopy surface. Within-canopy measurements of NH_3 were made at the soil surface and at 0.33 and 0.67 of canopy height. Ammonia samples were collected by drawing unfiltered air at a rate of 2.4 L min^{-1} through 0.1-L gas-washing bottles containing 0.020 L of $0.02 \text{ M H}_3\text{PO}_4$ for a period of 2 h. The air flow rate was monitored and a correction of 0.1 to 0.25 L min^{-1} was made for the measured pressure-drop between the flowmeter and the air inlet of the acid trap. The gas washing bottles were transported to a laboratory for NH_3 analysis by the phenol-hypochlorite method (Weatherburn, 1967).

The gradient-diffusion micrometeorological technique was used to determine above-canopy NH_3 flux densities and has been discussed by Harper et al. (1996). Environmental measurements included incident radiation, wind direction, rainfall, soil temperature, and soil water content (SWC). Dew formation was estimated visually once each hour and given a rating (0 = no water visible to 6 = large drops formed; Harper et al., 1983b). Occasionally dew on the grass during night and early morning was measured with a pH microelectrode. The dew was adsorbed into filter disks (10 mm diam.) and stored in $0.02 \text{ M H}_3\text{PO}_4$ for later NH_x concentration analysis.

RESULTS AND DISCUSSION

Ammonia transport

Figure 1 presents NH_3 fluxes for all 17 measurement periods, showing daily changes in rates of NH_3 exchange and variation throughout the measurement season (positive values indicate an efflux from the soil-plant system). Measurements usually began at midday. Often the fluxes were negative (toward the canopy surface) in the afternoon (Fig. 1B, F, I, L, M, N), decreasing in intensity towards evening. Average flux for the 17 dates indicated NH_3 absorption from the atmosphere suggesting a crop N deficiency (Harper et al., 1983b). This was unexpected, given the large amount of fertilizer N inputs.

Concentration gradients of NH_3 in the atmosphere near the plant canopy reflect either plant use, plant release, or nonuse of NH_3 by the plants, depending on plant N deficiency-sufficiency (Sharpe et al., 1988), plant age (Harper et al., 1987), plant type (Harper et al., 1989), and atmospheric NH_3 concentration (Harper and Sharpe, 1995). The NH_3 concentration profiles above the canopy in Fig. 2A and 2B show net transport to the atmosphere and to the plant canopy, respectively, while Fig. 2C indicates little net transport.

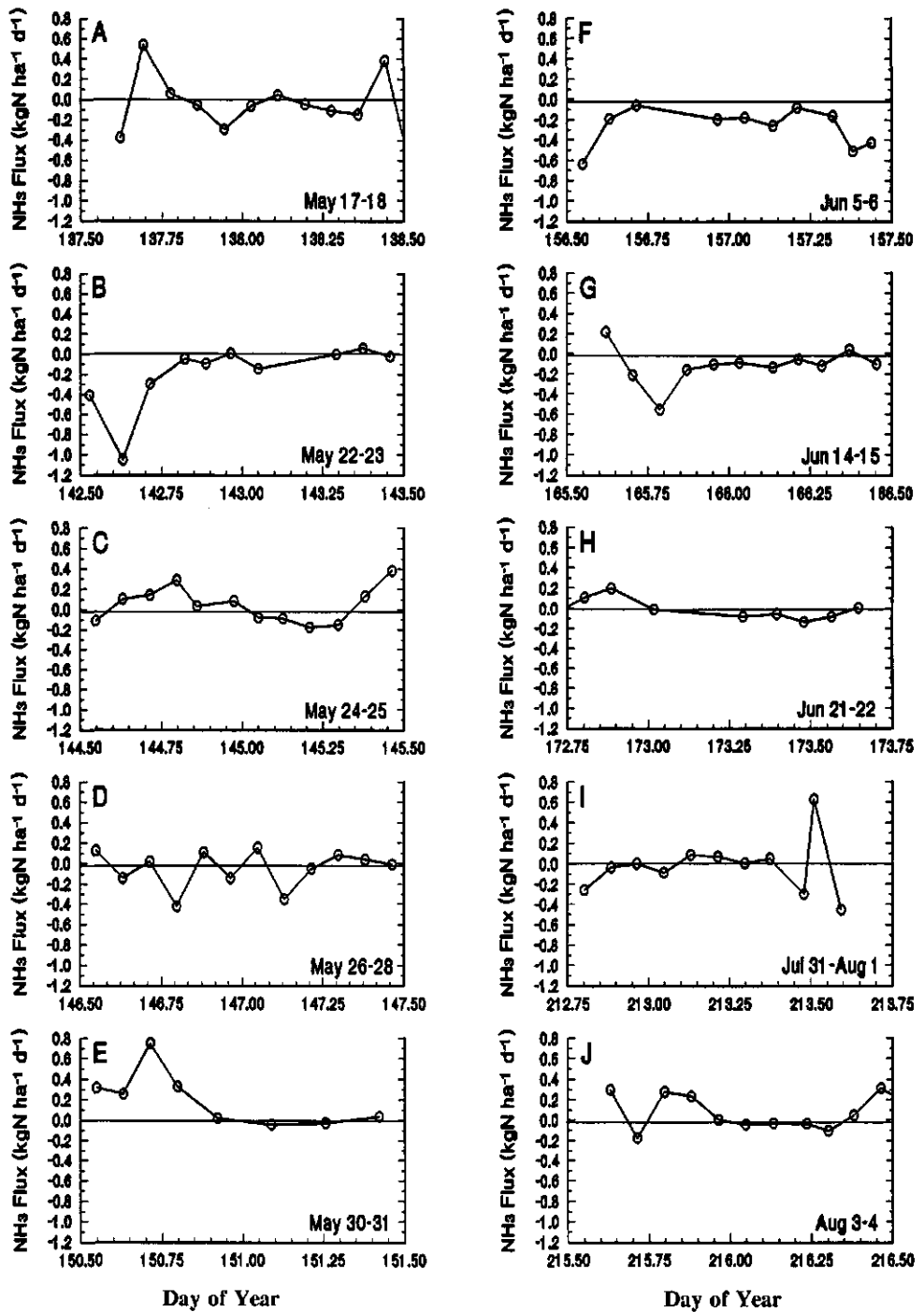
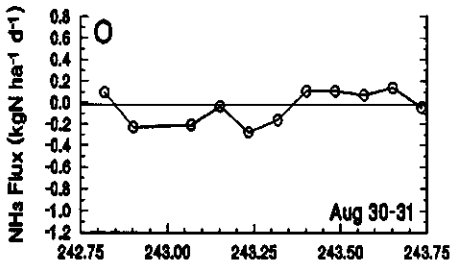
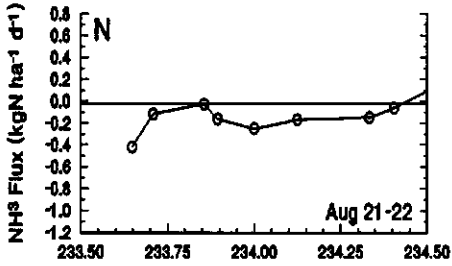
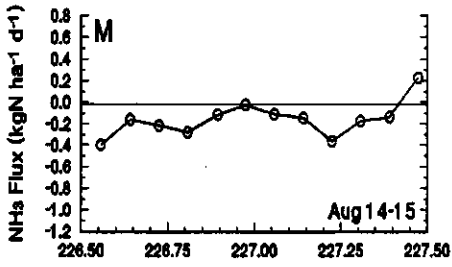
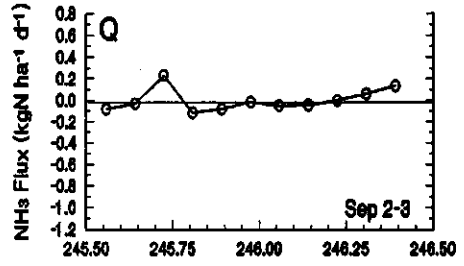
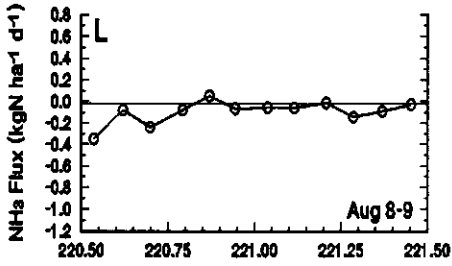
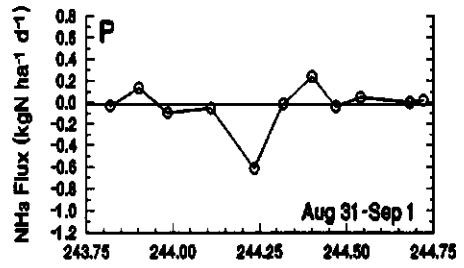
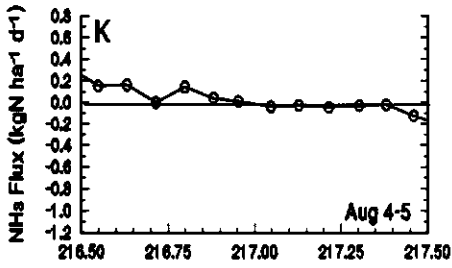


Fig. 1. Ammonia flux densities (positive values indicate an efflux from the soil-plant variation throughout the measurement season.

Ammonia transport in a temperate grassland: II.



Day of Year

system) for all 17 measurement periods, showing daily rates of exchange of NH₃ and

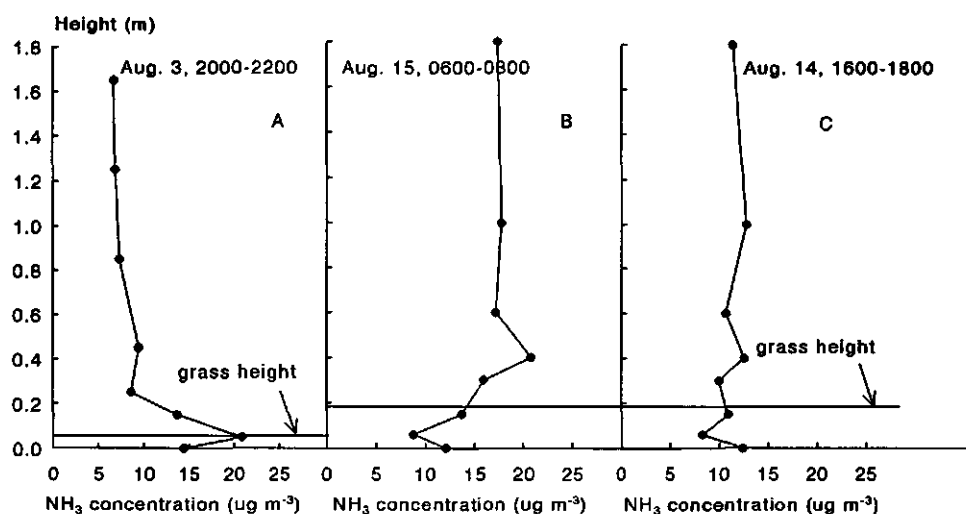


Fig. 2. Atmospheric NH_3 concentration profiles above the sward: (A) net NH_3 transport to the atmosphere; (B) net NH_3 transport to the plant canopy; (C) little net NH_3 transport.

Ammonia compensation point

The plant NH_3 CP has been suggested as being the controlling level at which NH_3 enters or exits the plant (Meyer, 1973; Farquhar et al., 1980). In this study, the compensation point was not determined directly from NH_3 concentrations measurements around the grass leaves, but rather in combination with flux density measurements and as a crop NH_3 CP. The NH_3 CP in this study is defined here as the concentration at which the crop NH_3 flux is zero in the regression of NH_3 concentration (at a height of 1.2 m above the surface) vs. flux density (see also Harper et al., 1996). (Note that at 1.2 m height, the canopy has only a limited effect on the ambient NH_3 concentration.) Others (Farquhar et al., 1980; Harper et al., 1987; Morgan and Parton, 1989; and Harper et al., 1989) have defined the NH_3 CP somewhat differently, depending on the measurement techniques used, but a similar value will be obtained as defined above.

A growing grass crop may release or take up NH_3 , depending on NH_3 CP. Because the NH_3 CP is affected by soil, plant, and atmospheric conditions, analyses were run on the daily 2-h measurement periods with respect to all measured factors. Only on three days during the growing periods of the second (DOY 156, 165 and 172) and fourth (DOY 220, 226, and 233) cutting, did substantial herbage production (range between 600 and 2700 kg DM ha⁻¹) coincide with the measurement of all factors on the same day. For

these six days, regression analysis showed that there was a good correlation (adjusted $R^2 = 73\%$, $df = 63$) between log aerial NH_3 concentration ($[\text{NH}_3]$, $\mu\text{g N m}^{-3}$), NH_3 flux density (N_{NH_3} , $\text{kg N ha}^{-1} \text{d}^{-1}$), and grass N concentration (N_g , $\text{g kg}^{-1} \text{DM}$). (A log transformation was necessary to obtain a normally distributed error.) The following relationship was derived:

$$\log(\text{aerial}[\text{NH}_3]) = 0.658 - 0.962(N_{\text{NH}_3}) + 0.06915N_g \quad (1)$$

(se = 0.182) (se = 0.212) (se = 0.00691)

Inclusion of surface soil temperature, SWC, radiation, or wind speed did not significantly improve the regression analysis.

The NH_3 CP can vary considerably with N_g . For example, according to Eq. (1), the NH_3 CP under optimum growing conditions ($N_g = 40 \text{ g kg}^{-1}$) was $30.7 \mu\text{g N m}^{-3}$, whereas it dropped to $7.7 \mu\text{g N m}^{-3}$ under N stress ($N_g = 20 \text{ g N kg}^{-1}$). Differences in the NH_3 CP between daytime (1300 to 2000 h) and nighttime (2200 to 0400 h) were also analyzed, with respect to soil, plant and atmospheric conditions, because N influx is often larger in the afternoon than towards the evening (Fig. 1B, D, I, L). This may be the result of an increase of the NH_3 CP; however, efflux decreases also at night (finally becoming an influx), as can be seen in Fig. 1E and 1K. Therefore it is more likely that an increase of diffusive resistance, because of partially closed stomata, is the major cause of lower influx or efflux at night. (Measured concentration gradients were larger during nighttime than daytime.)

Regression analysis (Table 1) showed that there was a good correlation (adjusted $R^2 = 78\%$, $df = 27$) between log (aerial $[\text{NH}_3]$) and N_{NH_3} , N_g , and SWC ($\text{cm}^3 \text{cm}^{-3}$). (A log transformation was necessary to obtain a normally distributed error.) Analysis showed that the model presented in Table 1 was significantly improved ($p < 0.05$) compared to the same model without inclusion of the time-of-day factor (day or night). Also the t probabilities of differences of regression coefficients (Table 1) suggested that the relationship of log (aerial $[\text{NH}_3]$) with N_{NH_3} , N_g , and SWC was different for day and night conditions. The much higher coefficient of the flux (N_{NH_3}) during nighttime than daytime suggests ($p < 0.108$) indeed a much higher diffusive resistance at night. This means that NH_3 is much more easily taken up or released by the crop during the day than at night. For example, to get an NH_3 flux density rate of $-0.1 \text{ kg N ha}^{-1} \text{d}^{-1}$ under maximum growing conditions ($N_g = 40 \text{ g N kg}^{-1}$ and $\text{SWC} = 0.4 \text{ cm}^3 \text{cm}^{-3}$), daytime NH_3 atmospheric concentration would have to be $1.4 \mu\text{g m}^{-3}$ higher than the NH_3 CP. To get the same uptake rate at night, atmospheric NH_3 concentration would have to be $8.2 \mu\text{g m}^{-3}$ higher than the NH_3 CP. For the above maximum growing conditions, the NH_3 CP is higher during nighttime ($39.1 \mu\text{g m}^{-3}$) than daytime ($33.0 \mu\text{g m}^{-3}$). However, for

Table 1. Regression calculation results for the NH₃ transport model.*

Coefficient	Estimate				Standard error of differences	Probability of differences
	Day	Se	Night	Se		
$a_{d,n}$	0.544	0.306	0.195	0.347	0.462	0.457
$b_{d,n}$	-0.415	0.286	-1.911	0.924	0.967	0.108
$c_{d,n}$	0.0548	0.017	0.100	0.021	0.027	0.134
$e_{d,n}$	1.90	1.17	-1.32	1.21	1.687	0.067

* $\log(\text{NH}_3 \text{ in air})_{(d,n)} = a_{(d,n)} + b_{(d,n)} N_{\text{NH}_3} + c_{(d,n)} N_g + e_{(d,n)} \text{SWC}$, where N_{NH_3} is the NH₃ flux density (kg N ha⁻¹ d⁻¹), N_g as grass N concentration (g kg⁻¹ DM), SWC is the soil water content (cm³ cm⁻³), and subscripts d and n indicate day and night, respectively. Model: $p < 0.001$, adjusted $R^2 = 78\%$.

the growing conditions $N_g = 20 \text{ g N kg}^{-1}$ and $\text{SWC} = 0.25 \text{ cm}^3 \text{ cm}^{-3}$, nighttime and daytime NH₃ CP are 6.5 and 8.3 $\mu\text{g m}^{-3}$, respectively. Paired testing for different N_g and SWC showed that these differences between daytime and nighttime NH₃ CP were generally not significant ($p < 0.05$). This means that Eq. (1) may still be used to calculate the NH₃ CP. However the daytime and nighttime regressions are needed to calculate influx or efflux for a given set of conditions.

Probably the effect of SWC on NH₃ CP is partly masked by soil temperature, though including soil temperature in our model did not improve the adjusted R^2 . Low SWC will often correspond with high soil temperatures and large temperature differences between day and night. It should be noted that equilibrium NH₃ pressure in air and, consequently NH₃ CP, will increase with temperature (Frenay et al., 1983).

We believe from these field studies that absorption of aerial NH₃ is governed mainly by the diffusive resistance, as is found in laboratory studies (Van Hove et al., 1989). However, further studies are necessary to differentiate between physical resistance to NH₃ transport, such as stomatal closure and reduced nighttime turbulence, and physiological processes of NH₃ conversion to amino acids in the leaf.

The effect of dew

During most nights we observed NH₃ absorption by the crop. Absorption can be through the stomata as NH₃ and/or through the leaf surface by ionic absorption from NH₃ adsorbed in the dew or guttation (Harper et al., 1987). Even an increase in air humidity,

which occurs at night, may cause an increase in NH_3 adsorption of leaves (Van Hove et al. 1989). The summer of 1989 was warm and dry. At the time of aerial NH_3 measurements during the growing period of the second and fourth cuttings, significant amounts of dew were observed on three dates, which made dew sampling and analysis possible. It is known that NH_3 adsorption on the leaf starts to increase when air humidity increases (Van Hove et al., 1989), normally occurring at night. Calculations of dew NH_3 partial pressure from measured NH_x concentrations, dew pH (around 6.5), and air temperature indicated a large NH_3 partial pressure gradient from the air to the dew on these three days. For example, on DOY 157 the partial pressure in the air above the crop was 0.045 Pa, while in the dew it was to 0.001 to 0.003 Pa. Harper et al. (1987) showed similar gradients in wheat.

Table 2 gives a comparison of our measured concentration and the maximum possible concentration that could occur in the dew at the local conditions of temperature and pH. The much lower concentration in dew than theoretically possible given the measured temperature and pH may be caused in part by lack of turbulence at the grass-air interface at night. This causes a much lower NH_3 concentration adjacent to the grass leaf than at 1.2 m height, resulting in a lower concentration in the dew. However, it is not possible to measure these leaf-surface/air interface concentrations. Part of the NH_x in the dew is from dry deposition, which was not measured.

During early morning, dew evaporation sometimes was coincidental with smaller influxes or even effluxes (Fig. 1B, D, E, G, M, P, Q). In Fig. 1C, 1J, and 1O, effluxes were also coincidental with fertilizer application on the previous day. On these days the NH_3 efflux is caused by excessive N uptake as a result of transpiration (as explained below). Interestingly, on one day (DOY 157), we observed a decrease in the dew NH_3 concentration during early morning, while at the same time, NH_3 influx increased (Fig. 1F). The measured NH_x concentrations in the dew first increased until around 0350 h, followed by a decrease until about 0750 h. By 0900 h, the dew had evaporated. Harper et al. (1996) provided evidence that on this day the grass crop was under N stress, because soil N availability rate index (Sharpe et al., 1988) was negative. The SWC at this period was around field capacity. The fact that NH_3 in the dew apparently was captured by the crop suggests a low NH_3 CP.

Management effects on NH_3 flux

Ammonia efflux was observed on days after fertilizer application (Fig. 1C, E, J, K, O). The high amount of available soil NO_3 (Fig. 1F and 2F in Harper et al., 1996) may cause a larger NO_3 uptake with water uptake and a resulting NO_3 concentration in the crop greater than what is needed for crop growth. Because of this excess NO_3 , NH_3 may have

Table 2. The measured NH_x concentration in the dew and the maximum NH_x concentration possible in the dew under local field conditions at a measured dew pH of about 6.5.

Sample date	Day of Year	Sampling time (h)	Air temperature (K)	Aerial NH_3 concentration ($\mu\text{N m}^{-3}$)	Maximum NH_3 concentration possible in dew (mg N L^{-1})	Measured NH_3 concentration (mg N L^{-1})
6 June	157	0300	275	27.2	428	11.9, 11.7, 31.0, 26.5
		0500	275	22.6	356	9.8, 9.3, 6.4
		0730	275	19.5	306	3.1, 7.9, 3.9
15 June	166	2300	285	17.2	79	0.4, 0.2
		0430	283	14.7	85	0.9, 10.0
22 Aug.	234	0400	288	18.1	58	36.5
		0830	288	17.9	57	39.6

been released by the crop. Early studies (Eggleton, 1935; Webster, 1959, p. 13) found a buildup of NH_3 in grass after fertilizer application due to NO_3 , with absorption being faster than it could be utilized. Hutchinson (1973) suggested, and Stutte et al. (1979) verified, that in senescing plants a net movement of N out of the leaves occurs in the presence of excess leaf N. Excess NO_3 in the crop can be reduced to NH_4 , which can then be released by the plant as NH_3 . Harper et al. (1987) and Harper and Sharpe (1995) have shown NH_3 released under high soil N during the vegetative growth period and during senescence in wheat and corn. Reduction of excess NO_3 occurs only during daytime because it is an energy intensive process. High NH_4 may then be expected. As shown, NH_3 CP is not significantly different between day and night for good growing conditions. Thus the high daytime efflux is caused by a low diffusive resistance (open stomata). Daytime emissions were less pronounced on DOY 243 (Fig. 10) when herbage yield was about $4000 \text{ kg DM ha}^{-1}$. (The unusual application of fertilizer at this growth stage was done for another study.) On DOY 145 (Fig. 1C) and 215 (Fig. 1J), the sward had just been recently cut. The large standing herbage on DOY 243 (Fig. 10) would have given the grass more opportunity for redistribution and utilization of the NO_3 uptake, resulting in less excessive N and less efflux.

After the second and fourth cut, the grass remained on the sward about two days for wilting. Measurement of NH_3 fluxes started as soon as possible, usually 1 to 2 h after mowing (Fig. 1B, I). Under these circumstances absorption was observed. Photosynthesis continues for some hours after cutting (Kormos and Chestnutt, 1967); however, cutting

disrupts the N supply from the roots. Aerial NH_3 is absorbed in an effort to satisfy N demand for assimilation of amino acids from the organic acids produced in photosynthesis before plant die-off. Under these conditions, there is a rapid change in the NH_3 CP.

The day after the fourth cut, a spike was observed (Fig. 1I). This spike could be a measurement error; however it was observed that the spike coincided with tedding and windrowing followed by removal of the wilted herbage. Tedding (i.e., scattering or spreading the mown grass to dry) stimulates water evaporation of the wilting herbage, and NH_3 may thereby be released, as with evaporating dew. As soon as the herbage was removed (at 1600 h), a sharp drop of the spike was observed. This spike cannot be seen in Fig. 1B, because aerial measurements were stopped before windrowing and removing the herbage. Additional measurements may elucidate this issue.

CONCLUSION

The NH_3 CP was related to grass N concentration and soil water content. Daily variation in flux was apparently caused by higher diffusive resistance during nighttime than daytime. Generally, there were no significant differences between daytime and nighttime NH_3 CP.

Ammonia flux density and the NH_3 CP were affected by management practices. Application of nitrate-containing fertilizer led to NH_3 emissions for the first few days after application probably due to the excessive N uptake by the crop. Mowing the crop followed by wilting rapidly decreased the NH_3 CP, creating an influx during the first few hours after mowing (caused by interruption of the N supply from the roots and consequent N deficit before plant die-off). Dew formation coincided with NH_3 influx, and NH_3 efflux occurred during dew evaporation. Nighttime NH_3 absorption from dew exceeded daytime release, with some of the N from the NH_3 absorption apparently being captured by the crop.

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CHAPTER 6

DIFFERENCES IN RAINFALL AND TEMPERATURE DEFINE THE USE OF DIFFERENT TYPES OF NITROGEN FERTILIZER ON MANAGED GRASSLAND IN UK, NL AND EIRE.

**DIFFERENCES IN RAINFALL AND TEMPERATURE DEFINE THE USE OF
DIFFERENT TYPES OF NITROGEN FERTILIZER ON MANAGED GRASSLAND
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ABSTRACT

There are distinct differences between the Netherlands (NL) and the United Kingdom (UK) in the use of urea (U) and (calcium) ammonium nitrate ((C)AN) fertilizers on grassland.

It has been known for some time that rainfall and temperature affect NH_3 volatilization from U and its agronomic efficiency. This study aimed (i) to examine how rainfall and temperature pattern in NL and UK relate to the observed U efficiency, and (ii) to provide a simple decision support model for farmers to enable them to choose the most appropriate N fertilizer. This study is based on straight forward and uniform statistical analysis (residual maximum likelihood) of existing data from numerous field trials.

The data came from trials in NL (1954-1989), Northern Ireland (NI, 1983-1985) and England (En, 1985-1988). The agronomic efficiency of U compared to CAN in field trials was expressed as (i) urea relative (N) yield (UR(N)Y), and (ii) apparent-urea relative (N) yield (AUR(N)Y).

In NL, URY did not significantly differ from 100% on peat grassland. Mean URY on sand and clay was 95%, in both cases. Mean seasonal AURY and AURNY for both soils together was 92.3 and 86.4%, respectively, without significant differences between first and later cuts. There was no significant improvement of AUR(N)Y in the last decades. In the first cut, mean AURY was lower than in En (100.9%) and NI (100.2%). Short-term rainfall and temperature defined the differences in efficiency between countries. By aggregating NL, NI and En data a simple regression equation was derived:

$$\text{AURY} = 89.48 (\pm 0.781) + 2.188 (\pm 0.148) * R3 - 1.091 (\pm 0.070) * T3$$

(R3 and T3; rainfall amount and average temperature within three days after fertilizer application, respectively). The decision support model based on this equation showed that under prevailing NL weather conditions it will be profitable for the farmer to apply U instead of CAN, for the first and second cut, only once every 5 and 7 years, respectively, because R3's exceeding 6 and 9.5 mm are required.

INTRODUCTION

In Western Europe, grasslands are intensively managed and supplied with relatively large amounts of N fertilizer. Ammonium nitrate ((C)AN) based fertilizers are by far the dominant

(more than 90 %) N fertilizers for grassland in the Netherlands (NL). By contrast, in the United Kingdom (UK) and especially Eire, urea (U) based fertilizers have a significant share in the use of N fertilizer on grassland. Major reasons for use of U based fertilizers are the relatively low price, the high N content and the suggested lower susceptibility for nitrate leaching, denitrification and N_2O emission compared with (C)AN (Velthof et al., 1996). Major objections for usage of U based fertilizers are the large potential for NH_3 volatilization (Freney et al., 1983) which on grassland can be as high as 60 % of the applied N (Black et al., 1987; Kunelius et al., 1987; Titko et al., 1987; Velthof et al., 1990), the lower maximum yield (Van Burg et al., 1982; Watson et al., 1990) and the soil acidifying effect (Van Burg et al., 1982). The general perception of the farmer is that U has a more uncertain effectiveness than CAN. In a review study, Watson et al. (1990) concluded that there was no evidence to indicate that U is significantly more variable than CAN for spring grass production in UK and Eire. There were large variations in the agronomic efficiency of both U and CAN when applied to grassland in spring. However, U was slightly less-effective than CAN in summer. Comprehensive field trials in NL, showed that over the whole season U was on average 15% less effective than CAN (Van Burg et al., 1982). These somewhat contrasting conclusions suggest significant differences in environmental conditions, and thereby in the effectiveness of U relative to CAN, between UK and NL.

Weather conditions such as temperature and rainfall have a significant effect on the agronomic efficiency of N fertilizers. Rainfall and low temperatures after fertilizer application suppress NH_3 volatilization from U (Black et al., 1987; Bouwmeester et al., 1985; Freney et al., 1983), thereby improving efficiency. In addition, rainfall increases nitrate leaching and denitrification from CAN, thereby decreasing CAN efficiency (Velthof et al., 1996). It has been shown (Van Burg and Rauw, 1972; Lloyd, 1992) that rainfall amounts of about 5 mm within a few days after fertilizer application resulted in an equal efficiency of U and CAN. For much larger amounts of rainfall, U became more efficient than CAN. Because effects of rainfall and temperature on U efficiency are general, and omnipresent, we hypothesize that variation in rainfall and temperature patterns define the observed differences in U efficiency, between NL and UK/Eire.

As the present environmental and economical constraints force European farmers to reduce costs, increase nutrient efficiency and minimize nutrient losses, the choice of N fertilizer type becomes more important.

This study defines criteria to improve fertilizer N use efficiency on grasslands in UK, NL and Eire. Data from a large number of fertilizer trials on representative grassland sites in these countries were analyzed uniformly. These analyses were used to test whether differences in rainfall and temperature patterns define the differences in U efficiency between these countries. Because experiments were carried out in different years, we first tested whether there is a general increase in agronomic efficiency of U from the early fifties to the

late eighties. This could be due to for example an improved fertilizer technology or a reduced biuret content in U (Watson et al., 1990) Results were also used to construct a simple model to help farmers to decide when U is profitable relative to AN-based fertilizer.

MATERIALS AND METHODS

Available data and sources

Available data from representative grassland areas in western Europe were analyzed, i.e. datasets from NL, Northern Ireland (NI) and southern England (En). General information about the datasets is given in Table 1. Available trials for NL varied from testing a single application in spring to a single application in autumn at different locations all over NL. In some trials applications of U and CAN were compared over all the growing season. Generally, dry matter yield (DMY) per cut ranged from 1500 to 4000 kg ha⁻¹, with the largest yields in the older experiments. Data for NI (Stevens et al., 1989) came from a trial in which during three years the effect of ten dates of application of CAN and U on DMY was studied in a randomized block experiment at four different sites. Fertilizer was applied at weekly intervals from 1 February to 5 April at 70 kg N ha⁻¹. At each site two control plots within each block received no N. Treatments were replicated three times (three blocks). The first cut was mown for all treatments on the same day, at the end of April. Within two days CAN and U were re-applied (50 kg N ha⁻¹). The second cut was mown, at the end of May. Data for En came from a four years old experiment (Peake, pers. comm.) in which DMY response of the first and second cut was determined. The DMY of the first and second cuts ranged from 5 to 7 and from 3 to 5 ton ha⁻¹, respectively. Generally, the sites of the trials differed each year. In total, 244 treatment data sets (of which 100 for the first cut) were analyzed, the control treatments excluded.

Rainfall and temperature (T) data were gathered for the trials in NL and NI for 10 days before N application up to mowing. The data came from official weather stations nearby the experimental sites. For En rainfall data within three days after application and average temperatures were available.

To predict the chance of a certain amount of rainfall after U application, probability curves were derived using rainfall statistics of NL in spring (period of 1930-1960), as an example. The probability of an amount of 'X' mm within 'Z' days was calculated.

Table 1. Datasets from NL, NI and En used in statistically analysis.

Data sets	Sites	Period	Number of trial data	Soil types	N-rate kg ha ⁻¹ cut ⁻¹	Number of cuts	Para-meters recorded
NL							
Oostendorp and Boxem pers. comm.), Boxem pers. comm.) and NMI data (partly published by Van Burg et al. (1982))	28	1954, 1955, 1958, 1964-1967, 1970, 1971 1987-1989	1092*	sand, clay and peat	0-200	1 to 6	DMY and NY, daily temperatures and rainfall
NI							
Stevens et al. (1989)	4	1983-1985	792	sandy-loam, clay, silty-clay-loam and clay-loam	70, 50	1 and 2	DMY and NY, daily temperatures and rainfall
En							
Peake, unpublished	27	1985-1988	244*	silt-loam, sandy-loam, sandy-clay, clay sandy-silt-loam, sandy-clay-loam and clay-loam	0-200	1 and 2	DMY, rainfall within three days after fertilizer application

* averaged over blocks

Comparison of fertilizer N trials

From a farmer's point of view, the effect of applied N on the yield of metabolizable energy or DM has to be considered rather than the effect on total herbage N yield (NY). However, from an environmental point of view the fraction fertilizer N recovered by the crop is important, as the remaining N is susceptible to losses. We decided to compare U and CAN on, both DMY and NY basis.

The efficiency of U and CAN in field trials with respect to DM yield can be expressed in terms of i) UEF (urea effectivity factor), ii) URY (urea relative yield) and iii) AURY (apparent-urea relative yield) i.e.,

$$\text{UEF} = \frac{(\text{CAN application needed to obtain yield X})}{(\text{U application needed to obtain yield X})} * 100\% \quad (1)$$

$$\text{URY} = \frac{(\text{DMY with U})}{(\text{DMY with CAN})} * 100\% \quad (2)$$

$$AURY = \frac{(DMY \text{ with U}) - (DMY \text{ of } 0 \text{ N plot})}{(DMY \text{ with CAN}) - (DMY \text{ of } 0 \text{ N plot})} * 100\% \quad (3)$$

Replacing DMY by NY in Equations (2) and (3) gives i) URNY (urea relative NY) and ii) AURNY (apparent-urea relative NY).

Probably, the most contrasting way (difference from 100%) of testing fertilizers is by UEF, followed by AURY and URY, as is demonstrated in Figure 1. The first two ways correct for the yield obtained at the control treatment. However, AUR(N)Y and UR(N)Y were mainly used in this paper, because i) most of the experiments did not contain enough N levels to apply the UEF method and ii) unless the maximum yield level for both fertilizers are the same UEF becomes biased (Van Burg et al., 1982). In the case of a low DMY or NY at the 0 N plot, UR(N)Y approaches AUR(N)Y. When there is no difference between the U and CAN fertilizers, AUR(N)Y and UR(N)Y are 100%.

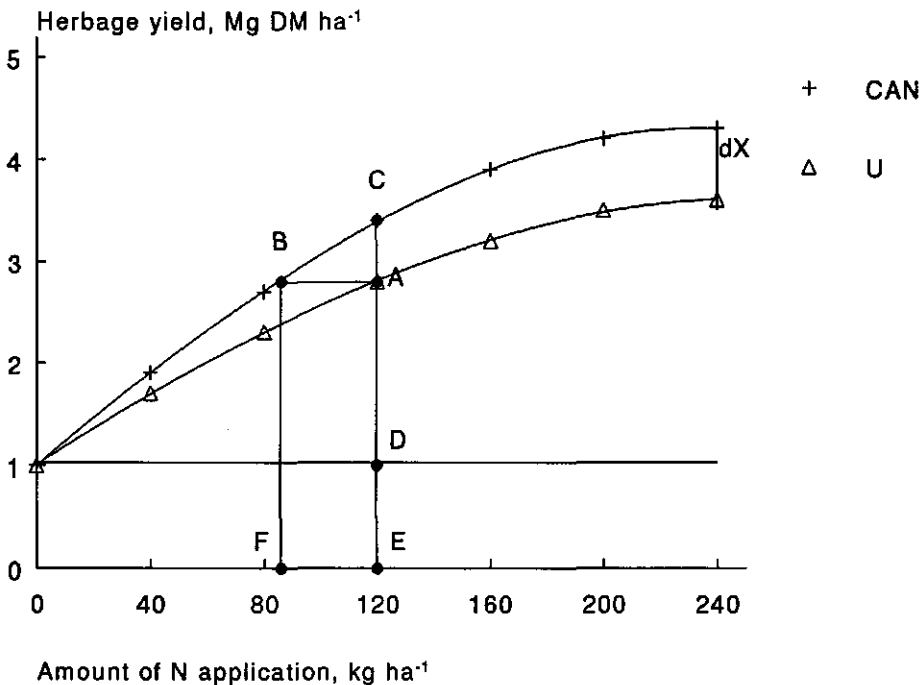


Figure 1. A schematic representation of how to estimate UEF (Urea Effectivity Factor), AURY (Apparent-Urea Relative Yield) and URY (Urea Relative Yield). UEF is $100 * F / E = 72\%$, AURY is $100 * (A - D) / (C - D) = 75\%$, URY is $100 * A / C = 82\%$ and dX is the yield difference between CAN and U at maximum yield.

Statistical analyses

Our dataset with N fertilizer trials (Table 1) contains information on treatment effects in similar experiments conducted at different times and places. To combine this information on treatment effects and to obtain information on sources and size of variability in the datasets we have to use the method of residual (or restricted) maximum likelihood. To do this we used the REML algorithm of the GENSTAT statistical package (Anonymous, 1994).

Models

The NL data were used to test whether there has been an increase of U efficiency in time and, also during the season using the following model:

$$A = \mu + FT + YR + ST + HD + \text{applN} + FT.YR + FT.ST + FT.HD + FT.\text{applN} \\ + YR.ST + YR.HD + YR.\text{applN} + ST.HD + ST.\text{applN} + \\ HD.\text{applN} + \epsilon_s + \epsilon_y + \epsilon_{sy} + \epsilon_{syr} \quad (4)$$

with:

A = either DMY, NY, (DMY - DMY of 0N plot) or (NY - NY of 0N plot) in kg ha⁻¹ yr⁻¹

FT = factor 'fertilizer type', being U or CAN

YR = factor 'years', divided into 3 periods (Table 2)

ST = factor 'soil type', being sand, clay or peat

HD = factor 'harvesting days', in numbers of day, divided into 4 periods (Table 2)

applN = 'amount of applied N, in kg ha⁻¹', divided into 3 groups (Table 2).

μ = constant, in kg ha⁻¹ yr⁻¹

The random terms ϵ_s , ϵ_y , ϵ_{sy} and ϵ_{syr} express the variance component of the experimental site, the experimental year, the site and year interaction and the rest, respectively.

To test whether differences in rainfall and temperature patterns adequately explain the observed differences in agronomic U efficiency and U use between NL, NI and En, we used three models. For NL the following model was used:

$$B = \mu + FT + \beta_1 \text{NoGD} + \beta_2 \text{Nappl} + \beta_3 \text{mT} + \beta_4 \text{tR} + \beta_5 \text{Rx} + \beta_6 \text{Tx} + \beta_7 (\text{RBy}) + \\ \beta_8 (\text{NoGD}^2) + \beta_9 (\text{Nappl}^2) + \beta_{10} (\text{Rx}^2) + \beta_{11} (\text{RBy}^2) + \beta_{12} (\text{FT.Nappl}) + \beta_{13} (\text{FT.Rx}) \\ + \beta_{14} (\text{FT.Tx}) + \beta_{15} (\text{Nappl.NoGD}) + \beta_{16} (\text{Nappl.tR}) + \beta_{17} (\text{Nappl.Rx}) + \\ \beta_{18} (\text{NoGD.Rx}) + \epsilon_s + \epsilon_y + \epsilon_{syr} \quad (5a)$$

with:

B = either DMY, NY, (DMY - DMY of 0N plot) or (NY - NY of 0N plot) in kg ha⁻¹ yr⁻¹

μ = a constant in kg ha⁻¹ yr⁻¹

Nappl = 'amount of N applied' (kg ha⁻¹)

NoGD = 'number of growing days'

mT = 'mean temperature' between time of fertilization and cutting in °C

tR = 'total rainfall' between time of fertilization and cutting in mm

Rx, RBy = 'amount of rainfall' in mm within, respectively, x days after and y days before fertilizer application

Tx = 'average temperature' in °C within x days after fertilizer application

The random terms ϵ_s , ϵ_y and ϵ_{syr} express the variance component of the experimental site, the experimental year and the rest, respectively.

For NI the following model was used:

$$B = \mu + FT + \beta_1 \text{NoGD} + \beta_3 \text{mT} + \beta_5 \text{Rx} + \beta_6 \text{Tx} + \beta_8 (\text{NoGD}^2) + \beta_{13} (\text{FT} \cdot \text{Rx}) + \beta_{14} (\text{FT} \cdot \text{Tx}) + \beta_{18} (\text{NoGD} \cdot \text{Rx}) + \beta_{19} (\text{FT} \cdot \text{NoGD} \cdot \text{Rx}) + \epsilon_s + \epsilon_y + \epsilon_{sy} + \epsilon_{sb} + \epsilon_{ysb} + \epsilon_{ysbr} \quad (5b)$$

The random terms ϵ_{sb} , ϵ_{ysb} and ϵ_{ysbr} express the variance component of site and block interaction and year, site and block interaction and the rest respectively.

For En the following model was used:

$$B = \mu + FT + \text{STY} + \beta_5 \text{Rx} + \beta_{10} (\text{Rx}^2) + \beta_{12} (\text{FT} \cdot \text{Rx}) + \epsilon_y + \epsilon_{yp} + \epsilon_{ypr} \quad (5c)$$

with:

STY = 'soil type' (8 types)

The random terms ϵ_{yp} and ϵ_{ypr} express the variance component paired data interaction and the rest respectively. No information was available on NoGD and short-term temperature.

RESULTS

NL data; effects of soil type, period of trial execution, harvesting day and amount of N applied

The URY frequency distributions shown in Figure 2 depict significant variations. Mean URY differed from 100% on sand and clay soils, but not on peat soils. These results were confirmed by statistical analysis using Equation 4, suggesting that the agronomic efficiency of U was less than that of CAN on sand and clay but not on peat soils. Peat soils were excluded from further analysis because of the limited data. The apparent N recovery in these experiments was low. The 'prediction' with REML was 56% and 48% for CAN and U, respectively.

Table 2. The predicted 'DMY response - DMY response of 0N plot' for CAN and U, 'difference in DMY' and 'AURY' as a function of the factors soil type (ST), periods of years (YR), periods of harvest days (HD) in day numbers, and applied amount of N (applN) in kg N ha⁻¹ of 459 pairs of yield data obtained in NL between 1954 and 1989.

Factor	Predicted 'DM yield - 0N DM yield' (kg ha ⁻¹)		Predicted 'DMY difference' (kg ha ⁻¹)	Average s.e.d.	Predicted AURY
	CAN	U			
FT ¹	1367 ^a	1270 ^b	106	27	92.3
<u>ST</u>					
sand	1354	1249	105	138	92.2
clay	1510	1377	130		91.2
<u>PoY</u>					
1954-1967	1562	1444	118	317	92.4
1970-1973	1542	1387	155		89.9
1987-1989	1193	1109	84		93.0
<u>PoHD</u>					
< 136	883	759	124	254	86.0
136-151	1819	1700	119		93.5
152-181	1649	1513	136		91.8
> 181	1378	1281	97		93.0
<u>applN</u>					
< 60	880	770	110	90	87.5
61-120	1504	1401	103		93.2
> 120	1913	1769	144		92.5

$$\sigma_s^2 = 1.126E+5, \sigma_y^2 = 9.74E+4, \sigma_{sy}^2 = 1.521E+5 \text{ and } \sigma_{syr}^2 = 1.207E+5$$

1) Obtained after reduction equation (4) to significant terms (superscripts a,b for $p \leq 0.001$)

Results presented in Table 2 indicate that AURY did not vary significantly between three classes of trials, grouped according to years. Trials carried out on sand and clay soils in the period 1954-1967 had similar AURY and also AURNY (data not shown) to the trials carried out in the period 1987-1989, suggesting no general increase in agronomic efficiency of U with time.

Results presented in Table 2 also indicate that AURY was affected neither by the harvesting day, nor by the amount of N applied. Similar results were obtained for AURNY (not shown). The fact that AUR(N)Y was independent of the number of cuts (HD) confirms the conclusions of Van Burg et al. (1982), except that a decreasing AURY with an increase in amount of N applied was not confirmed in the present study.

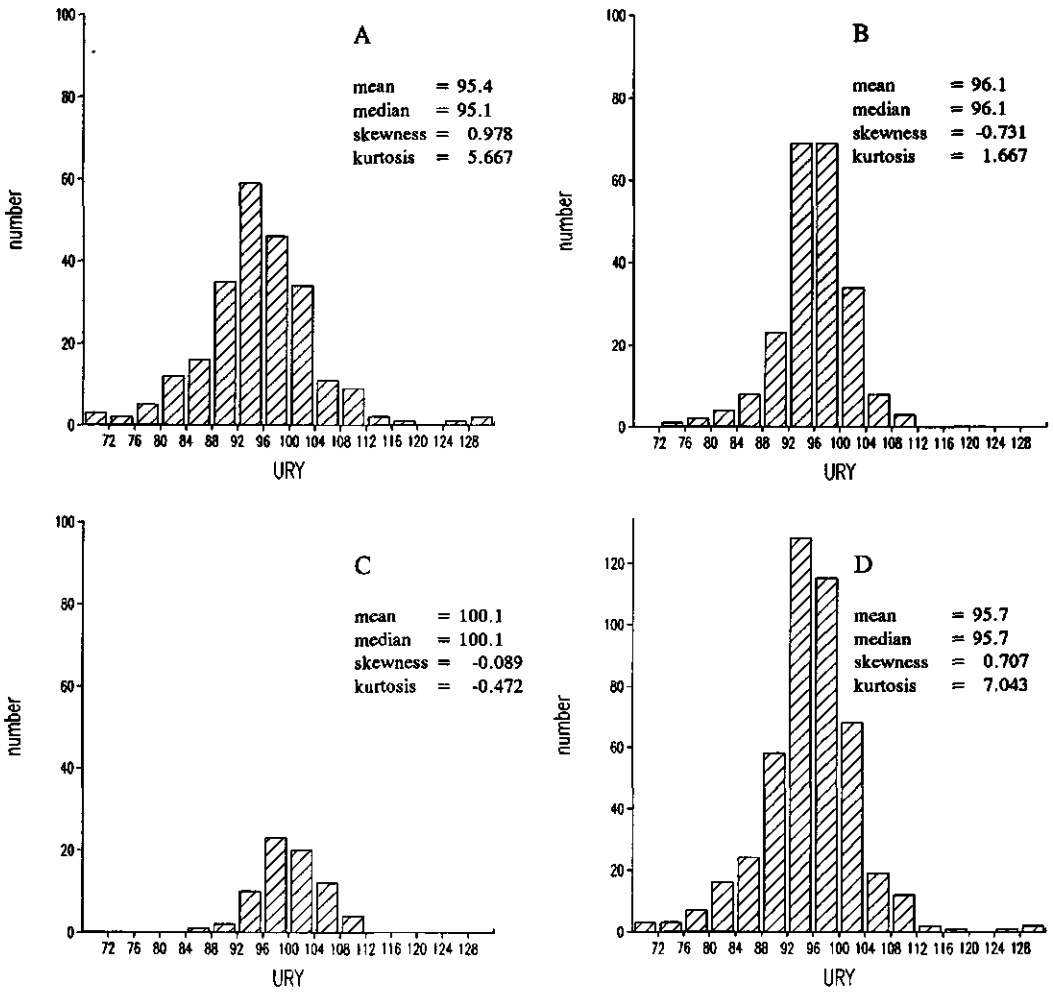


Figure 2. Frequency distribution of URY on sandy, clay, peat and sand + clay grassland of trials performed between 1954 and 1989 in NL.

Reducing Equation 4 to only the significant terms finally resulted in 'REML predictions' for the whole season for URY of 96%, for URNY of 93%, for AURY of 92% and for AURNY of 86%. All predictions were significantly different from 100% ($p < 0.001$). Because of the relative high DMY's and NY's at the control plots, UR(N)Y was markedly higher than AUR(N)Y.

NL data; effects of rainfall and temperature

Rainfall and temperature patterns during the trials may have contributed to the variation in URY. To test this, a more detailed analysis was performed based on Equation 5a. Data of the first cut and later cuts were separately analyzed, because of big differences in growing conditions. Analyses of DMY and NY response showed that best relationships with short-term weather conditions were obtained after fertilizer application for $R_x = R3$ and $T_x = T3$ and before fertilizer application for RB5 (cut 1) and RB7 (later cuts).

Results of the DMY response models (Table 3) indicate a significantly higher DMY with CAN than U for the first cut ($FT_{CAN} = 128 \text{ kg ha}^{-1} \text{ cut}^{-1}$) and for later cuts ($FT_{CAN} = 83 \text{ kg ha}^{-1} \text{ cut}^{-1}$), which is in agreement with our earlier analysis.

The DMY response of the first cut for U and CAN was positively related to tR , mT and negatively to $R3$ (Table 3). The DMY response of the later cuts was only related to short term weather conditions $R3$, $T3$ and $RB7$. The DMY response of first and later cuts showed no significant interactions between FT and weather conditions (i.e. $FT_{CAN} \cdot R3$).

NY response of the first cut showed significant interactions between FT and $R3$, $T3$ and $Nappl$, respectively (Table 3). An interaction between FT and $applN$ was not found with Equation 4 because all cuts were analyzed and weather parameters were not included. The summarized effects of these interactions (illustrated in Figure 3), show that AURNY decreases with $Nappl$, and increases with $R3$ and $T3$. In order to obtain an AURNY ≥ 100 , rainfall amounts of ≥ 6.0 and ≥ 12.5 mm are necessary for N rates of 60 and 100 kg ha^{-1} , respectively. These amounts of rainfall are not very common. The rainfall probability curve (Figure 3) shows that the chances of these amounts in spring is $\leq 22\%$ and $\leq 11\%$, respectively. At higher $Nappl$ the chances of obtaining an AURNY $\geq 100\%$ is even much lower than 10%.

For later cuts (Table 3), there were no interactions between FT and $R3$, $T3$ and $Nappl$ and it is predicted that use of U lowers N uptake with 5.9 kg ha^{-1} under all conditions.

NI data; effects of rainfall and temperature

Stevens et al. (1989) found a significant DMY difference between U and CAN in the first cut in only three out of the 120 fertilizer applications. Because of this, the current dataset was aggregated, by averaging the results per cut over three years and 10 application times to reduce the variance in the experiments. The reduced dataset (4 sites, 3 blocks and 2 cuts) was analyzed (Table 4). The second cut showed a significant difference from 100% for URY, AURY and AURNY. For both cuts it appeared that URY, AURY and AURNY increased together with the amount of rainfall (Table 4).

The effect of rainfall and temperature was tested in more detail by using Equation 5b for

Differences in rainfall and temperature

Table 3: DM yield (kg ha⁻¹ cut⁻¹) and N yield (kg ha⁻¹ cut⁻¹) response models for clay plus sand grassland of the first and later cuts for the NL dataset.

Model terms	DMY model			NY model		
	U	CAN	Se/Sed	U	CAN	Se/Sed
<u>Cut 1</u>						
Constant	-17163			-157.6	-161.7	
main effect	0	128	12.3	0	9.65	1.18
Nappl	3.705*		1.554	0.4233	0.5213	0.0360
R3	-8.43		5.75	-0.0007	-0.6114	0.2874
T3				1.526	0.5682	0.4854
mT	978.0		33.5		17.10	0.94
tR	2.973		1.682			
NoGD	116.4		9.6		1.011	0.059
NoGD ²	-0.558		0.0559			
Nappl.NoGD	0.1275		0.0314			
Nappl.tR	-0.0237		0.0101			
Rf5					0.6561	0.2849
Rf5 ²					-0.0198	0.0083
<u>Later cuts</u>						
Constant	4123			-22.41		
main effect	0	82.56	38	0	5.888	1.12
Nappl	7.86		0.8020		0.9272	0.0748
R3	-57.59		15.08		-0.1945	0.0735
R3 ²	-0.85		0.3228			
T3	-15.69		2.380		-0.1619	0.07062
tR						
NoGD	38.05		6.085		1.267	0.2443
NoGD ²	-1.81		0.3900			
Nappl ²	-0.0511		0.0087		-0.0022	0.0003
Nappl.NoGD					-0.0102	0.0024
Nappl.tR						
Nappl.R3	0.1747		0.0659			
NoGD.R3	1.956		0.4778			
Rf7	-8.380		2.713		0.1125	0.0714
Rf7 ²	-0.4071		0.1376		-0.0195	0.0038

DMY first cut: $\sigma_u^2 = 3.00E+5$, $\sigma_y^2 = 3.84E+5$ and $\sigma_{syr}^2 = 1.24E+5$; VC = 11.3%; n=323

DMY later cuts: $\sigma_u^2 = 2.21E+4$, $\sigma_y^2 = 7.31E+4$ and $\sigma_{syr}^2 = 1.35E+5$; VC=11.4%; n=380

NY first cut: $\sigma_u^2 = 175.9$, $\sigma_y^2 = 259.2$ and $\sigma_{syr}^2 = 68.9$; VC = 8.5%; n = 197

NY later cuts: $\sigma_u^2 = 139.8$, $\sigma_y^2 = 62.1$ and $\sigma_{syr}^2 = 118.1$; VC = 12.0%; n = 376

* identical values for U and CAN are placed between the U and CAN column.

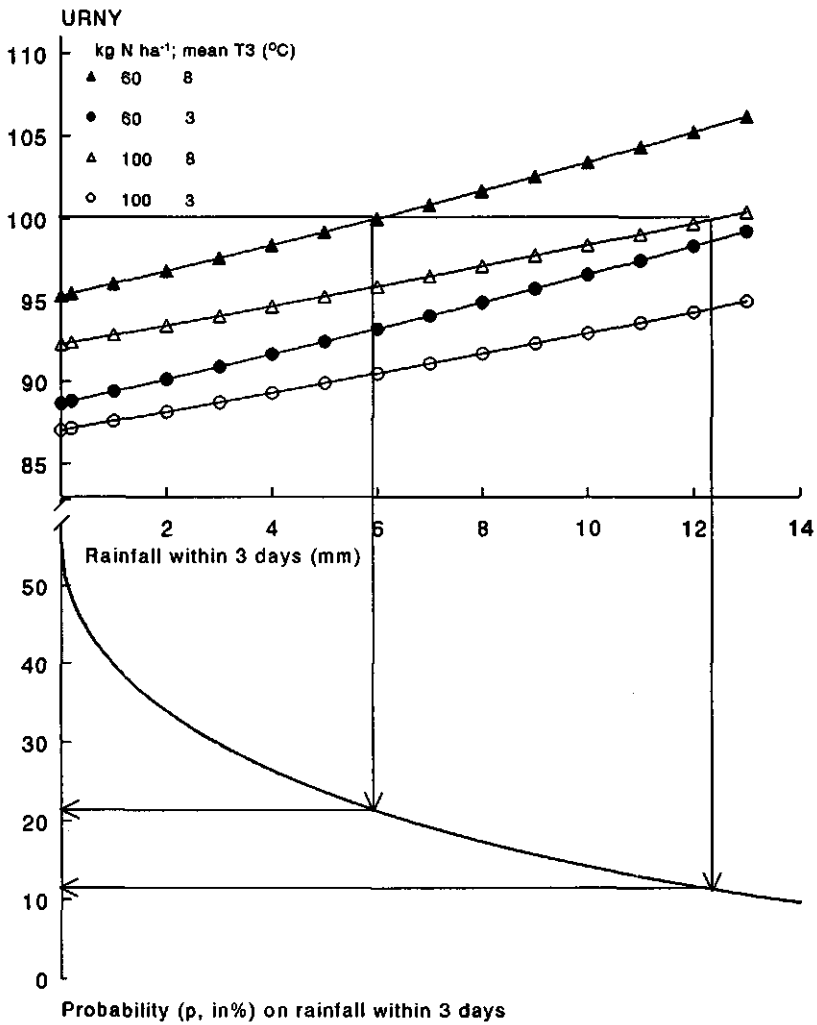


Figure 3. The effect of R3 for the first cut on AURNY for different NappI. In addition the probability of R3 greater or equal than the amount plotted on the X-axis (is shown on the lower Y-axis).

Table 4. The URY, AURY, AURNY and cumulative rainfall averaged over three years and 10 application times for the first and second cut of the NI experiment of Stevens et al. (1989).

Site	URY %	AURY %	AURNY %	Cumulative rainfall (mm)
<u>Cut 1</u>				<u>Feb, March and April</u>
S1 (Crossnacreevy)	102.9	104.4	100.5	192
S2 (Hillsborough)	98.9	96.7	95.6	186
S3 (Castle Archdale)	101.2	103.5	106.4	218
S4 (Greenmount)	98.5	96.6	95.0	182
Mean	100.1	100.2	99.5	
<u>Cut 2</u>				<u>May</u>
S1 (Crossnacreevy)	97.6	96.2	93.4	55
S2 (Hillsborough)	98.1	96.1	91.1	54
S3 (Castle Archdale)	101.3	103.6	102.5	63
S4 (Greenmount)	97.3	94.6	92.6	53
Mean	98.7*	97.4*	95.2**	

*, ** different from 100 at $p \leq 0.05$ and $p \leq 0.01$, respectively

the whole dataset. Analysis of DMY response of the first cut showed interactions between FT and Rx, Tx, NoGD and Rx.NoGD (Table 5). Short-term rainfall and temperature was best related to DMY response for Rx = R3 and Tx = T3. The difference in DMY and NY response between CAN and U is negatively related with T3 and R3.NoGD and positively with R3 and NoGD. The summarized effect of these interactions is illustrated in Figure 4.

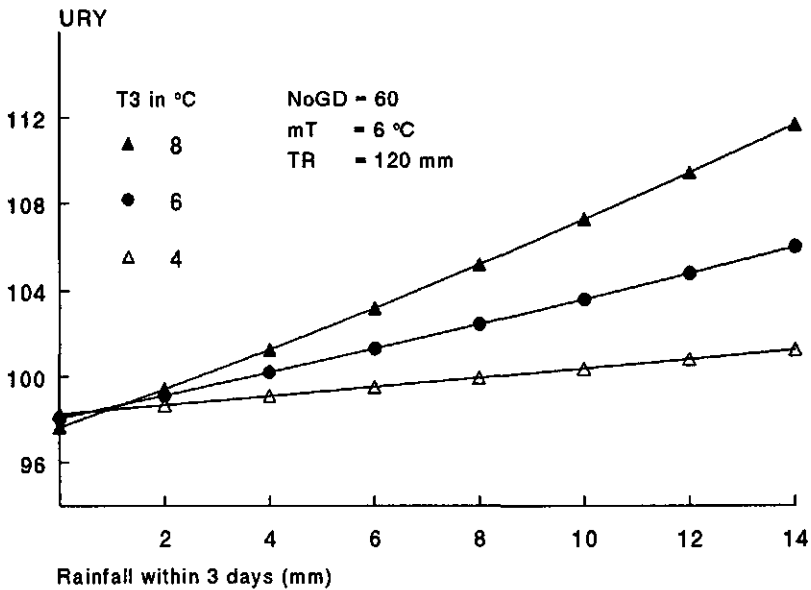
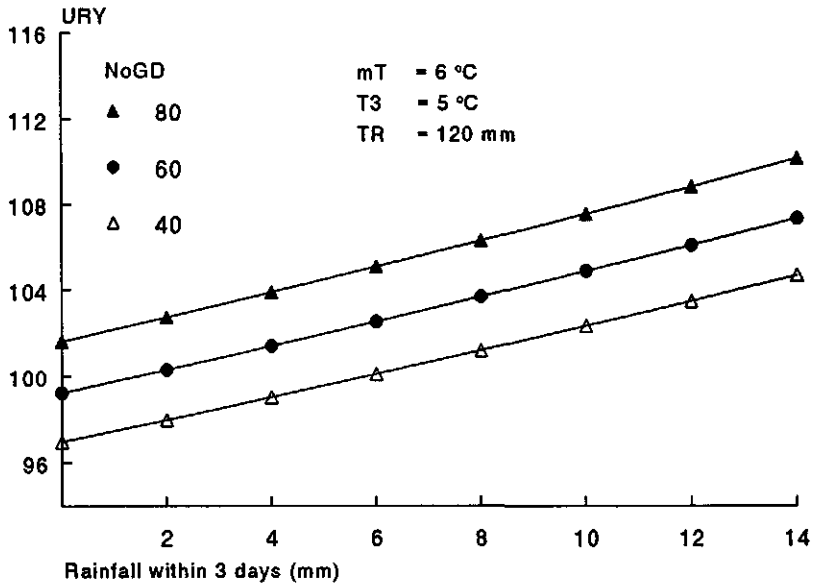


Figure 4. The effect of R3 on URY for varying NoGD, tR and mT in NI, using the results of Stevens et al. (1989).

Table 5. DM yield (kg ha⁻¹ cut⁻¹) and N yield response models of the first cut for the NI dataset of Stevens et al. (1989).

Model parameters	DMY model			NY model		
	U	CAN	Se/Sed	U	CAN	Se/Sed
Constant	-293.9	-137.5		19.27	14.51	
main effect	0	1.906	23.1	0	-0.1792	0.7338
R3	-0.3530	11.41	6.14	0.0653	0.3414	0.1951
T3	-1.825	-29.05	10.54	-0.3155	-1.106	0.3347
NoGD	50.28	50.76	1.49	0.8670	0.8778	0.0474
R3.NoGD	-0.0095	-0.4143	0.1322	-0.0014	-0.0125	0.0042
mT	160.8	27.3	3.976		0.865	
NoGD ²	-0.3791	0.0329	-0.0071		0.0010	

DMY: $\sigma_y^2 = 1.69E+5$, $\sigma_s^2 = 4.62E+5$, $\sigma_{sy}^2 = 3.05E+5$, $\sigma_{sb}^2 = 1.28E+4$, $\sigma_{ysb}^2 = 4.51E+3$ and $\sigma_{ysbr}^2 = 9.61E+4$; VC = 13.4%; n = 720
 NY: $\sigma_y^2 = 125$, $\sigma_s^2 = 485$, $\sigma_{sy}^2 = 114$, $\sigma_{sb}^2 = 18.3$, $\sigma_{ysb}^2 = 5.43$ and $\sigma_{ysbr}^2 = 96.9$; VC = 13.4%; n = 720

Table 6. DM yield (kg ha⁻¹) response models for the first and second cut of the En experiment of Peake (pers. comm.).

Model parameters	Cut 1			Cut 2		
	U	CAN	Se/Sed	U	CAN	Se/Sed
Constant	6543	6639		3429	3506	
main effect	0	-24.00	44.16	0	160.6	54.53
R3	-584.4	-595.1	6.7	86.67	72.92	7.59
Nappl		5.323	1.522		5.009	2.426
R3 ²		25.05	2.435		-4.74	2.882
ST _{silt-loam}					0	579.3*
ST _{sandy-loam}	-227		25.16*	-804.7		579.3*
ST _{loam}				670.6		579.3*
ST _{clay}	2680		25.16*	129.7		579.3*
ST _{sandy-clay-loam}	1893		25.16*	1070.1		579.3*
ST _{clay-loam}	0		25.16*	-796.7		579.3*
ST _{sandy-clay}				-188.0		579.3*
ST _{sandy-silt-loam}				741.8		579.3*

DMY cut 1: $\sigma_y^2 = 1.35E+4$, $\sigma_{yB}^2 = 1.898E+5$ and $\sigma_{ypB}^2 = 4.875E+4$; VC = 3.5% n = 100
 DMY cut 2: $\sigma_y^2 = 6.4E+3$, $\sigma_{yB}^2 = 6.257E+5$ and $\sigma_{ypB}^2 = 1.026E+5$; VC = 7.6%; n = 144

* average Sed

En data; effects of rainfall

The data of Peake (pers. comm.) showed a significant higher DMY with CAN than with U. Predicted URY for the first cut was 99.1% and for the second cut 94.8%. Predicted AURY for the first cut was 100.9% and for the second cut 91.1%. Using Equation 5c, we obtained a significant interaction between FT and R3 (Table 6). With U application, DMY increased by, respectively, 10.74 (\pm 6.68) and 13.75 (\pm 7.76) kg ha⁻¹ mm⁻¹ rainfall in the first and second cut, respectively, compared with CAN. Including STY in the model gave a significant improvement, because DMY differed significantly between the STY's.

Combined data of NL, NI and En

The analysis thus far showed that agronomic U efficiency increased with short-term rainfall and decreased with short-term temperature after fertilizer application. If rainfall and temperature patterns in NL, NI and En are different, then mean (A)UR(N)Y are different too in these countries. Aggregation of recorded R3 and T3 data in NL, NI and En clearly showed systematic mean differences (Table 7). In NL, low AUR(N)Y were found together with relatively low R3 and T3 in the first cut, and relatively large R3 and T3 in later cuts. Apparently, the increased R3 (which suppresses NH₃ volatilization) in later cuts was counteracted by the increase in T3 (which enhances NH₃ volatilization). In NI, a relatively

Table 7. The average AURY, AURNY and the average amount of rainfall and average temperature within three days after fertilizer application (R3,T3) in NL, NI and En.

Cut	AURY %	AURNY %	R3 (mm)	T3 °C	3 day periods without rain, (%)
Netherlands					
First	92.3	86.4	3.63	4.67	15.6
Later	92.3	86.4	8.90	14.21	24.4
Northern Ireland					
First	100.2	99.5	7.38	6.4	23.3
Second	97.3	95.2	7.42	9.1	16.7
En					
First	100.9	- ¹	8.94	-	10.0
Second	91.1	-	5.70	-	21.7

1) no data available

large AURY was combined with relatively large R3 and modest T3 in the first cut. In the second cut mean T3 was higher, which resulted in a decrease in AUR(N)Y. High temperatures and little rainfall promote NH₃ volatilization from U and reduce N losses through denitrification and NO₃ leaching from (C)AN. Both counteracting processes lead to low AUR(N)Y.

Combining all trials and all cuts leads to the following relationships between AUR(N)Y and R3 and T3:

$$\text{AURY} = 89.48 (\pm 0.781) + 2.188 (\pm 0.148) * \text{R3} - 1.091 (\pm 0.070) * \text{T3} \quad (R^2_{\text{adj}} = 98.9\%) \quad (6)$$

$$\text{AURNY} = 81.72 (\pm 1.93) + 3.665 (\pm 0.366) * \text{R3} - 1.815 (\pm 0.219) * \text{T3} \quad (R^2_{\text{adj}} = 97.6\%) \quad (7)$$

These relationships clearly indicate that rainfall and temperature define the agronomic efficiency of U in a similar way in NL, NI and En.

ECONOMIC EVALUATION OF THE USE OF (C)AN AND U

The farmer's choice of the amount and type of N fertilizer to be used on grassland is an economic decision; he wants to maximize the difference between the harvesting value (product quality in combination with yield) of herbage and the costs of fertilizer input. To facilitate decision analysis, we developed an empirical relationship to predict the profitability of U use. This relationship is based on Equation 6, but includes also the effect on soil acidification of U use, relative to CAN use:

$$U_p = \text{CAN}_p + \text{DM}_p * (\text{DMY}_{\text{fert}} - \text{DMY}_{\text{0N}}) * (0.8948 + 0.02188 * \text{R3} - 0.01091 * \text{T3}) / \text{Nappl} + (-2.94 + 1 / (\text{fraction of N contained in CAN})) * \text{lime}_p \quad (8)$$

with:

- U_p, CAN_p and DM_p are the prices of U, CAN and DM (Dfl. kg⁻¹ N) respectively.
- DMY_{fert} - DMY_{0N} is the DMY difference between the fertilized and the 0N plot (kg DM ha⁻¹)
- lime_p is the price of the limestone contained in CAN (Dfl. kg⁻¹)

CAN contains limestone, which is valued in Equation 8. Furthermore, it is possible to value the differences in NH₃ volatilization, N₂O emission and NO₃ leaching. These losses are unwanted. In future, farmers could be charged for these losses, if data are available.

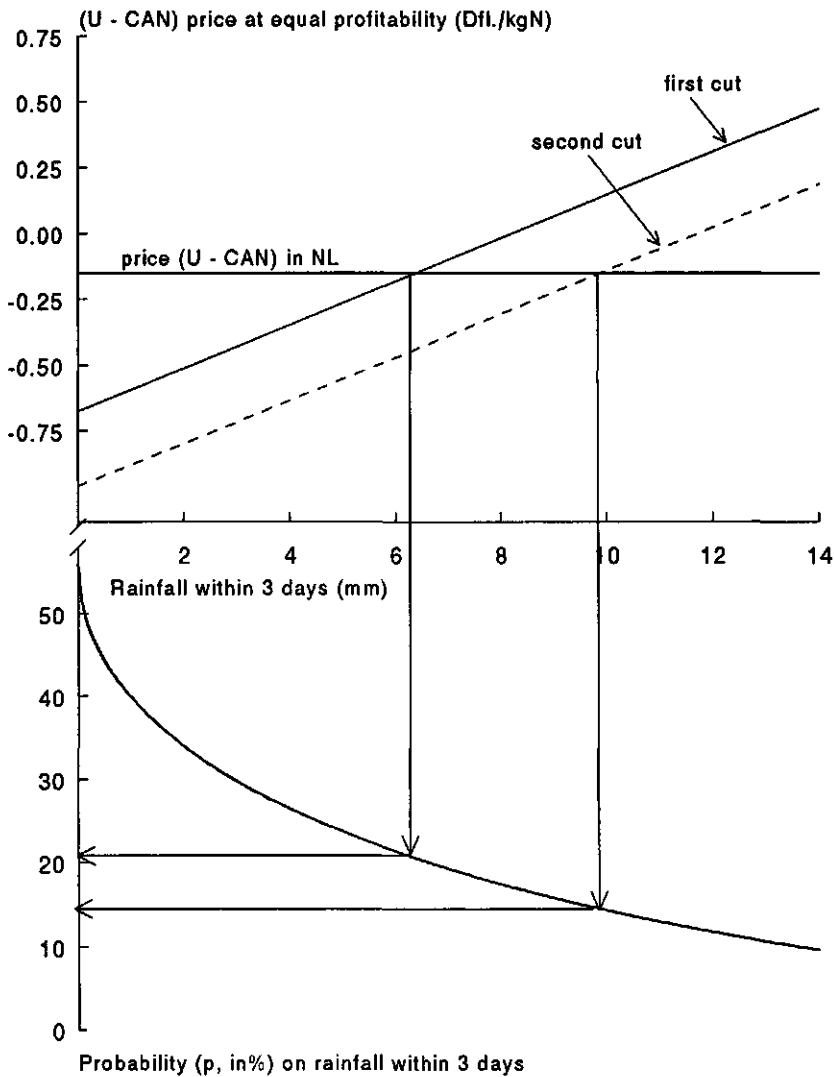


Figure 5. The effect of R3 on the price difference needed between U and CAN to obtain equal profits for different temperatures, based on NL and NI data.

However, at present there is not much evidence that fertilizer type affects N losses, let alone quantified estimates as a function of rainfall and temperature.

Examples of Equation 8 are shown in Figure 5. The calculations have been performed for DMY_{fert} and DMY_{ON} of 3000 and 1500 kg ha⁻¹ cut⁻¹, respectively, in the first cut ($T3 =$

5°C) and second cut ($T3 = 12^{\circ}\text{C}$). In NL one kg herbage DM has a value of Dfl. 0.20 and U is about Dfl. $0.15 \text{ kg}^{-1} \text{ N}$ cheaper than CAN (27%) (Anonymous, 1996). Figure 5 indicates that R3 must exceed 6 mm and 9.5 mm for the first and second cut, respectively, to obtain equal profits for U and CAN. In NL the probability of $R3 > 6 \text{ mm}$ and $R3 > 9.5 \text{ mm}$ is 20% and 16% for the first and second cuts, respectively, indicating that use of U for the first and second is only profitable once every 5 and 7 years, respectively. Assuming that the R3 values in Table 7 for NI and En are representative for the whole of NI and En, then usage of U is profitable for the first cut, because R3 is $> 6 \text{ mm}$ (Figure 5). For later cuts it is generally not profitable to use U. Of course there are differences within a country in rainfall and temperature pattern during spring. Improving the rainfall probability curve by using data of a local weather stations will greatly improve the accuracy of the predictions with Equation 8.

DISCUSSION

Effects of rainfall and temperature

Straightforward analysis of NL, NI and En data showed that rainfall and temperature have a marked and uniform effect on the agronomic U efficiency. These results confirm other findings (e.g. Black et al., 1987; Herlihy and O' Keeffe, 1988; Lloyd, 1992; Mahli, 1995; Van Burg et al., 1982; Watson et al., 1990). Thus far, however, no link had made to the fact that rainfall and temperature patterns also determine the differences in observed efficiencies between countries. Our study clearly shows that rainfall and temperature not only define (A)UR(N)Y in field trials within a country but also the observed differences in the use of fertilizer types between countries. Therefore, the conclusion of Watson et al. (1990) that U is generally as good as CAN early in the growing season, but less-effective in summer for NW-Europe conditions is too strict.

No significant increase of (A)UR(N)Y over the last 35 yrs was observed (Table 2). Such an increase might have occurred because of changes in grassland management, fertilizer granule quality and or variations in weather conditions. Data of 30-40 years of fertilizer trials are useful to test this provided the management of the trials is similar during the years. This was the case and was confirmed by statistical analysis. Improving fertilizer granule technology in the last decades (Anonymous, 1979), has resulted into more equal and less caking granules. This contributes to a better distribution of fertilizer on farms, but will hardly affect the distribution of fertilizer in trials with small plots and effects will therefore not be demonstrated.

For example, average R3 was 4.9, 5.3 and 7.7 mm and average T3 was 5.6, 10.5 and

13.5 °C during the periods 1954-1967, 1970-1973 and 1987-1989, respectively. Using Equation 6 this would give a mean AURY of 94, 89 and 91%, respectively, roughly the same variation as in Table 2.

We may conclude that (A)UR(N)Y values are similar in NL and UK where there are similar rainfall and temperature patterns. Variations in AURY between countries, during the season or between seasons can be mainly explained by these two variables.

Other important factors that may effect U efficiency

Van Burg et al. (1982) and Chaney and Paulson (1988) showed that UEF and URY decreased with Nappl increased, especially at high Nappl. Van Burg et al. (1982) found UEF's of 0.85 and 0.75 for Nappl of 70 and 140 kg N ha⁻¹, respectively. Lloyd (1992) found similar DMY increases per kg N applied with 80-160 kg N ha⁻¹. We found the same in our analysis. This suggests that URY decreases at high Nappl. Average Nappl for the first cut and later cuts was 110 and 80 kg ha⁻¹ in NL and 70 and 50 kg ha⁻¹ in NI. Nowadays, Nappl for the first cut and later cuts is decreasing and seldom exceeds 100 kg ha⁻¹. This may contribute to an improvement in U efficiency.

Results of Chaney and Paulson (1988) and Lloyd (1992) suggest that agronomic U effectiveness is different on calcareous compared with non-calcareous soils. The difference suggests that N losses from U through NH₃ volatilization are involved (ECETOC, 1994). The higher agronomic effectiveness on peat soils compared to sand and clay soils may be due to a combination of low NH₃ volatilization from U and relatively large N losses from CAN through denitrification. Peat soils are wet and this favors the dissolution and diffusion transport of U into the soil, thereby reducing the risk of NH₃ volatilization. Wet soil conditions also promote denitrification, thereby reducing the amount of NO₃-N from CAN. As a consequence, CAN-N derived emissions of N₂O, an intermediate component in both denitrification and nitrification processes, are much larger on peat soils than on sand and clay soils (Velthof et al., 1996). Denitrification measurements in NI by Jordan (1989) gave also much higher N losses from CAN than from U, especially under wet conditions. Data on peat soils should therefore be analyzed separately.

The form of N in fertilizers may also affect the efficiency of N fertilizers. Uptake of U by the crop is lower than the absorption of ammonium and nitrate (Bradley et al., 1989). Within a few days (even at low temperatures) U is hydrolyzed to ammonium (Gillman et al., 1995). Then the main N forms present in U and CAN fertilized soil are ammonium and ammonium nitrate, respectively. Perennial ryegrass uses nitrate-N more effectively than ammonium-N in DM production (Watson, 1988) and yields are highest when a mixture of nitrate and ammonium is supplied (Haynes, 1986). This suggests that a lower uptake efficiency in addition to N losses via NH₃ volatilization may be therefore one of the reasons

for the observed lower attainable maximum yield with U than with CAN (Van Burg et al., 1982; Watson et al., 1990).

Choice of fertilizer

With Equation 8 we obtained a simple decision support equation for farmers to enable them to choose between U and CAN, for spring application on grassland. In addition, the decision which N fertilizer to apply may also depend on the storage capacity at the farm. U requires less storage capacity than CAN because of its higher N content. Furthermore the cost of transportation from the retailer to the farmer may be lower for U than for CAN when distances are large. Equation 8 may therefore require some adaptations, depending on local circumstances.

ACKNOWLEDGEMENTS

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CHAPTER 7

AMMONIA VOLATILIZATION FROM NITRIC-ACID-TREATED CATTLE SLURRY SURFACE APPLIED TO GRASSLAND

By: D.W. Bussink, J.F.M. Huijsmans and J.J.M.H. Ketelaars. 1994. *Netherlands Journal of Agricultural Science* 42-4, 293-309

AMMONIA VOLATILIZATION FROM NITRIC-ACID-TREATED CATTLE SLURRY SURFACE APPLIED TO GRASSLAND

ABSTRACT

Much research is being done to lower NH_3 volatilization from animal manure. In this study, reduction in NH_3 loss from HNO_3 treated cattle slurry, surface applied to grassland, was measured on different soil types throughout the Netherlands from 1989 to 1992. In total, 13 micro-meteorological mass balance and 10 small wind tunnel experiments were carried out. Amounts varying between 7-17 and 10-30 $\text{m}^3 \text{ha}^{-1}$ were applied, respectively. Measurements were performed for 4 and 10 days, respectively. The pH of treated slurry ranged from 3.9 to 6.6. Acidified slurry was always compared with untreated slurry.

A mean total of 60% (range: 29-98%) of the $\text{NH}_4\text{-N}$ from untreated slurry was volatilized in the mass balance experiments. A reduction in NH_3 volatilization of 85, 72 and 55% was achieved for acidified slurry with a respective pH of c. 4.5, 5.0 and 6.0. Approximately 55% (range: 7-91%) of the total loss from acidified slurry was measured on the day of application. A mean total of 66% (range: 21-90%) of $\text{NH}_4\text{-N}$ from untreated slurry volatilized in the tunnel experiments. The reduction in NH_3 volatilization was 73% for slurry with pH 4.5. Approximately 27% (range: 6-91%) of the total loss from acidified slurry was measured on the first day. The lower reduction and the different pattern in NH_3 volatilization observed in the wind tunnel experiments might be the consequence of different climatic conditions in and outside the tunnels or they might be related to the higher rates of slurry application in these experiments.

Regression analysis indicated that high temperature, slurry pH, potential water evaporation and NH_4^+ concentration stimulated NH_3 loss in the mass balance experiments ($R^2=87\%$). It is suggested that the results obtained with acidified slurry were independent of the grassland soil type at the application levels employed.

INTRODUCTION

Livestock excreta are generally regarded as the main source of NH_3 input into the atmosphere (Apsimon et al., 1987; Schlesinger and Hartley, 1992). Losses may arise from grazing, housed livestock, slurry storage units and (surface) applied slurry. In Europe the largest losses are considered to result from surface applied slurry (Buijsman et al., 1987); ranging between 20 to 85% of the $\text{NH}_4^+\text{-N}$ applied (Bless et al. 1991; Pain et

al. 1989; Sommer et al., 1991). The large variation is due to differences in soil type, amount and composition of slurry (Sommer and Olesen, 1991) and environmental conditions (Horlacher and Marschner, 1990; Sommer et al., 1991).

Decreasing NH_3 losses will improve the N fertilizer value of land-applied slurry and decrease the impact of NH_3 on eutrophication and acid deposition (Roelofs et al., 1985). Slurry injection and soil tillage immediately after surface application on arable land (; Bless et al., 1991; Horlacher and Marschner, 1990; Mulder and Huijsmans, 1994; Van der Molen et al., 1990a) and slurry injection on grassland (Bussink and Bruins, 1992; Mulder and Huijsmans, 1994; Thompson et al., 1987; Van der Meer et al., 1987) proved to be efficient methods in reducing NH_3 losses. Because of the heavy application machinery and high draft requirement, injection on grassland is limited to light stone-free soils with a high bearing capacity. Under such conditions dilution of slurry or water irrigation after surface application (Bussink and Bruins, 1992; Sommer and Olesen, 1991) and band-spreading (Mulder and Huijsmans, 1994) are useful techniques.

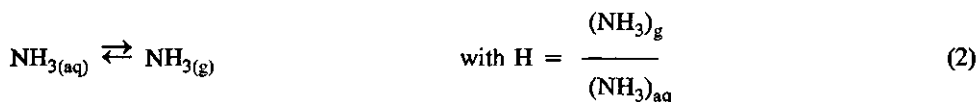
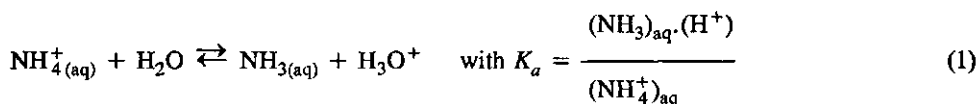
Acidification of slurry has also shown great potential in reducing of NH_3 losses (Frost et al., 1990; Pain et al., 1990; Stevens et al., 1989b). A key factor in the reduction of NH_3 losses is slurry pH at application (Stevens et al., 1992).

In the Netherlands much research has been done with respect to NH_3 loss reducing potential, the technical implementation in practice, the economics and the environmental aspects of nitric-acid-treated cattle slurry. This study examines the NH_3 losses from acidified cattle slurry surface-applied on grassland. Nitric acid (HNO_3) was chosen because the anion is a valuable plant nutrient and by varying the amount of HNO_3 applied it is possible to meet the total N demand of grass. However, this will lead to variations in slurry pH and thus in NH_3 losses. Therefore the main emphasis was placed on the effect of slurry pH and NH_4^+ activity on NH_3 volatilization and on changes in slurry pH after application. Results from 4 years of experimentation, using the micro-meteorological mass balance method and small wind tunnels at various sites and environmental conditions are described. The results were used to predict pH requirement for target volatilization reduction levels.

MATERIALS AND METHODS

Theory of NH_3 volatilization

Up to 80% of the mineral N in slurry originates from urea, which rapidly hydrolyses into $(\text{NH}_4)_2\text{CO}_3$. The NH_4^+ in the slurry is in equilibrium with NH_3 in the liquid and gas phases according to:



where $(\cdot)_{\text{aq}}$ and $(\cdot)_{\text{g}}$ are the activity (M) of the species in solution and in air, respectively; K_a is the dissociation constant (M) and H is the Henry constant (M M^{-1}). K_a and H are temperature (T , °C) dependent. Using the temperature corrections of Emerson et al. (1975) for K_a and of Dasgupta and Dong (1985) for $H/RT = K_h$ (M atm^{-1} , with $\text{atm} = 1.103 \times 10^5 \text{ Pa}$) and rewriting Equations (1) and (2) gives:

$$(\text{NH}_3)_{\text{g}} = \frac{K_a(\text{NH}_4^+)_{\text{aq}}}{K_h(\text{H}^+)} = (\text{NH}_4^+)_{\text{aq}} 10^{(4.117 + \text{pH} - 4507.053/(T + 273.15))} \quad (3)$$

By lowering the pH of the solution $(\text{NH}_3)_{\text{g}}$ decreases and thereby so does the potential for NH_3 losses. The relationship between $(\text{NH}_3)_{\text{g}}$, pH and T is shown in Figure. 1. For a slurry of average ionic strength (I) of 0.3 M and 2.2 kg $\text{NH}_4\text{-N m}^{-3}$, $(\text{NH}_4^+)_{\text{aq}}$ is 0.108 M (Vanysek, 1989), neglecting adsorption and complex formation. Lowering the pH from 7.5 to 4.5 gives a sharp decrease in $(\text{NH}_3)_{\text{g}}$ to values below background level in the atmosphere i.e. 5-25 $\mu\text{g NH}_3\text{-N m}^{-3}$ in our experiment. Due to water evaporation, I and $(\text{NH}_4^+)_{\text{aq}}$ will increase. At a relative humidity of 75%, the osmotic pressure of the slurry will rise to -38 MPa before evaporation ceases (calculated according to Koorevaar et al. 1983). This agrees with $I = 8.0 \text{ M}$, assuming a complete dissolution of the salts. As a consequence $(\text{NH}_4^+)_{\text{aq}}$ and $(\text{NH}_3)_{\text{g}}$ increase and, hence, NH_3 is released (Figure 1). In theory due to evaporation, there may be NH_3 volatilization at pH values as low as 4.5.

Description of sites and experimental treatments

Two separate data sets were available to analyse the effects of slurry acidification. One set of volatilization data had been obtained using the micro-meteorological mass balance method (Denmead, 1983) the other set using wind tunnel measurements (Lockyer, 1984).

All data originated from field experiments carried out at 5 sites, on clay (loam) soils near Swifterbant and Duiven, peat soil in Zegveld and sandy soils in Luttenberg and Wageningen. The location and soil characteristics of the sites are shown in Table 1. The

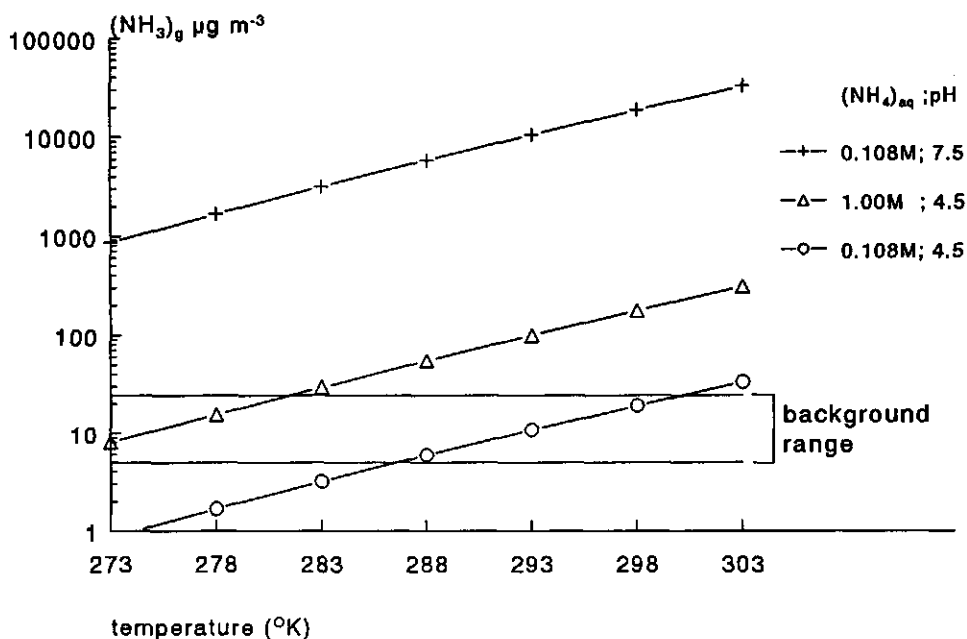


Figure 1. Equilibrium $(\text{NH}_3)_g$ concentration in air for a solution with NH_4^+ activity, (NH_4^+) of 0.108 and 1.0 M at different temperatures and solution pH's (1.0 M as example of the effect of water evaporation); background $(\text{NH}_3)_g$ range from 5 to 25 $\mu\text{g m}^{-3}$.

well established swards contained perennial ryegrass as dominant grass species and had been intensively managed in previous years. In all experiments untreated cattle slurry was compared with HNO_3 treated cattle slurry at similar levels of slurry application. Wind speed, air temperature at 1.5 m, humidity and sunshine duration and radiation were recorded on all sites. Water evaporation data for the sites were obtained from the meteorological office.

In the experiments using the mass balance method, slurry was surface applied before noon using a tanker fitted with a splash plate. Working width varied between 2.5 and 8 m. By spreading in parallel passes varying in length over a pre-marked area, circular plots were achieved with a radius varying between 20 and 24 m. The pH of the acidified slurry ranged from 3.9 to 6.6.

In the experiments using small wind tunnels slurry was applied with a watering can. The pH of the acidified slurry was c. 4.5.

Table 1. Location of the sites and characteristics of the 0-5 cm soil layer.

	Location		Soil type	pH-KCl	CEC mol _c kg ⁻¹	Organic matter %	CaCO ₃ %	Clay < 2μm %
	longitude	latitude						
Zegveld	4 52'	52 07'	peat	4.9	0.24	45.1	0	-
Luttenberg	6 21'	52 23'	sand	5.3	-	5.7	0	-
Duiven	6 01'	51 56'	heavy clay	5.2	-	13.7	0	44
Wageningen	5 40'	51 59'	sand	5.0	0.04	3.2	0	-
Swifterbant	5 40'	52 35'	loam	6.9	0.28	8.1*	6.4	18

* corrected for CaCO₃

Measurement of NH₃ losses by mass balance

The micro-meteorological mass balance method assumes that the vertically integrated product of wind speed and the difference in air-NH₃ concentration, between the centre and boundary of the plot, divided by the fetch (distance between upwind boundary and the centre of the plot) is equal to the NH₃ flux from the soil surface (Denmead, 1983).

As soon as the first half of the circular plots was covered with slurry (usually within 5 minutes) a mast supporting 7 to 8 NH₃ traps at heights between 0.25 and 3.30 m was placed in the centre of the plot. At the windward boundary of the plot, a mast was placed with 5 NH₃ traps at heights between 0.40 and 2.30 m. Fewer traps were placed at the boundary because the background concentration was low and essentially uniform with height. Each trap contained 20 ml 0.02 M H₃PO₄ or 0.02 M HNO₃ held in 100 ml collection tubes. Air was drawn through the acid via a sintered gas dispersion tube at rates of 2-4 l min⁻¹, measured with flow meters. A correction was made for the measured pressure drop between the flow meter and the air inlet of the trap.

The measurements continued for at least 4 days after slurry application. Traps were replaced five times in the first 24 h when the highest NH₃ loss rates occurred. From day 2 to day 4 the traps were replaced in early morning and late afternoon. Wind speed was measured on a mast outside the plot, at six different heights, between 0.40 and 3.30 m. A total of 13 experiments were conducted (see Table 2 for details).

Table 2. Slurry composition and measured NH_3 volatilization on grassland using the mass balance method. (In experiments 11-13 slurry was acidified immediately prior to application.)

Experiment nr.	Date	Soil type	Slurry composition			Amount $\text{NH}_3\text{-N}$ loss			Reduction by acidification	T		Rainfall			
			pH	DM %	$\text{NH}_4\text{-N}$ kg m^{-3}	applied $\text{m}^3 \text{ha}^{-1}$	% of $\text{NH}_4\text{-N}$ applied	% of 1st day loss		1st day $^{\circ}\text{C}$	2nd day $^{\circ}\text{C}$	1st day mm	2nd day mm		
1.	16-3-89	7	clay	7.5	-	2.7	10.0	28.5	98	99	4.5	3.3	3.0	7.1	
				4.5	-	3.3	10.0	0.4	91						
2.	19-6-89	5	sand	7.5	-	3.0	10.0	97.9	89	87	21.9	21.1	0.0	0.0	
				5.1	-	2.1	10.0	12.5	20						
3.	20-3-90	5	clay	7.3	8.0	2.3	6.5	42.3	95	94	13.0	10.7	2.5	0.5	
				3.9	11.2	2.2	7.0	2.6	8						
4.	24-4-90	4	peat	7.5	7.3	2.2	10.2	58.3	92	81	12.2	12.4	0.0	0.0	
				4.5	11.1	1.7	9.0	11.1	50						
5.	29-5-90	4	peat	7.1	8.3	2.3	9.8	44.2	87	69	12.3	15.1	0.0	0.0	
				4.6	11.6	1.7	8.1	13.5	29						
6.	12-6-90	4	sand	7.2	8.3	2.3	9.9	33.9	88	99	12.0	12.4	0.0	0.0	
				4.3	9.7	1.7	8.7	0.2	60						
7.	26-6-90	4	sand	7.4	8.3	2.3	9.8	51.1	98	86	19.2	19.7	0.0	20	
				4.3	8.8	1.7	8.6	7.0	90						
8.	28-8-90	4	peat	7.1	7.3	2.0	12.7	52.0	72	87	20.3	22.8	0.0	0.0	
				4.4	8.1	1.3	13.2	7.0	7						
9.	4-9-90	4	peat	7.4	7.6	2.3	9.6	49.7	91	73	15.7	13.9	0.0	0.0	
				4.5	8.1	1.4	8.2	13.2	59						
10.	11-9-90	4	peat	7.3	7.3	2.1	8.7	58.1	85	65	13.5	13.9	2.2	0.4	
				5.0	8.1	1.5	7.7	20.4	35						
11. ¹	16-7-91	10	heavy clay	7.0	7.2	1.5	9.8	96.7	85	52	16.4	16.9	0.0	0.0	
				6.0	7.5	1.6	10.1	46.5	73		51				
				5.8	7.6	1.3	10.3	47.8	62						
12. ¹	10-3-92	3	heavy clay	4.9	7.9	1.4	10.2	20.6	50	79					
				7.4	6.6	2.1	17.3	85.8	96		29	7.4	5.9	0.0	2.1
				6.6	6.7	2.2	14.9	60.5	84						
13. ¹	19-5-92	10	heavy clay	6.3	7.0	2.2	16.7	29.5	79	84					
				5.8	7.3	2.3	15.1	13.5	65						
				6.8	8.7	2.0	11.6	88.9	93		48	19.1	18.8	0.0	0.0
				5.7	9.1	2.2	13.0	46.1	60						
				5.6	9.3	2.3	12.0	41.3	77			54			
5.2	9.6	2.4	15.8	38.0	62	57									

Measurement of NH_3 losses by wind tunnels

The design of the small wind tunnels followed essentially the description by Lockyer (1984). A U-shaped transparent tunnel of polycarbonate covers an experimental plot (2.0 x 0.5 m). The tunnel is connected to a circular steel duct housing an electrically powered fan. In principle the method consists of sampling a controlled airflow (generated by the fan) before and after it passes over the experimental plot in the tunnel. The difference in concentration between inlet and outlet multiplied by the airflow and corrected for the experimental area is

equal to the NH₃ flux for a certain measurement period.

The NH₃ concentrations in inlet and outlet of the tunnel were measured by drawing air continuously via a sintered gas dispersion tube at a rate of 13 l min⁻¹ through 0.3 M H₃PO₄ held in 100 ml collection tubes. These traps were usually replaced on a 24 h basis during a 10-day measurement period. Air passed through the tunnel at rates of 2 m s⁻¹ in two experiments and 1 m s⁻¹ in the other eight experiments (see Table 3 for details).

Table 3. Slurry composition and the measured NH₃ volatilization on pasture using wind tunnels.

Experiment nr.	date	Measurement days	Soil type	Slurry composition			Amount applied m ³ ha ⁻¹	NH ₃ -N losses		Reduction by acidification %	T		Cumulative potential evaporation mm
				pH	DM %	NH ₄ -N kg m ⁻³		% of NH ₄ -N applied	of 1st day % of total loss		1th day °C	2nd day °C	
1.	16-3-89	7	clay	7.5	-	2.7	14.8	21	94		4.5	3.3	
				4.5	-	3.3	10.6	1.5	16	93			
2.	26-6-89	5	sand	7.5	-	3.0	10.2	82	63		13.0	10.7	
				5.1	-	2.1	9.9	9	91	89			
3.	26-3-91	10	sand	6.8	10.8	2.5	22	90	57		6.6	8.3	18.4
				4.5	-	2.5	22	3	81	97			
4.	16-4-91	10	sand	6.8	10.8	2.5	22	75	45		5.9	5.1	20.4
				4.5	-	2.5	22	8	11	89			
5.	2-4-91	10	sand	6.8	10.8	2.5	30	59	44		7.7	7.5	21.3
				4.5	-	2.5	30	30	6	49			
6.	14-5-91	10	sand	6.8	10.8	2.5	22	75	50		10.2	7.1	26.3
				4.5	-	2.5	22	30	15	60			
7.	28-5-91	10	sand	6.8	10.8	2.5	30	60	51		11.1	13.2	26.8
				4.5	-	2.5	30	33	12	46			
8.	11-6-91	10	sand	6.8	10.8	2.5	30	74	59		14.2	14.1	21.9
				4.5	-	2.5	30	14	20	82			
9.	25-6-91	10	sand	6.8	10.8	2.5	30	62	52		17.4	15.9	29.1
				4.5	-	2.5	30	15	8	75			
10.	9-7-91	10	sand	6.8	10.8	2.5	30	58	61		15.5	19.4	29.3
				4.5	-	2.5	30	20	7	65			

Analytical methods

The NH₄⁺ concentration in the H₃PO₄ solutions was measured colorometrically (Weatherburn, 1967; Bietz, 1974), whereas ion-chromatography was used for analysis of the NH₄⁺ concentration in the 0.02 M HNO₃ solution.

In the mass balance experiments 12 and 13 and in the tunnel experiments 4, 6, 8 and 10 slurry surface pH was measured after application using a flat-surface combined glass electrode after moistening the slurry with dionized water. Per plot three readings were obtained during the course of the experiment.

RESULTS

NH₃ losses from untreated slurry

The mass balance measurements showed a high NH₃ loss rate from untreated slurry during the first hours after application (Figure 2). The average total NH₃ loss was 60% (range: 29-98%) of the NH₄-N applied at an average slurry application of 10.4 (range: 6.5-17.3) m³ ha⁻¹ (Table 2). On average 90% (range: 72-98%) of the total losses were measured on the first day after application. One day after application the rate of loss decreased sharply.

Results obtained with the tunnel method were comparable to those obtained with the mass balance method. Total average loss was 66% (range: 21-90%) of the NH₄-N applied (Table 3) at an average slurry application of 24.1 (range: 9.9-30) m³ ha⁻¹. On average 60% (range: 44-94%) of the total NH₃ loss was measured on the first day. Hence, volatilization continued longer in the tunnel than in the mass balance experiments (e.g. Figures 2 and 3).

NH₃ losses from acidified slurry

The mass balance experiments gave a reduction in NH₃ volatilization for acidified slurry of 29 up to 99% of that found with untreated slurry. Ammonia volatilization was strongly related to slurry pH (Table. 2). A mean reduction in NH₃ volatilization of 85, 72 and 55% was achieved for acidified slurry with a respective pH of c. 4.5, 5.0 and 6.0.

The NH₃ loss from acidified slurry was very low in the first hours after application, but increased later. On average, 55% (range: 7-91%) of the total NH₃ loss was measured on the first day with application rates averaging 10.8 (range: 7.0-16.7) m³ ha⁻¹. The percentage of NH₄-N volatilized (%NH₄-loss) on the first day was strongly related to initial (NH₃)_g (Equation 3; using the initial slurry pH, the average temperature of the first day at 1.5 m and using the initial NH₄⁺ concentration instead of NH₄⁺ activity) and soil type according to:

$$\%NH_4\text{-loss} = 5.42 (\pm 0.77) * 10^7 (NH_3)_g + 4.25 (\pm 2.03) * \text{peat} + 10.44 (\pm 2.74) * (\text{heavy clay}) \quad (4)$$

with: R²_{adj} = 90.5 % and n=19 (all treated slurries of Table 2)

It was tested that clay and sandy soil did not differ from each other. Peat and heavy clay showed higher volatilization rates for the same (NH₃)_g than clay and sandy soil.

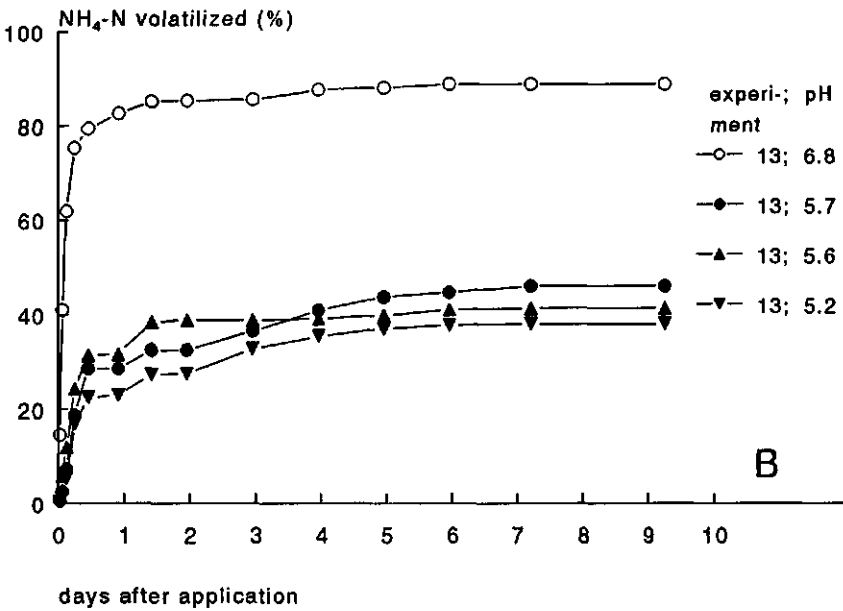
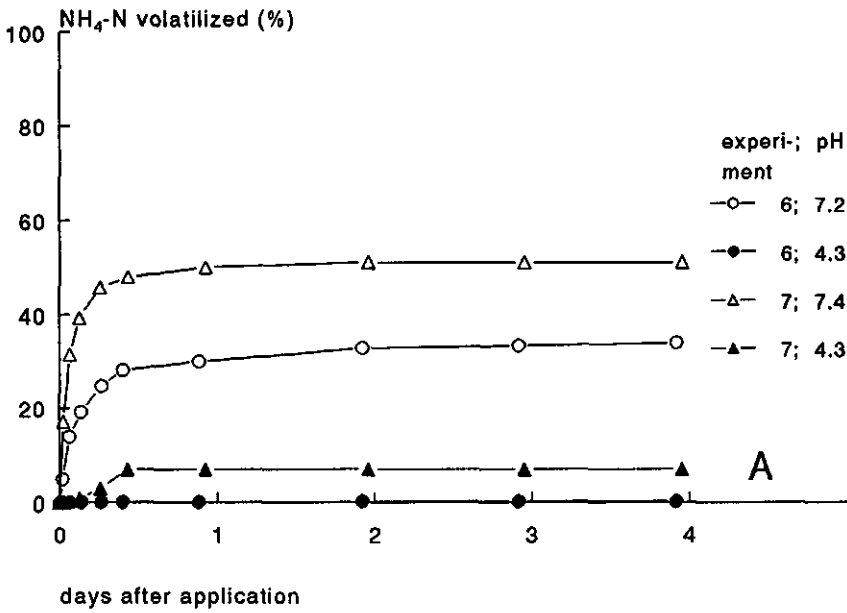


Figure 2. Pattern of NH₃ volatilization in the mass balance experiments 6 and 7 (A) on sandy soil and experiment 13 (B) on heavy clay soil.

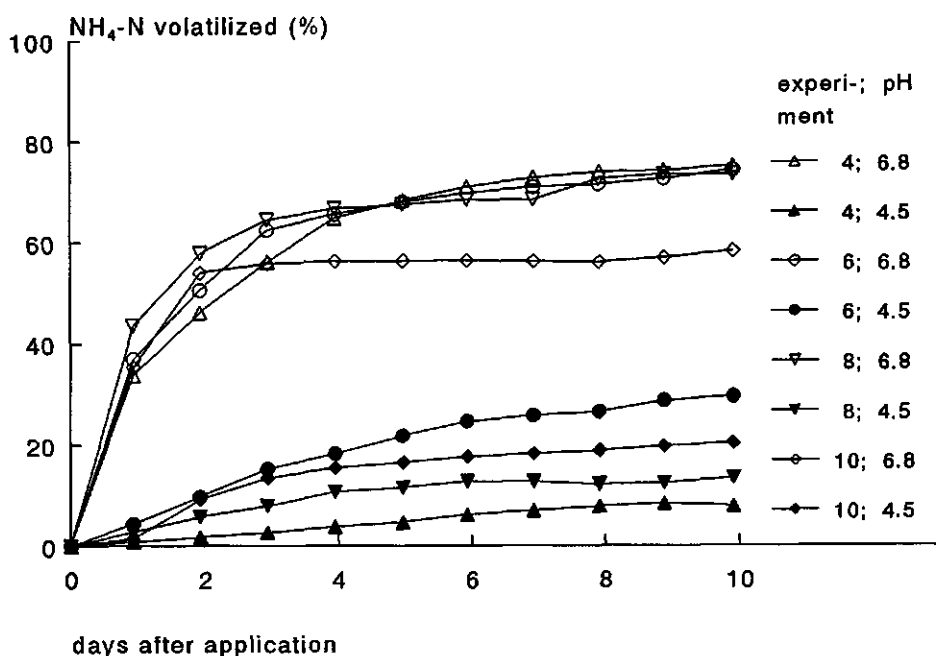


Figure 3. Pattern of NH₃ volatilization in the wind tunnel experiments 4, 6, 8 and 10.

Inclusion of (wind speed)*(NH₃)_g, (water evaporation)*(NH₃)_g or (application level)*(NH₃)_g did not improve R²_{adj}. The total percentage of NH₄-N (%TNH₄-loss) volatilized during the experimental period was strongly related to initial (NH₃)_g, soil type and 4-day cumulative water evaporation (cumE_p4, mm), according to:

$$\%TNH_4\text{-loss} = (3.61 (\pm 1.68) + 1.58 (\pm 0.86) * \text{cumE}_p4) * 10^7 (NH_3)_g + 12.09 (\pm 2.96) * \text{peat} + 17.87 (\pm 4.24) * (\text{heavy clay}) \quad (5)$$

with: R²_{adj} = 87.4 % and n=19

The tunnel experiments also showed a reduction in NH₃ losses from acidified slurry of 46 up to 97% to that of untreated slurry (Table 3). At pH ≈ 4.5 the mean reduction with the tunnel (73%, range: 46-97%) was less, than with the mass balance method (85%, range: 69-99%). Furthermore, there was a difference in variation and volatilization continued longer in the tunnel experiments than in the mass balance experiments (Figures 2 and 3). On average 27% (range: 6-91%) and 68% (range: 48-100%) of the total NH₃ loss was

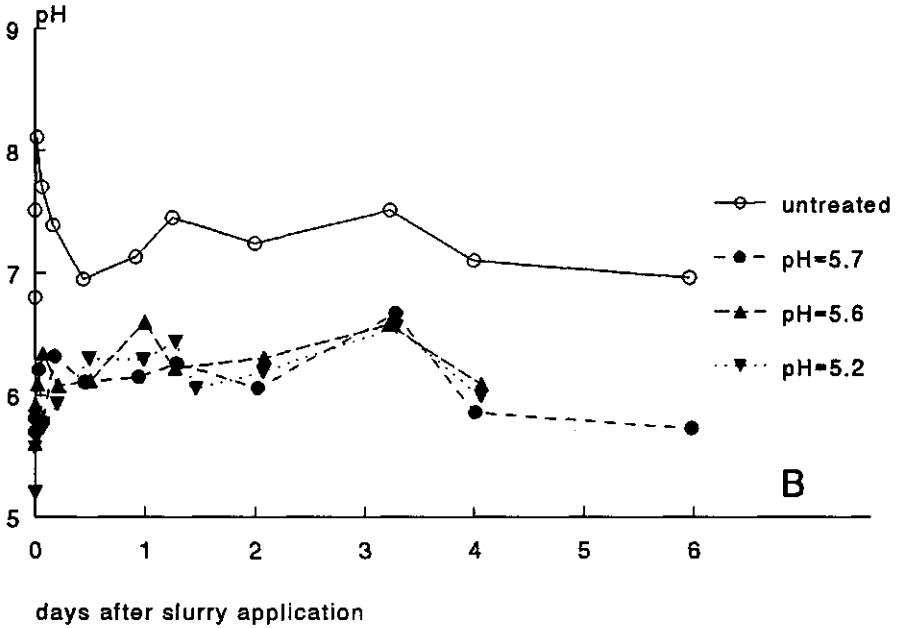
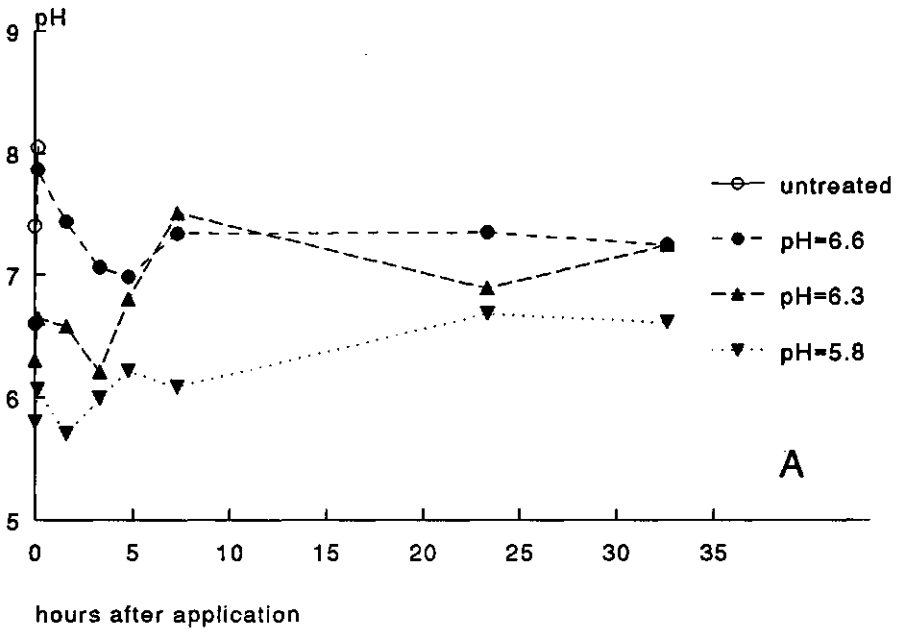


Figure 4. Slurry pH after application on heavy clay soil in the mass balance experiments 12 and 13.

measured during the first and up to the fourth day, respectively.

Surprisingly, %NH₄-loss on day one was not significantly related to NH_{3(g)} or any weather parameter. This is probably due to the low losses on day one and the constant initial pH of the slurry. Also, %TNH₄-loss was not related to NH_{3(g)}, but only slightly to the 10-day cumulative E_p (cumE_p10, mm):

$$\%TNH_4\text{-loss} = 0.565 (\pm 0.097) * \text{cumE}_p10 \quad (R^2_{\text{adj}} = 23.6\% \text{ and } n=8) \quad (6)$$

for tunnel experiments 3-10 (1 and 2 are excluded because of differing experimental design).

Changes in slurry pH

In the mass balance experiments 12 and 13, there was a rapid increase in pH immediately after slurry application, followed by a decrease in pH (Figure 4). After several hours a small rise in pH was observed.

In the tunnel experiments the pH of acidified slurry increased steadily (Figure 5). Experiment 10 showed the largest pH increase with c. 1.5 units. This did however not result in the highest NH₃ loss rate (Figure 3, experiment 6), despite the fact that cumE_p10 was also the largest (Table 3). Untreated slurry gave a sharp rise in pH.

DISCUSSION

Effect of slurry acidification on NH₃ loss

Slurry acidification proved to be an efficient method of reducing NH₃ losses. The reduction achieved strongly depended on initial slurry pH and air temperature (Figure 1), which was confirmed by regression analysis (Equation 5). Ammonia losses increased progressively with increasing pH and temperature and according to Equation 5 NH₃ losses increased also with cumE_p4.

Other experiments also showed marked reductions in NH₃ loss due to acidification. In Northern Ireland, a slurry pH of 5.5, 6.0 and 6.5 resulted in a reduction of NH₃ loss of > 85% (Frost et al., 1990), 90% (Stevens et al., 1992) and 75% (Stevens et al., 1992), respectively. Our experiments showed lower reductions for these pH values (Table 2), e.g. pH values of 4.5 to 5.0 were needed in the mass balance experiments - and even lower pH values in the tunnel experiments - to obtain similar reductions. This might be attributed to (i) the used measurement technique in Northern Ireland (discontinues mea-

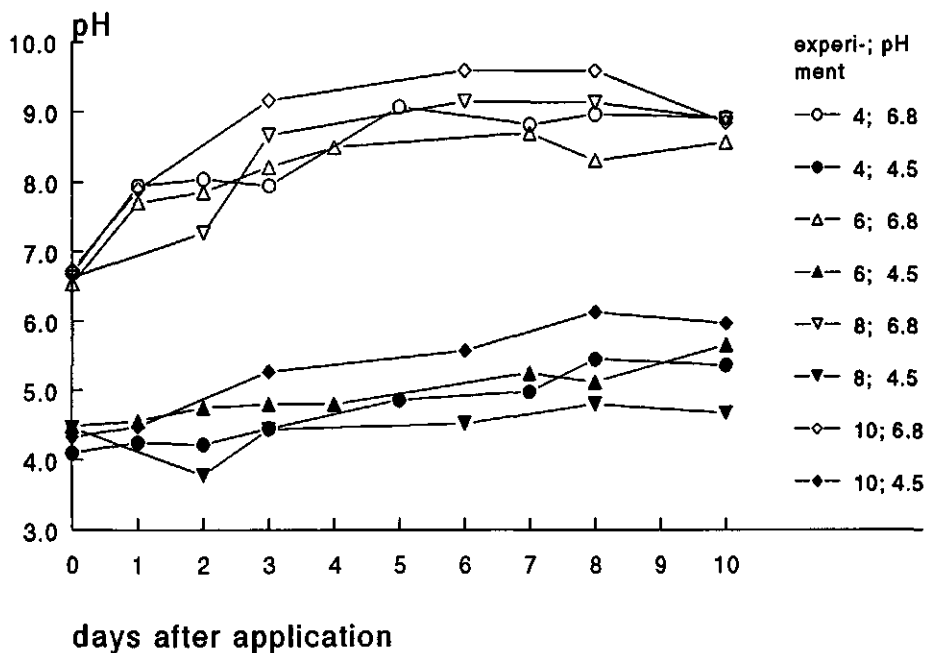


Figure 5. The pH of acidified slurry after application on sandy soil in the wind tunnel experiments 4, 6, 8 and 10.

surements using ventilated enclosures) which underestimated NH_3 loss rate (Frost et al., 1990) and (ii) the slightly higher temperature and evaporation in the Netherlands, which enhance NH_3 loss as observed from Figure 1. Consequently lower pH values are needed to obtain the same levels of reduction. Also the smaller amount of slurry applied (e.g. Döhler, 1991) and the high slurry DM content may stimulate NH_3 loss rate (Sommer and Olesen, 1991), in comparison to other experiments on grassland (Frost et al., 1990; Pain et al., 1990; Stevens et al., 1989b and 1992).

Comparison of measuring techniques

Two factors may account for the higher loss rates and the continuing loss (Figure 3) in the tunnel experiments. Firstly, differences in conditions in and outside the tunnel may stimulate NH_3 volatilization. In tunnels any rainfall is intercepted and due to the continuous wind speed dew formation is possibly prevented and evaporation is possibly stimulated. These factors may lead to a lower infiltration of NH_4^+ into the soil and to an increase

in $(\text{NH}_4^+)_{\text{aq}}$ and I. In a study of Ryden and Lockyer (1985) no difference was found between mass balance and tunnel measurements with urea fertilizer provided that there was no rainfall and that wind speed in the tunnel was adjusted to wind speed outside the tunnel at a height of 0.25 m. A lengthy NH_3 loss was also observed by Pain et al. (1990) where the tunnels were only moved to an adjacent area of the plots if more than 2 mm of rain fell within a 24 h period.

Secondly, the rate of slurry application in most wind tunnel experiments was 2 to 3 times higher than in the mass balance experiments. This difference may have also created a more favourable environment for a prolonged volatilization.

Whatever the cause of the differences between techniques may be it seems wise to move tunnels at least twice a day to adjacent spots with the same treatment and to adjust wind speed in the tunnel to local conditions.

Changes in slurry pH

In the mass balance experiments 12 and 13, where the slurry was acidified shortly before application (Figure 4), a rapid increase immediately after application of up to 1.2 pH units was observed, especially for the higher pH values. This was caused by faster volatilization of CO_2 than of NH_3 (calculated with help of a chemical equilibria model; Keizer and van Riemsdijk, 1994), probably enhanced by the fact that the freshly prepared acidified slurry had not reached a chemical equilibrium and much carbonate remained. Similar rapid pH increases due to a faster volatilization of CO_2 than of NH_3 were observed in aeration experiments performed by Husted et al. (1991) with HCl treated slurry. The initial pH values of experiments 12 and 13 and probably also of experiment 11, used in the regression analysis (Equation 4 and 5) were underestimated in contrast to the initial pH at lower values (Figure 5). Consequently this results in a different behaviour of the heavy clay soil in Equations 4 and 5, since all the freshly prepared acidified slurry with high pH values was applied on this soil type. On the peat soil a pH increase of the applied slurry with respectively 0.5 and 1 unit after 1 and 4 days may have caused the different behaviour in Equations 4 and 5 according to statistical analysis. This suggests some denitrification. However no pH or denitrification measurement data were available to confirm this. In addition it is possible that NH_3 loss from acidified slurry at low application rates ($7\text{--}17 \text{ m}^3 \text{ ha}^{-1}$) to grassland, is independent of soil type, since it was observed that the slurry made almost no direct contact with the soil surface in dense grass swards. Equations 4 and 5, without the peat and heavy clay terms, may then be applied for all grassland soil types if the slurry is stable and almost free of carbonate, due to acidification. In experiments 12 and 13 the rapid initial increase in pH is followed by a decrease during the next hours, due to NH_3 loss (Figure 2B). Thereafter a slow increase

in pH is observed, followed by a sharp decrease after day 3. This increase in pH may be due to denitrification. Experiments conducted by Velthof and Oenema (1993) with acidified cattle slurry of pH 4.5 and 6.0, surface applied to grassland, gave N_2O -N losses of <0.1 and 1.4% of applied nitrate. Taking into account that N_2O losses may be accompanied by substantial N_2 losses, then the pH increase of acidified slurry after the first hours (Figure 4) may result from denitrification. For pH values below 5.0 denitrification is probably lower, the more because N efficiency trials with acidified slurry of pH 4.5 (Schils; pers. comm.) showed an N recovery of applied mineral N which was similar to that of calcium-ammonium-nitrate fertilizer.

Treated slurry (Figure 5) in the tunnel experiments showed a slow uniform pH increase. This may be due to denitrification and or pH buffering by the soil.

Target slurry pH for various conditions

Because of the possible environmental impact of NH_3 losses, legislative targets have been formulated for the reduction of NH_3 losses from livestock, especially from manure application. In the Netherlands the target is 80% reduction by the year 2000. This target can be met by slurry acidification as follows.

The measured mean total loss in the mass balance experiments of untreated slurry was 61%. A loss of 12% is thus sufficient to meet the target reduction of 80%. By rearranging Equation 6 for the sandy and clay soil, the required pH can be estimated from Equation 7 as a function of initial NH_4^+ concentration, average T, $cumE_p4$ and maximum NH_3 loss (12%):

$$pH = \log(12) - \log((3.61 + 1.58 * cumE_p4) * [NH_4^+]) - 11.117 + 4507.053 / (T + 273.15) \quad (7)$$

As discussed it is likely that there is no difference between the four grassland soil types in NH_3 volatilization. Therefore Equation 7 is also used for peat and heavy clay soil. The pH needed to obtain the reduction target of 80% on grassland then ranges from 6.0 for an average temperature of 5 °C and $cumE_p4$ of 4 mm, whereas it has to be 4.5 for an average temperature of 20 °C and $cumE_p4$ of 16 mm (Figure 6).

CONCLUSION

Acidification of cattle slurry gave a marked reduction in NH_3 losses from surface applied slurry, irrespective of the method employed to measure NH_3 volatilization.

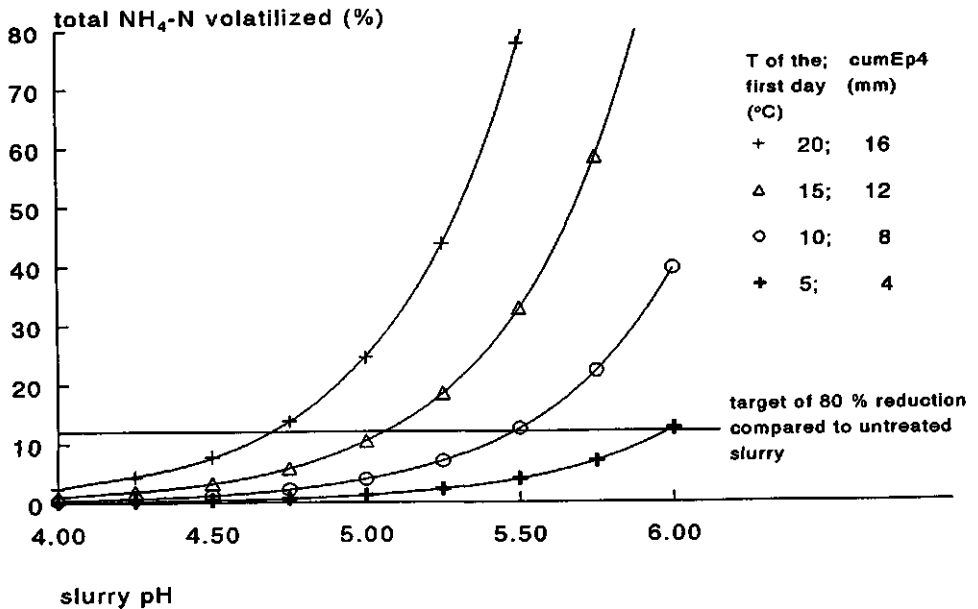


Figure 6. Expected rate of loss in total NH_3 for different pH, cumulative evaporations and temperature values according to Equation 5 for an initial NH_4^+ concentration of 0.157 M, assuming that peat and heavy clay soil do not differ from sand and clay soil.

Key factors in determining the NH_3 loss rate are T, pH and potential evaporation. To obtain a low volatilization by acidification all the carbonate should be removed from the slurry (via CO_2). It was hypothesized that the pH required to obtain a certain reduction in NH_3 loss was independent of the grassland soil type at the application levels used in the experiments, because of the limited contact of slurry with the soil. At low temperatures and water evaporation a pH of about 6.0 is needed to achieve a reduction in NH_3 loss of 80% of that of untreated slurry. At high temperatures and water evaporation this is approximately 4.5.

The measured pH rise in the experiments with acidified slurry after the initial hours after application, is probably caused by denitrification of slurry with a pH between 5.0 and 6.0.

ACKNOWLEDGEMENTS

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CHAPTER 8

**AMMONIA VOLATILIZATION FROM DAIRY FARMING SYSTEMS IN
TEMPERATE AREAS; A REVIEW**

By: D.W. Bussink and O. Oenema. Submitted to Nutrient Cycling in Agroecosystems

AMMONIA VOLATILIZATION FROM DAIRY FARMING SYSTEMS IN TEMPERATE AREAS; A REVIEW

ABSTRACT

Ammonia (NH_3) emissions from dairy farm systems cause environmental problems. This paper reviews and quantifies the major loss routes of NH_3 in dairy farms. Furthermore, management options are discussed that reduce NH_3 losses.

Losses of NH_3 occur during slurry application, housing, slurry storage, grazing, fertilizer application and from crops, in descending order of importance. Animal waste is the major source in four of the six cases. This ranking varies between farms and between countries, depending on environmental conditions and management practices. Total NH_3 losses range from 17 to 46 kg N cow yr^{-1} , reflecting the variability in amount and composition of animal excreta (urine + faeces), management of the slurry and soil and environmental conditions. The amount and composition of urine and faeces depend on N transformations in the digestive track of the cow. Urea has the highest potential for NH_3 volatilization followed by allantoin, uric acid and creatinine in decreasing order. Creatine, xanthine and hypoxanthine have a low NH_3 volatilization potential.

Reducing the excretion of urea and urea like products by optimizing N Intake (NI) and N Retention (NR) is one solution to reduce potential NH_3 losses. Improvement is possible since NR is about 20% of NI in practice, whereas 43% is theoretically possible. The second solution is to reduce NH_3 loss rate by technical means like direct incorporation of slurry into the soil, dilution or acidification of slurry, covering of the slurry storage and/or acidification or dilution of slurry in the storage. These techniques have been known for long and become available now on a large scale in practice. Reducing the surface area per cow in the shed and sprinkling floors with water to remove and to dilute urine reduce also NH_3 loss rates.

Reducing NH_3 loss requires a whole farm system approach, because it shows how intervening in one part may affect NH_3 losses in other parts of the system. Reducing NH_3 loss may increase nitrate leaching and denitrification. To prevent this the achieved reduction in NH_3 loss should lead to a reduction of total N input of fertilizers, concentrates and forage on the N budget of the farm, which is possible as a reduction of NH_3 loss improves the N fertilizing value of slurry. Model calculations showed great scope for reducing NH_3 losses on dairy farms by improved management. Up to three fold reductions in NH_3 loss are possible together with marked reductions in N fertilizer usage. The rate at which improved management techniques will be introduced in practice depends on legislation, the applicability of new techniques and the expected increase in net production costs. To comply with environmental targets requires a huge effort of farmers with associated high costs.

INTRODUCTION

Ammonia (NH_3) losses from livestock wastes have been recognized since early 19th century (Boussingault, 1851; Sprengel, 1839). Around 1900, direct and indirect measurements proved that storage and handling of livestock wastes, and the application of these wastes to land were all associated with NH_3 losses. Because livestock waste was the main nitrogen (N) fertilizer in those days, research was undertaken to find ways to reduce NH_3 losses and to improve the N fertilizer value of livestock waste. Heiden (1887) and Wagner et al (1897) were the first to write about the use of chemicals to reduce N losses from (liquid) waste during storage. Early 20th century it was shown that dilution of slurries (Blanck, 1918a), addition of acids, salts and formaline (e.g. Blanck, 1918b and 1918c; Gerlach, 1919; Liechti and Ritter, 1913) and closing storage tanks (Heiden, 1887; Kristensen, 1907) may improve the fertilizer value of livestock wastes. Incorporation of (liquid) waste in the soil by harrowing immediately after application (Blanck, 1918b; Heck, 1931; Iversen 1934) or by injection (Gerlach, 1918; Iversen 1934) were also shown to be successful measures in improving the N fertilizer value, by reducing NH_3 losses. However, the costs and technical difficulties made these measures often inapplicable for practice at that time.

With the large-scale introduction and use of N fertilizers from the 1950s onwards, research interest in gaseous N losses from livestock waste faded away in Europe and North America. Renewed interest emerged after NH_3 volatilization became an environmental issue after the recognition that it may seriously contribute to soil and surface water acidification and eutrophication, and to forest dieback (e.g.; Ellenberg, 1985; Fangmeier et al., 1994; Roelofs et al., 1985; Skeffington and Wilson, 1988; Van Breemen et al., 1982). The development of field techniques for the direct measurement of NH_3 volatilization greatly improved the reliability of measured NH_3 losses, and further promoted the interest in NH_3 volatilization. A large number of measurement campaigns have been carried out in the last two decades to quantify NH_3 losses from the various sources in a farming system. Development of simulation models have further improved the insight in the critical factors for NH_3 losses from e.g. slurry applied to arable land (Van der Molen et al., 1990b), from housing (Muck and Richards, 1983), and from urea fertilizers (Kirk and Nye, 1991; Rachhpal-Singh and Nye, 1986; Sadeghi et al., 1988).

Recent estimates show that in Europe up to 90% of the total NH_3 burden in the atmosphere originates from agriculture, with livestock wastes as major source (Asman, 1992; Buijsman et al., 1987; ECETOC, 1994). Cattle farming and especially dairy farming is regarded as the largest animal husbandry source of NH_3 emission. Total NH_3 losses from animal husbandry have increased by about 50% between 1950 and 1980 (Apsimon et al., 1987), mainly because of the increased number of animals and the increased dietary N content. The increased use of N fertilizers (Figure 1) and the import of fodder and

concentrates until about 1985 have given a strong impetus to both, the increase in number of animals and the increase in dietary N content, and hence to the increase in NH_3 burden in the atmosphere. For a variety of reasons, e.g. introduction of low-emission techniques for application of slurry, decrease of fertilizer N consumption and a decrease in animal numbers, the NH_3 losses from livestock holdings in Western Europe have started to decrease from about 1990 onwards, especially in the Netherlands and Denmark. Policies to control air pollution and eutrophication, and to conserve nature have also strongly contributed to the introduction of measures to reduce NH_3 emissions at the farm level. Considerable progress has been made, but as the understanding of the environmental impacts of NH_3 emissions has improved, it becomes evident that further reductions are necessary. Detailed insight and knowledge into the various pathways and controls of NH_3 losses on livestock farms are necessary to obtain the best environmental benefits against the lowest control costs.

Despite the facts that the total NH_3 burden of the atmosphere is known reasonably well, and that NH_3 loss potential of livestock wastes is known for almost two centuries, estimates of NH_3 losses at the farm level are still facing large uncertainties. These uncertainties slow down the introduction of cost-effective abatement measures. Major NH_3 losses from livestock

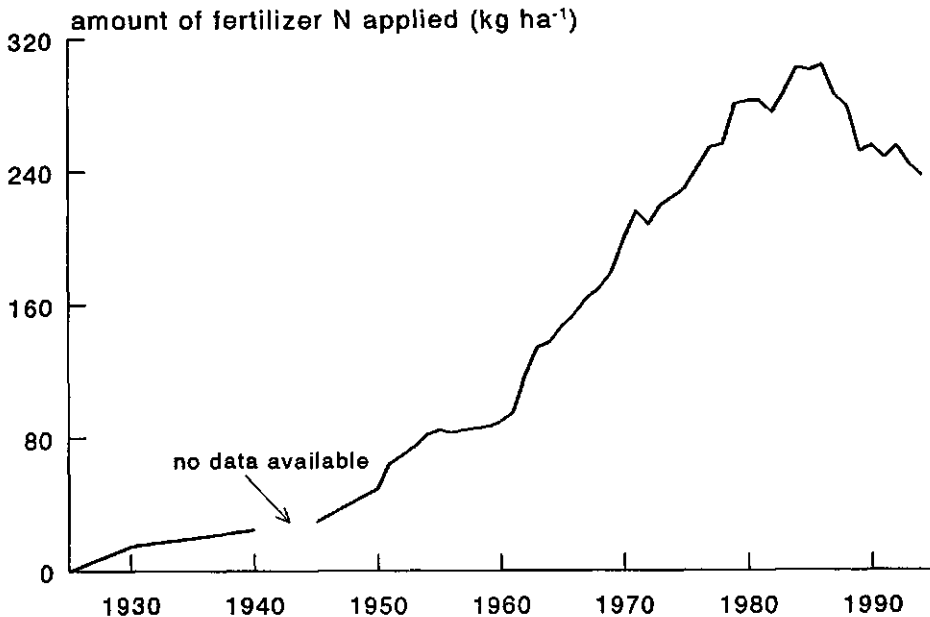


Figure 1. The annual use of N fertilizer on grassland in the Netherlands (after Keuning, pers. commun.).

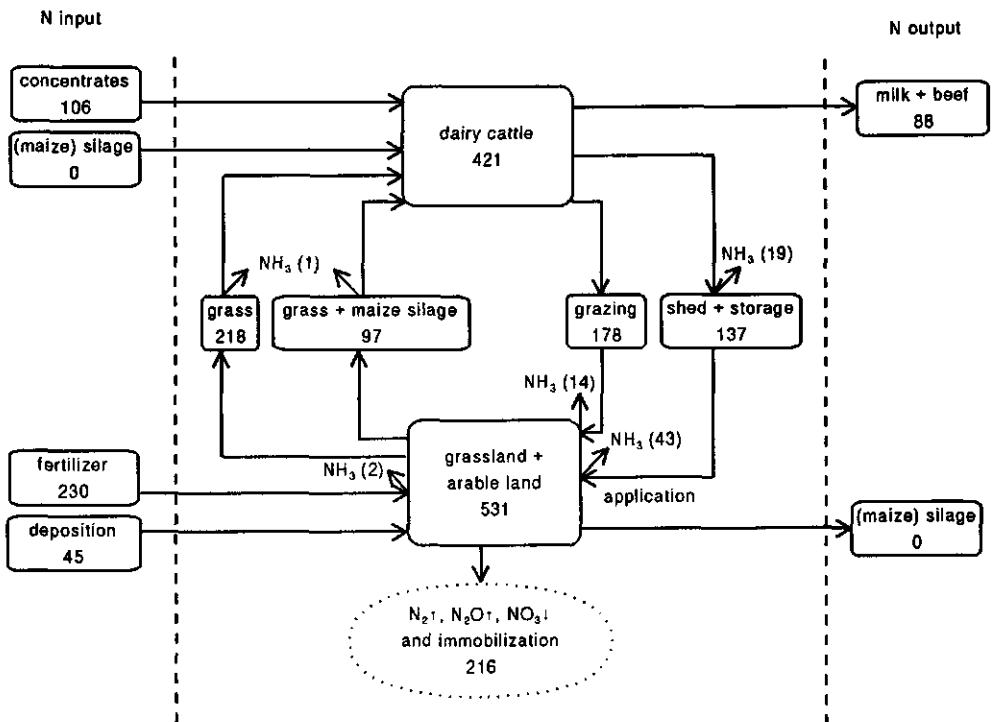


Figure 2. The N flows ($\text{kg ha}^{-1} \text{yr}^{-1}$) on a dairy farm with grass and maize as main forages and the major pathways of NH_3 losses. The numbers represent situation B in Table 4.

farms occur during storage and spreading of wastes, and during grazing and housing cattle (Figure 2). There are further possible losses from ammoniacal fertilizers and senescent crops and crop residues. These very different (point and diffuse) NH_3 sources, combined with the fact that weather and soil type, and waste composition and management have a large effect on NH_3 losses from these sources, make estimates about NH_3 losses from farming systems uncertain.

Better quantitative estimates insight into the losses from the various sources on livestock farms and more quantitative knowledge of the factors that govern these losses are necessary to allow progression of the introduction of cost-effective abatement measures in practice. A whole farm approach is an essential tool to obtain this better insight, because all the components of the farming system are taken into account. It shows how intervening in one component may affect other components of the system and the NH_3 losses at other sites.

It is the purpose of this paper (i) to provide an overview of current estimates of NH_3 losses from the various sources in dairy farming (ii) to review the dominant factors that determine the size of the NH_3 losses from dairy farms, (iii) to identify abatement measures,

and (iv) to show the relationship between the various NH_3 losses and abatement measures, using a simple model, so as to provide justification for a whole farm approach. Emphasis is given to physiological processes in dairy cattle, because these determine the composition and amount of wastes, the distribution between faeces N and urine N, and the urinary composition. A further emphasis is on N fertilizer use, because this affects the amount and composition of forage and thereby the number of cattle.

Overview of NH_3 losses from dairy farming

Volatile ammoniacal N is produced from dairy waste, fertilizers, soils and crops. Conveniently however, five major NH_3 volatilization sites are distinguished on dairy farms (Figure 2 and Table 1). Dairy waste is the major source of NH_3 in four of the five sites. Soils and crops are generally not considered as major sources of NH_3 : the net loss from crops is probably $< 2 \text{ kg } \text{NH}_3\text{-N ha}^{-1} \text{ yr}^{-1}$ (Holtan-Hartwig and Bøckman, 1994), and from unfertilized soils even less.

Factors that affect NH_3 losses from N fertilizers have been examined and discussed extensively (Bock and Kissel, 1988; Fenn and Hossner, 1985; Freney et al., 1983; Terman, 1979). Generally, NH_3 losses decrease in the order urea containing fertilizers, ammonium sulphate, ammonium nitrate, and nitrate fertilizers. Large losses (up to 30%) are associated with urea containing fertilizers (e.g. Fenn and Hossner, 1985; Lightner et al., 1990; Terman, 1979) and with ammonium based fertilizers applied to high-pH soils (Hargrove et al., 1977; Whitehead and Raistrick, 1990). Losses from ammonium nitrate based fertilizers are generally less than 5% (e.g. Sommer and Jensen, 1994; Velthof et al., 1990; Whitehead and Raistrick, 1990). The range in losses seems to be somewhat larger in studies using enclosure techniques than in studies using meteorological techniques (ECETOC, 1994).

Enclosure measurements indicate that 4 - 41% of the N from applied cattle urine may volatilize (Ball and Ryden, 1984; Lockyer and Whitehead, 1990; Ryden et al., 1987; Vallis et al., 1982; Vertregt and Rutgers, 1991; Whitehead and Raistrick, 1993a), with an extreme of 66%. Results for faeces range from 1-13% (MacDiarmid and Watkin, 1972b; Ryden et al., 1987; Sugimoto and Ball, 1989; Vertregt and Rutgers, 1991).

Grazing derived NH_3 losses, as estimated by meteorological techniques, range from 0 - 28% of the N voided in urine and dung, depending on N application rate, climatic conditions and CEC (Table 2).

The few estimates for housed dairy cattle have been obtained from N budget studies and from direct measurements in mechanically and naturally ventilated buildings (Table 2) (Oldenburg, 1989). Direct measurements of NH_3 losses from natural ventilated housings are still in a testing phase (Scholtens and Van 't Ooster, 1994). In the budget studies, all N losses are assumed to be NH_3 losses. This assumption may lead to an overestimation of NH_3 losses,

Table 1. Range of measured of NH_3 losses for the different steps of the NH_3 loss cycle.

Compartment	Range of measured NH_3 losses	Factors affecting NH_3 loss	References
Artificial ^x fertilizer	6 - 42 % ^a of urea-N applied	T^1 , swc^2 , CEC^3 , soil pH, fertilizer type, N input, CaCO_3 , vegetation	Black et al., 1985; Bussink, unpublished results; Harper et al., 1983b; Sherlock et al., 1989
Application ^x of slurry	1 - 100% of $\text{NH}_4\text{-N}$ applied on grassland 3 - 70% of $\text{NH}_4\text{-N}$ applied on arable land	T, rainfall, swc, CEC, pH, % DM, amount applied, application technique, vegetation	Beauchamp et al., 1982; Bless et al., 1991; Bussink et al., 1994; Bussink and Bruins, 1992; Brunke et al., 1988; Döhler, 1991; Horlacher and Marschner, 1990; Huijsmans et al., 1996; Pain et al., 1989; Sommer, 1989; 1992; Stevens and Logan 1987; Van der Molen et al., 1990a;
FYM	45-100% of $\text{NH}_4\text{-N}$ applied		
Grazing ^x	0 - 18% of the N excreted per grazing or 3.1 - 8.5% of the N excreted per year 1.3 - 27.7% of N excreted per grazing 9.8 - 12.1% of urinary N per year	T, swc, CEC, N input grassland management urease activity, rainfall	Bussink, 1992 and 1994a Ryden et al., 1987 Jarvis et al., 1989b
Housing in slurry system	0 - 70 % of N excreted ^b 5 - 38 g N $\text{cow}^{-1} \text{day}^{-1}$ ^c	T, stable type N content urine, residence time, ventilation	Muck and Richards, 1983 Groenestein, 1994; Monteny and Verboon, 1994; Oldenburg, 1989; Oosthoek et al., 1991
Storage of slurry	0 - 20% of total N 16 - 50% of total N ^d 3 - 66% ^b	time, T, N content storage type, aeration	Beauchamp and Burton, 1985; De Bode, 1991; Gracey, 1979; Muck and Steenhuis, 1982; Pami and Jui, 1986; Sommer, 1992 Van der Holm, 1975
FYM			Bucher, 1943; Iversen, 1931; Köhnlein und Vetter, 1953; Schuchardt, 1990
Crops	<0 - 156 g N $\text{ha}^{-1} \text{d}^{-1}$	N status, fysiological status, crop type	Holtan-Hartwig and Böckman, 1994

x) results obtained with micrometeorological techniques, 1) T is temperature, 2) swc is soil water content and 3) CEC is cation exchange capacity, a) no data obtained with micrometeorological techniques were available for other fertilizers, b) part of it may got lost by denitrification, c) measured during the winter period, d) lagoons

because N may get lost also via reduction of nitrate to N_2O and N_2 , e.g. in the rumen of cattle (Kaspar and Tiedje, 1981). Losses of NH_3 from housed dairy cattle range from 5- 38 g N cow⁻¹ day⁻¹ in winter (equal to 2 - 10% of the N voided with urine and dung) (Table 2). They are much higher in summer (Oosthoek et al., 1991). Losses up to 70% have been reported (Muck and Richards, 1983).

Losses during storage range from 0 to 20% of the N contained in the slurry (Table 1). The residence time, slurry composition and slurry mixing, temperature and the type of covering are key factors in determining the NH_3 loss rate.

Effects of method of slurry application and environmental conditions on NH_3 volatilization from slurry have been studied frequently. There is a wide range in losses. Under optimal conditions (e.g., warm, dry), essentially all inorganic ammoniacal N may volatilize from surface applied slurry, whereas under rainy conditions almost no NH_3 volatilizes. Losses increase with temperature, and tend to be higher on grassland than on arable land. Horlacher and Marschner (1990) reviewed the effect of environmental factors influencing NH_3 losses from slurry application.

Total NH_3 losses from dairy farms in NW Europe range from 36 to 105 kg N ha⁻¹ yr⁻¹, and from 17 to 46 kg N per livestock unit per year (Aarts et al., 1992; Isermann, 1990a; Jarvis, 1993; Koorevaar and den Boer, 1990). The wide range reflects the variability in amount and composition of slurry, the management of the slurry, stocking density and soil and environmental conditions. The N content of urine and faeces depends on the NI via forage and concentrates. The composition of urine and faeces depends in large on the N transformations in the digestive track, as discussed below.

NITROGEN METABOLISM IN THE COW

Pathways and transformations of N

Most of the N in forage and concentrates is contained in proteins, which have to be digested in order to be retained by the cow in milk and beef. The first part of the digestion takes place in the rumen, where enzymes secreted by microorganisms breakdown 70 to 85% of the digestible proteins (Bondi, 1987). The true digestibility of proteins ranges from 80 to 100% (Ørskov, 1992). The proteins are degraded into peptides, which are further degraded to fatty acids, carbon dioxide and NH_3 . Micro-organisms may use the NH_3 in the presence of carbohydrates or other energy sources to synthesize new proteins. Generally however, only a small amount of NH_3 is fixed because of the limited energy supply (Ørskov, 1992; Sniffen and Robinson, 1987;). Most of the remaining NH_3 is adsorbed and transformed into urea in the liver and, subsequently, excreted via the urine.

Urinary N is derived from various sources. The rumen is the major source if dietary N exceeds 24 g N kg⁻¹ DM. In intensive dairy farming systems in West Europe, grass based diets often contain between 30 and 40 g N kg⁻¹ DM, and rumen losses are thus a major source for urinary N. The turnover of ingested dietary protein into microbial nucleic acids, and the conversion of amino acids into milk and body proteins are also associated with N losses that contribute to urinary N. These sources amount to 10 and 10-15% of ingested N, respectively (Tamminga, 1992). In addition, there are contributions from maintenance and metabolic processes (Table 2). Urinary N excretions can be reduced by reducing the rumen losses, and relatively by increasing milk yield.

Transformations of N compounds in animal excretions

Upon deposition to the soil or stable floor, urea is rapidly hydrolyzed by the enzyme urease according to:



The formation and subsequent dissociation of ammonium carbonate ((NH₄)₂CO₃) gives urea a high potential for NH₃ volatilization.

Hydrolysis of hypoxanthine (Ladd and Jackson, 1982) finally results also in urea, according to: hypoxanthine --> xhantine --> uric acid --> allantoin --> allantoic acid --> urea + ureidoglycolic acid --> 2 urea + glyoxylic acid --> (NH₄)₂CO₃ + glyoxylic acid.

There is a lack of information on the decomposition of creatine and creatinine in soils. Hippuric acid decomposes easily into glycine and benzoic acid. Experiments with solutions of urinary N components (Whitehead et al., 1989) showed that NH₃ volatilization after 8 days amounted to 15% of the N applied from urea, about 11% from allantoin, almost 4% from creatinine but < 1% from creatine and hippuric acid. The latter appeared to stimulate urea hydrolysis (Doak, 1952). Uric acid, a main N source in excreta of poultry, also has a high NH₃ loss potential though there was a delay of a few days before volatilization started (Valli et al., 1991; Van Beek, 1990). The NH₃ loss potential of hypoxanthine and xanthine is low probably. In summary, the NH₃ volatilization potential decreases in the order: urea > allantoin > uric acid > creatinine > creatinine ≈ hippuric acid > xanthine > hypoxanthine.

Cattle faeces contains low amounts of rapidly decomposable N (Van Faassen and Van Dijk, 1987; Wagner et al., 1897). Only a few per cent of the N in fresh faeces is NH₄⁺ or urea (Ettalla and Kreula, 1979), suggesting that the NH₃ volatilization potential of fresh faeces is relatively low. The major part of the N in faeces is organically bound N. Up to

50% of this N may become mineralized during storage for 6 months (Snel, 1990). The mineralization rate increases with temperature (Whitehead and Raistrick, 1993b).

Estimation of urinary compounds with high NH₃ volatilization potential

As discussed before urea, allantoin, uric acid and NH₃ in urine and faeces have a high NH₃ volatilization potential. In the following these four are treated similar, as urea-like (U) components. The non-urea-like components (non-U) in urine are excreted in fairly constant amounts. On the basis of data from Aafjes and De Groot (1961), Bristow et al. (1992) and Osinga (1970) we calculate a non-U excretion rate of 31 ± 4.3 g N cow⁻¹ d⁻¹. The total excretion rate of U via urine can now be estimated as follows:

$$U = \Sigma(\text{N in urine}) - \text{non-U} = \text{NI} - \text{NR} - \text{N in faeces} - 31 \quad (\text{g N cow}^{-1} \text{ d}^{-1}) \quad (3)$$

Total NI is calculated from the NI via herbage, forage and concentrates. The NR can be calculated from the live weight N gain and the Milk N Yield (MN_y). The live weight N gain is constant (8.7 g N cow⁻¹ d⁻¹); MN_y (g N cow⁻¹ d⁻¹) is related to milk protein yield. Excretion of N via faeces is linearly related to DM intake of grass based diets by the cattle (DM intake * 7.8 g N cow⁻¹ d⁻¹; Lantinga et al., 1987). Hence,

$$U = \text{NI} - \text{MN}_y - (7.8 \times \text{DM intake}) - 39.7 \quad (\text{g N cow}^{-1} \text{ d}^{-1}) \quad (4)$$

MANAGEMENT FACTORS AFFECTING NH₃ LOSSES

Adjusting N intake

Reducing NI and increasing milk protein yield reduces the production of U compounds via urine (Eq. 4) and as a result the NH₃ volatilization potential. Theoretically not more than 43% of the NI of lactating cows can be retained in milk and liveweight gain (Van Vuuren and Meijjs, 1987). In practice however, NR is often less than 20% (Van Vuuren and Meijjs, 1987).

A reduction in NI can be achieved by (i) lowering the N content in grass through improved grazing and grassland management, and (ii) replacement of grass by low-protein concentrates and forages in the diet. Lowering the N fertilizer application rate strongly reduces the NI of the cow and thereby the excretion of U compounds. Volatilization of NH₃ from grazed swards has been shown to increase progressively with fertilizer N application rate (Bussink, 1992 and 1994a). Delaying the start of grazing is another effective measure

to reduce N content due to the inverse relationship between herbage yield and herbage N content (Meijs, 1981). However, lowering herbage N content may reduce grass DM (energy) digestibility and thereby NR in milk and beef. Therefore, grass N content should not drop below 30 and 20 g N kg⁻¹ DM for lactating and non-lactating cows, respectively (Oldham, 1984). Increasing stocking density increases grazing efficiency and decreases selectivity (Bussink, 1994a; Meijs, 1981), leading to a lower N content of consumed herbage and lower total NI (Meijs, 1981). This would suggest that mean NI and thus NH₃ volatilization potential is lower with rotational grazing than with continuous grazing. However, the only comparison showed the opposite (Jarvis et al., 1989b), suggesting that other factors like the distribution of urine and faeces, and interactions with environmental conditions outcompeted the effects of grazing efficiency and selectivity.

There is still uncertainty about how a lowering in NI will effect urinary N excretion. A lower NI may lead to (i) a lower N content in the urine, (ii) less urinations but with unchanged N content and unchanged amount of urine per urination, and (iii) less urine voided per urination but with unchanged N content. Replacing 30% of the grass by maize silage in the diet of dairy cows showed a decrease in the amount of urine, while the urinary N content remained the same or slightly increased (Valk, personal comment and own results). Feed additives like salts may increase water consumption of the cattle and may dilute the urea content of urine. It has been observed that NH₃ volatilization is linearly related with the urea content of urine (Elzing and Kroodsma, 1993). The uncertainty in the effect of changes in NI on urinary N excretions also follows from the complexity of N transformations in the digestive track, and the large diurnal variations and inter-animal variations in urinary composition, which all make comparisons laborious.

Optimizing N retention

Evidently, decreasing the herd and increasing the NR in the cattle (Eq. 3) will reduce total N excretion and thereby NH₃ volatilization potential. Breeding and selection of dairy cattle for milk protein is attractive, both from economic and environmental points of view (Tamminga, 1992). Reducing the numbers of herd-replacement and fattening cattle is also attractive, because NR is much higher in high-yielding milking cows than in calves and fattening cattle (Coppoolse et al., 1990)

Housing systems

There are a number of housing systems, which differ in the use of straw and the storage of cattle excretions: (i) housings with straw, e.g. free stall with farm-yard manure (straw yard), (ii) housings with slatted floors, e.g. cubicle houses with a slurry storage below the slats, and

(iii) housings with solid floors and a scraper system to remove the slurry from the stable into a storage basis. Combinations also exist. There are also 'open cubicle housings', e.g. without wall and roof. Measurements have shown that NH_3 losses per housed cow increase in the order cubicle houses < free stall with straw yard < open housing with solid or slatted floors (Groenestein, 1994; Monteny and Verboon, 1994).

In farm-yard manure (FYM) systems, the amount of straw used determines whether all urine and faeces are stored as FYM or that part of the urine is stored as liquid manure. Adsorption of urine by straw may effectively reduce NH_3 losses (Hümbelein et al., 1980; Meyer and Sticher, 1983; Van Faassen and Van Dijk, 1979) whereas no reduction (Köhnlein and Vetter, 1953) and increased losses (Bucher, 1943) also have been reported. The effectivity of straw in reducing NH_3 volatilization depends mainly on the duration and conditions of the FYM storage.

In slurry systems, NH_3 volatilization starts immediately after deposition of urine on the floors and on and under the slats (Oosthoek et al., 1991), due to the immediate start of urea hydrolysis (Ketelaars and Rap, 1994). As already reported one century ago, NH_3 losses from slurries can be reduced by fast removal of the liquid slurry to a closed pit (Heiden, 1887; Kristensen, 1907), by dilution with water (Blanck, 1918a), by acidification (Blanck, 1918c; Heiden, 1887; Wagner et al., 1897), by adding salts (Heiden, 1887), and by combinations of two or more of these measures. There is renewed interest in these measures, nowadays. Sprinkling (slatted) floors with water, fast removing of the urine to the storage by sloping solid floors, and sprinkling with additives like formaline and acids may reduce NH_3 loss by 15-30% (Monteny and Verboon, 1994). Rinsing the floor with strong acids decreased floor bound urease activity temporarily and thereby NH_3 losses (Ketelaars and Rap, 1994). In addition restricting the area per cow in open housings, may result in a lower urine and faeces contaminated area like in a tying shed. All these measures are rather effective, but adoption in practice is still hampered by the high costs, as was the case one century ago. The wide range in NH_3 losses from housing systems suggests that there is scope to further optimize the management of slurries in housing systems so as to reduce NH_3 volatilization.

Slurry and manure storage systems

Losses of NH_3 are much larger from slurry stored in open tanks and lagoons than from slurry stored in closed (underground) pits. Losses from open tanks can be reduced by decreasing the surface area per m^3 slurry stored (De Bode, 1991; Sommer, 1992), by adding oil (Blanck, 1918a; Sommer, 1992) or straw (Sommer, 1992) on the slurry surface, by dilution with water, which requires extra storage capacity (Blanck, 1918a; Kellems et al, 1979), and by slurry acidification. Reductions in NH_3 losses up to 90% have been achieved. Similar solutions can be applied to lagoons.

Losses from slurry and FYM stored outside increase with an increase in temperature and surface area, and with the duration of storage. An increase in temperature increases the mineralization of organically bound N in slurry. Hence, storage during summer should be minimized because NH_3 losses are much higher in summer than in winter (De Bode, 1991; Sommer, 1992). The effect of temperature on mineralization rate also explains why covering manure heaps is not always effective, because the effect of increased mineralization may outcompete the effect of reduced exchanged rates of NH_3 from the manure with the atmosphere. In addition, the more straw, the higher temperature, the more NH_3 loss (Köhnlein and Vetter, 1953; Schuchardt, 1990). A high moisture content of FYM may reduce NH_3 losses due to reduced gas exchange (Isermann, 1990a; Schuchardt, 1990).

Slurry Application

Various application methods have been developed and tested already at the beginning of this century, to reduce N losses from slurries after application to land. Dilution with water, treatment with acids, salts and disinfectants, and direct incorporation of slurries into the soil were tested by comparing the N response of crops. In recent experiments these treatments and techniques were compared by measuring the NH_3 volatilization directly. These experiments showed that tine injection, disc injection, incorporation of surface applied slurry in the soil, acidification, band spreading, dilution with water and irrigation immediately after surface spreading are proper techniques to reduce NH_3 volatilization losses (Bless et al., 1991; Bussink and Bruins, 1992; Bussink et al., 1994; Döhler, 1991; Huijsmans et al., 1996; Pain et al., 1989 & 1990; Sommer, 1992; Stevens et al., 1992; Thompson et al., 1987; Van der Molen et al., 1990a).

There is a wide range in efficacy for some techniques with respect to the reduction of NH_3 emissions, reflecting in part its weakness and unsuitability for practice. The wide ranges may also reflect the variable composition of slurries, the variable environmental conditions during testing and the limited number of tests for some of the techniques. The efficacy of tine injection ranges from 95-100%, disc injection from 80-100%, soil incorporation after surface spreading from 35-95%, acidification prior to surface spreading from 30-100%, band spreading from 35-95%, and the efficacy of dilution with a 1:3 slurry:water ratio ranges from 20-80%. In addition to the efficacy and financial costs, the choice for a certain technique depends on the bearing capacity of the soil when heavy machinery is involved and on the stoniness of the soil. The latter restrict the possibilities for slurry injection into the soil.

It appears that there is still large scope for optimizing the various techniques. When bandspreading is used, slurry must be applied in low amounts and preferably in a growing crop. Acidification is effective only when the slurry pH is less than 5 (Bussink et al., 1994). Most important for the efficacy of slurry incorporation is the time gap between slurry

application and incorporation. This holds for irrigation as well. There is also scope for minimizing NH_3 losses by proper timing and adjustment of the amount of slurry to actual climatic conditions. Proper conditions generally prevail in early spring when temperatures are low and the incidence of rainfall is high.

Despite the introduction of low-emission techniques in practice, slurry application to land is still a major source of atmospheric NH_3 . Estimates for Denmark and the Netherlands (NL) indicate that on average about 60% of the $\text{NH}_4\text{-N}$ in slurry was lost to the atmosphere, when broadcast applied (ECETOC, 1994; Sommer, 1992). Estimates for Germany and the UK are in the range of 40% (Isermann, 1990a; Jarvis, 1993). Estimates for southern European countries are rather uncertain, due to the limited number of measurements. For Western Europe as a whole 46% of the $\text{NH}_4\text{-N}$ in slurry is calculated to get lost as NH_3 (ECETOC, 1994).

Fertilizers

Addition of urease inhibitors to urea containing fertilizers (e.g. Watson et al., 1994), placement (Mahli, 1995) and incorporation of the fertilizer into the soil (Terman, 1979) are all effective measures to reduce NH_3 losses.

CALCULATING NH_3 LOSSES FROM DAIRY FARMS

Integration of NH_3 losses on farm scale

Large NH_3 losses are associated with housing, grazing, slurry storage and slurry application, and application of urea and ammonium based mineral fertilizers. A whole farm system analysis is most appropriate to quantify the various NH_3 sources (e.g. Hutchings et al., 1996). In this whole farm approach various simulation models for specific components of the farming system are combined to analyze the loss from the whole farm system.

A simple model was developed to simulate the effects of farm management and soil and environmental conditions on total NH_3 losses from dairy farms (Figure 2) that are self supporting with forage. In the model, grass production is determined by N fertilization, soil type and weather conditions. Grass production together with grazing management, amount of concentrates and fodder crops (e.g. maize) fed and milk yield per cow determine the diet and stocking density. Dietary NI and NR determine the N contained in excreta. This amount is distributed between shed (slurry) and grassland, depending on grazing management. Slurry handling affects NH_3 loss from housing, storage and application, thereby determining the

amount of N available for plant uptake and N effectivity. Total fertilizer N requirement by the crop minus effective slurry N determine the amount of applied mineral N fertilizer. The amount and type of fertilizer determine the NH_3 loss from mineral fertilizer.

Table 4 summarizes the mean results for 6 management options for farms with only dairy cows. Optimizing farm management may result in a more than threefold reduction in total NH_3 losses relative to the standard situation.

In the standard situation, total NI is about $188 \text{ kg cow}^{-1} \text{ yr}^{-1}$ (Table 4). The major part of the N excreted is contained in urea-like (U) components (Eq. 4). On sandy soil and for average environmental conditions ($750 \text{ mm rainfall yr}^{-1}$ and annual temperature of $9.5 \text{ }^\circ\text{C}$) the mean calculated NH_3 loss is 97 kg N ha^{-1} . Additional calculations (not shown) indicate that these losses may range between 75 and 113 kg N ha^{-1} under cold and wet and under dry and warm conditions during the growing season, respectively.

Partial replacement of grass silage by silage maize (situation B, Table 4) to reduce NI leads to 17% less grassland at the expense of maize land. Under the assumption of a linear relationship between U excretion and NH_3 loss, it results in a reduction of shed, storage and application losses totalling 19% compared with situation A.

Situation B resembles roughly the situation for NL in 1990. The calculated loss of $31.7 \text{ kg N cow}^{-1} \text{ yr}^{-1}$ is in agreement with estimates of Asman (1992), Isermann (1990) and Klaassen (1992) being respectively 32.7, 28.8 and $29.3 \text{ kg N cow}^{-1} \text{ yr}^{-1}$. Extrapolation of situation B to a nationwide emission from cattle would result in 101 Gg N yr^{-1} . These results are achieved by dividing the cattle population of 1990 in three groups; above 2 yr (2.171 million), between 1 and 2 yrs (0.964 million) and below 1 yr (1.695 million). Estimated total NH_3 losses are in agreement with the 90.5 and $92.3 \text{ Gg N yr}^{-1}$ estimated by Asman (1992) and Van der Hoek (1994), respectively.

Keeping the cows at night in the shed to replace grass partially by silage maize (situation C, Table 4) gives an additional reduction in NI. This leads to less grassland (65%) at the expense of maize land. The amount of U has been decreased to 71% of situation B. Total NH_3 losses are however higher than in situation B due to i) high shed (and storage losses) in summer and ii) an increase in application loss due to more slurry production. Mineral fertilizer requirement reduces due to i) more slurry production and ii) a lower N requirement.

Usage of slurry application techniques low in NH_3 emissions (situation D, Table 4) reduces NH_3 losses with 47% compared to situation B. Slurry application in the growing season increases slurry N effectivity and reduces mineral fertilizer N requirement.

Increasing the milk yield per cow reduces the number of cows. This reduces total feed requirement (situation E, Table 4) and thereby mineral N fertilizer requirement. The NH_3 loss per cow remains almost unchanged but combined with the lower number of cows, NH_3 loss per ha is reduced with 55% compared to situation B. Finally, a reduction of NH_3 losses with 67% is possible by reducing the NH_3 losses from the shed (situation F, Table 4).

Table 4. Effect of management on NH₃ losses on a dairy farm with a fixed milk quatum of 15000 kg ha⁻¹ yr⁻¹.

	A standard situation	B A + maize in the diet	C B + cows in the shed at night in summer + more maize	D C + 80% reduction of storage and application losses	E D + 1750 kg increase in milk yield per cow	F E + 50% reduction in shed losses
Cows per ha ²	2.4	2.4	2.4	2.4	1.875	1.875
Milk yield (kg cow ⁻¹) (3.4% protein)	6250	6250	6250	6250	8000	8000
Fraction grassland (ha ha ⁻¹)	1.0	0.83	0.65	0.65	0.69	0.69
Fraction maizeland (ha ha ⁻¹)	0.000	0.17	0.35	0.35	0.31	0.31
N rate grassland (kg ha ⁻¹)	306	306	255	255	171	171
Grazing hours in summer (h day ⁻¹)	20	20	9	9	9	9
Summer diet (cow⁻¹):						
Grass (kg DM)	13	13	8.1	8.1	9.6	9.6
N content (g kg ⁻¹ DM)	38.3	38.3	37.4	37.4	35.4	35.4
Maize silage ¹ (kg DM)	0	0	5	5	5.5	5.5
Concentrates ¹ (kg)	3.4	3.4	3.4	3.4	4.2	4.2
Winter diet (kg cow⁻¹):						
Grass silage (kg DM)	10	5	5	5	5.9	5.9
N content (g kg ⁻¹ DM)	30.0	30.0	29.4	29.4	27.5	27.5
Maize silage ¹ (kg DM)	0	5	5	5	5.9	5.9
Concentrates ¹ (kg)	5.5	5.5	5.5	5.5	6.7	6.7
Mean crude protein content (%)	20.1	18.7	16.2	16.2	15.6	15.6
N intake (kg cow ⁻¹ yr ⁻¹)	188.0	175.0	151.1	151.1	172.9	172.9
N retention (kg cow ⁻¹ yr ⁻¹)	36.5	36.5	36.5	36.5	45.8	45.8
N in U (kg cow ⁻¹ yr ⁻¹)	94.6	81.9	58.1	58.1	61.7	61.7
Slurry effectivity (kg N cow ⁻¹ yr ⁻¹)	25.7	20.5	22.6	32.6	39.9	44.6
Required fertilizer (kg N ha ⁻¹)	245	230	158	134	90	81
NH₃ losses (kg N yr⁻¹)						
Grazing (cow ⁻¹)	6.0	6.0	2.4	2.4	2.6	2.6
Shed + storage (cow ⁻¹)	9.8	7.7	10.0	10.0	11.0	5.5
Application (cow ⁻¹)	23.4	17.9	22.3	4.4	4.9	5.3
Fertilizer (ha ⁻¹)	2.4	2.3	1.6	1.2	0.9	0.9
Total (ha ⁻¹)	96.6	78.3	84.9	41.8	35.4	25.9
Total (cow ⁻¹)	39.2	31.7	34.7	16.9	18.4	13.4
Balance surplus	303	293	220	197	150	145

1) In the calculations the N concentration of maize silage and concentrates was about constant at respectively 14 and 27 g N kg⁻¹ DM. The recommended N rate on maize land is 150 kg N ha⁻¹ yr⁻¹. It was assumed that effective DM yield of maize silage was 12.1 ton DM ha⁻¹.

2) Based on the N response of productive sandy soil in the Netherlands.

To prevent a potential increase of other N losses (e.g. nitrate leaching), reductions of NH₃ loss in a whole farm approach requires that on the N budget total N input of fertilizers, concentrates and forage minus N output in milk and beef should be reduced with the achieved amount of NH₃ loss reduction. This condition is met in Table 4. The decrease of the balance surplus exceeds the decrease in total NH₃ loss per ha.

CONCLUSIONS

The results of simple calculations show that there is great scope for reducing NH_3 losses on dairy farms by improved management. The first farm-scale results in NL indicate that marked reductions in NH_3 losses are possible e.g. Koorevaar and Den Boer (1990) achieved a 50 % reduction in NH_3 losses on a practical dairy farm within a few years. The feasibility of a reduction up to 80 % is tested on the experimental farm The Marke (Aarts et al., 1992). However, one has to be careful to extrapolate these results to other countries in Europe because management systems and the environment may be different. Also the applicability of methods to reduce NH_3 losses may differ between countries e.g. application of slurry injection is not feasible in large parts of Europe due to stoney soils. The model includes possible interactions which may modify the effectiveness of the various management options

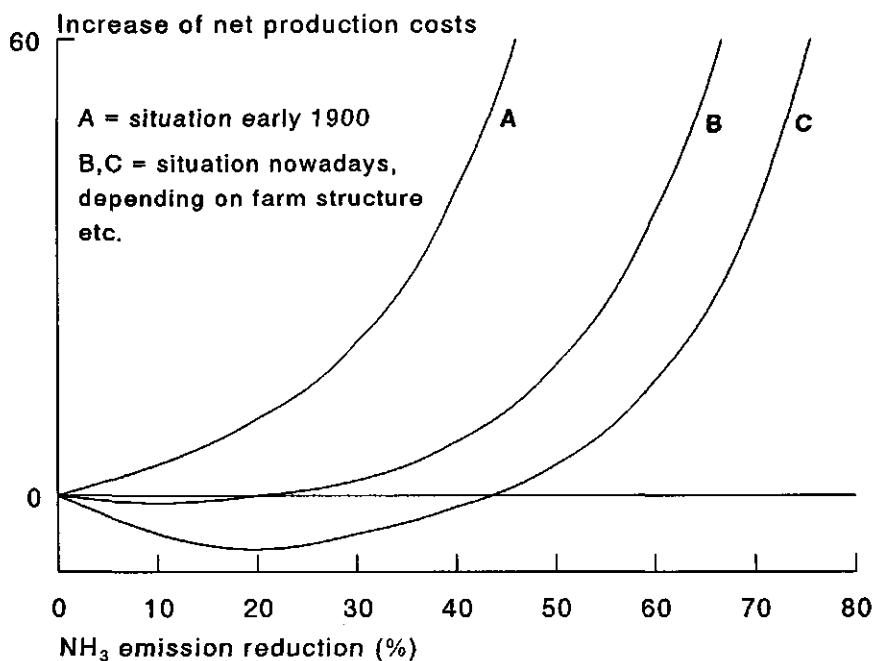


Figure 3. The possible effect of NH_3 emission reduction on the increase of net production costs of a farm.

e.g. the amount of $\text{NH}_4\text{-N}$ saved by reducing the shed emissions will get lost partly if no improved slurry application techniques are used. The understanding of these interactions is

essential in reducing the NH_3 losses on farm scale (see also Figure 2). A whole farm approach is therefore a prerequisite to reduce NH_3 emissions.

Of the different pathways of NH_3 losses on a farm, the results for housing are limited and most uncertain. This uncertainty is reflected in the wide range of NH_3 losses from housing systems. Furthermore, there is uncertainty about how a lower NI will affect urinary N excretion. Studying NH_3 losses from housing and the effect of dietary NI on urinary N excretion and as a result on NH_3 losses deserves more attention.

The rate at which improved management techniques to reduce NH_3 loss will be introduced in practice, depends on legislation and the expected increase in net production costs. Figure 3 indicates possible patterns of change in production costs. Dietary improvements to reduce U excretion and more efficient slurry application techniques in combination with application during the growing season reduce production costs (curve B and C), because of a better animal performance and a reduction in mineral fertilizer requirement, respectively. To comply with environmental targets concerning the reduction of NH_3 losses (70% in NL by the year 2000 compared to the year 1980) requires however a huge effort of farmers with associated high costs.

CHAPTER 9

SUMMARY AND GENERAL DISCUSSION

SUMMARY AND GENERAL DISCUSSION

During the last decade it became clear that NH_3 emissions from agriculture are substantial and that they are causing negative effects on the natural environment (Ellenberg, 1985). The first emissions inventories (Buisman et al., 1987) were rough estimates due to lack of data. Quantification of the magnitude of NH_3 losses was needed to improve these inventories in order to improve the predictions of NH_3 emission/deposition on the natural environment. Furthermore there was a need to investigate how to reduce NH_3 emissions to decrease the negative effects on the environment. We studied NH_3 losses of N fertilized grasslands under grazing by dairy cows, of mown N fertilized grassland during regrowth, of cattle slurry application and of N fertilizers.

AMMONIA EMISSIONS FROM (UN)GRAZED GRASSLAND

Grazed grassland

In the period 1987-1990 NH_3 volatilization was measured from rotationally grazed perennial ryegrass swards on a loam soil in Oostelijk Flevoland using the micrometeorological mass balance method (Chapter 2 and 3). Annual fertilizer rates as calcium ammonium nitrate (CAN) varied between 250 and 550 kg N ha⁻¹. On the same soil NH_3 cycling was measured on a sward used only for forage production and fertilized with calcium nitrate (Chapter 4 and 5). The experiments showed large variations in NH_3 emissions between individual cuts. On a seasonal basis there was not much difference in NH_3 emissions between years. On the 550N treatment losses in 1987, 1988 and 1990 were 8.5%, 7.7% and 6.9% of the N returned to the sward in urine and faeces, on the 250N treatment losses in 1988 and 1990 were 3.1% and 3.3%, respectively. Whole season measurements are required to obtain reliable data on NH_3 volatilization. Rainfall and sward management affected the size of NH_3 volatilization rate. Volatilization could be related to N excretion and N application rate. A calculation procedure was developed to estimate NH_3 volatilization from N application rate (Chapter 3).

The fraction emitted as NH_3 from voided urine and faeces was clearly lower than what was estimated by Buisman et al. (1987) (40% for urine and 5% for faeces, respectively), based on data from the (sub)tropics and laboratory experiments. The results obtained in this study are roughly in line with data from the south east of the UK (Jarvis et al., 1989a and 1989b) on a similar soil type. These studies confirm that field scale data are required, which take into account, local environmental conditions to obtain reliable data.

Ungrazed grassland

The NH_3 emission from grazed swards is the sum of NH_3 losses from fertilizer application, decaying grass, excreta and reabsorption by the sward grass. Losses from decaying grass and applied CAN fertilizer are probably negligible (Chapter 2). The measured losses are predominantly the net result from deposited excreta and reabsorption of volatilized NH_3 by the sward. A sward can take up and release NH_3 (Chapter 4 and 5). Our experiments indicate that a well fertilized growing pasture sward mown-only has a net uptake of aerial NH_3 ; during the growing period of the second and fourth cut there was a net uptake of 2.3 and 3.9 kg N ha⁻¹ (Chapter 4). During a few days after calcium nitrate fertilization a release of NH_3 was observed. Thereafter a net uptake was observed until harvest. The first few hours after cutting the sward showed an uptake of NH_3 later on followed by a release, probably due to tedding and windrowing. The observed net uptake was not expected, because the sward received about 100 kg N ha⁻¹ cut⁻¹. However soil inorganic N levels dropped to low values, resulting in relatively low N concentrations in the crop, and probably in low ammonium concentrations in the leaf tissue, causing a gradient from the atmosphere towards the crop (Holtan-Hartwig and Bóckman, 1994). The measured NH_3 fluxes were much greater during the day than during the night, indicating that the uptake is controlled by stomatal behaviour (Chapter 5, Holtan-Hartwig and Bóckman, 1994). The NH_3 compensation point of the grass (aerial NH_3 concentrations above this point cause an uptake of NH_3 by the grass crop), which was on average 14 $\mu\text{g m}^{-3}$, could be related to grass N content and soil water content.

Reabsorption of NH_3

The net uptake was measured on a sward where no NH_3 sources (grazing cattle, sheds) were present in the neighborhood of the experimental field. At grazing there are many point sources, resulting in NH_3 concentrations close to the grass surface which were 1-50 times higher than on ungrazed swards. Quantification of the reabsorption in our grazing experiments is not possible, but it is likely that the reabsorption of emitted NH_3 is (much) higher than the absorption of aerial N by the ungrazed swards. However, from deposition calculations it becomes clear that part of the emitted NH_3 is deposited (is reabsorbed) close to the source (Figure 1). According to these calculations 20% of the emitted NH_3 may become deposited on the measurement field.

Increasing the reabsorption of emitted NH_3 may be a possibility to reduce net emission from grazed swards. This could be done by decreasing N fertilizer rate, because it decreases grass N content, which may result in a decrease of the NH_3 compensation

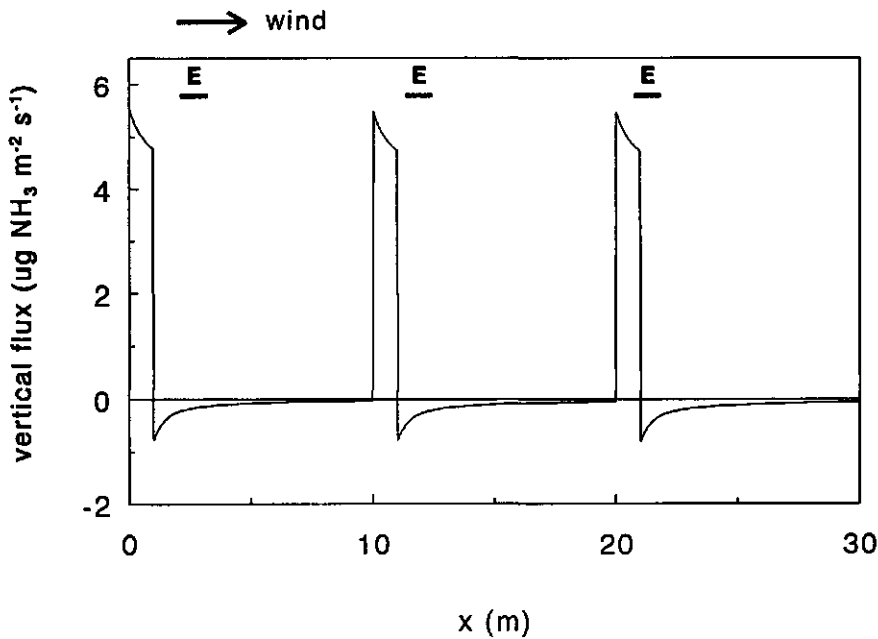


Figure 1. Vertical NH_3 flux (emission is positive) as a function of the upwind edge of a field with three urine patches (obtained from Asman, 1996).

point. This causes a larger NH_3 gradient from the atmosphere towards plant canopy. Increasing the absorptive area is another possibility to increase reabsorption of NH_3 . The taller sward at continuous grazing might have some potential. Jarvis et al. (1989b) measured a 42% decrease in NH_3 emission per grazing animal under continuous grazing compared to rotationally grazing, which might be due to more reabsorption and reduced exchange rates of NH_3 due to a larger boundary layer. However it should be stressed that the measurement of NH_3 emission is less accurate at low grazing intensities such as occurs with continuous grazing.

Emission measurements techniques

In our experiments (Chapter 2 and 3) and in those of Jarvis et al. (1989b) the micrometeorological mass balance or the so called integrated horizontal flux (IHF) method has been used. This technique is laborious and expensive. Often wind tunnel techniques as described by Lockyer (1984) have been used to measure NH_3 emission from urine, faeces, fertilizer and decaying grass (Sherlock and Goh, 1985; Vertregt and

Rutgers, 1991; Whitehead and Lockyer, 1989; Whitehead et al., 1989). Results of both methods have been used in emission inventories although the results are radically different.

Firstly, using the IHF method the sum of NH_3 losses from fertilizer application, decaying grass, excreta and reabsorption by the sward is measured, while with the windtunnel method every source is measured individually. Losses of NH_3 from decaying grass and fertilizer application in case of CAN are probably small, but reabsorption of emitted NH_3 is significant, as mentioned before. A correct estimation of this short distance deposition is very important in calculating the long range transport of $\text{NH}_3/\text{NH}_4^+$ (Asman, 1996). Therefore, the emissions for grazing obtained with the IHF method will be lower than results based on wind tunnel experiments with urine and faeces.

Secondly, the wind tunnel method does not or only partly take into account (i) the variability in N composition of urine between cows and in time, (ii) the spatial variability in urine spot sizes and the amount of urine voided per unit area of urine spots and (iii) variability in soil characteristics (e.g. soil water content) and sward density over space and time. The composition of the (artificial) urine in wind tunnel experiments reflects only part of the variance of cattle urine. Not only the urea N content but also the other N components like allantoin and creatine/creatinine can contribute to NH_3 volatilization (Whitehead et al., 1989) whereas the amount of hippuric acid may determine urea hydrolysis rate (Whitehead et al., 1989; Bussink, 1994b). In wind tunnel experiments a fixed area is treated by urine. Under grazing the area of urine spots is variable. Published data about the average area range from 0.26 to 0.68 m^2 per spot (Doak, 1952; During and McNaught, 1961; Keuning, 1977; Whitehead and Raistrick, 1993). Between individual cuts the average area of urine spots varied between 0.50 and 0.76 m^2 (Keuning, 1977). The variation in urine spot sizes depends on the amount of urine voided per urination, windspeed, slope and probably soil type and sward density. The effects of the mentioned parameters are generally non additive as can be seen from Bussink (1994b). Using average values for the individual parameters may thus lead to different results between the IHF and tunnel method.

Thirdly, climatic conditions in the tunnel often differ from those outside and combined with a different airflow over the surface this may affect NH_3 exchange and thereby NH_3 emission (Chapter 7). In a study with surface applied slurry Ryden and Lockyer (1985) only found a close relation between the wind tunnel and IHF method when windspeed in the tunnel was adjusted to windspeed outside the tunnel at the same height. The effect of rainfall in tunnel experiments is often lacking, but can be overcome by moving the tunnel once or twice a day (Velthof et al., 1990).

For the above reasons, micrometeorological techniques are to be preferred over wind

tunnel techniques to quantify NH_3 losses from grazing. However, there are some problems with micrometeorological techniques. Since, these techniques are expensive, measurements are often not instantaneous, but on a daily or diurnal basis with periods without measurements (Chapter 2, 3, 4 and 5). This might cause errors in the measuring of NH_3 emission because of short term variations in windspeed and concentration profile. A 10% underestimation of NH_3 emission may result when 4 measurements per 24h are replaced by a 24h measurement (Chapter 2). In our measurements (Chapter 2, 3 and 7) only the convective flux was measured. The flux due to horizontal diffusion is neglected, which may lead to an 10% overestimation of the real flux (Raupach and Legg, 1983). To overcome the problems associated with non-instantaneous measurements and neglecting horizontal diffusion, Denmead (1983) proposed the development of a NH_3 trapping device in which the air flow through is linearly related to windspeed. Leuning et al. (1985) developed such a NH_3 trap, which became commercially available in 1992/93. It is even possible to replace the IHF measurements by a measurement at a single height, which depends on roughness length and the radius of the measurement field (Denmead, 1983 and Wilson et al., 1982).

Other difficulties associated with IHF measurements in grazing studies is that the dung and urine spots have to be equally distributed over the plot (Denmead, 1983) to give a uniform source strength as demonstrated in an experiment by Ferm et al. (1991). An even distribution was obtained in our rotationally grazing experiments. Furthermore back diffusion could lead to an overestimation of the background concentrations at the windward side, leading to an underestimation of the emission. Placing the windward mast several meters from the border of the field, could overcome these problems. Circular plots are required to obtain a constant fetch (the distance between the center of the plot and the upwind boundary). In the 1987 grazing experiment only a square plot was used and thus the fetch became wind direction dependent.

To conclude micrometeorological techniques are needed to obtain representative data about the net NH_3 emission from grazing. With wind tunnel methods, the gross NH_3 emission is determined, which is a potential overestimation of the field scale emission. The wind tunnel method can be used to test the effects of certain parameters in comparative experiments.

Representativeness of the data for the Netherlands

Our experiments have been carried out on a soil which represents only a fraction of the total grassland area in the Netherlands. A major part of the grassland is on sand grassland with a low CEC. This factor appears to be dominant in determining NH_3 emissions from

urine (Whitehead and Raistrick, 1993; Bussink 1994b). The higher the CEC, the lower the NH_3 emission from urine. Also, in wind tunnel experiments of Vertregt and Rutgers (1988) with artificial urine, a higher emission was observed from sand (10.5%) than from clay (4.5%) grassland. Curves 4 and 5 in Figure 5 of Chapter 3 are therefore too optimistic. It is possible to include a CEC correction in equation 9 in Chapter 3 to improve the extrapolation of this equation to other soil types, by using the slope of the linear regression analysis on the grassland emission data of Whitehead and Raistrick (1993) and tune this slope on the average annual emission of the 550N plot of 7.71%. This resulted in the following correction factor for CEC ($\text{mmol}_c \text{ kg}^{-1}$) $(7.71 - 0.02793(\text{CEC}-280))/7.71$. For sandy soils this means that equation 9 in Chapter 3 has to be multiplied by a factor 1.8.

In the experiments of Whitehead and Raistrick (1993), a fixed area was treated by urine. Under grazing the area of urine spots is variable (Keuning, 1977) and may depend on soil characteristics resulting in different urine spot sizes for similar amounts of voided urine. Since only a part of the urinary N volatilizes, it is expected that NH_3 emission increases when urine spot size increases per litre of voided urine. This may be the reason of the high emission in the autumn of 1989, when rainfall may have reduced urine infiltration, thereby increasing the urine treated area. It has to be tested whether the urine treated area per urination is soil type dependent and causes major differences in NH_3 emission between soil types other than a CEC effect.

Results with dairy cows on the loamy soil have to be extrapolated to heifers and calves, sheep and to less grass-based diets. Heifers and calves have a different urinary N composition (due to a lower N retention) and void smaller amounts of urine, which may result in a different amount of urine voided per unit of urine spot area. The expected higher concentration of urinary N may increase emission (Whitehead, 1989; Bussink, 1994b). Linear extrapolation may thus underestimate NH_3 for heifers and calves. Extrapolation of dairy cow data to sheep is difficult. Jarvis et al. (1991) measured NH_3 emissions of less than 10 kg N ha^{-1} from a 420N sward continuously grazed by sheep, which is much less than from dairy cows (Jarvis et al., 1989b). The results in Chapter 2 and 3 are mainly from grass based diets. However, on many farms the diet of the grazing cow contains silage maize. It is not clear how this affects NH_3 emission, because replacing 30% of the grass by silage maize in the diet of dairy cows decreased the amount of urine, while urinary N concentration remained the same or slightly increased (Valk, pers. comm.; unpublished results). The first effect lowers NH_3 volatilization potential, whereas the second effect increases it (Whitehead and Raistrick, 1989; Bussink, 1994b). Nevertheless, there are possibilities to reduce urea concentration in urine by diet optimization, which can be further enhanced by feeding extra salt (Van Vuuren and

Smits, 1996).

At present the best estimate to calculate emissions from grazing is the proposed procedure at the end of Chapter 3 corrected for the CEC effect. To improve the estimates for grazing on other soil types and by other animals and for other diets additional field scale measurements are required. With modified field scale techniques (single point measurements and the Leuning sampler) this can be done with much less labor input and lower costs of analysis.

Our measurements on the ungrazed fertilized pasture showed a net uptake of aerial NH_3 . Other experiments on grassland (Holtan-Hartwig and Bøckman, 1994) all showed a net average release of NH_3 . These experiments were carried out in areas with much lower aerial concentrations of NH_3 than in our experiments, which typically ranged between 10 and 25 $\mu\text{g NH}_3\text{-N m}^{-3}$. Normal aerial concentrations in rural areas are often much below 14 $\mu\text{g NH}_3\text{-N m}^{-3}$ (WHO, 1986; Allen et al., 1988; Grünhage and Jäger, 1990), the seasonal NH_3 compensation point found in our experiments (Chapter 4). From 1990 onwards NH_3 emissions started to decrease. This resulted in a decrease in NH_3 background concentrations and will result in decreased NH_3 uptake by the grass crop and may even change into a net release of NH_3 . In large parts of the Netherlands, NH_3 concentrations in the air are much higher than at our measurement site in Flevoland. Therefore, it is expected that a growing grass crop will remain a sink for aerial NH_3 .

APPLICATION OF NITROGEN

Fertilizer

To stimulate grass production N fertilizer or slurry is applied. Losses of NH_3 from CAN are low in contrast to those of urea (Chapter 6). Agronomic trials in The Netherlands confirmed the superiority of CAN compared to urea (Van Burg et al., 1982; Chapter 6). However, in the UK and Ireland urea was as effective as CAN, especially in the first cut (Watson et al., 1990). Agronomic trials show the net effect of N losses, including differences in nitrate leaching, denitrification and N_2O emission. It could be proved that the amount of short term rainfall and temperature after N fertilizer application caused the observed difference in urea and CAN efficiency between years as well as between the Netherlands and the UK (Chapter 6). High rainfall and low temperatures decrease NH_3 volatilization, but especially high rainfall increase nitrate leaching, denitrification (Jordan, 1989) and N_2O emission (Velthof et al., 1996b). Minimizing NH_3 losses from fertilizer application, may thus increase other N losses, which is not desired. Optimizing herbage

yield, thereby minimizing N losses may be the best approach to decide which fertilizer to use. We developed a calculation model to improve the decision analysis whether to use urea or CAN, taking into account economic constraints (Chapter 6). Under prevailing Dutch conditions for the first and second cut it is only once every 5 and 7 years profitable for the farmer to use urea in stead of CAN.

Slurry

Slurry application is a major source for NH_3 emission. Reduction of these losses on grassland is possible by decreasing (i) the surface area of the slurry (injection, bandspreading), (ii) the concentration of ammonium in slurry (dilution, irrigation) or (iii) the pH of the slurry. We tested the latter by using nitric-acid-treated cattle slurry. Our mass balance results showed that the mean total emission of 60% of the $\text{NH}_4\text{-N}$ applied with surface applied untreated slurry could be reduced with 85, 72 and 55% when acidified slurry was used with pH values of 4.5, 5.0 and 6.0, respectively (Chapter 7). Our tunnel experiments showed 73% reduction at pH 4.5. The lower reduction and the different pattern of NH_3 volatilization (Chapter 7) might be due to different conditions in and outside the tunnels and higher slurry application rates compared to the mass balance experiments. The measured losses in the mass balance experiments could be related to temperature, slurry pH, potential water evaporation and NH_4^+ concentration. It was possible to calculate which slurry pH would be required to obtain a certain reduction in NH_3 emission. Experiments from the UK also showed that acidification of cattle slurry has great potential in reducing NH_3 emissions (Pain et al., 1990; Stevens et al. 1989).

The results obtained with acidified slurry are comparable to those obtained by decreasing the surface area of slurry. Averaged over all experiments in the Netherlands (Huijsmans et al., 1996), injection (closed slot), shallow injection (open slot) and narrow bandspreading decreased NH_3 emission with 98, 83 and 69%, respectively.

The treatment of slurry with nitric acid, reduces NH_3 emission, but may increase denitrification. The concept of acidification of cattle slurry was originally, to apply it to the slurry pit of the housing. It would than reduce NH_3 losses from the shed and slurry storage as well as from slurry application. The in this way acidified slurry contains more $\text{NH}_4\text{-N}$ which together with the added nitric acid could than be used as enriched manure. Field experiments showed that the N efficiency of acidified slurry on the basis of its inorganic N content was 110 and 90% (Van Lent et al., 1995), for first and later cuts, respectively, compared to that of CAN. However, substantial denitrification losses were measured of about 20% of the N contained in the added nitric acid for slurry stored in the pit of cubicles with a pH of 4.5 (Van Lent, 1995). This was caused by inadequate mixing of acidified slurry along the walls and floors of the pit, resulting in local pH values

ranging between 5-7, which stimulated denitrification. A large part of this N was lost as N_2O as became clear from incubation studies (Oenema and Velthof, 1993). Losses of this greenhouse gas should be prevented. Acidifying immediately before slurry application became an alternative (Huijsmans and Mulder, 1996) to prevent the denitrification losses in the shed. Thus far however surface application of acidified slurry on grassland is not allowed, because it is difficult to control by authorities.

PERSPECTIVES OF REDUCING NH_3 LOSSES

Losses of NH_3 occur from slurry application, housing, slurry storage, grazing, fertilizer application and from crops, in descending order of importance (Chapter 8). Total losses range from 17 to 46 kg N $cow^{-1} yr^{-1}$, reflecting the variability in amount and composition of animal excreta, management of the slurry and soil and environmental conditions. The amount and composition of urine and faeces depend on N transformations in the digestive track of the cow. Urea has the highest potential for NH_3 volatilization followed by allantoin, uric acid and creatinine in decreasing order. Creatine, xanthine and hypoxanthine have a low NH_3 volatilization potential.

The main strategies to reduce potential NH_3 losses are lowering the dietary N intake of the cows to reduce the excretion of mainly urea and/or technical means like the use of new slurry application techniques and the development of low emission housing. Reducing NH_3 loss may increase other N losses. To prevent this the achieved reduction in NH_3 loss must lead to a reduction of total N input from fertilizers, concentrates and forage on the N budget of the farm. This is possible because a reduction of NH_3 loss improves the N nutrient value of slurry. Model calculations showed great scope for reducing NH_3 losses on dairy farms by improved management. Up to three fold reductions in NH_3 loss are possible together with marked reductions in N fertilizer use (Chapter 8).

Pure grassland farming

One of the main reasons of the sharp decline in NH_3 emission reported in Chapter 8 is that farmers on sandy soil can grow maize, to reduce N intake of the dairy cattle. Especially when cows are kept in the shed at night, marked reductions in the N budget and NH_3 losses are possible (Aarts et al., 1992; Koorevaar and Den Boer, 1990; Chapter 8). However, in parts of the Netherlands with peat and wet and heavy clay soils maize growing and harvesting is difficult. Lowering N fertilizer rate becomes than the main strategy to reduce NH_3 emission from (grazed) grassland. This may reduce herbage yield.

Furthermore, under grazing NH_3 losses are relatively low (Chapter 2 and 3) compared to slurry application (Chapter 6) and housing (Chapter 8). Therefore, it seems that there is no urgent need to lower N fertilization, if less than 8% of the N voided in urine and faeces volatilizes on loam grassland. However if the remaining N is not used by the grass crop large denitrification and leaching losses may occur. Keuning (1977) found a 15% increase in annual herbage yield on urine spots deposited in April on sandy grassland receiving $273 \text{ kg N ha}^{-1} \text{ yr}^{-1}$. Deenen and Middelkoop (1992) found with urine spots on sandy grassland deposited late July, a 5% increase at 250 kg N ha^{-1} applied as fertilizer and a decrease of 7% at 400 kg N ha^{-1} , respectively. Moreover, of the N contained in dung and urine 8 and 16%, respectively was recovered in herbage on the 250N sward, whereas they were negligible on the 400N sward. Generally, urine spots deposited later in the growing season and higher N application rates decrease N recovery (Van der Meer and Whitehead; 1990, Van der Putten and Vellinga, 1996), though urine spots deposited in autumn may increase herbage yield in the first cut of the next growing season (Keuning 1977). Because, NH_3 volatilization and N recovery by herbage makes up only a part of the N voided urine and dung, the remainder of the N must nitrify and emit N_2O , leach, denitrify ($\text{N}_2/\text{N}_2\text{O}$) and/or accumulate. Measured nitrate leaching (Macduff et al., 1990), denitrification (De Klein, 1994), N_2O emission (De Klein and Van Logtestijn, 1994; Velthof et al., 1996a) and accumulation (Hassink and Neeteson, 1991) can be substantial, especially under grazing. Possibilities to reduce fertilizer N input under grazing (without reducing grass yield) are of great interest in reducing NH_3 loss, and particularly in reducing the other N losses. Lowering N application rate reduces N emissions from the applied fertilizer itself. Moreover it will result in a much lower herbage N concentration and thereby in a lower N intake and lower N (urea) excretion which will reduce NH_3 emissions (Fig. 2, Chapter 3) and other N losses from grazing.

Until recently, all grassland soils, except peat, had the same fertilizer recommendations. In 1994 an improved fertilizer recommendation scheme was introduced (Vellinga et al., 1993). The main criteria in this scheme are N delivery capacity of the soil, apparent N recovery, target yield and time of year. The soils are divided in four groups based on the first two criteria. Recently, Hassink (1996) showed that it is possible to improve the prediction of the N delivery capacity, thereby optimizing fertilizer application rate. A further possibility, is to avoid urine spots when fertilizer is applied. Such a spot contains $400 - 600 \text{ kg N ha}^{-1}$. All fertilizer N on such a spot is superfluous. Vellinga et al. (1996) expect that a reduction of $55-110 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ compared to the present recommendations should be possible by improvement of the prediction of N deliver capacity, by avoiding fertilization of urine spots, by adjustments of N fertilization to actual growing conditions and target herbage yields. Furthermore, if sward damage occurs as on sandy

soil due to urine scorching and poaching (Deenen, 1994) the optimum N fertilizer rate should be reduced.

Improvement in grass breeding practices resulting in new cultivars with higher N efficiencies can also lead to a reduction of N input on grassland. Over the last 20 years a 10% improvement of production has been realised. If such an improvement could also be realized in future, than N fertilization could possibly reduce to two thirds of the present optimum recommendations (Vellinga and Van Loo, 1994).

Continuous grazing is also a possibility to reduce NH_3 losses from grazing. However, because net animal production of continuous and rotational grazing are generally similar (Ernst et al., 1980; Schlepers and Lantinga, 1985) other losses like nitrate leaching or N_2O emission must be somewhat higher for continuous than for rotationally grazing. Total N losses are similar for both systems and therefore it makes no difference which grazing system is used. However, continuously grazing is more difficult to manage.

Emission reduction in practice

The whole farm approach of Chapter 8 demonstrates that there is much scope to reduce NH_3 emissions from grassland as well as at farm scale. However, using fixed emission factors is too simplistic and may be too optimistic. Firstly, NH_3 emission and also the other N loss processes are dynamic processes. Due to changing weather conditions large differences in emission loss rates may exist within the season and between individual seasons (like the very dry spring of 1996). This requires a dynamic approach of calculating emissions at farm scale and calculating the effects for fertilizer requirement and feed purchases (Hutchings et al., 1995).

Secondly, emission factors (e.g. slurry application and housing) are obtained from designed experiments. For slurry injection with open slots the recommended amounts are applied on flat and not to wet uniform fields in order to prevent overfilling of the slots. In practice, fields are uneven and sometimes slanting, the amounts applied are often larger than recommended in order to reduce the costs of bandspreading or injection. Also the soil may be too wet to allow a proper infiltration of slurry. This means that emission reductions in practice will be lower than under experimental conditions. Introduction of a correction term is recommended to prevent overestimation of the obtained emission reductions.

Thirdly, due to legislation more slurry is applied in spring and summer. This increases the potential of NH_3 emissions, despite the usage of low emission slurry application techniques. These factors may partly explain the systematically lower modelled NH_3 and NH_4^+ concentrations in air than actually are measured (Erisman et al., 1996).

Further research with respect to NH₃ emissions

Several estimates for NH₃ emissions have been made in the last five years, which have resulted in comparable emissions levels. However, the NH₃ emission pattern during the season is less well known. For example, the reduction of the time of slurry application may result in a peak in emission in spring and summer and probably also in deposition peaks of NH₃/NH₄⁺. Asman (1992) estimated the seasonal variation in the emission rate from information on agricultural activities and from measurements of NH₄⁺ in air and precipitation and found large discrepancies between the results of both methods. It is important to know seasonal variation in the emission rate as peak emissions in spring and summer may cause less reduction of eutrophication of land and water than expected, e.g. phytoplankton will only utilize additional N sources between March and October (Horstmann, pers communication).

Quantification of NH₃ losses under grazing on a field scale on other soil types is required, because the amply studied loam soil represents only a part of the grassland soils in the Netherlands. Extrapolation of these results of loam soil to other soil types is difficult.

Farming is a dynamic process, depending on inputs and weather conditions. The approach of Hutchings et al. (1995) is one tool to minimize NH₃ losses. However, emissions of NH₃ and other N losses are related to each other. This requires a broad approach in which all N flows on grassland are taken into account dynamically. This is done in the model "Ntegratie" (Vellinga et al., 1996). The aim is to predict the grass growth as a function of actual soil and weather parameters. In this way, optimum N application rate can be calculated taking into account the expected N delivery by the soil and given a set of restrictions like the required yield or the maximum permitted nitrate leaching. Implementation of the model results in practice is urgently needed, given the legislation on the reduction of N surpluses on farms.

MAIN FINDINGS

The main findings of the experiments described in this thesis are as follows:

- * Quantitative data have been obtained about the NH₃ emissions from grazing, slurry application and the uptake and release of NH₃ from a growing grass crop.
- * Volatilization of NH₃ on grazed pastures could be related to N excretion, N application rate and CEC, which resulted in a calculation procedure to estimate NH₃ volati-

lization.

- * Grassland mown-only and fertilized according to current recommendations showed a net uptake of aerial NH_3 during grass regrowth.
- * The recognition that NH_3 fluxes in grassland mown-only have a diurnal pattern as well as a pattern during the grass regrowth period.
- * The recognition that reabsorption of emitted NH_3 by grazed swards is important.
- * The recognition that the amount of short-term rainfall and temperature after N fertilizer application determine the observed differences in N efficiency between urea and CAN, between years as well as between countries.
- * Acidification is a good method to reduce NH_3 emissions from surface applied slurry. With a simple relationship it was possible to calculate the required pH in order to meet a target emission reduction.
- * The recognition that a whole farm approach is needed to reduce NH_3 emissions and to prevent the increase of other N losses.

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SAMENVATTING

Aan het begin van deze eeuw waren organische meststoffen de belangrijkste bron voor de stikstofbemesting op landbouwbedrijven. Het was bekend dat het gebruik, de opslag en de toediening van mest gepaard ging met ammoniakverliezen. Door toediening van chemicaliën aan de mest of door direct inwerken van mest werd getracht zo min mogelijk ammoniak verloren te laten gaan uit de mest om zodoende een maximaal profijt te hebben van de stikstof (N) in de mest. Echter de kosten en technische problemen zorgden ervoor dat deze maatregelen in die tijd niet toepasbaar waren. Met de opkomst van kunstmest in de vijftiger jaren verflauwde de interesse in ammoniakverliezen uit dierlijke mest. De belangstelling nam echter weer sterk toe nadat in de tachtiger jaren bekend werd dat ammoniakvervluchtiging milieubelastend was. Uit schattingen die vooral gebaseerd waren op onderzoeksgegevens uit het buitenland, bleek, dat de landbouw veruit de grootste bijdrage leverde aan de ammoniakemissie. Ruim 60% hiervan kwam voor rekening kwam van de rundveehouderij, waarbij de melkveehouderij de grootste bijdrage leverde.

In de melkveehouderij treedt ammoniakemissie op uit mest- en urineplekken bij beweiding, door toediening van mest en kunstmest en uit het gewas zelf. Andere belangrijke bronnen van ammoniak binnen de melkveehouderij zijn de huisvesting en de mestopslag. De stikstofverbinding die in belangrijke mate bijdraagt aan de ammoniakvervluchtiging is het in urine aanwezige ureum. Vanwege de negatieve effecten van ammoniak op het milieu bestaat sinds 1985 de behoefte om de ammoniakemissie te kwantificeren voor de Nederlandse omstandigheden en belangrijker nog de emissie van ammoniak te beperken. Hoge concentraties aan ammoniak kunnen namelijk leiden tot gewasschade. Verder leidt de vervluchtiging van ammoniak tot een toename van de stikstofdepositie. Deze kan daarmee bijdragen aan bodemverzuring en aan de eutrofiëring van natuurgebieden, hetgeen leidt tot veranderingen in flora en fauna.

Deze studie handelt over de ammoniakemissie van grasland in de melkveehouderij. De onderzoeksdoelen zijn (i) het kwantificeren van de ammoniakemissie van grasland, (ii) het vergroten van de kennis over ammoniakemissieprocessen op grasland en (iii) het bestuderen van maatregelen om de ammoniakverliezen op grasland, maar ook op bedrijfsniveau te beperken.

AMMONIAKEMISSION VAN BEWEID EN GEMAAID GRASLAND

Beweid grasland

In een eerste studie naar de omvang van de ammoniakemissie werd op basis van litera-

tuurgegevens geschat dat uit urine en mest respectievelijk 40% en 5% van de aanwezige N zou emitteren. Door de ammoniakemissie bij omweiden met melkkoeien te meten, hebben we getracht de ammoniakemissie nader te kwantificeren.

Gedurende de periode 1987-1990 is de ammoniakemissie gemeten op jonge zeeklei in Oostelijk Flevoland (Hoofdstukken 2 en 3). Daarbij is gebruik gemaakt van een volveldse meetmethode (de micrometeorologische massabalansmethode). In 1987 is de ammoniakemissie gemeten bij een stikstofgift van $550 \text{ kg ha}^{-1} \text{ jr}^{-1}$, in 1988 bij 250 en $550 \text{ kg ha}^{-1} \text{ jr}^{-1}$ en in 1989 (tijdens de laatste twee sneden) en 1990 bij 250, 400 en $550 \text{ kg ha}^{-1} \text{ jr}^{-1}$. De stikstofbemesting werd gegeven als kalkammonsalpeter verdeeld over 7 tot 9 sneden. Bij omweiden begon de emissie vrijwel direct na inscharen en liep door tot ongeveer 10 dagen na uitscharen. Tussen de sneden traden grote verschillen op in ammoniakemissie, met als extremen 0 en 18% emissie van de N aanwezig in de op het perceel uitgescheiden urine en mest. Het emissieniveau per snede werd sterk beïnvloed door de weersomstandigheden en het graslandmanagement. Regenval voorafgaand aan de beweiding resulteerde in een hoge ammoniakemissie terwijl regenval direct na de beweiding resulteerde in een lage emissie.

Tussen de jaren waren er echter geen grote verschillen in ammoniakemissie. Bij een jaargift van 550 kg N ha^{-1} bedroegen de ammoniakverliezen in 1987, 1988 en 1990 respectievelijk 42,2, 39,2 en $32,8 \text{ kg N ha}^{-1}$, hetgeen overeenkomt met 8,5%, 7,7% en 6,9% van de op het perceel uitgescheiden N in urine en mest. Bij $250 \text{ kg N ha}^{-1} \text{ jr}^{-1}$ bedroegen de verliezen in 1988 en 1990 respectievelijk 8,1 en $9,1 \text{ kg N ha}^{-1}$ overeenkomend met 3,1% en 3,3% en bij $400 \text{ kg N ha}^{-1} \text{ jr}^{-1}$ bedroeg het verlies $27,0 \text{ kg N ha}^{-1}$ overeenkomend met 6,9% van de op het perceel uitgescheiden N in urine en mest.

Metingen gedurende het gehele seizoen waren nodig om betrouwbare data te verkrijgen met betrekking tot de ammoniakvervluchtiging. We vonden een goede relatie tussen ammoniakvervluchtiging en de stikstofuitscheiding cq. de stikstofgift. Op basis van deze relatie en met literatuurgegevens is een rekenprocedure ontwikkeld waarmee het mogelijk is om de ammoniakvervluchtiging af te leiden uit de stikstofresponsecurve, de stikstofuitscheiding en de kationenuitwisselingscapaciteit van de grond (Hoofdstukken 3 en 9). Hiermee is het mogelijk de ammoniakvervluchtiging per grondsoort te berekenen. In deze rekenprocedure wordt rekening gehouden met de beweidingsefficiëntie en -selectiviteit, de stikstofretentie in melk en vlees, de hoeveelheid krachtvoer tijdens beweiding en de tijd die dieren 's zomers bij het melken niet in de weide zijn. Aanvullende metingen op andere grondsoorten zijn gewenst om dit rekenmodel te toetsen. Daarnaast is het onvoldoende bekend welk effect bijvoeding met stikstofarme producten heeft op de ammoniakemissie bij beweiding.

Gemaaid grasland

Het was bekend dat planten zowel ammoniak kunnen opnemen als afgeven. Van goed bemest grasland waren echter nauwelijks gegevens beschikbaar. Wij hebben getracht de opname en afgifte van ammoniak door gras op bemest grasland te kwantificeren in een experiment op jonge zeekei in Oostelijk Flevoland uitgevoerd in 1989. Het grasland werd alleen gemaaid en per snede bemest met ongeveer 100 kg N ha^{-1} grasland (Hoofdstukken 4 en 5). De bemesting is uitgevoerd met kalksalpeter om ammoniakemissie uit de meststof te vermijden. Ammoniakfluxen zijn om de twee uur volvelds gemeten (flux gradiënt methode) gedurende een aantal etmalen tijdens de groeiperiode van de tweede en vierde snede. Onze metingen gaven een netto opname te zien van 2,3 en 3,9 kg N ha^{-1} gedurende de groeiperiode van de tweede en vierde snede (Hoofdstuk 4). Gedurende een paar dagen na bemesting met kalksalpeter werd een afgifte van ammoniak door het gras gemeten. Overtollig opgenomen N werd via het blad afgegeven als ammoniak. Na een paar na bemesting tot aan het maaien van de snede werd een opname van ammoniak gemeten. De eerste uren na maaien werd een opname van ammoniak gezien, later gevolgd door een afgifte, waarschijnlijk ten gevolge van schudden en wiersen. Deze netto opnames waren niet verwacht vanwege de stikstofgift van 100 kg N ha^{-1} per snede. De gemeten ammoniakfluxen waren overdag veel groter dan 's nachts, hetgeen er op duidde dat de opname en afgifte werd gecontroleerd door het open zijn van de huidmondjes. De concentratie aan ammoniak waarbij geen opname of afgifte van ammoniak door het gewas optrad, het ammoniakcompensatiepunt, was gemiddeld $14 \mu\text{g m}^{-3}$. Het compensatiepunt daalde bij het afnemen van het stikstofgehalte in het gras en afnemen van het bodemvochtgehalte.

Reabsorptie van NH_3

Met de volveldse meetmethode wordt de resultante gemeten van de emissie uit mest- en urineplekken, van de toegediende kunstmest, van afstervend gras en de reabsorptie van geëmitteerde ammoniak door het gras. De emissie van afstervend gras en uit de gebruikte kunstmeststikstof zijn gering (Hoofdstuk 2). Reabsorptie van geëmitteerde ammoniak op het beweide perceel is belangrijk. Berekeningen geven aan dat 20% van de uit urine- en mestplekken geëmitteerde ammoniak weer wordt opgenomen. Dit verklaart ten dele waarom puntmetingen (windtunnelmetingen) aan urine- en mestplekken hogere emissies geven dan volveldse metingen.

TOEDIENING VAN STIKSTOF

Kunstmest

Belangrijke stikstofmeststoffen op grasland zijn (kalk)ammonsalpeter (KAS) en ureum. Bekend is dat in Nederland de werking van KAS op grasland beter is dan die van ureum. Daarentegen vindt men in Ierland en het Verenigd Koninkrijk (UK) dat de werking van ureum vooral in de eerste snede vrijwel gelijk is aan die van KAS. Bekend is dat ureum bemesting tot meer ammoniakvervluchtiging leidt dan KAS-bemesting. Het risico op nitraatuitspoeling en denitrificatie (lachgasemissie) is daarentegen groter bij KAS- dan bij ureumbemesting. De resultante van deze verliezen komt tot uiting in veldproeven waarin de stikstofwerking van deze meststoffen is getoetst.

Onze analyse van Nederlandse en UK-veldproeven laat zien dat de verschillen in stikstofwerking tussen ureum en KAS vooral terug te voeren zijn op de temperatuur en de hoeveelheid neerslag kort na de bemesting. Dit geldt zowel voor verschillen tussen proefjaren als voor verschillen tussen landen. Door aggregatie van Nederlandse en UK data kunnen we een goede relatie afleiden tussen de relatieve stikstofwerking van ureum (ten opzichte van KAS) en de hoeveelheid neerslag en de gemiddelde temperatuur drie dagen na bemesting. Op basis hiervan is een beslissingsmodel afgeleid. Voor Nederlandse omstandigheden voorspelt dit model dat het voor de eerste en tweede snede gemiddeld respectievelijk eens in de vijf en zeven jaar financieel aantrekkelijk is voor de boer om ureum te gebruiken in plaats van KAS.

Dunne rundermest

Toegediende dunne mest op grasland is een belangrijke bron van ammoniakemissie. Vermindering van deze emissie is mogelijk door (i) het met mest bedekte oppervlak te verkleinen (injectie, zodebemesting, sleepvoeten), (ii) het verlagen van de ammoniumconcentratie in de mest (verdunnen of verregenen) of (iii) het verlagen van de pH van de mest. Wij hebben de mogelijkheden van de laatste methodiek getest voor met salpeterzuur direct voor toediening of in de mestopslag aangezuurde dunne rundermest (Hoofdstuk 7) met een pH die varieerde tussen 3.9 en 6.6. De hoeveelheden mest die werden toegediend in de volveldse metingen varieerden tussen 7 en 17 m³ ha⁻¹. De emissie van breedwerpig toegediende onbehandelde mest bedroeg gemiddeld 60% van de in de mest aanwezige ammoniumstikstof. Deze kon met 85, 72 en 55% verminderd worden door aangezuurde mest te gebruiken met een pH van respectievelijk 4.5, 5.0 en 6.0. We vonden een goede relatie tussen de gemeten ammoniakemissie en de luchttemperatuur, de pH van de mest,

de verdamping en de ammoniumconcentratie in de mest ($r^2 = 87\%$). Met deze relatie kan berekend worden welke pH de mest moet hebben om een bepaalde emissiereductie te realiseren. Door het niet bereiken van een evenwichts pH gaf direct voor toedienen aangezuurde mest een hogere emissie dan in de mestopslag aangezuurde mest bij eenzelfde pH voor toedienen van de aangezuurde mest. Uit de resultaten kon afgeleid worden dat de ammoniakemissie uit aangezuurde mest onafhankelijk is van de grondsoort en de hoeveelheid toegediende mest (Hoofdstuk 7) bij toediening van hoeveelheden kleiner dan $17 \text{ m}^3/\text{ha}$.

Beperking ammoniakverliezen en stikstofoverschot in de melkveehouderij

In Hoofdstuk 8 wordt een overzicht gegeven van de grootte van de ammoniakverliezen in de melkveehouderij uit de verschillende bronnen, welke factoren deze verliezen bepalen en hoe de verliezen te verminderen zijn. Bronnen van ammoniakverliezen zijn toegediende mest, stallen, mestopslag, weidend vee, kunstmest en gewassen in afnemende volgorde van belangrijkheid. De totale gerapporteerde verliezen variëren tussen de 17 en 46 kg N per koe per jaar, hetgeen de variabiliteit weergeeft in de hoeveelheid en samenstelling van urine en mest, het gebruik van dierlijke mest en bodem en omgevingscondities. De hoeveelheid en samenstelling van urine en mest hangt af van de stikstofopname door en stikstofomzettingen in de koe. Van de stikstofverbindingen in urine heeft ureum de hoogste potentie voor ammoniakvervluchtiging, gevolgd door allantoïne, urinezuur en creatinine. Creatine, xanthine en hypoxanthine hebben een lage potentie voor ammoniakvervluchtiging. Er is een relatie afgeleid waarmee berekend kan worden hoeveel van de door het dier opgenomen N als ureum-achtige (ureum plus allantoïne plus urinezuur plus creatinine) verbindingen wordt uitgescheiden.

De belangrijkste mogelijkheden om de ammoniakemissie te verminderen zijn i) het verminderen van de stikstofopname door het dier met het voer en verhoging van de stikstofretentie om de uitscheiding van ureum-achtige producten te verminderen en ii) technische aanpassingen zoals het toepassen van emissiearme mesttoedieningstechnieken of emissiearmere huisvesting. Berekeningen voor een bedrijf op zandgrasland tonen aan dat indien deze mogelijkheden goed op elkaar zijn afgestemd de ammoniakemissie met meer dan 65% gereduceerd kan worden, waarbij tevens het stikstofoverschot op bedrijfsniveau sterk wordt verminderd. Dit kan door het melkvee in de zomer 's nachts opstallen en bij te voeren met snijmais (om de N-opname te verminderen), het toepassen van emissiearme toedieningstechnieken, het verhogen van de melkproductie van de koe en het toepassen van emissiearme huisvesting.

Een hogere melkproductie per koe leidt tot een vermindering van het aantal koeien

en daarmee tot een geringere voerbehoefte. De stikstofbemesting op grasland kan worden verlaagd. Dit gecombineerd met de toegenomen stikstofwerking van dierlijke mest (meer mest en emissiearm toegediend) leidt tot een flinke besparing op het stikstofkunstmestverbruik (Hoofdstuk 8). Daarmee neemt het stikstofoverschot op het bedrijf sterk af.

Op puur graslandbedrijven zijn dergelijke forse emissieverminderingen moeilijker te realiseren doordat bijvoeding met stikstofarme voedergewassen om de stikstofopname en -uitscheiding te verlagen veelal niet mogelijk is en doordat niet de meeste efficiënte mesttoedieningstechnieken kunnen worden gebruikt. Verlaging van de N-opname door de koe met het gras kan door de stikstofgift te verlagen. Volgens een recentelijk ontwikkeld model "Ntegratie" is het mogelijk om 55 tot 110 kg N ha⁻¹ te besparen op de stikstofgift op grasland ten opzichte van het huidige landbouwkundige advies zonder gevolgen voor de grasopbrengst. Implementatie van deze modelresultaten in de praktijk is dringend gewenst, niet alleen om de ammoniakverliezen terug te dringen, maar ook het stikstofoverschot op de bedrijven verder te beperken.

DE BELANGRIJKSTE RESULTATEN DIE HET ONDERZOEK HEEFT OPGELEVERD

- * Kwantitatieve gegevens over de ammoniakemissie bij beweiding en dunne mest toediening en de ammoniakopname en -afgifte door gras.
- * De vervluchtiging van ammoniak op beweid grasland kon gerelateerd worden aan de stikstofgift, de stikstof uitscheiding in mest en urine en de kationeneuittwisselingscapaciteit, hetgeen resulteerde in een rekenprocedure om de ammoniakemissie te bepalen.
- * Grasland dat alleen werd gemaaid en werd bemest volgens de huidige adviezen vertoonde een netto opname van ammoniak uit de lucht.
- * Onderkenning dat er patroon bestond in de opname en afgifte van ammoniak zowel per etmaal als over de hergroeiperiode van gemaaid grasland.
- * Onderkenning dat de hoeveelheid regenval en de temperatuur kort na bemesting de verschillen in stikstofwerking tussen kalkammonsalpeter en ureum bepalen, zowel tussen jaren als tussen landen.
- * Aanzuren van dunne mest is een goede methode om de ammoniakemissie van oppervlakkig toegediende dunne mest te beperken. Het was mogelijk een relatie af te leiden waarmee het mogelijk werd om te berekenen welke pH nodig is om een bepaalde emissiereductie te realiseren.
- * Onderkenning dat een benadering op bedrijfsniveau nodig is om ammoniakverliezen te beperken zonder dat dit leidt tot een verhoging van andere stikstofverliezen.

CURRICULUM VITAE

Wim Bussink werd 24 september 1962 op de ouderlijke boerderij in het Gelderse Aalten geboren. Hij volgde de VWO-opleiding aan de Christelijke Scholengemeenschap te Aalten en haalde in 1980 het eindexamen. In datzelfde jaar begon hij met de studie Bodemkunde en Bemestingsleer aan de Landbouww Universiteit te Wageningen. In 1984 liep hij een half jaar stage aan de landbouwfaculteit van de TU München te Weihenstephan. Nadat hij in 1987 de doctoraalsbul had gehaald, trad hij in dienst bij het toenmalige Nederlands Meststoffen Instituut en het huidige Nutriënten Management Instituut (NMI). NMI is een stichting die gefinancierd wordt door het meststoffenbedrijfsleven en de distributie. Als belangrijkste doelstelling heeft NMI het bevorderen van een efficiënt gebruik van nutriënten bij bemesting en op bedrijfsniveau. Hij is gestationeerd bij het Praktijk Onderzoek Rundvee, Schapen en Paarden (PR) te Lelystad. Van 1987-1990 hield hij zich bezig met het meten van de ammoniakemissies bij beweiding. Van 1989-1992 was hij betrokken bij het onderzoek naar het meten van de ammoniakemissies bij het toedienen van dunne mest op grasland. Van 1988-1996 was hij tevens betrokken bij een NMI-project: "Beperking van nutriëntenverliezen in de melkveehouderij". De doelstelling van dit project was de verliezen van nutriënten door ammoniakvervluchtiging, uit- en afspoeling te reduceren met behoud van een rendabele melkveehouderij. Zijn huidige interesse gaat uit naar het optimaliseren van het nutriëntenmanagement op rundveebedrijven.