Landbrugsministeriet
Statens Planteavlsforsøg

Ammonia volatilizaton from cattle and pig slurry during storage and after application in the field

Ammoniakfordampning fra kvæg- og svinegylle under lagring og efter udbringning på jorden

Ph.D. dissertation

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Tidsskrift for Planteavls Specialserie

Beretning nr. S 2209 - 1992

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2. Forord

Denne afhandling er udarbejdet med henblik på erhvervelse af Ph.D.-graden ved Den Kongelige Veterinær- og Landbohøjskole. Hermed afsluttes 3 års studier financieret af Forskerakademiet og Statens Planteavlsforsøg. Det eksperimentelle arbejde er udført på Askov Forsøgsstation med kontakter til sektion for Kulturteknik og Planteernæring, Landbohøjskolen.

Studiets hovedfag har været Planteernæring og fysiologi under vejledning af professor Niels Erik Nielsen med bifag i analytisk fysisk kemi under vejledning af lektor Søren Storgaard Jørgensen og lektor Leif Skibsted. Vejledere på projektet har været afdelingsforstander Bent Tolstrup Christensen, professor Niels Erik Nielsen og lektor Jan Kofoed Schjørring.

Jeg vil gerne rette en tak til Bent T. Christensen, fordi jeg fik muligheden for at gennemføre dette studium på Askov Forsøgsstation, og for en grundig, positiv og ikke mindst konstruktiv kritik af de artikler, jeg har forfattet i løbet af de 3 år. Niels Erik Nielsen takkes for ideer og inspiration til projektet. En tak til Jan K. Schjørring for et godt samarbejde gennem årene, samt for interessante og behagelige samtaler og diskussioner. Endelig vil jeg takke medarbejderne på Askov Forsøgsstation, fordi de tog godt imod mig og gav en stor hånd til gennemførelse af eksperimenterne. Især skal Kirsten Vang takkes for sin store og dygtige indsats i forbindelse med opbygning af forsøgsudstyr og gennemførelse af forsøgene.

Til slut en stor tak til min kone Birgitte og mine børn Niels og Tine, fordi I tog med til Jylland, og ovenikøbet accepterede, at jeg det følgende år drog til København næsten ugentligt.

I løbet af studiet er der publiceret følgende artikler, hvori resultaterne fra studiet beskrives i detaljer. I denne afhandling gives en sammenfatning af artiklerne, hvortil der henvises ved numrene I-XII.

Artikler publiceret internationalt:

I. *Schjørring, J.K, Sommer, S.G. and Ferm, M.* 1992. A simple passive sampler for measuring ammonia emission in the field. Water Air Soil Pollut. 62, 13-24.

II. *Sommer, S.G. and Jensen, E.S.* 1991. Foliar absorption of atmospheric ammonia by ryegrass in the field. J. Environ. Qual. 20, 153-156.

III. *Sommer, S.G., Kjellerup, V.K. and Kristjansen, O.* 1992. Determination of total ammonium nitrogen in pig and cattle slurry: Sample preparation and analysis. Acta. Agric. Scand. In press.

IV. *Sommer, S.G. and Olesen, J.E.* 1991. Effects of dry matter content and temperature on ammonia loss from surface-applied cattle slurry. J. Environ. Qual. 20, 679-683.

V. *Sommer, S.G., Olesen, J.E. and Christensen, B.T.* 1991. Effects of temperature, wind speed and air humidity on ammonia volatilization from surface applied cattle slurry. J. Agric. Sci. Camb. 117, 91-100.

VI. *Sommer, S.G., Christensen, B.T., Nielsen, N.E. and Schjørring, J.K.* 1992. Ammonia volatilization during storage of cattle and pig slurry: Effect of surface cover. J. Agric. Sci. Submitted.

VII. *Sommer, S.G., Jensen, E.S. and Schjørring, J.K.* 1992. Leaf absorption of gaseous ammonia after application of pig slurry on sand between rows of winter wheat. 395-402. In **Air Pollution Research Report 39; Field Measurements and Interpretation of Species related to Photooxidants and Acid Deposition.** Eds. Angeletti, G., Beilke, S. and Slanina, S. Udgivet af EEC. Belgien.

Artikler publiceret i Tidsskrift for Planteavl og Grøn Viden, Landbruget:

VIII. *Sommer, S.G.* 1989. Udspredning af gylle: Fordampning af ammoniak og fordeling af udbragt gylle. (Spreading of slurry: Volatilization of ammonia and distribution of applied slurry). Tidskr. Planteavl. 93, 323-329. (Summary and legends in English).

IX. *Christensen, B.T. and Sommer, S.G.* 1989. Fordampning af ammoniak fra udbragt gødning. Metode og ammoniaktab fra urea og urea-ammonium nitrat. (Volatilization of ammonia from fertilizers and manure. Methodology and loss of ammonia from urea and urea-ammonium-nitrate). Tidsskr. Planteavl. 93, 177-190. (Summary and legends in English).

X. *Sommer, S.G. and Christensen, B.T.* 1989. Fordampning af ammoniak fra svinegylle udbragt på jordoverfladen. (Volatilization of ammonia from surface-applied pig slurry). Tidsskr. Planteavl. 93, 307-321. (Summary and legends in English).

XI. *Sommer, S.G.* 1990. Ammoniakfordampning fra svinegylle på nykalket jord. (Ammonia volatilization from pig slurry applied to recently limed soil). Grøn viden, Landbrug. 51, 1-4.

XII. *Sommer, S.G. and Christensen, B.T.* 1990. Ammoniakfordampning fra fast husdyrgødning samt ubehandlet, afgasset og filtreret gylle efter overfladeudbringning, nedfældning, nedharvning og vanding. (Ammonia volatilization from solid manure and raw, fermented and separated slurry after surface application, injection, incorporation into the soil and irrigation) Tidskr. Planteavl. 94, 407-418. (Summary and legends in English).

3. Sammenfatning

Fordampning af ammoniak reducerer husdyrgødnings indhold af plantetilgængelig kvælstof. Ammoniakken tabes i stalden, fra lager, under udbringning, fra gødning der ligger på jorden og fra græssende dyr. Den fordampede ammoniak vil blive afsat som ammoniak eller ammonium, og kan derved medføre uønskede ændringer af kvælstofbegrænsede plantesamfund. I dette studie er faktorer af betydning for ammoniaktabet fra gyllebeholdere, under udbringning og fra udbragt gødning, blevet undersøgt.

Forskellige metoder til bestemmelse af ammoniaktabet fra handelsgødning og fra husdyrgødning er benyttet eller afprøvet. Størrelsen af ammoniaktabet kan som regel ikke bestemmes som forskellen i tilført og genfundet kvælstof eller udtrykt som merudbytter af tørstof eller indhøstet kvælstof. Ammoniaktab målt i et kammer kan ikke direkte relateres til tab i marken. Kammerteknikken kan derfor mest hensigtsmæssig anvendes under kontrollerede forhold i laboratoriet, i forsøg hvor ammoniaktabet ved forskellige behandlinger ønskes sammenlignet. Målinger af ammoniaktabet fra gylle med vindtunneler har i markforsøg givet samme værdier som målinger med meteorologiske metoder, når vindhastighed og nedbør i vindtunnelerne kontinuert justeres til samme niveauer som udenfor. Vindtunnelerne er meget anvendelige til undersøgelser i marken, hvor effekten af forskellige faktorer ønskes bestemt, og til at tilvejebringe data for modellering af ammoniaktabsprocessen. Til direkte målinger af ammoniaktabet fra udbragt gødning i markskala-forsøg, anses meteorologiske massebalance-metoder for at være mest velegnede. En ny metode baseret på passive flux målere har i en afprøvning vist sig at give korrekte tabsmålinger. Metoden viste sig enkel at anvende i et forsøg, hvor ammoniaktabet fra seks forsøgsfelter i en mark blev bestemt samtidig. Forsøgene er imidlertid arealkrævende, og målingerne kan ikke gennemføres, hvis der i vindretningen er en ammoniakkilde inden for en afstand af 50-100 m.

Vindtunneler blev benyttet til måling af ammoniakfordampningen fra gylle lagret i pilot-skala gyllebeholdere (0,90 × 2,89 m), og fra gylle nedfældet direkte, nedharvet i jorden eller udbragt på jorden (0,5 × 2,0 m). Ammoniaktabet ved udspredning af gylle blev undersøgt i et enkelt forsøg og blev målt som differencen i ammoniumindholdet før og efter udbringning.

Fra gyllelagre med ugentlig omrøring var ammoniaktabet 3-5 g NH_3-N m^{-2} dag^{-1}. Om sommeren (16,9 °C) var ammoniaktabet 50% større end i en vinter-forårs periode (7,3°C), som følge af de højere temperaturer. Tilstedeværelse af et flydelag begrænsede ammoniaktabet med 80% i forhold til tabet fra gylle omrørt ugentligt. Et forsøg fra en vinterperiode viste, at et lag halm på 15 cm kunne erstatte flydelaget. Ekstra overdækning i form af leca sten, rapsolie, sphagnum, flydende plastfolie og et trælåg begrænsede ammoniaktabet væsentligt. Der er blevet udviklet en model til beregning af ammoniaktabet fra lagret gylle, og de beregnede tab er i overensstemmelse med tabene målt med vindtunneler.

Under udbringning af gylle, dvs. fra gyllen forlader gyllesprederen til det rammer jorden, er ammoniaktabet mindre end 4% af det udbragte ammonium i et forsøg med klapspredere.

Ammoniakfordampningen fra gylle udbragt på jordoverfladen påvirkes af klimaet, gyllens sammensætning, beskaffenhed af jordens overflade og tiden fra gyllen udspredes til den nedbringes i jorden. I de første 6 timer efter udbringning steg ammoniaktabet eksponentielt med temperaturen, hvorefter tabet steg lineært med temperaturen. Ammoniaktabet øgedes med stigende vindhastighed indtil 2-3 m s^{-1}. Ved vindhastigheder derover ændredes tabsraten ikke. Nedbør eller vanding reducerede ammoniaktabet fra overfladeudbragt husdyrgødning.

Ammoniaktabet øgedes med stigende tørstofindhold i gyllen samt ved stigende pH og alkalinitet. Det akkumulerede ammoniaktab efter 6 timer steg lineært med tørstofindholdet i gyllen; men derpå var forløbet kurvet. Hvis tabsraterne blev korrigeret for effekten af temperatur og pH, var tabet sigmoidalt relateret til tørstofindholdet. Dette resultat antyder, at ændringer i tørstofindholdet ved niveauer under 4% og over 12% er af mindre betydning for størrelsen af ammoniaktabet.

Efter nedfældning eller omhyggelig nedharvning var ammoniaktabet ringe. Hvis jorden blev harvet (til 10 cm dybde) før overfladeudbringning af gylle, blev ammoniaktabet begrænset med ca. 50% i forhold til gylle udbragt på ubehandlet jord. Udlægning af gylle mellem rækker af afgrøder ved slangeslæbning kan begrænse ammoniaktabet fra gyllen, idet forflygtigelsen af ammoniak fra gyllen mindskes, og ammoniak optages af planterne.

4. Summary

Volatilization losses of ammonia reduces the fertilizer value of animal manure for plant production. Ammonia losses related to livestock farming occur from animal houses, from manure storages, during spreading of manure, from surface applied manure and from grazing animals. Deposition of aerial ammonia and ammonium may cause undesired changes of oligotrofic ecosystems. The objective of this study was to increase the knowledge of the factors, which influences the ammonia loss potential from slurry during storage, spreading and from slurry applied in the field.

Techniques for measuring ammonia losses from slurry were tested and are discussed. It is concluded, that changes in the nitrogen content of slurry and crop responses are not adequate for determination of ammonia loss from slurry stored or applied to the field. The use of small enclosures should be used only for comparing relative ammonia loss rates between treatments, as losses cannot be related directly to losses in the field. The technique is best for measurements in the laboratory where the environment can be controlled. A wind tunnel system gave results similar to measurements in the open, if wind speed and precipitation in the tunnels were adjusted to the environment. The tunnels can be used under field conditions in studies of the effect of various treatments in replicate experiments. The systems have been shown to provide reliable data for modelling the process of ammonia volatilization. The demand for big homogeneous areas with a uniform source strength restricts the applicability of the eddy correlation techniques, the gradient technique and the ZINST mass balance technique. A test of a new passive flux sampler used in a mass balance method gave accurate determinations of the ammonia loss from a circular plot.

Wind tunnel systems were used for determining ammonia volatilization losses from stored slurry and from slurry applied in the field. Ammonia loss during spreading was determined by the change in nitrogen content of the slurry.

From slurry storages which were stirred weekly, average ammonia losses were 3-5 g NH_3-N m^{-2} d^{-1}. The losses during summer (16.9°C) were 50% higher than during winter-spring (7.3°C) due to higher temperatures. Surface crustings reduced ammonia losses by 80% compared to the losses from slurry stirred weekly. One experiment showed that a layer of chopped straw (15 cm) could replace a surface crusting layer. Ammonia losses from slurry covered by rape oil, leca pebbles, sphagnum peat, floating foil or a wooden lid were less than 60% of the loss from stirred slurry.

A model for predicting ammonia loss from stored slurry was developed. The model predictions agreed with ammonia loss values from uncovered slurry determined with wind tunnels.

During application of slurry with conventional spreaders ammonia losses were less than 4% of the ammonium content.

Ammonia loss from surface applied slurry is influenced by climate, slurry composition, soil conditions and time from application until incorporation of the slurry. Ammonia losses were exponentially related to air temperature during the first 6 hours. Subsequent loss rates were linearly related to temperature. Ammonia losses increased with wind speed up to 2-3 m s^{-1}. At higher wind speeds, loss rates were not influenced by change in wind speed. Rain or irrigation reduced ammonia losses from surface applied slurry.

Ammonia losses increased with increasing slurry dry matter content and pH. The accumulated ammonia loss after six hours was linear related to slurry dry matter content, but in following periods the relation was curved. After adjusting the results for temperature and pH effects the relationship was sigmoidal. Changes in slurry dry matter content, therefore, had little effect on ammonia loss, when the dry matter content was higher than 12% or lower than 4%.

Little ammonia was lost from slurry injected directly into the soil, and from slurry incorporated into the soil. Cultivation before application of slurry onto the soil reduced ammonia losses compared to an unharrowed soil by 50%. Ammonia loss from slurry applied to a crop may be reduced by application on the soil between rows of the crop. The reduction is caused by a reduced transfer of ammonia from the slurry to the atmosphere and absorption of ammonia by the plant leaves.

5. Nomenclature

Symbol	Definition	Units
K_H	Henrys constant	atm kg mol^{-1}
K_N	The equilibrium constant of NH_4^+ and NH_3	mol l^{-1}
F	Vertical flux of ammonia	mol NH_3 m^{-2} s^{-1}
NH_{3g}	Concentration of gaseous ammonia in equilibrium with the concentration of NH_{3l} in the slurry solution	atmosphere
NH_{3a}	Ammonia concentration in the immediate atmosphere	atmosphere
TAN	Concentration of total ammoniacal nitrogen $[NH_4^+]+[NH_3]$	mol l^{-1}
NH_{3l}	Concentration of ammonia in solution	mol l^{-1}
NH_4+	Concentration of ammonium in solution	mol l^{-1}
J	Diffusive transport of TAN in the slurry	mol cm^2 s^{-1}
D	Diffusion coefficient of TAN	cm^2 s^{-1}
K(v)	Transfer coefficent for ammonia volatilization	mol NH_3-N m s^{-1}
R_a	Resistance of the turbulent layer above the slurry	s m^{-1}
R_b	Resistance of the laminar layer between the surface of the slurry and the turbulent layer	s m^{-1}
l	The height of the internal boundary layer	cm

Symbol	Definition	Units
z_o	Roughness length	cm
z_o	Roughness length	cm
k	von Karmans constant	k=0.4
v_*	Roughness speed	$m\ s^{-1}$
v(z)	Mean wind speed at different heights above the slurry	$m\ s^{-1}$
T	Air temperature	°K
z	Distance from the surface of the slurry, zero is the surface of the slurry, negative is downward and positive is upwards.	cm
x	The distance downwind from the edge of the slurry treated area or the slurry tank	cm

6. Introduction

In Denmark about 60% of the nitrogen excreted from housed cattle and pigs is collected and transported in form of slurry, equivalent to a yearly production of 180.000 ton N (Kofoed and Hansen, 1990). More than half the nitrogen is ammonium-N which is readily available to plants. Ammonia volatilization, therefore, reduces the value of slurry for plant production.

In Denmark and in Europe, emission of ammonia from animal manures represents the most important source of atmospheric ammonia (Buijsman **et al.** 1987). The deposition of ammonia may be detrimental to nitrogen limited ecosystems (Roelofs, 1986). In Denmark the use of animal manure, therefore, has been regulated by law.

Ammonia volatilization losses related to livestock farming occur from animal houses, manure storages, applied manure and from grazing animals. As stated by Jarvis and Pain (1990), there are few dependable measurements of ammonia loss from stored manure. From applied slurry it has been shown that ammonia volatilization is related to the general weather conditions, slurry composition, soil characteristics and method of application (Brunke **et al.** 1988; Pain **et al.** 1989; Döhler 1991; Horlacher and Marschner 1990; Thompson **et al.** 1990). Experiments under different environmental regimes, and differences in the origin and chemical composition of the slurries employed have given a qualitative understanding of the factors influencing ammonia loss. However, the limited number of experiments have not allowed a general quantitative relationships to be established between ammonia loss rates and the various variables influencing ammonia losses.

6.1 Objective of the study

- To increase the understanding of the factors influencing ammonia loss from stored and surface applied animal slurry.
- To evaluate different techniques for determining ammonia losses from confined areas.
- To obtain quantitative relationship between the rate of ammonia loss (F) and the intensity of various factors affecting ammonium concentrations, eg. pH and dry matter content of the slurry.

6.2. Processes of volatilization used in the development of a model

The main source of ammonium in slurry is urine which contains more than 60% of the excreted nitrogen from pigs and cattle (Koefoed and Hansen, 1990). In urine about 70% of the nitrogen is in urea (Muck and Richards, 1983; Jarvis **et al.** 1989). Ammonium and carbonate are produced during the hydrolyses of urea by the enzyme urease:

$$CO(NH_2)_2 + 2H_2O \rightleftharpoons 2NH_4^+ + CO_3^-$$

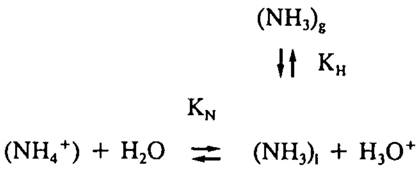
Urease is released from living and disintegrating microbial cells and is found in a wide range of environments including soil and the floors of animal houses. Due to high temperatures and the moist substrate, this reaction will be rapid in slurry produced in animal houses. Only little of the excreted urea therefore is left in stored slurry, and the conversion of urea is not included in the model for describing the ammonia loss from slurry storages.

Ammonia volatilization from a liquid surface such as recently stirred slurry can be considered to be the transfer of ammonia from the liquid surface of the slurry to the immediate atmosphere. The rate of ammonia loss is given by:

$$F=K(v)(NH_{3,g} - NH_{3,a}) \qquad (1)$$

K(v) depends mainly on wind speed, surface roughness and temperature (Rachpal-Singh and Nye, 1986a).

The concentration of atmospheric ammonia in equilibrium with a solution will be proportional to the concentration of NH_{3l} in solution. The relationship between the different ammoniacal species in solution is as follows:



$$\begin{tikzcd} & (NH_3)_g \arrow[d, shift left] \arrow[d, leftarrow, shift right, "K_H"'] \\ (NH_4^+) + H_2O \arrow[r, shift left, "K_N"] & (NH_3)_l + H_3O^+ \arrow[l, shift left] \end{tikzcd}$$

The concentration of NH_3 at equilibrium can be calculated by the equations:

$$[TAN]=[NH_{3l}] + [NH_4^+] \tag{2}$$

$$[NH_4^+]=[NH_{3l}][H_3O^+]/K_N \tag{3}$$

$$[NH_{3l}]=[TAN]/(1 + [H_3O^+]/K_N) \tag{4}$$

The atmospheric ammonia concentrations in equilibrium with the concentrations of TAN in the surface of the slurry can be calculated by the Henry's Law equation:

$$NH_{3,g}=K_H[NH_{3l}] \tag{5}$$

Combining 1, 4 and 5 gives the equation:

$$F=K(v)(K_H([TAN]/(1 + [H_3O^+]/K_N)) - NH_{3,a}) \tag{6}$$

Volatilization of ammonia from the surface of the slurry reduces the concentrations of TAN in the surface layers. For the volatilization process to continue, TAN must be transported to the surface layer. Depletion of TAN will cause a decrease in concentrations toward the top layer, and TAN will diffuse to the surface. This transport can be described by Fick's law:

$$J= -D\ d[TAN]/dz \tag{7}$$

It is assumed the slurry is not stirred, and that turbulent transfer caused by wind or temperature gradients in the slurry may be neglected due to the viscosity and dry matter content of most slurries.

The transfer coefficient K(v) used in equation (1) may be calculateded by the equations (Molen et al. 1990):

$$K(v)= 1/(R_a+R_b) \quad (8)$$

$$R_a = \ln (l\, z_o^{-1})\, k^{-1}\, v_*^{-1} \quad (9)$$

$$v_* = v(z)\, k\, (\ln(z\, z_o^{-1}))^{-1} \quad (10)$$

$$l(\ln(l/z_o)-1)=k^2\, x \quad (11)$$

R_b is the resistance of the laminar layer dependent on slurry surface roughness and v_*. The relation between R_b, surface roughness and v_* is not known, and has to be estimated from ammonia loss measurements.

The temperature dependent equilibrium constant (K_N) and Henry Law constant (K_H) can be calculated by the equations (Beutier and Renon, 1978):

$$\ln K_N=-177.95292-1843.22/T+31.4335\ln(T)-0.0544943T \quad (12)$$

$$\ln K_H =160.559-8621.06/T-25.6767\ln(T)+0.035388T \quad (13)$$

7. Techniques for measuring ammonia volatilization losses

Ammonia losses may be determined indirectly from the crop response to nitrogen in applied manure, or as the difference in ammonium content added and the recovery of inorganic nitrogen in the soil. The direct methods of determining ammonia losses from slurry are based on changes in atmospheric ammonia concentration in enclosures placed over the treated surface, or on micrometeorological techniques in which the volatilization is determined in the free air above the surface.

7.1. Indirect measurements

Ammonia volatilization from slurry added to the soil and determined by indirect techniques will be influenced by leaching, denitrification, mineral fixation of ammonia and mineralization/immobilization processes. Estimating ammonia volatilization from crop responses (dry matter yield or plant uptake of nitrogen) to the field applied manure do not discriminate between these processes. Ammonia loss estimated from cropping methods will depend on the crop response to the added nitrogen (the crop/nitrogen response curve). If the yield is at the maximum of the crop response curve, there will be no significant increase in crop production due to the applied nitrogen, and the ammonia volatilization is overestimated. Christensen (1986) found that the ammonia loss determined with indirect methods tends to be twice as high as losses found by direct methods. Using the nitrogen uptake, additional errors arise due to variations in uptake of nitrogen induced by climate or infection of the crop, and to the exchange of nitrogen between the atmosphere and the crop (Farquhar **et al.** 1980). Introducing ^{15}N will not reduce the errors as the assimilated ^{15}N will take part in the exchange processes (Schjørring **et al.** 1989). Therefore recovery of nitrogen in the harvested crop only broadly reflect differences in the gaseous loss measured with wind tunnels (Larsen **et al.** 1992; Thompson **et al.** 1987).

Nõmmik (1966) studied ammonia volatilization from nitrogen fertilizers by the N-recovery technique. To reduce leaching, the experiments were carried out in periods with no precipitation, and in dry soils to avoid denitrification. Furthermore, the soil had a low ammonium fixing capacity and the experimental periods were kept short to reduce effects of fertilizer nitrogen on net-mineralization.

The precaution needed for this technique, however, limits its use for estimating ammonia volatilization from surface applied slurry, as the soil will be moistened and inorganic nitrogen, therefore, exposed to denitrification (Thompson and Pain, 1988; Molen **et al.** 1988). Molen **et al.** (1988) established a mass balance for nitrogen applied to the soil surface in urine, using micrometerorological measurements and the nitrogen recovery technique. Between 10-30 % of the nitrogen added was not accounted for. The authors suggested that this was due to denitrification, as all nitrogen added was recovered when nitrification inhibitors were added.

The nitrogen recovery approach was used in a study of ammonia absorption by leaves after application of slurry on the soil between the rows of winter wheat (**VII**). ^{15}N enriched ammonium was added to the slurry. Immobilization, mineralization and denitrification processes were inhibited by mixing mercury chloride into the slurry. To improve the calculation of the nitrogen balance, the slurry was applied to nitrogen-free sand. From this system, ammonia loss was higher than the losses determined with direct methods in the field. The higher losses were ascribed to the low CEC of the sand and the absence of nitrification which reduces ammonia losses.

Recovery of TAN in stored slurry cannot be used for determination of the ammonia loss, because ammonia is formed by net-mineralization of nitrogen during the experiments (Bode, 1991). The loss of ammonia is small compared to the total-N content in the slurry. Differences in total-N, therefore, may give erroneous estimates of ammonia loss due to sampling variability. Inhomogenity of total-N is great in stored slurry, as the organic nitrogen precipitates or floats to the surface.

Ammonia loss during application (i.e. from the slurry leaves the spreader and until it hits the ground) was measured by determining the difference in content of ammonium (**VIII**). The slurry in the slurry tanker was stirred to eliminate variations in TAN content of the samples related to inhomogenity. In this experiment the experimental period was short, and microbial processes, therefore, of minor importance.

7.2. Direct measurements

7.2.1. Enclosures

Enclosures used in the field have been made of cylinders with a lid on the top, and an inlet and outlet at the top for air to pass over the experimental plot (Ferguson **et al.** 1988; Kissel **et al.** 1977). Ammonia loss was measured by collecting the gaseous ammonia in acid. The air may be drawn through the enclosure continuously, the enclosures being permanently closed (Sherlock and Goh, 1984). In the system of Kissel **et al.** (1977) the enclosures were periodically closed with the lid, and air was only drawn through the enclosure during closure.

Ammonia losses measured with enclosures increase with the air flow up to 15 volume changes/minutes (Kissel **et al.**, 1977; Ferm 1986). At higher flow rates, ammonia loss was not significantly influenced by change in air flow rate (Kissel **et al.** 1977). Hoff **et al.** (1981) proposed that change in aerodynamics caused 41% of lost ammonia from slurry applied on a plastic foil not being accounted for by the determination with enclosures only closed during measurements. The direct measurements were compared to the loss determined by the N-recovery technique, but the difference could not be ascribed to denitrification or immobilization. When determined with an enclosure, ammonia loss from urea spread upon soil covered by a 3 cm layer of chopped wheat straw, was much lower than determined by a micrometerological method (Ferguson **et al.** 1988). The straw seemed to have directed the air flow over the surface of the wheat straw, by that increasing the diffusion resistance. If windspeed is high and the roughness of the surface low, the accumulated loss from a treated plot determined with an enclosure will be similar to direct measurements in the open. This was shown by determining ammonia loss from urea broadcasted to a pasture (grass height 1 cm) with a permanent closed enclosure (air change 17 volume minute^{-1}), compared to simultaneous measurements with an aerodynamic technique. During the experiments, the wind speed was high and there was no rain (Black **et al.** 1985).

The most appropriate use of the enclosure technique is determinations of the ammonia loss potential from animal manure or fertilizers applied to an uncovered soil in the laboratory (Döhler, 1991; Whitehead and Raistrick, 1990). The air exchange should be 17 volumes minute^{-1} or more. The enclosures change the air temperature with less than 2°C at this flow rate (Sherlock and Goh, 1984).

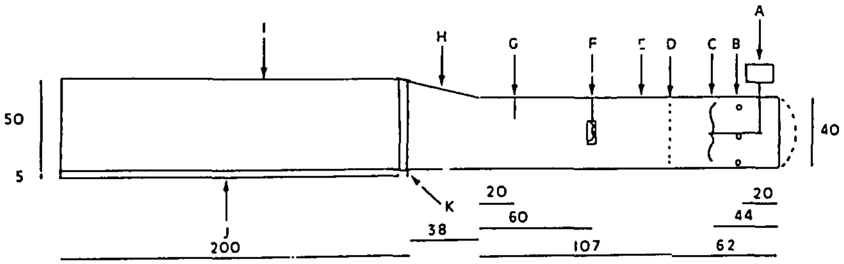


Figure 1. Cross section of a wind tunnel unit. Dimensions are given in cm (XI). A, motor; B, air sampling points; C, fan; D, Steel-net; E, steel duct; F, vane anemometer head; G, temperature sensor; H, steel funnel; I, tunnel of polycarbonate; J, metal frame; K, spade-edge.

7.2.2. Wind tunnels

A system of portable wind tunnels (Fig. 1) has been designed to allow measurements of ammonia volatilization in the field without inducing marked changes in the microclimate (Lockyer, 1984; IX). The loss of ammonia from the plot is calculated by the product of air flow and the difference in ammonia concentration of air entering and leaving the tunnels.

Wind speed within the tunnels is controllable, and a test showed that air temperatures inside the tunnel generally are less than 1 °C lower than ambient air temperatures (2 m height) and soil temperatures outside tend to be 1.9°C higher than inside (V; Ryden and Lockyer, 1985). Compared to the micrometeorological mass balance method, similar ammonia losses were determined with wind tunnels, provided the wind speeds in the tunnels were adjusted to ambient wind speeds 0.25 m above the ground (Ryden and Lockyer, 1985). Wind tunnels may, therefore, be used for estimating the effect of wind speed on ammonia volatilization from surface applied cattle slurry (V; Thompson et al. 1990). Due to turbulence, the wind tunnels could not be used for estimating the reduction in ammonia volatilization when slurry was applied on the soil in a tall crop (X).

The coefficient of variation in ammonia loss between wind tunnels with similar treatment was less than 25%. There were no significant differences in ammonia losses determined in two trials with similar treatments and climate (Fig. 2). This gives an opportunity for comparing experiments epeated during different periods, examining the effect of climate or comparing the effect of treatments, slurry composition etc. by more measurements during the same period.

In the studies **IV-VI** and **IX-XII**, wind tunnel systems were used to study the effect of climate and slurry composition factors on ammonia loss from surface applied animal manure and stored slurry. Ammonia loss was measured from the soil plots of 50 × 200 cm and from pilot slurry tanks of 90 × 289 cm.

7.2.3. Micrometeorological methods

The micrometeorological methods may be divided into three categories, eddy correlation methods, gradient diffusion methods and atmospheric mass balance methods (Denmead, 1983).

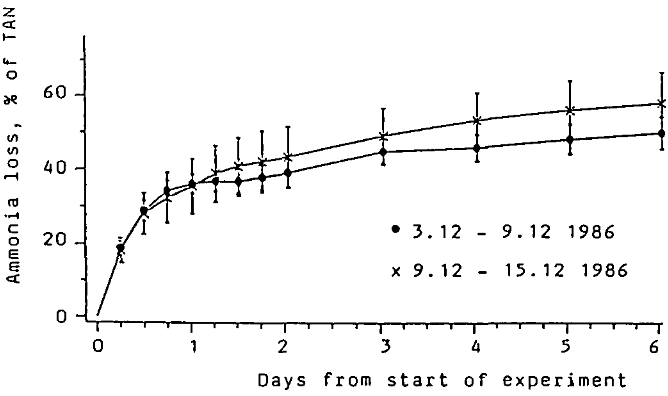


Fig. 2. Cumulative ammonia loss as percentage of TAN (Ammonium + ammonia) in surface applied slurry determined with three wind tunnels. Both experiments were carried out in December 1986 during periods with near similar climatic conditions (V).

With the Eddy correlation technique ammonia loss is determined by simultaneously measuring the vertical wind speed and ammonia concentration during short time intervals. The gradient diffusion technique requires measurement of mean gas concentrations at different heights above the surface and knowledge of the appropriate eddy diffusion coefficient. The eddy diffusion coefficient is calculated either from wind speed and temperature (Aerodynamic method) or temperature and air humidity (energy balance method), at different heights above the surface. These techniques can only be used in situations where the air has transversed a field with homogeneous ammonia source strength and uniform surroundings, as horizontal concentration gradients must be negligible. The experimental area has to be large (several ha). Therefore the methods are not widely used for determination of ammonia loss from areas treated with ammonium fertilizer or manure.

Mass balance techniques have been used for measuring ammonia volatilization from smaller land areas treated with sewage sludge, pig or cattle slurry or grazed areas (Beauchamp **et al.** 1978; Denmead **et al.** 1982; Ryden and McNeill, 1984; Pain **et al.** 1989; Bless **et al.** 1991). The ammonia volatilization is calculated from the difference in the horizontal flux of gaseous ammonia through hypothetical vertical planes windward and leeward of a treated experimental area.

The profile of the ammonia flux is often calculated from determination of ammonia by gas traps and of wind speed by cup anemometers at five or more heights. The method is most simply applied when circular plots are used with the leeward sampling position at its centre. By that the distance between the leeward and windward sampling position (ie the fetch) is constant despite changing wind direction (Denmead, 1983). The method is usefull for agricultural studies because it only needs small experimental areas and due to the simplicity of the method.

For circular plots located in large and uniform areas, the ammonia flux profiles have a theoretically predictable shape determined by surface roughness, plot geometry and atmosphere stability (Wilson **et al.** 1982; McInnes **et al.** 1985). Wilson **et al.** (1982) predicted a height (ZINST), at which the ratio of the horizontal to the vertical flux ($u \times c/F$) has almost the same value in all atmospheric stability regimes. The ratio $u \times c/F$ may be calculated knowing surface roughness, plot geometry and atmospheric stability, and the vertical flux of ammonia can be calculated from determinations of the horizontal flux $u \times c$. Determination of ammonia volatilization from circular plots 20 or 50 m in radius by the ZINST method, agreed satisfactorily with estimates based on a mass balance which employed ammonia fluxes determined in five or more heights (Wilson **et al.** 1983; Pain **et al.** 1989). The labour needed for the measurements of the horizontal flux of ammonia can be reduced by using a rotating passive flux sampler (Leuning **et al.** 1985; Sherlock **et al.** 1989). The ZINST method has been used measuring ammonia losses from a circular experimental area with a radius of 3.5 m (fetch), and determination of ammonia fluxes 12.5 cm above the surface (Gordon **et al.**, 1988).

Knowing the mean air temperature and wind speed at a reference height z and surface temperature, u ×c/F can be calculated as the function of the fetch (McInnes **et al.** 1985). The fetch and the reference height may, therefore, be varied, and the vertical flux of ammonia can be determined at a reference height where the coefficient of variation of the measurements are small. A test showed (Mcinnes **et al.**, 1985) this method to agree better with the mass balance technique where the flux was measured at 5 heights, than the method of Wilson **et al.** (1982), because the concentration of ammonia may be low at the height ZINST. The techniques do not account for the horizontal flux in the plant canopy, and the methods cannot be used in studies of ammonia loss from slurry applied to a tall crop.

A new mass balance technique was developed (I). This method does not make extensive demands to the surrounding area, climatic variables have not to be measured and no electricity is needed. The ammonia flux is determined with passive flux samplers, each made of two glass tubes connected in series. The inner surface of the tubes is coated with oxalic acid which absorbs the ammonia in the air flowing through the tubes. The passive flux samplers are mounted at four heights on four masts. The masts are placed at right angles to each other on the periphery of a circular experimental plot. At each mast, the flux of ammonia into and out of the experimental plot is measured. The vertical flux of ammonia from the plot is calculated as the difference in the flux of ammonia into and out of the plot, measured at the four masts. The vertical flux per square meter is calculated, by dividing the horizontal flux by the diameter (fetch, m) of the experimental plot.

The vertical flux from the circular plot determined with passive absorbers was in good agreement with the determination based on gas traps and wind speed measurements (Fig. 3).

The passive flux samplers were used in a study of ammonia loss from slurry applied to plots of 15 ×15 m in a winter wheat field (Sommer and Pedersen, unpublished). The slurry was applied onto the crop with splash plates, injected into the soil or applied with trail hoses on the soil between the rows of the crop. Six experiments were carried out during the same period. The method performed very well on these relatively small plots placed with a distance of 40 m between plots,

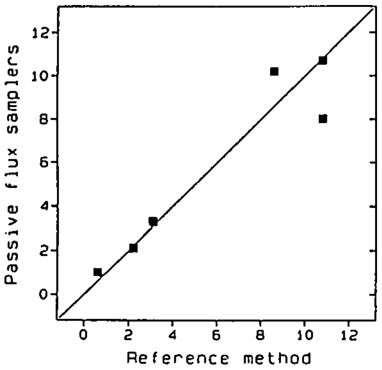


Fig. 3. Relationship between vertical flux densities of NH_3 (μg NH_3-N m^{-2} s^{-1}) measured by a micrometeorological method with a new type of passive flux sampler and a conventional micrometeorological method (reference method) (I).

and about 30 m to the nearest building or hedge. It is therefore suggested, that this method provides a research tool able to compare the effects of differences in slurry composition and different application techniques. The experiments may be carried out in the same field and in the same period, excluding the effect of differences in soil conditions and climate.

In the experiment three of the flux samplers were mounted above the canopy and one flux sampler 5 cm below the top of the canopy (Sommer and Pedersen, unpublished). Within the crop canopy, about 10% of the total horizontal flux from the plot was measured, assuming that the ammonia flux measured 5 cm below the top of the wheat represents the flux gradient within the crop (see Denmead et al. 1982). Consequently the horizontal flux profile within the canopy must be determined, if ammonia loss from slurry applied to a tall crop (>20 cm) is examined by a mass balance technique.

8. Factors influencing ammonia losses

Ammonia loss during storage and from surface applied slurry will partly be influenced by similar factors, i.e., climate, dry matter content and pH of the slurry. Due to the different environments, the factors may act different. The process of ammonia volatilization from stored slurry is not significantly influenced by the material of the storage tank, whereas the loss from surface applied slurry is influenced by the soil. The ammonia loss may, therefore, be related to the same factors, but the influence of the factors must be dealt with separately.

8.1. Concentration of TAN

8.1.1. Concentration gradient in stored slurry

Wind tunnel measurements of the ammonia loss from a weekly stirred slurry showed that losses increased two to three fold after stirring (**VI**). Mixing of the slurry increased the TAN concentrations in the surface layers, causing the transfer of ammonia to the atmosphere to increase. One to two days after stirring the loss rates declined, as concentrations of TAN in the surface layers declined. The reduction of TAN in the surface is supposed to be caused by the slow diffusive transport of TAN from the layers below, which cannot replace ammonia lost by volatilization, and a curvated decline in TAN concentrations towards the surface of the slurry is created. This gradient has been measured in the pilot slurry storages (Olesen and Sommer, not published), and is depicted by a model describing the diffusion of TAN during ammonia volatilization (Muck and Steenhuis, 1982).

8.1.2. The ammonia flux related to the content of TAN in surface applied slurry

In the experiments **IV**, **V**, **X** and **XI**, the amount of slurry applied was generally 3 l m^{-2}. The accumulated loss of ammonia during the experiment was expressed as percentage of TAN added in the slurry, and the loss during a period was expressed as percentage of TAN remaining in the slurry at the beginning of the period. This transformation enables comparison of accumulated ammonia losses from slurries with different contents of TAN, because of the linear relation between ammonia loss and concentration of TAN (Equation (6); Brunke **et al.** 1988). The transformation will give an opportunity to relate the determined ammonia losses to factors such as climate, differences in compositions of slurry and soil conditions (**IV**; **V**; Beauchamp **et al.** (1978)).

In most experiments ammonia loss rates were high the first 24 hours after surface application, thereafter the losses decreased (Fig. 2). This pattern is due to the reduction in the content of applied TAN caused by ammonia volatilization, but also to changes in slurry acidity and infiltration of slurry into the soil (Lauer **et al.** 1976; Beauchamp **et al.** 1982). In most experiments more than half the total ammonia loss during a 6-day period occured within the first day (**IV**,**V**, **IX-XII**), a pattern demonstrated in several other studies (Thompson **et al.** 1987; Pain **et al.** 1989).

8.2. Acidity in the slurry

8.2.1. Changes in pH in the stored slurry

Initially it was assumed that pH in the surface of newly stored slurry would be modified, mainly due to transport and loss of the acidic ammonium ion and the basic bicarbonate (Fig. 4). Similar processes have been described by a model of ammonia volatilization from urea applied on the soil (Rachpal-Singh and Nye, 1986ab). The model predicted, and an experiment showed, that in this system pH declined 1-1.5 units at the soil surface. The decrease in pH in the soil surface was due to a faster diffusive transport to the surface of TAN compared to carbonate species, and thereby a greater volatilization of ammonia. Loss of ammonia decreases pH, while the loss of carbondioxide increases pH.

In stored slurry the system differs from the one described by Rachpal-Singh and Nye (1986ab). In recent produced slurry pH will rise as urea is hydrolysed to ammonia and carbonate ions. If the buffer system only consisted of TAN and carbondioxide pH would be 9.3 after hyrolyzes of the urea. In slurry organic acids modify pH to between 7 and 8, and TAN and carbondioxide are mainly ammonium and bicarbonate. In a soil with recently hydrolysed urea, pH is about 9, and TAN and carbondioxide are mainly ammonia and carbonate.

These processes have to be examined. In this study, therefore, pH in the surface of stored pig slurry was determined in a wind tunnel experiment, carried out to provide data for the development of a model. Immediately after stirring, bulk pH in one m depth was 6.9-7.0 and four days later pH

Table 1. Initial bulk pH after stirring of the slurry and surface pH of slurry during the experiment (Sommer and Olesen, not published). Immediately after the slurry was stirred pH was measured in samples from 0.75 m depth. After that pH was determined at the slurry surface with a flat glass membrane electrode.

Wind speed	Days from stirring of the slurry			
m s^{-1}	0	3	8	10
	pH			
8.7	6.9	7.7	7.3	7.3
5.3	7.0	8.0	7.8	7.9
2.2	6.9	7.7	7.4	7.7

in the surface was 0.4 to 1.0 units higher (Table 1). The high surface pH was probably due to a greater loss of carbondioxide than of ammonia after stirring. Surface pH did not decrease from day 4 to day 10, indicating that ammonia volatilization did not cause an increase in the acidity of the surface layers. This may be due to a greater loss of carbondioxide compared to ammonia, or to aerobic digestion of fatty acids in the slurry surface, a process which also will increase pH (Georgacakis et al. 1982; Husted et al. 1991)).

8.2.2. Ammonia loss related to pH of applied slurry

Accumulated ammonia loss during 6 day periods increased with the initial bulk pH in the surface applied pig slurries (X). Interaction of dry matter content of the slurry and air temperature weakened the relationship, and the ammonia flux could not be related to initial differences in ammonia/ammonium ratios induced by proton activity. This may be due to buffering of pH by volatile organic acids, the bicarbonate system and ammonium (Husted et al. 1991). Husted et al. (1991) showed that a slurry with a high bulk pH may have a low total alkalinity, and losses of small amounts of ammonia vill reduce pH, while a slurry with a lower bulk pH may have a high

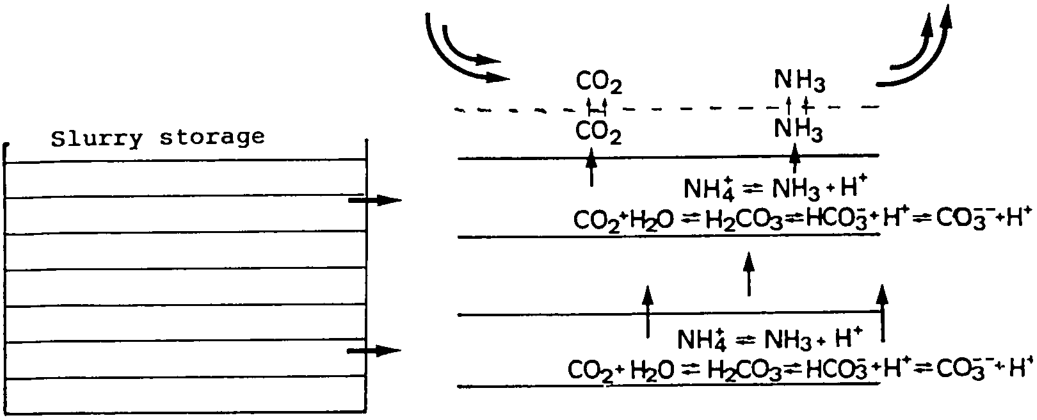


Fig. 4. Description of proton and hydroxylic ion producing processes during volatilization of ammonia and carbondioxide from a slurry tank.

total alkalinity, and loss of ammonia does not change the acidity significantly. This could explain why the accumulated ammonia loss during 6 days in some experiments was higher from slurries with a low bulk pH than a high bulk pH (X). Anaerobic digestion of slurry increased pH, but ammonia loss values were similar from surface applied anaerobic digested and raw slurry (**XII**; Pain et **al.** 1990). This may be due to an unchanged alkalinity of the slurry.

Immediately following application of a pig slurry, pH in the surface increased to 8.4 from an initial bulk pH of 7.6 in the stored slurry (V). The increase was due to a greater loss of carbondioxide than of ammonia, because water solubility of carbondioxide is lower than that of ammonium. Within 3-4 days, pH declined to 7.4 as ammonia volatilization produced protons in the surface. The initial high pH could explain the high ammonia loss rate during the first day after application (Fig. 2). Subsequently the acidification of the slurry has influenced the reduction in ammonia loss rate.

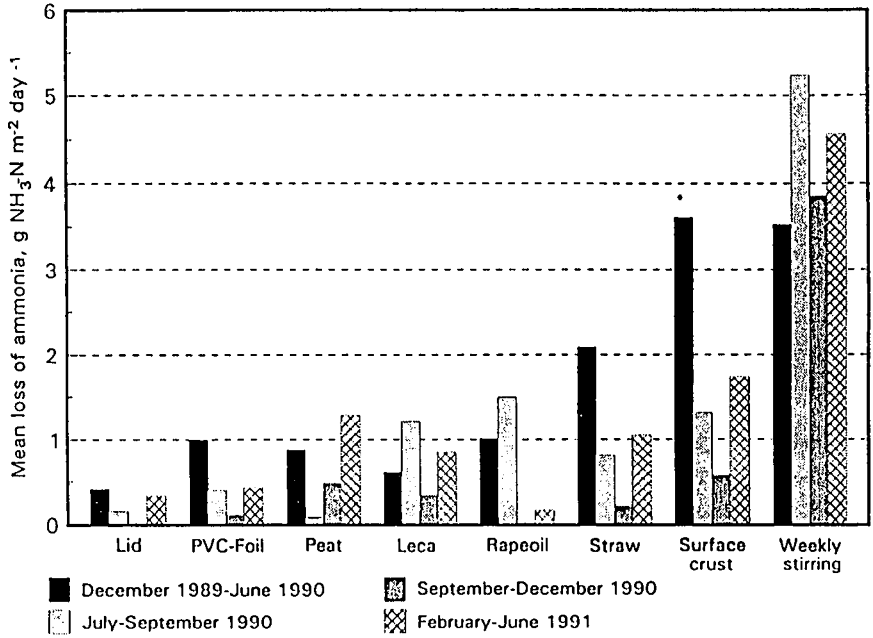


*Fig. 5. Mean daily ammonia loss rates from stored cattle (Dec. 1989-Sep. 1990) and pig slurry (Sep. 1990-Jun. 1991) with eight different surface coverings. * No formation of surface crust. Ammonia losses were measured with wind tunnels on slurry tanks (0.90 m × 2.89 m). Mean air temperatures during the experiments were: Dec. 1989-Jun. 1990, 7°C; Jul.- Sep. 1990, 17°C; Sep.- Dec. 1990, 7°C; Feb.-Jun. 1991, 6 °C.*

8.3. Structure material in the slurry

8.3.1. Effect of surface crusting on ammonia loss from stored slurry

Ammonia loss from a slurry with a surface crust was less than 20% of the losses from a weekly stirred slurry (VI). The surface crust created a stagnant air layer above the liquid slurry and increased the surface roughness. Thereby the surface resistance increased and the transfer coefficient (K(v) decreased, (Equation 8). Ammonia loss rate from a cattle slurry with no surface crust was similar to the loss rates from a stirred slurry (Fig. 5). The great loss of ammonia from unstirred slurry with little dry matter content may be due to a low viscosity and an increase in natural convection of the slurry. Furthermore the transfer coefficient is higher above a rough surface with surface crust than above a liquid surface. In Dutch wind tunnel experiments similar ammonia losses from stored cattle slurry were determined (Bode 1991). In the present study **(VI)** ammonia losses from stored pig slurry were lower than in the Dutch, probably due to the development of a surface crust, which did not appear in the study of Bode (1991).

8.3.2. Effect of dry matter content on loss of ammonia from surface applied slurry

Ammonia loss rates from surface applied cattle slurry adjusted to different dry matter contents were related to the content of dry matter (Fig. 6). The ammonia loss from 0 to 6 h was linearly related to dry matter content, while the relationship during following periods was nonlinear. A lower dry matter content in the slurry may cause an increased infiltration into the soil. Sorption to soil colloids reduces the concentration of ammonium in the solution, and the transfer of ammonia from the liquid in the soil to the atmosphere is reduced. In addition the transport of gaseous ammonia is reduced in soil.

When the effect of pH and temperature was eliminated from the ammonia loss data, the loss of ammonia during the periods 0-6 h, 6-12 h, 12-24 h and 24-144 h tended to be sigmoidally related to dry matter content. This shows that at low (< 4%) and high contents (> 12%) of dry matter, small changes in dry matter have a limited influence on ammonia loss. Probably little liquid remains on the soil at dry matter content lower than 4% and little liquid infiltrates the soil at dry matter content higher than 12%.

Higher loss values were determined from cattle slurry than from adjusted slurry with similar dry matter content **(XII)**. Visually it appeared that the cattle slurry had a higher viscosity than the adjusted slurry, the high viscosity may have contributed to a smaller infiltration compared to the adjusted slurry. Soluble carbohydrates, proteins and fatty acids contribute to the viscosity of the slurry, but may not be related to the dry matter content. Therefore viscosity may be an additional factor in the ammonia loss process.

In winter experiments, high losses were determined from the fibrous fraction (20% DM) but not from the liquid fraction (1% DM) of mechanical separated pig slurry. This indicates that dry matter content and thus infiltration interact with temperature **(XII)**.

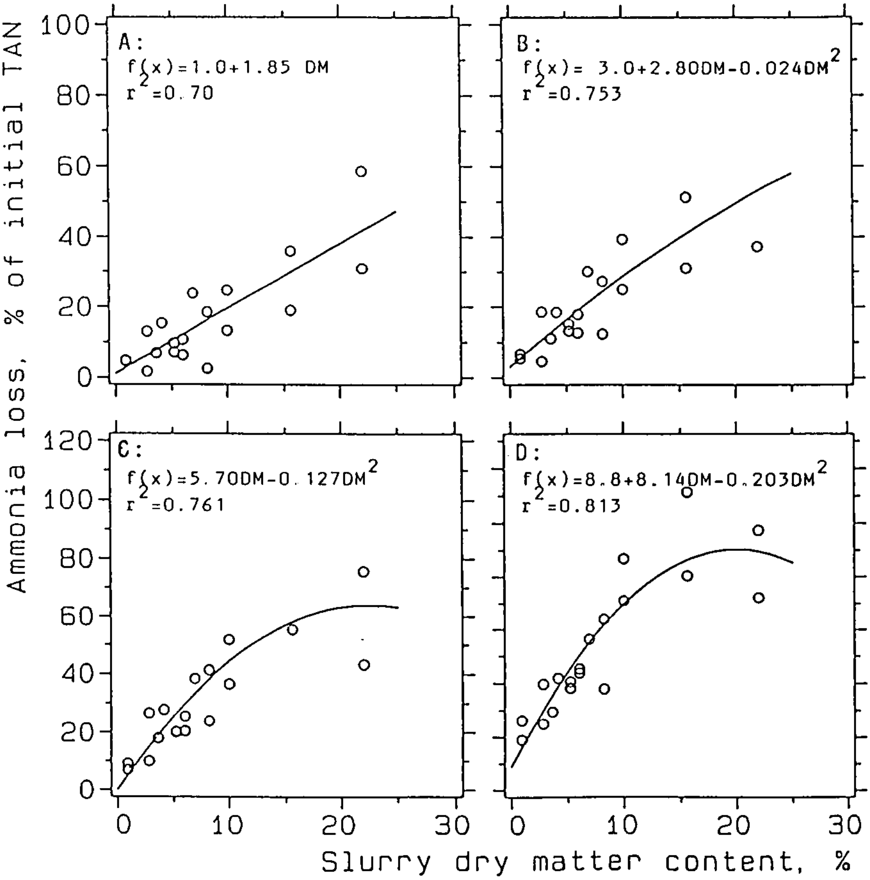


Fig. 6. Accumulated ammonia loss in percent of TAN in applied cattle slurry related to slurry dry matter content for four time periods (IV). The ammonia loss was measured with wind tunnels (0.5 × 2 m). Slurry dry matter content was adjusted by mixing the fibrous and liqued fraction of mechanical separated cattle slurry. Mean air temperatures were from 0.5 to 19.6°C.

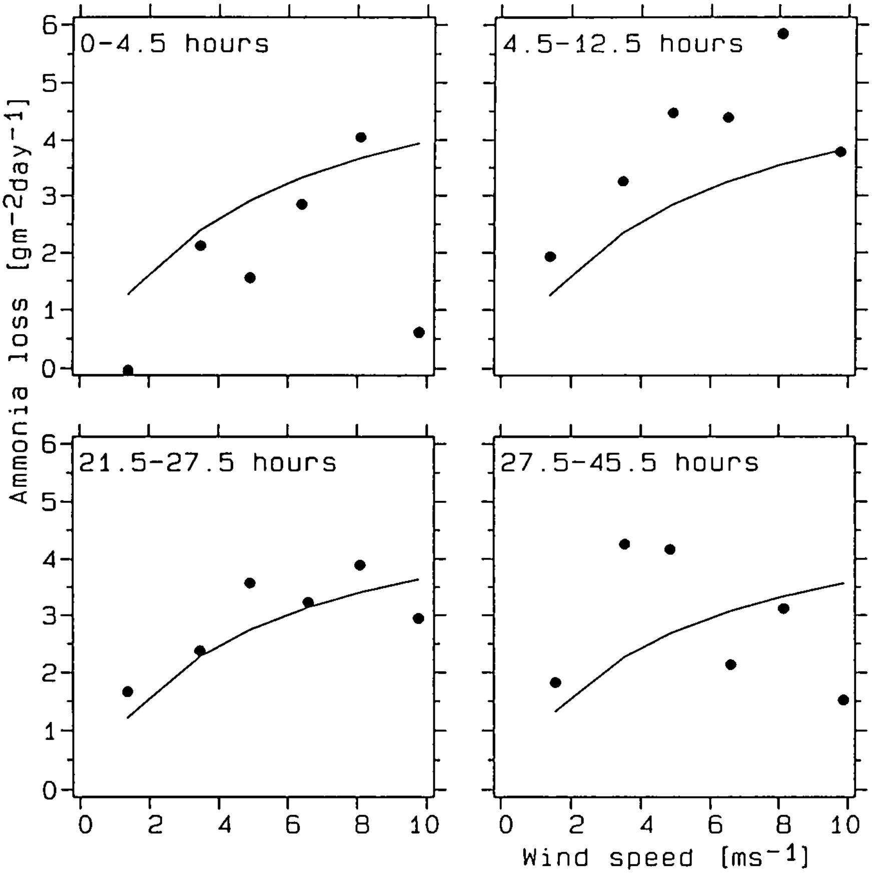


Fig. 7. Predicted (solid line) and measured (points) ammonia loss from stored pig slurry at different wind speeds. The slurry was stirred initially. Ammonia loss was determined with wind tunnels on pilot slurry tanks (0,9 × 2,89 m), mean air temperature was 3°C. The laminar resistance was assumed to be R_b=20 s m^{-1}. (Olesen og Sommer, unpublished).

8.4. Climate

8.4.1. The effect of wind speed and air temperature on ammonia loss from stored slurry

By increasing wind speeds the boundary resistance at the surface of stored slurry will be reduced (Equation (9)-(12)), and the transfer of ammonia from the slurry to the atmosphere increases. At high wind speeds transfer of ammonia through the boundary layers to the atmosphere will be faster than the rate of diffusive transport of TAN to the surface layers, and the slow diffusive transport of TAN will limit the rate of ammonia volatilization. The flux of ammonia from stored pig slurry, therefore, showed a curvated relationship with increasing wind speed in the periods 0-4.5 h, 4.5-12.5 h and 21.5-27.5 h after an initial stirring (Fig. 7).

From stored cattle slurry, ammonia loss at mean air temperatures of 17°C was 50% higher than at 7°C. During the day the slurry was stirred, ammonia loss was related to air temperature (VI). On the day of stirring, TAN concentrations in the surface only varied a little during the experimental period, and there was little interaction from differences in TAN concentrations and development of surface crust.

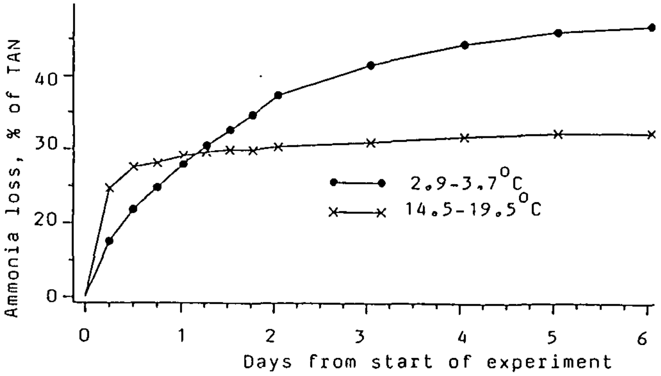


Fig. 8. Accumulated ammonia loss in percent of added TAN in surface applied cattle slurry (3 l m^{-2}) during a summer and a winter period (V). Ammonia loss was measured with wind tunnels (0,5 × 2 m).

8.4.2. The effect of air temperature, air humidity and wind speed on ammonia loss from surface applied slurry

At low temperatures, the rate of ammonia loss was generally reduced (Fig. 8). The accumulated loss during 6 days was high, however, due to an appreciable loss rate from day 2 to day 6. During the experiment the soil was saturated with water and partially frozen, factors assumed to promote ammonia losses (V). Sustained ammonia losses from slurry during periods with low temperatures have also been observed in a study of Thompson et al. (1987). At 19°C initial loss rates were high but after 12 h almost no further loss occurred (Fig. 8). This was ascribed to surface crusting and rapid infiltration into the relatively dry soil.

The results of 20 wind tunnels-experiments with near identical cattle slurries were related to climatic conditions (Fig. 9). During the initial 6 h, the accumulated ammonia loss was exponentially related to temperature. During the three succeeding periods of 6-12 h, 12-24 h and 24-144 h, the ammonia volatilization rate was low and only slightly related to temperature. In these periods the ammonia loss pattern shifted to a linear relationship to temperature. The reason for the increase in loss rate with temperature is that equilibrium-constants change with temperature. At a given concentration of TAN, an increase in temperature will cause a higher ammonia/ammonium ratio in the slurry, and the solubility of ammonia declines with increasing temperature. Initially pH is high (8.5) and changes in temperature will influence ammonia loss significant, as small changes in pH produce significant changes in the ammonia/ammonium ratio (V). Therefore the ammonium loss rate is exponential related to temperature during the first six hours. In the following periods pH declined to 7.5, at this level the ammonia/ammonium ratio is less influenced by changes in pH. After a period factors like infiltration and soil properties interact with temperature.

Four equations describing the relationship between ammonia loss and temperature were determined for the four periods (Fig. 9). For all experiments 46 % of the measured loss over 6 days was accounted with the models (V), indicating that other factors like soil properties influenced the ammonia losses.

The ammonia loss rate after 6 h increased when tunnel wind speed increased up to 1.75 m s^{-1}. No consistent increase in volatilization was found when the wind speed increased from 1.75 to 2.8 m s^{-1} (V). In a study of Thompson et al. (1990), the accumulated ammonia loss from cattle slurry was measured with similar wind tunnels. The loss of ammonia increased with wind speed up to

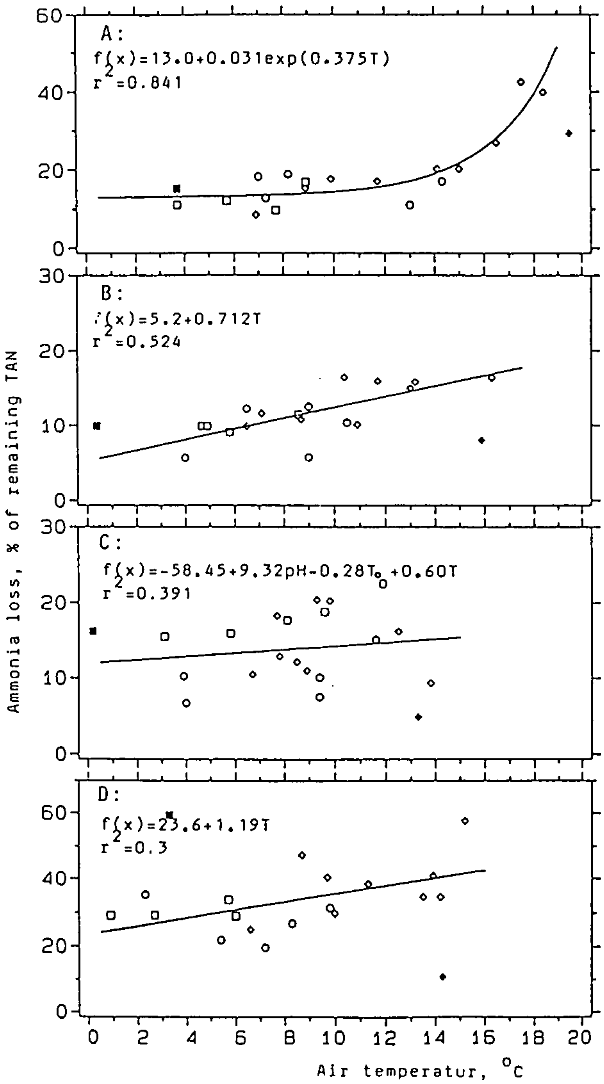


Fig. 9. Cumulative ammonia loss from surface applied slurry during the periods (a) 0-6 h, (b) 6-12 h, (c) 12-24 h and (d) 24-144 h. The loss is presented as a percentage of TAN remaining at the start of a period in relation to mean air temperature during the period (V). Solid symbols indicate observations not included in estimation of the lines shown. Surface type: stubble (circle), grass or clover grass (square), harrowed soil or cultivated stubble (diamond).

3 m s^{-1} during the first two hours, but during 5 h or more the accumulated loss only increased with wind speed up to 2.5 m s^{-1}. The increased ammonia loss with increasing wind speed is due to a decrease in the boundary resistance. In the experiments, wind speeds higher than 2-3 m s^{-1} did not increase ammonia loss rates, probably because the boundary resistance was insignificant at the high wind speeds. The ammonia loss related to wind speed in the open, may deviate from the measured values, as turbulence created by the tunnels changes the wind profiles (Rasmussen and Mikkelsen, 1988), but the relation with wind speed will show a similar pattern.

Rain simulated with 5 and 10 mm irrigation immediately after application of pig solid manure and after 1, 2 and 3 days reduced ammonia losses (**XII**). Irrigation with 10 mm had greatest effect during the first two days, after which the rate of ammonia loss increased compared to 5 mm irrigation. The ammonia loss after six days did not differ between the two irrigation treatments.

An increase in ammonia volatilization with increasing water vapor pressure deficit was considered an effect of temperature (**V**).

8.5. Methods for reducing ammonia losses

8.5.1. Slurry storages

The ammonia loss from stored slurry covered by seven surface coverings was compared to a weekly stirred slurry (**VI**). The coverings were natural surface crust, crude rape seed oil, sphagnum, chopped cereal straw, floating PVC-foil, leca pebbles (floating granules of burned montmorillonitic clay) and a lid (Fig. 5). Ammonia losses from the weekly stirred slurry were 3-5 g NH_3-N m^{-2} d^{-1}.

From an undisturbed slurry that developed no natural surface crust, ammonia loss was similar to losses from stirred slurry (Fig. 5). A layer of surface crust reduced ammonia loss rates with 80% compared to stirred slurry. This reduction was attributed to the development of a stagnant liquid and air layer in the surface crust. During addition of slurry to the storage, these barriers should be protected by injecting the slurry below the surface.

The surface coverings reduced ammonia loss rate to less than 60% of the loss from the stirred slurry (Fig. 5). In the study by Bode (1991), roofings or floating covers reduced ammonia loss to 20% of the losses from an uncovered slurry with no surface crustings.

Rape seed oil surfaces, lids and PVC-foils reduce transfer of ammonia from the slurry to the air. Losses observed from slurry tanks with these coverings (Fig. 5) were considered to be due to cracks developing in the rape seed oil surface and slits between the foil or the roof and the sides of the slurry storages. The effect of surface crust, sphagnum, leca and straw was ascribed to the development of a stagnant air layer above the slurry surface and a reduced natural convection in the slurry.

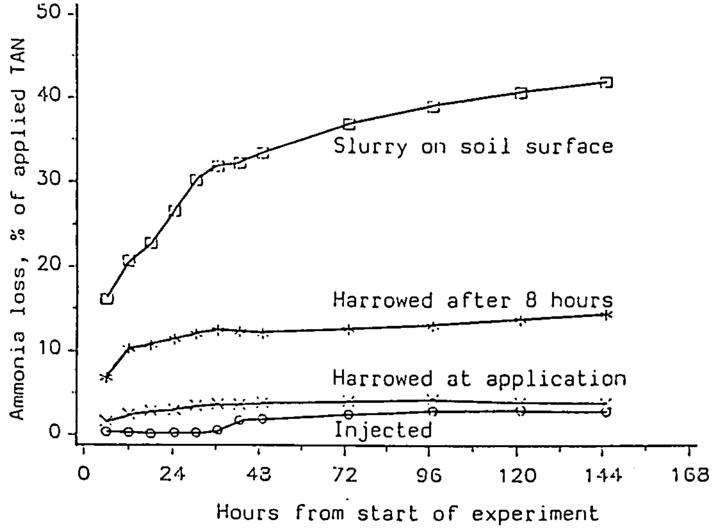


Fig. 10. Accumulated loss of ammonia from anaerobic fermented pig slurry (3 l m^{-2}) measured with wind tunnels. The slurry was either directly injected into the soil, surface applied and cultivated into the soil immediately or after 8 hours, or surface applied. Mean air temperatures during the experiments were 11-17°C (Larsen et al., 1992).

8.5.2. Methods for reducing losses following application

Injection of slurry (10 cm depth) or immediate incorporation into a soil reduced ammonia loss to low values (Fig. 10). More ammonia was lost by injecting the slurry to a depth of 10 cm into a wet soil compared to injection into a moist soil (**XII**), reflecting the furrow in the wet soil stayed open after the injection knifes. Soil injection to 30 cm reduced ammonia loss to less than 2% of the applied ammonium (Hoff **et al.** 1981; Thompson **et al.** 1987).

Application of slurry onto the soil between rows of plants with hoses trailed on the surface may reduces ammonia losses (Bless **et al.** 1991). The effect is highest when the slurry is applied under a well developed plant canopy (**VII**), as the reduction in wind speed increases with the size of the plants. Furthermore a reduced wind speed within the crop canopy will increase the gaseous ammonia concentration, by which leaf absorption of ammonia increases (**II**). Similar ammonia

Table 2. Volatilization of ammonia from surface applied pig slurry (3 l m^{-2}) to a newly cultivated (5-10 cm depth) and an uncultivated soil (Sommer, unpublished).

Experi-mental period	Temperature	Wind speed	Soil water content	Cultivated soil	Uncultivated soil
	°C	m s^{-2}	% V/V	Ammonia loss in % of TAN	Ammonia loss in % of TAN
19.-25. Mar.1991	6	3.0	17	19	43
3.-9. Jul.-1991	20	3.2	11	17	25
25.Sep.-1.Oct.1991		3.0	14	15	33
5.-11. Nov.1991	8	3.0	17	12	22

losses were estimated after surface application of slurry applied with trail hoses and splash plates to a winter wheat crop, rows spaced with 22 cm and plant height 40 cm (Sommer and Pedersen, unpublished). High wind speed during the experiments was assumed to cause a high convective transport within the waving crop canopy, and to reduce the boundary layer. This shows that the trail hose application technique do not reduce ammonia losses when used in a crop with a small leaf area and in periods with high wind speed.

Cultivating the soil surface before surface application of slurry reduced ammonia loss values compared to losses from an uncultivated soil (Table 2). The reduction was caused by higher infiltration rate of slurry into the soil (Horlacher and Marschner, 1990) and by an increased surface roughness. The effect of trail hose application may be improved by harrowing the soil before application.

8.6. Loss of ammonia from slurry applied to a recently limed soil

After 6 days the accumulated loss of ammonia from slurry applied to the surface of a recently limed soil was 21-28% higher, than from an untreated soil (**XI**). The difference was mainly caused by a high loss rate from the limed soil from day one and two. This supports the suggestion that ammonia loss the first day after application may be significantly influenced by changes in acidity (**V**).

8.7. Ammonia volatilization during application of slurry

During spreading with conventional slurry spreaders equipped with a central splash-plate, loss of ammonia was less than 4 % of applied ammonium (**VIII**). Volatilization was determined by the difference in TAN content in slurry before and after spreading. There were no differences in ammonia losses when the slurry was applied in a spreading fan with a length andwidth of respectively 11 and 10 m or 6 and 4 m (**VIII**). Direct measurements have shown, that ammonia losses during spreading were less than 1% of the applied ammonium with conventional spreaders, trail hose application and a cable driven irrigator (Pain **et al.** 1989, Phillips **et al.** 1991). These results are not supported by the observations reported by Boxberger and Gronauer (1990), who found that ammonia losses increased from 4% to 6.7% of applied ammonium, when the spreading length increased from 1.5-10 m to 5-15 m. Spreading of slurry using an irrigation device having a spreading length of 25-30 m resulted in losses of 9.6% of the applied ammonium (Boxberger and Gronauer, 1990). The ammonia loss was determined by the difference in TAN of slurry collected before and after spreading. The greater losses in their study compared to the results of **VIII**, Pain **et al.** (1989) and Phillips **et al.** (1991), may be due to losses of ammonia from the collected slurry (**VIII**).

9. Modelling ammonia volatilization from stored slurry

In the model ammonia volatilization from stored slurry was calculated using the equations (6) to (13), knowing temperature, wind speed, pH and TAN concentrations of the slurry, and the geometry of the slurry tank (Olesen and Sommer, unpublished). TAN determined by addition of MgO, distillation and titration, has been shown to be the soluble fraction (III). It is assumed that convection of the slurry can be excluded because of the high viscosity and dry matter content of the slurry. TAN, therefore, is only transported by diffusion to the surface layer of the slurry.

Changes in surface acidity, CO_2 volatilization and microbial digestion of organic acids of the slurry cannot be calculated by the model. The buffer system of slurry, acid and base producing processes, has to be examined further, before changes in acidity of slurry can be calculated. Therefore the measured pH in the surface of the slurry is an input variable in the model. This approach was also used in models of ammonia volatilization from stored slurry (Muck and Steenhuis, 1982), from surface applied slurry (Molen **et al.** 1990) and from urea applied to flooded soil systems (Jayaweera and Mikkelsen, 1990).

The model was tested with ammonia loss values determined with wind tunnels covering pilot slurry tanks (Olesen and Sommer, unpublished). Wind speed within the tunnel was adjusted from 1.8 to 10 m s^{-1}. There was agreement between predicted and measured loss of ammonia from an uncovered slurry, except for the losses from 27.5 to 45.5 h after initiating the measurements and stirring the slurry (Fig. 7). The development of a surface crust in this period may have caused a change in surface roughness. The effect of a 15 cm straw layer could be simulated with the model by increasing r_b to 100 s m^{-1} compared to 20 s m^{-1} from an uncovered slurry.

10. Conclusion

Erroneous ammonia loss values may arise from determination of ammonia losses by the N-recovery technique.

Enclosures can be applied in the laboratory for the study of potential ammonia losses related to soil variables or slurry compositions.

Wind tunnels may be used for studying ammonia loss from animal manure and fertilizers in the field, when estimating the effect of climate, soil property, slurry composition or application techniques.

Eddy correlation and gradient techniques are not usable for studying ammonia volatilization from confined areas to which manure or fertilizers can be homogeneous applied. For measurements in the field micrometeorological mass balance techniques have shown to be appropriate. A new mass balance technique using passive absorbers gave reliable ammonia loss values, the method is labour saving and the loss can be determined easily and cheaply.

Ammonia loss from weekly stirred pig and cattle slurries were 3-5 g NH_3-N m^{-2} d^{-1}. Ammonia losses from stirred slurry were related to temperature and wind speed. Surface crustings reduced NH_3 losses to 20% of the losses from stirred slurry. Ammonia losses from an unstirred slurry without a surface crust were similar to the losses from a stirred slurry. A layer of chopped straw (15 cm) could replace a surface crusting layer. Ammonia losses from slurry covered by rape seed oil, leca pebbles, sphagnum peat, a wooden lid or floating foil were low.

With a simple model ammonia loss from stored slurry was predicted. There was agreement between model prediction and measured ammonia losses from uncovered slurry and slurry covered with af straw layer.

Ammonia losses were low during application of slurry with conventional spreaders.

From surface applied slurry, ammonia losses were exponentially related to air temperature during the first 6 hours after application and linearly related in following periods. Ammonia losses from surface applied slurry increased with wind speed. Irrigation reduced ammonia losses from surface applied animal manure.

Ammonia losses from surface applied slurry increased with increasing slurry dry matter content. If the results were adjusted for pH and temperature, losses tended to be sigmoidal related to the dry matter content, indicating that changes in content of dry matter have little effect on ammonia loss at dry matter contents higher than 12% and lower than 4%. Slurry pH had an effect on ammonia loss, but the relation was not significant. It is proposed that ammonia loss should be related to both slurry alkalinity and acidity.

Generally no ammonia is lost from slurry injected into the soil, and after incorporation of slurry into the soil only little ammonia is lost. Ammonia loss from surface applied slurry may be reduced by harrowing the soil before application. Ammonia loss from slurry applied to a crop may be reduced by trail hose application to the soil between the rows of the crop.

11. Outlook

A simple model for calculating ammonia loss from stored slurry was developed. With the model pH changes in the surface of the slurry cannot be calculated. Submodel predicting surface pH by the transport of carbondioxide species and TAN in the slurry and the transfer of gaseous carbondioxide and ammonia from the slurry should be developed.

It was shown that ammonia loss from surface applied slurry is related to slurry dry matter content, and equations describing the effect of slurry dry matter were developed. Furthermore infiltration of slurry into the soil may be influenced by the slurry viscosity. The effect of viscosity should be examined.

Ammonia is related to acidity, but accumulated loss from surface applied slurry was not significantly related to initial bulk pH. It is assumed that pH of the slurry changed during the experiment, and this change was influenced by initial proton activity, alkalinity and volatilization of carbondioxide and ammonia. These processes are not well described and should be examined.

The model developed for measuring ammonia loss from stored slurry may be expanded to describe ammonia volatilization from slurry applied to the soil surface. For that purpose, processes of infiltration of slurry into the soil should be included, the infiltration being influenced by both soil and slurry characteristics. The influence of infiltration and the effect of sorption of ammonium to soil colloids must be quantified.

Future studies of ammonia loss from stored and applied animal manure will include meteorological mass balance measurements in the open. These measurements will be used for evaluating the models developed for depicting the wind tunnels measurements.

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A SIMPLE PASSIVE SAMPLER FOR MEASURING AMMONIA EMISSION IN THE FIELD

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(Received May 13, 1990; revised september 5, 1991)

Abstract. A new type of passive sampler for the determination of NH_3 emission from land surfaces and manure storages was tested in a micrometereological mass balance method. The sampler consists of 2 glass tubes, each with a length of 10 cm and an internal diameter of 0.7 cm. The two glass tubes are connected in series, with one end fitted with a thin stainless steel disc having a 1 mm hole in the center. The inner surface of each glass tube is coated with oxalic acid. The results show that the passive flux sampler can be used to give accurate determinations of NH_3 emission. The passive flux sampler makes gas washing bottles, pumps, flow meters, anemometers, and electricity unnecessary and ammonia loss can be determined easily and cheaply without the requirement of a large labor force.

1. Introduction

Ammonia is a major air pollutant. The principal sources of atmospheric NH_3 are generally concluded to be animal manure and N fertilizers. Ammonia that enters the troposphere is readily transferred from the air into acid cloud droplets, neutralizing acidity by accepting H^+ to form NH_4^+. Removal of NH_4^+ and NH_3 from the atmosphere takes place by wet and dry deposition. Close to sources, dry deposition of NH_3 is the most important removal process, while at greater distances wet removal of particulate NH_4^+ aerosols is most important. The deposited NH_3/NH_4^+ contributes to several undesirable environment changes like acidification and eutrophication of oligotrophic ecosystems (Schulze *et al.*, 1989).

Estimates of NH_3 emission are still very uncertain. In order to improve the estimates there is a great need for data on NH_3 volatilization from manure storages and from manure and fertilizers applied to the surface of agricultural land. Furthermore, very few results are available on the emission of NH_3 from the foliage of agricultural crops.

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Water, Air, and Soil Pollution 62: 13–24, 1992.

Ammonia volatilization is strongly influenced by air temperature and wind speed. The frequently used chamber technique alters the microclimatic conditions and may give incorrect estimates of NH_3 emission (Ferm, 1983; Ferguson *et al.*, 1988). Instead, wind-tunnels (Vallis *et al.*, 1982; Thompson *et al.*, 1987; Sommer and Olesen, 1991) or micrometeorological techniques (Beauchamp *et al.*, 1982; Brunke *et al.*, 1988) have to be used. A disadvantage is that both wind-tunnels and micrometeorological methods require expensive instrumentation and a large labor force. In addition, micrometeorological measurements based on energy balance or aerodynamics require extensive and uniform land areas. Such requirements are not necessary in micrometeorological measurements based on mass balance (Denmead, 1983). Hence, mass balance methods are suitable for measuring NH_3 emissions from smaller plots.

The requirement for a large labor force in the micrometeorological mass balance methods has partly been overcome by development of the ZINST mass balance approach (Wilson *et al.*, 1983) and the 'theoretical profile shape solution' (McInnes *et al.*, 1985). By application of these simplified methods, NH_3 emission (vertical NH_3 flux density) can be determined from measurements of horizontal NH_3 flux in one height only. The nearby surroundings must be uniform and it is assumed that the flux of NH_3 from the surroundings into the area is negligible. The suitability of the ZINST method for determination of NH_3 loss from manure applied on a circular area has recently been demonstrated by Sherlock *et al.* (1989). In their study, the horizontal NH_3 flux was measured by a rotating sampler, automatically aligning its opening to the wind direction (Leuning *et al.*, 1985).

The purpose of the present work was to test a new, simple, non-rotating sampler for measuring horizontal NH_3 fluxes in the atmosphere (product of NH_3 concentration, wind speed and cosine of the angle between wind direction and axis of the sampler). The sampler has the potential advantages of being easy to operate, no climatic variables have to be measured, no electricity is needed, and there are no specific restrictions to the surroundings of the experimental area. An additional advantage is that NH_3 emissions may be integrated over long periods.

2. Materials and Methods

2.1. EXPERIMENTAL AREA

The experimental area in experiment 1 was a square with a side length of 21 m. In the rest of the experiments, the experimental area was a circle with an area of 707 m^2 (radius 15 m). The NH_3 source consisted of 140 flat beakers (diameter 15 cm, height 3 cm), evenly distributed on the experimental area and containing an $(NH_4)_2SO_4$ solution. The experiments were started by adding a $NaHCO_3/Na_2CO_3$ solution to the beakers. The total volume of the solution was 0.5 L with a NH_4^+ concentration about 1 *M*. The pH of the solution was initially 8.5 to 9.0 and dropped during the experiments to around 8.0 (Table I). The amount of NH_3 volatilized

TABLE I

Climatic conditions (1 m above soil surface) and pH of ammonia source (NH_4^+/HCO_3^- solution) in experiments with a passive sampler for measuring ammonia emission in the field

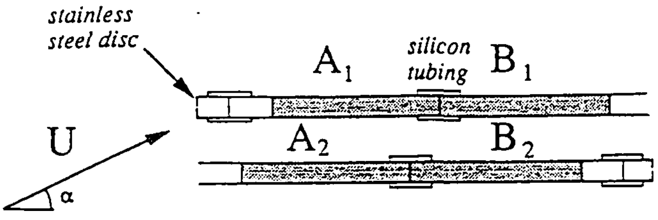
Parameter	Experiment					
	1	2	3	4	5	6
Wind speed, m s^{-1}	4.1	1.1	1.9	2.4	3.7	4.3
Air temperature, °C	14.5	4.3	9.6	12.1	17.4	16.3
Air humidity, %	65	70	49	47	72	67
Wind direction	NW	NE	NE	W	NW	W
Initial pH	8.6	8.5	8.6	8.3	8.9	9.1
Final pH	8.0	-	8.4	8.0	8.0	8.2

was estimated on basis of the difference in NH_4^+ content in the beakers before and after an experiment. Immediately after sampling, the solution was acidified by addition of 0.6 *M* H_2SO_4 to stop NH_3 volatilization. The NH_4^+ concentration of the solution was determined by distillation followed by titration.

The climatic conditions during the experiments are summarized in Table I.

2.1. MASS BALANCE METHOD WITH PASSIVE FLUX SAMPLERS

The passive flux sampler consists of glass tubes with a coating of oxalic acid on the inner surface (Figure 1, hatched part). The oxalic acid coating was made by drawing methanol containing 3% oxalic acid into each glass tube. After allowing



$$F_{hz}\cdot\Delta t = \int_{t_1}^{t_2} U\cdot\cos\alpha\cdot[NH_3]\cdot dt \approx \frac{(A_1+A_2)}{2\cdot\pi\cdot r^2\cdot 0.77}$$

Fig. 1. Passive NH_3 flux sampler. NH_3 is collected in tubes A_1 and A_2 but not in B_1 and B_2 when wind direction and windspeed is represented by thge vector U. Tubes A_1 and A_2 collect the same amount of NH_3 if α is 0°. When α increases, the amount of NH_3 collected by A_1 decreases more rapidly with α than does cos α, while A_2 collects an amount of NH_3 that decreases more slowly with α than does cos α. However, the average amount of NH_3 collected by the two tubes as a function of α corresponds approximately to cos α (Figure 2). Thus, the NH_3 flux through a plane perpendicular to the longitudinal axis of the samplers can be determined. F_{hz} is the horizontal flux density of NH_3, $[NH_3]$ is the atmospheric NH_3 concentration, r is the radius of the hole in the stainless steel disc, and t is time.

the methanol solution to drain, the tubes were dried with NH_3 free air. The tubes were closed immediately after drying. Sixteen tubes connected to a manifold were coated simultaneously. We have subsequently observed that a more uniform coating may be obtained when acetone is used as solvent instead of methanol (see also Leuning *et al.*, 1985).

Each glass tube was 100 mm long with an inner and outer diameter of 7 and 10 mm, respectively. Two tubes were connected by means of a small piece of silicon tubing (Figure 1). To each pair of glass tubes was furthermore connected a stainless steel disc (thickness 0.5 mm in Experiment 1, 2, 3, and 4 and 0.05 mm in experiments 5 and 6) with a hole (diameter 1 mm) in the center. The disc was glued onto a 10 mm long glass tube that was connected to the oxalic acid coated glass tubes by use of a piece of silicon tubing (Figure 1). The purpose of the stainless steel disc was to decrease the air speed inside the tubes in order to achieve a low friction resistance and a high NH_3 collection efficiency. The air speed inside the tubes will be approximately proportional to the wind speed outside the tube multiplied with the cosine of the angle between the wind direction and the tube axis (Figures 1 and 2). Tubes and stainless steel discs were manufactured by Mikrolab Aarhus A/S, Axel Kiers Vej 34, DK-8270 Hoejbjerg, Denmark.

The passive flux samplers were mounted at four heights (0.75, 1.5, 2.25, and 3 m) on four masts placed at right angles to each other on the periphery of the circular experimental area. In each height the two units of a passive flux sampler (Figure 1) were mounted, one unit having the stainless steel disc facing towards the experimental area, the other unit having the disc facing away from the experimental area. Ammonia coming from the experimental area was thus collected through the stainless steel disc of the first unit and through the open end of the second. Conversely, NH_3 from the surroundings was collected through the open end of the first unit and through the disc of the second.

At the end of the 9 hr exposure period the flux samplers were taken down from the masts and closed with plastic caps. In the laboratory, 3 mL deionized water was added to each glass tube in order to dissolve the oxalic acid coating. The ammonium concentration in the leachate was analyzed by use of a Flow Injection Analyzer (Tecator model 5020). Application note ASN 50-01/84 was followed except for 0.1 *M* NaOH which was replaced by 0.3 *M* NaOH in order to neutralize the sorbent (see also Svensson and Anfält, 1982).

The horizontal flux of NH_3 (F_{hz}, μg NH_3-N m^{-2} s^{-1}) through two glass tubes facing in the same direction (see e.g. A_1 and A_2 in Figure 1) was calculated on basis of the following equation:

$$F_{hz} = \frac{A_1 + A_2}{2 \cdot \pi \cdot r^2 \cdot \mathrm{K} \cdot \Delta t}, \qquad (1)$$

where A_1 and A_2 are the amounts of NH_3 in the two glass tubes, r is the radius of the hole in the stainless steel disc (0.5 mm), Δt is the time between the start

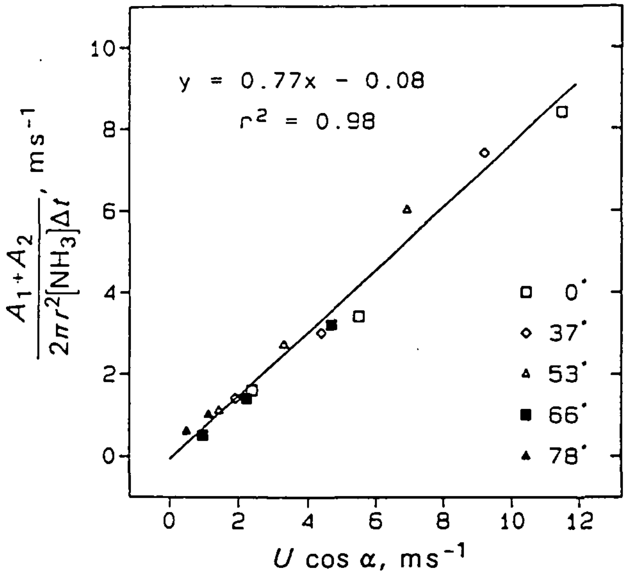


Fig. 2. Average air speed through the hole of the stainless steel disc of a passive NH_3 flux sampler as a function of ambient wind speed (U) and angle between wind direction and longitudinal axis of sampler (α). Measurements were carried out in a wind tunnel at 3 wind speeds (2.4, 5.4, or 11.5 m s^{-1}) and with α adjusted to 0°, 37°, 53°, 66°, or 78°. The air speed through the sampler was calculated as $(A_1 + A_2)/(2\pi r^2[NH_3]\Delta t)$ where A_1 and A_2 are the amounts of NH_3 in the two glass tubes facing in the wind direction (see e.g. $A_1$and A_2 in Figure 1), r is the radius of the hole in the stainless steel disc (0.5 mm), Δt is the time between the start and the conclusion of the measurements, and $[NH_3]$ is the atmospheric NH_3 concentration in the wind tunnel as determined by use of a denuder (Ferm 1986).

and the conclusion of the measurement, and K is a correction factor ($K = 0.77$; Figure 2). The correction factor was determined in wind tunnel experiments in which the air speed through the hole of the stainless steel disc was calculated as a function of of ambient wind speed (U) and cosine of the angle α between the wind direction and the longitudinal axis of the sampler (Figure 2). Independent of the size of α there was a very good correlation between air speeds within and outside the sampler ($r^2 = 0.98$; Figure 2). However, the slope of the regression line, which corresponds to K in Equation (1), was not equal to 1 but amounted to only 0.77. This was likely due to the fact that the stainless steel disc creates some turbulence which reduces the air speed within the sampler.

The vertical net-flux of NH_3 from the experimental area (F_v) was calculated using the following equation:

$$F_v = \frac{1}{2r} \sum_{h=1}^{h=4} \sum_{m=1}^{m=4} (F_{hz,p} - F_{hz,s})\Delta h \, , \qquad (2)$$

where $F_{hz,p}$ and $F_{hz,s}$ is the horizontal flux from the experimental area and surroundings, respectively, at each height of measurement (h) with each mast (m), Δh is the height interval represented by the flux samplers ($\Delta h = 1.125$ m for flux

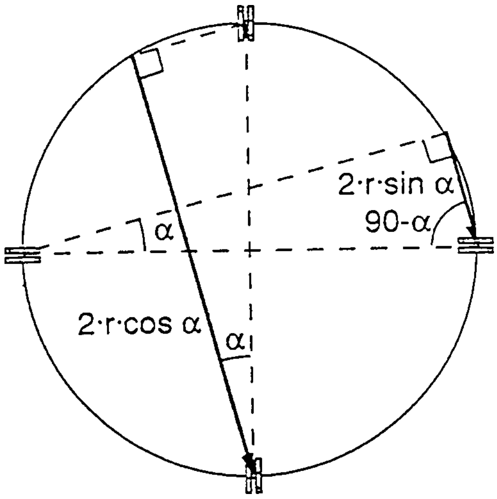


Fig. 3. Graphical presentation of the fetch represented by passive flux samplers on four masts surrounding a circular plot. Further explanation of the Figure is given in the Text.

samplers in 0.75 m height, and Δh = 0.75 m for flux samplers in 1.5, 2.25 and 3 m height), r is the radius of the experimental plot (15 m), corresponding to half of the fetch (the stretch the wind had passed over the experimental area).

That the fetch is equal to $2r$ can be derived from Figure 3. Two pairs of flux samplers receive air that has passed a stretch of $2r \cdot \cos\alpha + 2r \cdot \sin\alpha$ over the experimental plot (bold arrows in Figure 3). The fetch thus varies beween $2r$ and $2.83r$ when α varies between 0° and 45°. However, the flux is not only proportional to the amount of NH_3 emitted (here assumed to be proportional to the fetch) but also to the cosine of the angle between the wind direction and the longitudinal axis of the samplers (Figure 1). Accordingly, the effective fetch will be the sum of the products $2r \cdot \cos^2\alpha$ and $2r \cdot \sin\alpha \cdot \cos(90\text{-}\alpha)$ which is equal to $2r$.

2.3. REFERENCE METHOD

The downwind mast, placed in the center of the experimental area, was equipped with NH_3 traps placed at 0.25, 0.5, 0.75, 1.1, 1.5, 2.25, and 3.75 m height above the soil surface. A mast with four air temperature sensors (Rotronic MP100TST-010) at 1, 1.5, 2, and 3 m height above soil surface and seven anemometers (Vector Instruments A101M) at 0.25, 0.5,0.75, 1.1, 1.5, 2.25, and 3.75 m height above soil surface was placed 1 m from the central mast. The signals from the air temperature sensors and from the anemometers were recorded by a datalogger (Cambell CR10/WP). Two masts with an NH_3 trap at 1, 2, and 3 m height above soil surface were placed at the upwind edge of the experimental area.

The NH_3 traps consisted of a 250 mL test tube with a bottle head supporting a gas dispersion tube. The traps contained 60 mL 0.05 M H_2SO_4. The air flow through the trap was 8 L min^{-1} provided by a Neuberger membrane pump. The traps were changed every 3 hr. The concentration of ammonium in the traps was measured spectrophotometrically by use of an autoanalyzer and a method based on reaction between ammonium, phenol, and hypochlorite (Hinds and Lowe, 1980).

The horizontal flux of NH_3 at each height of measurement was calculated as the product of mean wind speed and mean atmospheric concentration of NH_3. The NH_3 loss from the experimental area (the vertical flux of NH_3) was calculated using the following equation (Denmead, 1983; Ryden and McNeill, 1984):

$$F_v \approx \frac{1}{r} \int_{z_0}^{z_p} (\bar{u}_z \bar{c}_z - \bar{u}_z \bar{c}_{b_z}) \mathrm{d}z \ . \qquad (3)$$

Mean windspeed (u) and mean atmospheric NH_3 concentration (c) in the 3-hr periods of measurement were used in the calculations of F_v. In Equation (3), r is the fetch (i.e. the radius of the circular experimental plot which was 15 m), c_b is the mean background concentration of NH_3, z_p is the height at which the concentration of NH_3 equalled its background value (i.e. the height of profile development), and z_0 is the height at which wind speed fell to zero.

3. Results and Discussion

The horizontal flux of NH_3 determined with the new type of passive flux sampler is shown in Table II. The highest NH_3 flux from the experimental plot was in all cases observed at the downwind edge of the plot (compare Tables I and II). As an example, a high horizontal NH_3 flux from the experimental plot to the surroundings ($F_{hz,p}$) was observed on the eastern and southern mast in experiment 1 (Table II) in which the prevailing wind direction was north-west (Table I). Conversely, the horizontal NH_3 flux from the surroundings to the experimental plot was highest at the upwind edge of the plot.

The horizontal net flux of NH_3 ($\Sigma F_{hz,p}$ – $\Sigma F_{hz,s}$ in Table II) decreased in all of the experiments with the logarithm of height (z) (Table III). This shows that the flux samplers are able to measure a NH_3 flux profile.

There was a strong linear relationship between horizontal net flux densities of NH_3 measured by the passive flux samplers and by the reference method ($F^{\mathrm{net}}_{\mathrm{flux\text{-}samplers}} = 1.24F^{\mathrm{net}}_{\mathrm{NH_3\text{-}traps}} + 0.02$, r^2=0.96; Figure 4). The 95% confidence limit for the slope was 0.13. Thus, the slope was significantly higher than 1. The high slope of the regression line between the horizontal fluxes obtained with the two methods is mainly due to results obtained at the lowest height of measurement (0.75 m) in Experiments 5 and 6 (compare Table II and Figure 4). Exclusion of these data from the regression analysis reduces the slope to 1.08 with a 95% confidence limit of 0.22. In Experiments 5 and 6, the thickness of the stainless steel disc was reduced to 0.05 mm. We do not think, however, that the overestimation of the fluxes in Experiment 5 and 6 was due to a systematic error introduced by reducing the

TABLE II

Horizontal NH_3 fluxes from experimental plot ($F_{hz,p}$) and from surrounding ($F_{hz,s}$) as a function of mast and height in experiments with a passive sampler for measuring ammonia emission in the field

Exp.	Height (cm)	Flux, µg NH_3-N m^{-2} s^{-1}								Net flux[a]
		North		East		South		West		$\Sigma F_{hz,p}$-$\Sigma F_{hz,s}$
	(cm)	$\Sigma F_{hz,p}$	$\Sigma F_{hz,s}$	$\Sigma F_{hz,p}$	$\Sigma F_{hz,s}$	$\Sigma F_{hz,p}$	$\Sigma F_{hz,s}$	$\Sigma F_{hz,p}$	$\Sigma F_{hz,s}$	
1	300	0.0	6.1	12.2	0.0	15.3	6.9	3.1	10.7	6.9
1	225	2.3	4.6	19.9	5.4	16.1	5.4	0.8	6.9	16.8
1	150	0.0	10.7	36.0	6.9	22.2	5.4	0.0	7.7	27.5
1	75	2.3	15.3	84.2	7.7	59.7	3.8	5.4	16.8	107.9
2	300	0.0	1.5	1.5	0.8	5.4	1.5	1.5	0.8	3.8
2	225	0.8	2.3	3.1	1.5	3.8	1.5	3.8	1.5	4.6
2	150	0.0	1.5	1.5	0.0	6.1	0.8	3.8	1.5	7.7
2	75	0.8	1.5	0.0	1.5	11.5	0.8	6.9	0.0	15.3
3	300	3.1	6.1	6.1	7.7	16.1	7.7	12.2	8.4	7.7
3	225	9.9	9.9	5.4	4.6	13.8	9.2	18.4	7.7	16.1
3	150	6.1	3.8	4.6	6.1	11.5	5.4	26.8	8.4	25.3
3	75	0.8	9.2	4.6	5.4	20.7	4.6	59.7	10.7	55.9
4	300	13.8	10.7	14.5	4.6	6.1	8.4	7.7	19.1	-0.8
4	225	7.7	9.2	13.8	4.6	6.1	6.9	4.6	8.4	3.1
4	150	9.9	6.1	24.5	7.7	7.7	4.6	9.9	9.2	24.5
4	75	4.6	10.7	44.4	6.1	13.0	6.1	6.9	7.7	38.5
5	300	13.8	16.8	31.4	6.1	11.5	17.6	5.4	8.4	13.0
5	225	10.7	16.8	34.4	14.5	21.4	11.5	4.6	8.4	19.9
5	150	13.0	16.1	51.3	2.3	33.7	13.0	6.9	8.4	65.0
5	75	10.7	12.2	116.3	3.1	101.8	4.6	7.7	9.2	207.4
6	300	12.2	13.8	36.0	6.9	8.4	9.9	5.4	24.5	6.9
6	225	19.1	13.0	49.0	9.9	17.6	13.8	9.2	9.9	48.2
6	150	10.7	22.2	97.9	3.8	13.0	9.9	13.8	26.8	72.7
6	75	14.5	13.0	205.1	9.2	26.8	13.0	3.1	13.0	201.3

[a] µg NH_3-N m^{-2} s^{-1}.

thickness of the stainless steel disc. Other things may have been involved. For example, some beakers with NH_4^+/HCO_3^- solution may have been too close to a flux sampler in these experiments thus affecting the results in a non representative way. It must also be remembered that there are uncertainties associated with the reference method which may lead to an under estimation of NH_3 fluxes (Wilson *et al.*, 1983). If the stainless steel disc used in connection with the passive flux samplers is too thick there may be a risk that the air flow inside the glass tubes is too low when the wind direction is oblique to the axis of the sampler.

The vertical flux densities of NH_3 determined using the passive flux samplers and the reference method are shown in Figure 5. There was a good agreement

TABLE III

Linear regression equations and correlation coefficients for the relationship between horizontal net flux of ammonia ($\Sigma F_{hz,p}$-$\Sigma F_{hz,s}$, μg NH_3-N m^{-2} s^{-1}) measured with a new type of passive sampler (Table II) and logarithm of height (z, m) above the surface emitting ammonia

Experiment	Linear regression equation	Correlation coefficient
1	$\Sigma F_{hz,p}-\Sigma F_{hz,s} = -\ 73.2\ \ln(z) + 76.9$	$r^2 = 0.91$
2	$\Sigma F_{hz,p}-\Sigma F_{hz,s} = -\ 8.6\ \ln(z) + 12.2$	$r^2 = 0.96$
3	$\Sigma F_{hz,p}-\Sigma F_{hz,s} = -\ 34.6\ \ln(z) + 43.8$	$r^2 = 0.98$
4	$\Sigma F_{hz,p}-\Sigma F_{hz,s} = -\ 29.9\ \ln(z) + 31.4$	$r^2 = 0.95$
5	$\Sigma F_{hz,p}-\Sigma F_{hz,s} = -145.4\ \ln(z) + 150.0$	$r^2 = 0.94$
6	$\Sigma F_{hz,p}-\Sigma F_{hz,s} = -137.0\ \ln(z) + 151.7$	$r^2 = 0.96$

between the vertical flux densities of NH_3 obtained by the two methods.

The amount of NH_3 volatilized from the beakers with NH_4^+/HCO_3^- solution varied from 171 mg NH_3-N per beaker in the experiment with lowest NH_3-emission to 3240 mg NH_3-N per beaker in the experiment with the highest NH_3 emission. Expressed per unit land area these NH_3 losses correspond to a NH_3-N flux between 1.1 and 20.0 μg NH_3-N m^{-2} s^{-1} (Table IV). The highest losses of NH_3 took place

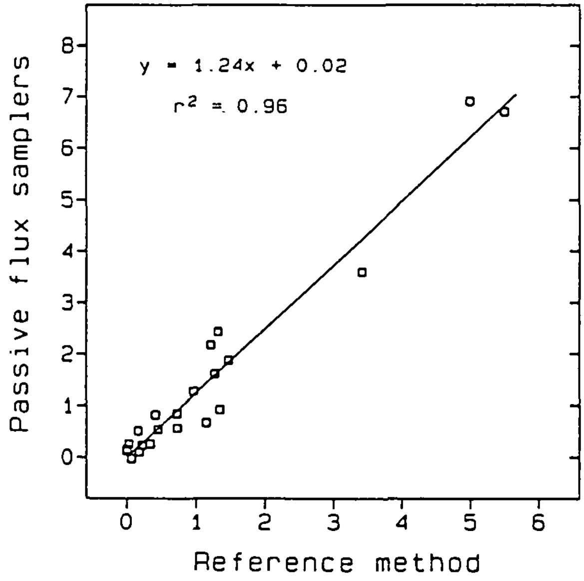


Fig. 4. Relationship between normalized horizontal net flux densities of NH_3 (μg NH_3-N m^{-2} s^{-1} per m fetch) measured by a micrometeorological method with passive flux samplers and a conventional micrometeorological method (reference method) with acid traps at 0.75, 1.5, 2.25 and 3 m height above the surface of the experimental plot. Normalisation of horizontal fluxes (i.e. division by fetch) was done in order to eliminate differences in the distance the wind had travelled over the experimental area (15 m in reference method, 30 m for passive flux sampler).

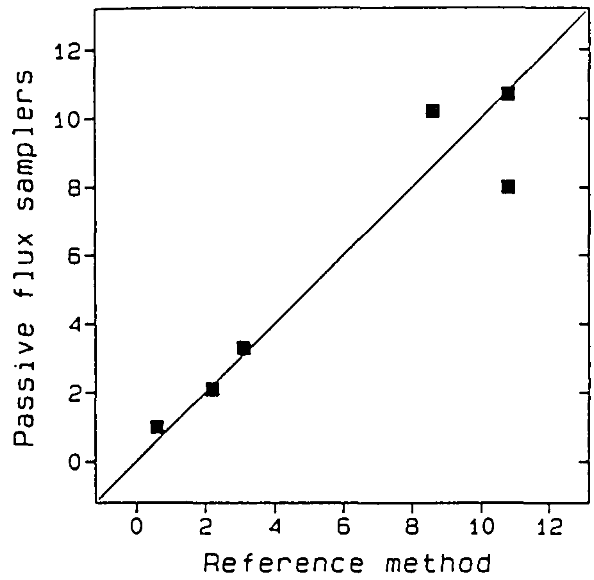


Fig. 5. Relationship between vertical flux densities of NH_3 (µg NH_3-N m^{-2} s^{-1}) measured by a micrometeorological method with passive flux samplers and a conventional micrometeorological method (reference method).

in experiment 6, in which air temperature and wind speed were relatively high (Table I). This is in accordance with the fact that NH_3 volatilization from aqueous solutions increases exponentially with temperature (Vlek and Stumpe, 1978). The amount of NH_3-N volatilized, relative to the initial amount of NH_4^+ in the beakers, varied from about 40% in experiment 6 to only 3% in experiment 2.

The NH_3 emissions measured with the two micrometeorological methods were smaller than close calculated on basis of the amounts of NH_3 lost from the source. The differences were most likely caused by deposition of NH_3 and subsequent

TABLE IV

Comparison of vertical NH_3 flux densities as measured by loss of NH_3 from beakers with NH_4^+/HCO_3^- solution and micrometeorological mass balance methods

Exp.	NH_3 loss from beakers µg NH_3-N m^{-2} s^{-1}	Vertical NH_3 flux, µg NH_3-N m^{-2} s^{-1} Micrometeorological method[a]
1	11.7 ± 0.8	9.4
2	1.1 ± 0.4	0.8
3	8.3 ± 0.8	3.2
4	6.1 ± 0.6	2.2
5	19.4 ± 1.9	9.4
6	20.0 ± 1.4	10.8

[a] Means of fluxes measured with reference method and passive flux samplers (Figure 5).

absorption of NH_3 to the soil surface. The NH_3 deposition was greatest in experiments 5 and 6 which were carried out in spring on a ploughed field with moist soil while experiment 1 was carried out on a stubble field with a relatively dry surface. Closely above the beakers there was a detectable odor of NH_3. This means that the concentration of NH_3 in the air just above the beakers was between 10 and 50 mg m^{-3} (Ahlberg, 1985; Jones, 1973). Calculated on basis of these concentrations, a deposition of e.g. 9.2 μg NH_3-N m^{-2} s^{-1} (difference between 20 and 10.8 μg NH_3-N m^{-2} s^{-1}; Table IV, Experiment 6) would require a deposition velocity between 0.02 and 0.1 cm s^{-1}. Velocities of 1 to 2 cm s^{-1} have been measured for dry deposition of NH_3 on vegetation (Duyzer *et al.*, 1987). In a mathematical simulation model, Asman and Janssen (1987) used velocities of 0.06 to 0.5 cm s^{-1} for ammonia dry deposition to bare soils.

4. Conclusion

The passive flux sampler can be used in a micrometeorological mass balance method to give accurate determinations of the vertical flux density of NH_3 from a circular field. The passive flux sampler make pumps, flow meters and anemometers unnecessary and NH_3 loss can be determined easily and cheaply without the requirement of electricity and large labor force.

Acknowledgments

This work was conducted under the N, P and Organic Matter Research Programme 1985–1990, funded by the National Agency of Environmental Protection, Denmark.

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II.

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Vol. 20, no. 1, January-March 1991, Copyright © 1991, ASA, CSSA, SSSA
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Foliar Absorption of Atmospheric Ammonia by Ryegrass in the Field

S. G. Sommer* and E. S. Jensen

ABSTRACT

The dry deposition of ammonia (NH_3) in the field was measured simultaneously at increasing distances from a point source (a dairy farm) using a biomonitor. The biomonitor was Italian ryegrass (*Lolium multiflorum* Lam.) grown in pots and supplied with ^{15}N-labeled N. The use of ^{15}N improved the precision and lowered the detection limit of the method compared with calculating the NH_3 deposition using the difference method (N-balance method). Atmospheric NH_3-concentrations were measured by drawing air through traps containing sulfuric acid. At the end of a 6-wk period in the growing season, the deposition of N was 3.0 g N/m^2 and 0.7 g N/m^2 at average atmospheric concentrations of 89 and 6 μg NH_3-N/m^3, respectively. Estimated deposition velocities ranged from 0.7 to 3.4 cm/s with an average of 1.6 cm/s (s.d. 1.2 cm/s).

IT HAS BEEN SHOWN that atmospheric ammonia (NH_3) can be absorbed as well as released from plants (Dabney and Bouldin, 1985; Harper et al., 1987; Schjørring et al., 1987; Whitehead and Lockyer, 1987). The flux of NH_3 is controlled partly by atmospheric NH_3 concentrations, as plants can absorb NH_3 at high concentrations of atmospheric NH_3 and lose NH_3 at low concentrations. In most natural ecosystems the supply of N is low and plants are in general N-deficient. It is therefore unlikely that plants in these ecosystems will lose N in the form of NH_3 during growth. However, during senescence ammonia volatilization can occur from ryegrass (*Lolium multiflorum* Lam.) (Whitehead et al., 1988). Micrometeorological measurements have shown that heather [*Calluna vulgaris* (L.) Hull] and pine (*Pinus* sp.) woods absorb atmospheric NH_3 (Duyzer et al., 1987). It has been demonstrated that Douglas fir [*Pseudotsuga menziesii* (Mirbel) Franco] absorbs ^{15}N-enriched NH_3 in the field (Nason et al., 1988) and laboratory (Pang, 1984). Plants exposed to atmospheric NH_3 in chambers increase their absorption of NH_3 almost linearly with concentrations of NH_3 in the air in the range 14 to 700 μg NH_3/m^3 (Whitehead and Lockyer, 1987).

The aim of the present investigation was to simultaneously measure atmospheric NH_3 concentrations and foliar absorption of NH_3 by plants in the field. The plants were grass grown in pots (biomonitors) with a low supply of N. The biomonitors were placed in the field at increasing distances from a point source of atmospheric NH_3. It was evaluated whether or not plant absorption of NH_3 was correlated with the average concentration of atmospheric NH_3. Deposition velocities of NH_3 were estimated.

MATERIAL AND METHODS

Plant Growth and Analysis

Absorption of atmospheric NH_3 was estimated by measuring dilution of ^{15}N in Italian ryegrass grown in pots. The pots (area 491 cm^2, volume 8.8 L) contained 7.4 kg N-free sand. On the sand surface 0.75 g seed (0.018 g N) was spread evenly and covered with a 1-cm layer of sand. Initially, the pots were watered with a N-free nutrient solution (Sommer, 1988). Ten and 25 d after sowing, 0.224 g N as KNO_3 with 2.786 atom % ^{15}N excess was supplied to each pot with the nutrient solution. Nutrient solution without N was supplied when needed.

The pots were placed in a greenhouse for 28 d after sowing. Groups of four to five pots were placed in the field 20, 40, and 60 m east and 20, 40, 60, 80, and 130 m west of a dairy farm dung yard in the prevailing wind direction. One group was placed 10 m south of the source. When the pots were placed in the field, plants from other five pots were harvested and analyzed (control). Pots were positioned such that the plants were at the same height as the crop in the field.

After 47 d exposure, plants from all pots were harvested. The roots were recovered by gently washing the sand from the roots. The plant material was oven-dried at 80 °C for 24 h, weighed, and ground.

Analyses for total N and ^{15}N enrichment in the dried and finely ground plant material were carried out using an elemental analyser (Carlo Erba NA 1500) interfaced to an isotope ratio mass spectrometer (Delta, Finnigan MAT).

Measurements of Atmospheric Ammonia and Inorganic Nitrogen in Rain Water

The atmospheric NH_3 concentration was measured by drawing air at 0.5 L/min through traps containing 60 mL 0.1 *M* H_2SO_4. The trap consists of a 100-mL test tube with a gas dispersion tube. The flow was provided by a diaphragm pump (Neuberger NMP 8.0 L, 12 V DC). The traps situated 1.2 m above the crops were changed weekly and the concentration of NH_4^+ measured colorimetrically (Dansk Standardiseringsråd, 1975). The measurements were carried out in two 7-d periods 1 and 2 wk after the start of exposure.

Rain was collected in funnels (area 452 cm^2) giving an estimate of the bulk deposition. Ammonium concentrations were analyzed colorimetrically and NO_3^- was analyzed with a HPLC (Perkin Elmer, series 10).

Calculations

The content of labeled N (N_{lab}) in the plant material, and N-deposition (N_{dep}) was calculated, using the following equations.

$$N_{lab} = N_{total} \times \frac{\text{atom \% } ^{15}\text{N excess (plant)}}{\text{atom \% } ^{15}\text{N excess (N added)}}$$

$$N_{dep} = N_{total} \times 1 - \left[\frac{\text{atom \% } ^{15}\text{N excess (exposed plant)}}{\text{atom \% } ^{15}\text{N excess (control plant)}}\right]$$

In the plume of NH_3 from the dairy farm, the background concentration of NH_4^+ is constant (Allen et al., 1988; Asman and Janssen, 1986), and in rural areas background NO_x concentrations in the air are also constant. In this study, differences in the amount of N deposited are therefore related

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Published in J. Environ. Qual. 20:153-156 (1991).

to differences in atmospheric NH_3 concentrations. One is able to calculate the deposition velocity for NH_3, dividing differences in uptake of N with differences in atmospheric NH_3 concentration at two distances from the farm. The uptake of atmospheric NH_3 is then expressed as the deposition velocity (V_d):

$$V_d = \frac{R\,(x) - R\,(130)}{[NH_3\,(x) - NH_3\,(130)]\,E_T}$$

where

V_d = deposition velocity, cm/s
$NH_3\,(x)$ = atmospheric NH_3 concentrations in the air x m from the farm, μg NH_3-N/m^3
$NH_3\,(130)$ = atmospheric NH_3 concentrations in the air at 130 m from the farm, μg NH_3-N/m^3
$R(x)$ = rate of N deposition to biomonitor x m from the farm, g/m^2
$R\,(130)$ = rate of N deposition to the bio-monitor at 130 m from the farm, g/m^2
E_T = period of exposure, s

An analysis of variance was carried out using the procedure ANOVA in SAS, and LSD values were used to compare treatment means when the treatment effect was significant.

RESULTS AND DISCUSSION

Atmospheric Ammonia Concentration and Wet Deposition of Nitrogen

The mean concentration of atmospheric NH_3 increased from 6 μg NH_3-N/m^3 130 m east of the farm up to 89 μg NH_3-N/m^3 10 m south of its dung yard (Table 3). East and west of the farm the concentrations of NH_3 were at identical levels. The east and west NH_3 concentrations measured were much higher than those found in natural ecosystems unaffected by animal production (Ferm et al., 1988). The highest concentrations were equivalent to reported concentrations from areas with high livestock production (Pinksterboer et al., 1987).

Table 1. Dry matter production, N concentrations in dry matter, and ^{15}N enrichment of Italian ryegrass tops and roots as influenced by biomonitor placement.

Distance†	Dry matter	N	Atom % ^{15}N excess
m	g/pot	%	
		Plant top	
−60	17.9	1.52	2.22
−40	21.9	1.31	2.07
−20	18.7	1.61	2.09
0	26.1	1.27	1.99
+20	24.2	1.21	2.08
+40	25.3	1.15	2.16
+60	23.5	1.19	2.25
+80	22.8	1.15	2.33
+130	25.5	1.02	2.43
LSD_{95}	2.2	0.10	0.24
Control	8.21 (SD 1.10)	3.64 (SD 0.20)	2.62 (SD 0.10)
		Plant root	
−60	60.9	0.35	2.21
−40	73.2	0.29	2.03
−20	65.6	0.34	2.06
0	82.8	0.30	1.99
+20	78.4	0.31	2.02
+40	79.1	0.29	2.09
+60	80.1	0.27	2.13
+80	83.9	0.23	2.23
+130	70.5	0.31	2.32
LSD_{95}	22.0	0.08	0.09
Control	4.63 (SD 0.20)	1.90 (SD 0.10)	2.47 (SD 0.05)

† − East, + west of dung yard.

With funnels continuously open, deposition of ions and particles with rain and dry deposition on the funnel sides is measured as bulk deposition. In rain water, the respective concentrations of NO_3^- and NH_4^+ were 0.723 mg NO_3^--N/L and 0.866 mg NH_4^+-N/L. Precipitation during the measuring period was 94 mm and the bulk deposition of N was therefore 0.007 g N/pot.

Nitrogen Accumulation in Control Plants

The top dry matter production of the control plants harvested at the initiation of the exposure period, was higher than that of the roots (Table 1). The concentration of N in the top material was twice the concentration in the roots and 77% of total N of the plants were found in the top. There was found 79% of the labeled N in control plants (Table 2). It was found that 0.04 g N/pot was derived from sources other than the labeled N. Approximately half of this N was derived from the seeds, the rest was probably added in the deionized water or derived from assimilation of NH_3 from the air.

The labeled N that was unaccounted for (21%) was probably still present in the sand or lost when the roots were washed free of sand (Janzen and Bruinsma, 1989). It is unlikely that denitrification occurred in the sandy soil containing no organic material. Due to the high N status of the plants and low atmospheric NH_3

Table 2. Total and labeled N uptake and recovery of labeled N in the plant biomass as influenced by biomonitor placement.

Distance†	N-total	N_{lab}‡	Recovery§
m	g N/pot	g N/pot	%
−60	0.48	0.37	82
−40	0.50	0.35	78
−20	0.52	0.47	82
0	0.57	0.48	86
+20	0.53	0.47	83
+40	0.52	0.38	85
+60	0.48	0.47	81
+80	0.45	0.46	81
+130	0.47	0.49	86
LSD_{95}	0.05	0.04	NS
Control	0.39 (SD 0.03)	0.35 (SD 0.05)	79 (SD 11)

† − East, + west from the dung yard.
‡ Based on atom % N in labeled N.
§ Recovery of added labeled N.

Table 3. Concentration of NH_3 and deposition velocities (Vd) as influenced by the distance to the dung yard of a dairy farm.

Distance†	NH_3-N	Vd
m	$\mu g/m^3$	cm/s
−60	25	2.4
−20	46	1.2
0	89	0.8
+20	41	1.5
+40	17	3.4
+60	16	1.5
+80	16	0.7
+130	6	N.D.

† − West from the dung yard, + east from the dung yard.

concentrations, some of the N taken up may have been lost as NH_3 from the plant tops (Harper et al., 1987).

Nitrogen Accumulation in Exposed Plants

After 6 wk exposure in the field, the mean recovery of labeled N was 83%; this is not significantly different from the uptake in the control plants (Table 2), indicating no fertilizer N was lost during this period.

The N concentration in plants exposed in the field was low (Table 1), and plants were N-deficient during field exposure, labeled N was translocated from the top to the roots. Atmospheric NH_3 was assimilated by the plant tops and some of it was apparently translocated to the roots, because the amount of the N deposited in the roots exceeded the amount added to the plants in rain. Although N was translocated from the tops to the roots, the concentration of N in the roots was very low.

Foliar Absorption of Ammonia

The ^{15}N-enrichment of the control plants was used for calculating the deposition of N to plants exposed in the field. As the plants were growing in sand only containing labeled N, it is not necessary to assume the same amount of soil N was taken up by plants exposed to elevated concentrations of atmospheric NH_3 as plants grown in an NH_3-free atmosphere (Lockyer and Whitehead, 1986). The uptake of soil N may be depressed when the plants are absorbing large amounts of gaseous N (Okano and Totsuka, 1986). Nitrogen lost or gained while the plants were grown in the greenhouse will not affect the estimated deposition, because the ^{15}N-enrichment in the control plants is used for calculating the deposition of N to the plants in the field.

Absorption of atmospheric N can also be estimated by the difference method (Okano and Totsuka, 1986; Sommer, 1988). Using this method, the absorption is estimated as the difference between the total N of the plants harvested and the amount of N added in seeds and fertilizer. In this study, a positive correlation between the methods was observed (Fig. 1), but the N difference method underestimated the deposition. This difference could have been caused by ammonia volatilization from the plants 1 to 2 wk after fertilizer application (Harper et al., 1987) and release of root exudates into the rhizophere (Janzen and Bruinsma, 1989).

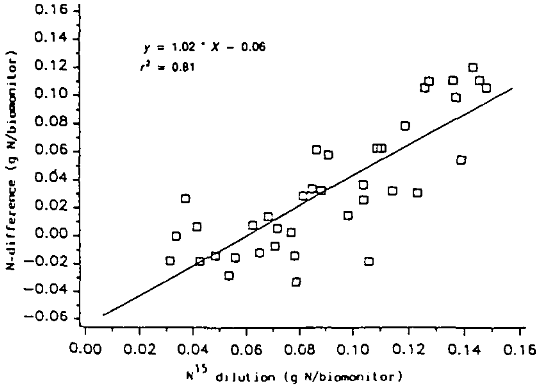

Fig. 1. Correlation between estimates of NH_3 deposition using N-difference or ^{15}N-dilution method.

The source of NH_3 was a dairy farm [80 cows (*Bos* sp.)], which produced ca. 5.7 × 10^3 kg NH_4^+-N/yr (Hansen and Sibbesen, 1989). From the stable and dung yard it is assumed that 20% (Kruse et al., 1989) of the NH_4^+ evaporated giving an estimated ammonia loss of 1.1 × 10^3 kg NH_3-N/yr. This emission caused a deposition of N to the biomonitors, which declined rapidly to the west and east of the farm due to falling concentration of atmospheric NH_3 (Fig. 2). Ten meters south of the farm, the measured deposition is equivalent to 3.0 g N/m^2 and 130 m east of the farm the deposition is equivalent to 0.7 g N/m^2 for the 47 d the biomonitors were exposed in the field. At the end of this period, the bulk deposition was 0.14 g N/m^2, indicating dry deposition of NH_3 contributes large amounts of N to the vegetation and crops near a farm with livestock.

The amount taken up from NH_3 increased with increasing concentrations in the air (Fig. 3). It has been

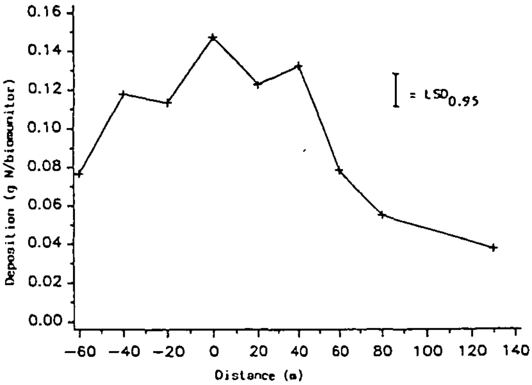

Fig. 2. Deposition of NH_3 east (+) and west (−) from the dung yard. Measured with biomonitors, area 492 cm^2.

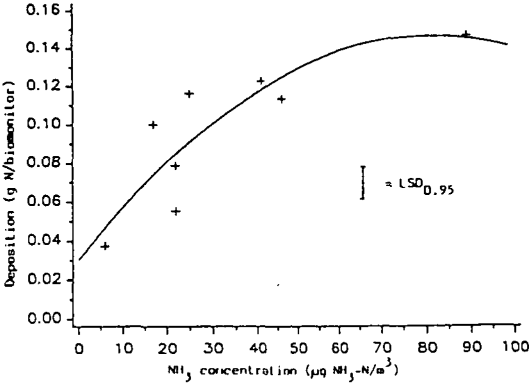

Fig. 3. Deposition of NH_3 measured with Italian ryegrass grown in post, area 492 cm^2.

shown that at atmospheric NH_3 concentrations from 14 to 709 $\mu g\ NH_3/m^3$ the assimilation of NH_3 was linearly correlated to the concentration (Whitehead and Lockyer, 1987). In the present experiment, the deposition of NH_3 deviates from linearity at the high NH_3 concentration near the farm. This could be an artifact caused by the wind conditions near the farm buildings, which affect the NH_3 concentration gradients above the plants. Alternatively, the plants near the farm may have been saturated with NH_4^+ during the fairly long exposure period with high concentrations of atmospheric NH_3.

Deposition velocity is an unknown function of experimental conditions (Sehmel, 1980) and shows a wide numerical range for even the same type of deposition surface. The reference heights have normally been 1.0 to 1.5 m for land surface. In this study NH_3 concentrations were measured 1 to 1.2 m above the biomonitor. The estimated average deposition velocity of NH_3 was 1.6 cm/s (SD 1.2 cm/s) (Table 3). Using a micrometeorological gradient method, a total yearly average of Vd = 1.92 cm/s (SD 1.09 cm/s) was estimated over heather (Duyzer et al., 1987).

ACKNOWLEDGMENTS

The National Agency of Environmental Protection, the N, P, and Organic Matter Research Program 1985-1990, Denmark, supported this study by a grant.

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Determination of Total Ammonium Nitrogen in Pig and Cattle Slurry: Sample Preparation and Analysis

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In order to supply the correct amount of ammonium to the crop when slurry is spread on the field, it is necessary to know the ammonium concentration. Slurry is a heterogeneous substance and there is a risk that organic N-compounds and the ionic strength will interfere with the determination of ammonium. The usability of five different methods for the determination of ammonium in solution has been tested on 18 different cattle and pig slurries and compared to a manual distillation titration technique. Colorimetric determination using an autoanalyzer and an automatic titration distillation device using MgO were highly accurate, and the precision was close to 1%. Distillation with NaOH caused interference from hydrolysable organic compounds. An ammonium electrode could be used, but the accuracy was not good. When using the automatic titration distillation device, samples should immediately be transferred to Kjeldahl flasks with water or acidified to prevent loss of volatile ammonia, unless they are to be distilled within 30 min.

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Key words: ammonium; autoanalyzer; manual titration-distillation; automatic titration–distillation; ion-selective electrode; sample preparation.

Introduction

Large amounts of animal manure are collected and applied to fields in form of slurry. Owing to the low costs of mineral fertilizers, the plant nutrients in slurry have not been highly valued and slurry has been treated as a waste product. This can generate environmental problems, as increasing amounts of nitrogen will leach to ground- or surface water if the nutrient load exceeds crop requirements. In field experiments at Askov Experimental Station, the total ammonium nitrogen (TAN) determined with a manual distillation titration method has been shown to have a nutritional effect equivalent to inorganic nitrogen in fertilizers. The content of TAN in slurry is highly variable (Kjellerup, 1986), and the TAN concentration has to be known in order to calculate the amount of slurry necessary to satisfy the nitrogen requirement of the crop.

Before slurry is applied, the TAN concentrations can either be determined by the farmer (Kjellerup, 1986) or at the local laboratory. It is known that commercial laboratories often determine the concentration of TAN with existing methods for soil- or water analysis. These methods include ammonia gas and ammonium ion electrodes, direct distillation of TAN or colorimetric determination using an autoanalyzer. Ammonia-sensing electrodes have been shown to give the same TAN concentrations in slurry as standard distillation titration methods (Kluge et al., 1989; Manca et al., 1989). Direct distillation with MgO has often been used for determination of TAN in slurry (Lauer et al., 1976; Hoff et al., 1981; Kirchman & Witter, 1989; Manca et al., 1989). At Askov Experimental Station, TAN in farmyard manure and slurry ~~has~~ been determined by direct distillation with MgO, collection in boric acid indicator solution and titration with standard HCl solution (Hansen, 1927).

The question of whether the methods often used for soil analysis are suitable for determination of TAN in slurry has not been reported. Such methods were compared to the manual distillation procedure using MgO which ~~has~~ been used since 1927 as the standard method for analyzing TAN in manure at Askov Experimental station. Laboratories often prepare many samples at a time, which can result in loss of ammonia by evaporation during storage. Therefore, the effect of sample preparation was examined, and methods to preserve TAN were developed.

Experimental

Five methods for the determination of ammonia in slurry have been tested: a manual distillation–titration method using MgO, distillation on an automated distillation–titration unit for Kjeldahl nitrogen determination using either MgO or NaOH, use of an ammonium electrode, and an automated spectrophotometric method using an autoanalyzer. The water used was purified by ion exchange (Silborko MC equipment, model DP1) and boiled, and all reagents were analytical grade.

Manual distillation–titration (MDT)

Determinations of TAN using manual distillation were made according to Hansen (1927). An aliquot of 5–10 g of slurry was transferd to a 250 ml Pyrex flask. Five grams of MgO, four drops of paraffin oil (antifoam) and 200 ml of water were added. The flask was connected to the distillation device and a receiver flask containing 25 ml 4% boric acid and three drops of indicator (methyl red an methyl blue). The slurry solution was heated until 100–150 ml had distilled into the receiver flask (10–13 min). TAN in the distillate was determined by titration with 1/14 M HCl. When the colour changed from green to red the distillate was heated to boiling for 5 min to remove dissolved carbon dioxide, and the colour changed ~~from~~ back to green. Thereafter the distillate was titrated until the colour changed to red again.

Table 2. Determination of TAN in pig (no. 13) and cattle (no. 14) slurry by the manual distillation titration method with and without addition of $CuSO_4$ ($n = 5$)

Slurry no.	$CuSO_4$	TAN* (g N l^{-1})	c.v. (%)
2	+	2.48	1.5
2	–	2.48	0.6
11	+	4.52	1.0
11	–	4.47	0.3

* There was no significant difference ($p = 1\%$) between the determinations with and without $CuSO_4$.

Table 1. Characteristics of the cattle and pig slurries used in the experiments

Sample no.	Slurry source	Total-N (g N l^{-1})	TAN-N (g N l^{-1})	pH	Dry matter (% w/w)
1	Pig	5.44	4.33	8.15	2.44
2	Pig	2.80	2.50	7.45	1.05
3	Pig	3.50	2.60	7.20	2.23
4	Pig	3.80	3.10	7.40	2.01
5	Pig	4.60	3.50	7.45	3.73
6	Pig	5.60	3.80	7.35	8.13
7	Pig	6.71	5.30	8.10	4.08
8	Cattle	3.80	2.30	7.45	6.15
9	Cattle	4.34	2.60	7.35	7.06
10	Cattle	4.20	2.80	8.70	6.08
11	Cattle	*	2.48	*	*
12	Cattle	*	3.97	*	*
13	Pig	6.04	4.56	6.40	5.50
14	Cattle	3.86	2.42	6.29	7.96
15	Cattle	5.81	4.59	6.68	8.06
16	Cattle	5.40	3.26	7.20	8.52
17	Pig	3.00	2.44	7.50	2.05
18	Pig	6.10	4.61	7.60	4.42

* Not measured.

Automated distillation–titration (ADT)

The TAN concentration was determined with an automated steam distillation titration system, Kjeltec Auto 1030 Analyzer (Tecator, Sweden). The system was used and reagents prepared as described in the manual. An aliquot of 5–10 g slurry was transferred to a destruction tube. Five grams of MgO and four drops of silicone oil (antifoam) ~~was~~ added, and distillation started immediately. Determination of TAN using 25 ml 33% NaOH added automatically instead of MgO was also examined.

Ammonium electrode (AE)

An F2322 NH_4 electrode (Radiometer A/S, Copenhagen) was employed. Potentiometric measurements were performed with a Radiometer TTT 85 instrument. The electrode consists of a silver chloride insert mounted in a tube containing ammonium chloride electrolyte solution. The tip of the tube is a membrane through which the electrolyte solution is in contact with the sample solution. The sample solution was diluted 100 times with water and stirred with a magnetic stirrer. The electrode and calomel reference electrode were immersed into the slurry solution, and stirring was stopped. After 1 min the potential was read. TAN standard solutions were prepared by diluting a 500 ppm NH_4Cl solution to give TAN concentrations of 2.5, 5.0, 10.0, 25.0, 50.0, 100.0 and 200.0 ppm.

Autoanalyzer (AA)

A Technicon autoanalyzer (Technicon autoanalyzer II, Segmented Flow Analytical Instruments) was used essentially as described by Crooke and

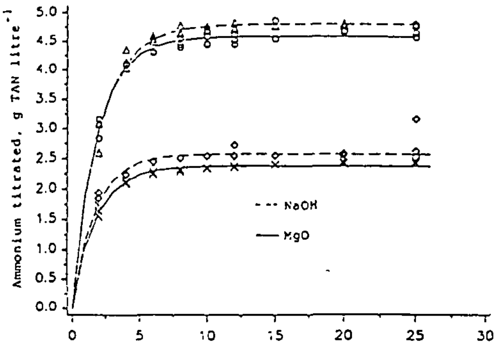

Fig. 2. Recovery of TAN added to the slurry as NH_4Cl measured with the standard manual distillation titration method adding MgO.

Simpson (1971). In this system the TAN is dialysed over a membrane and determined with a Berthelot reaction using salicylate and dichlorisocyanurate as coloring reagent and nitroprusside as catalyst. An automatic pipette ~~from which the end of the tip had been removed~~ was used to transfer 1 g of slurry to a 100 ml volumetric flask containing 10 ml water. A solution of 1 mM KCl was added to make the volume up to 100 ml.

Slurries and treatments

Eighteen samples of pig and cattle slurry were used for the test (Table 1). The content of TAN was determined with the manual–distillation titration method, and total-N using the Kjeldahl method. The dry matter content was determined gravimetrically and slurry bulk pH with a standard electrode (Radiometer). The slurries are referred to by the numbers in Table 1. The slurry was stored frozen and after thawing kept in closed 200 ml polyethylene bottles and analyzed within 3 days.

Test of distillation procedure: Recovery of added ammonium from slurry was studied with the standard MDT method by adding 4, 8, 12 and 15 ml of a 100 ppm NH_4Cl solution to slurry sample no. 1. The effect of the duration of distillation was examined with the MDT method using MgO and NaOH with slurries nos. 13 and 14. Addition of NaOH was compared to MgO addition with the ADT method using slurries nos. 12–16. The effect of addition of $CuSO_4$ on the analysis was examined with the MDT, on slurry nos. 2 and 11.

Comparison of methods: TAN in slurry determined with the ADT using MgO, the AA and the AE methods was compared to the determination by the standard MDT method. Slurries nos. 2–18 were used for this test.

Reproducibility: Ten samples of slurries nos. 6 and 15 were analyzed with each of the four methods, the MDT and ADT methods using MgO, the AA and the AE method.

Sample preparation: The effect of having the samples stored in open beakers (liquid depth 1 cm and surface area 25 cm^2) and in Kjeldahl flasks (liquid surface area 12.6 cm^2) for 3, 6, 9, 12, 15, 18, 21, 30, 60, 120, 240 and 240 min was tested with slurries nos. 12 and 13. Furthermore, the effect of addition of MgO and water or preservation with phosphoric acid (when stored in the flasks) was examined.

Calculations

The results were analyzed using two-way analysis of variance (SAS Institute, 1988). Adjusted r^2 correlation values were used to test the relation between two treatments. The NLIN procedure in the SAS statistical package (SAS Institute, 1988) was used to test the effects of different treatments.

Results and discussion

Manual distillation

Addition of $CuSO_4$ to the slurry prior to analysis with the MDT method reduced the accuracy of the method, and the coefficient of variation increased two- to three-fold (Table 2). There was no significant difference ($p = 1\%$) between the two methods. Copper sulphate was originally added to the manure (Hansen, 1927) to precipitate hydrogen sulphide, which upon distillation can blur the colour

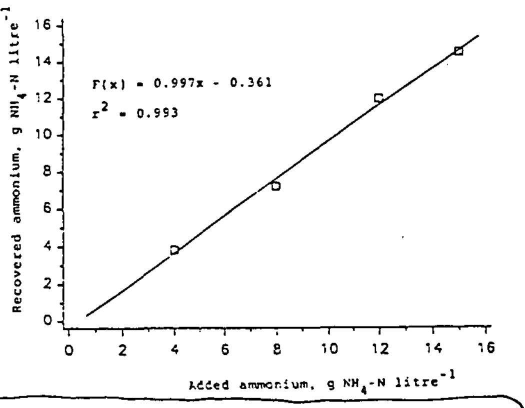

Fig. 1. Effect of distillation time and addition of NaOH and MgO on the amount of TAN distilled from pig slurry (upper) and cattle slurry (lower).

change during titration. The test showed that this precaution is not necessary.

Recovery of TAN (Fig. 1) was highly correlated with the amount of added ammonium chloride ($r^2 = 0.993$) in the determination with the MDT method. The recovery of added ammonium was confirmed by the observations, as the correlation line goes through the origin ($p = 5\%$) and the slope is 1.0 ($p = 5\%$).

The effect of distillation time was tested using the MDT method using either MgO or NaOH. Maximal amounts of TAN were obtained after 7–8 min of distillation (Fig. 2). After that time no more TAN was distilled, but significantly more TAN ($p = 5\%$) was distilled with NaOH than with MgO. NaOH probably hydrolyses alkali-labile organic N-compounds in the slurry (Fordham & Schwertmann, 1977), as ~~was~~ shown for soils by Bremner & Keeney (1965). These results show that MgO should be used in the analysis, and that distillation times of 8 min are necessary if reliable results are to be obtained. The distillation time corresponded to 150 ml distillate, as used in the standard procedure (Hansen, 1927).

Automatic distillation titration method

Distillation of TAN for ~~3 min~~ three min. by the ADT method with NaOH was highly correlated with the MDT method with MgO ($r^2 = 0.9997$), but the values obtained are significantly different, since the slope of the curve is significantly different ($p = 5\%$) from 1 (Fig. 3A). Using the more reactive base possibly caused interference from amino acids. By contrast, determination of TAN by adding MgO to the slurry and distilling with the ADT for ~~3 min~~ three min. was identical with the MDT method, as the linear regression line ($r^2 = 0.997$) had a slope not significantly different from 1.0 ($p = 5\%$) and an intercept not different from zero ($p = 5\%$) (Fig. 3B). The result indicates that when MgO is used, there is no interference with TAN determination by steam distillation; this

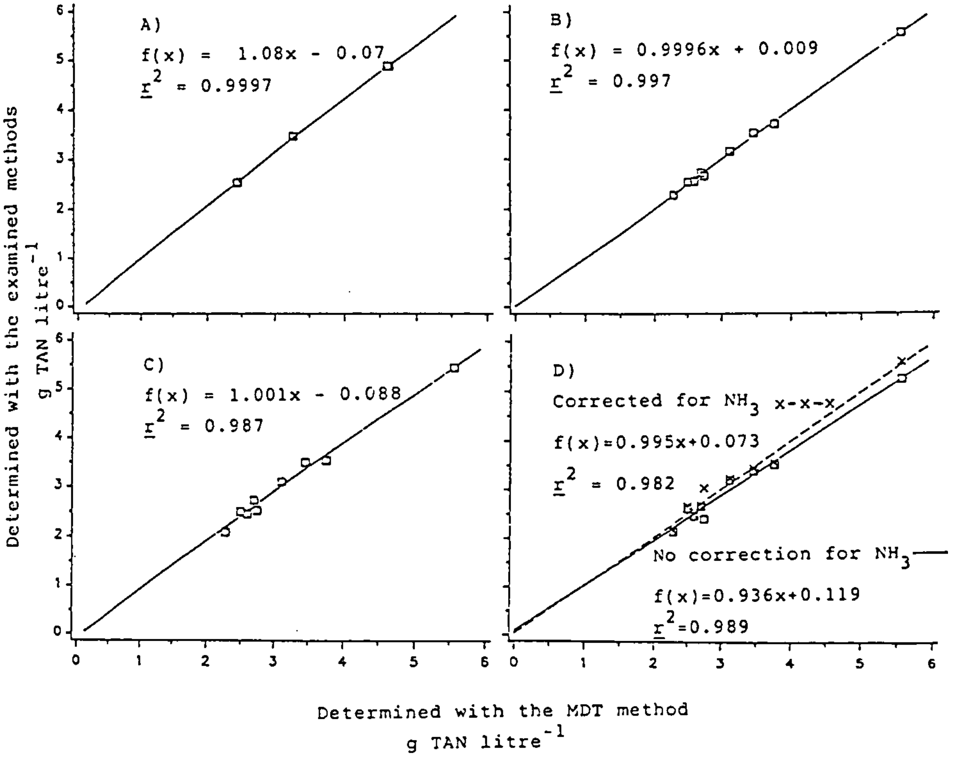

Fig. 3. Determination of TAN in slurry measured with an automated distillation titration unit after addition of either NaOH (A) or MgO (B), an autoanalyzer (C) and an ammonium electrode (D) compared to the standard manual distillation titration method adding MgO.

Table 3. The precision of the four methods tested with pig (no. 6) and cattle (no. 15) slurry ($n=10$)

Method	Pig slurry TAN* (g N l^{-1})	Pig slurry c.v. (%)	Cattle slurry TAN (g N l^{-1})	Cattle slurry c.v. (%)
Manual distillation titration (MgO)	3.97^{a,b}	1.1	4.55^{a}	1.2
Automatic distillation titration (MgO)	3.96^{a}	1.1	4.58^{a}	0.4
Automatic distillation titration (NaOH)			4.89^{b}	0.1
Ammonium electrode	3.76^{c}	1.3	4.40^{c}	1.6
Autoanalyzer	4.01^{b}	1.9	4.54^{a}	0.9
LSD (0.95)	0.04		0.04	

* Figures with the same letter are not significantly different.

has also been shown for soils by Burton et al. (1989).

Autoanalyzer

Determination of TAN estimated with an autoanalyzer was linearly correlated ($r^2=0.987$) with the standard MTD (Fig. 3C), but had a regression coefficient smaller than that obtained using the ATD method in the presence of MgO. The slope of the regression line was not significantly different from 1.0 ($p=5\%$) and the intercept was not significantly different from zero ($p=5\%$). The method is therefore suitable for the determination of TAN in slurry. The comparison showed that there is no interference with colour formation when the temperature is 37°C and nitroprusside is used as the catalyst (Searle, 1990).

Ammonium electrode

Determination of TAN in diluted slurry with an electrode was linearly correlated with the MDT method (Fig. 3D), the regression coefficient being 0.988. The slope is significantly different from 1.0 ($p=10\%$) and the intercept is significantly different from zero ($p=5\%$). The reason for the difference could be that the electrode only estimates ~~that~~ part of the TAN present as the NH_4^+ ion; if the pH of the slurry is higher than 8.0, less than 95% of the TAN will be in the NH_4^+ form. The ammonia content of the slurry was added to the estimate using the equation

$$TAN = [NH_4^+] \times (1 + K/[H^+])$$

where K is the equilibrium constant for the reaction, $[NH_4^+]$ is the ammonium content measured with the electrode and $[H^+]$ is the hydrogen ion concentration in the diluted slurry. The calculation improved the relation to the MDT method, giving a regression line ($r^2=0.982$) having a slope not different from 1.0 at the 10% level, and an intercept not different from zero ($p=5\%$). The sample has to be diluted to reduce the effect of ionic strength on the activity of the ammonium ions.

Precision

The precision of the MDT and the ADT methods was generally the best of the methods shown to be usable for determination of TAN in slurry (Table 3). The precision of the autoanalyzer was lower than of the distillation methods. The sample pattern was seen in the work of Crooke & Simpson (1971) who compared estimates of TAN in Kjeld-

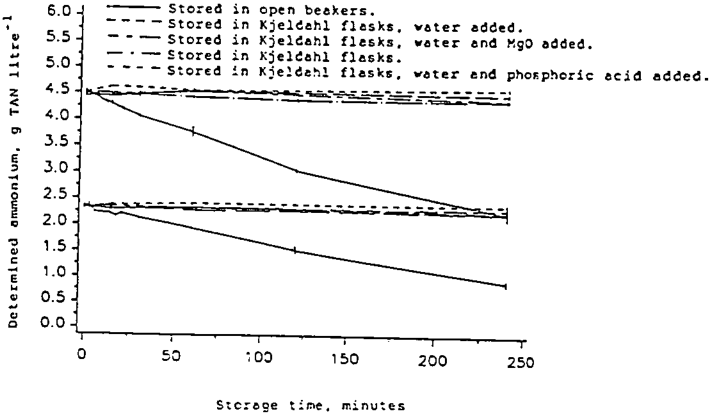

Fig. 4. Effect of pretreatment and storage period on TAN determination in pig slurry (upper) and cattle slurry (lower).

ahl digests determined with an autoanalyzer method and a manual distillation titration method.

Sample preparation

From the time when the samples were weighed until ~~to when~~ they were transferred with water to the Kjeldahl flasks and distilled and titrated, a significant ($p = 5\%$) amount of ammonium was lost owing its evaporation if the slurry was stored for 6 min or more in the beakers (Fig. 4). However, when the samples were transferred to Kjeldahl flasks there was no significant loss of TAN for at least 30 min, even in the presence of added water with or without MgO. The necks of the Kjeldahl flasks appear to provide a sufficient barrier to diffusion to prevent significant loss compared with the thin layer of liquid in an open beaker. However, significant loss of TAN could be observed even in the Kjeldahl flasks over longer periods; this could be completely prevented by acidifying the samples with phosphoric acid. Under these conditions samples were stable for at least 4 h ($p = 5\%$).

Conclusions

The automatic distillation titration method using MgO and the autoanalyzer method are accurate and have a high precision when used for analyzing TAN in slurry. The accuracy of the ammonium electrode is not high; to calculate the TAN content, the pH of the diluted sample has to be known, because the ammonia content must be calculated and added to the ammonium content measured. The precision of the ammonium electrode is not as good as ~~for~~ the autoanalyzer and the automatic distillation–titration unit. Sodium hydroxide cannot be used for the titration, since organic N-compounds will be hydrolyzed and will interfere with the analysis.

There is a great risk of loss of ammonia from the samples if they are stored in the beakers used for weighing. It is therefore recommended that the samples should be analyzed immediately. If a small series of samples is prepared at the same time, there is no significant risk of ammonia loss within 30 min if the samples are transferred to the Kjeldahl flasks with addition of 75 ml water and MgO. MgO addition to the Kjeldahl flasks should be avoided, and acidification may be used if a large series of samples is prepared at the same time.

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IV.

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Effects of Dry Matter Content and Temperature on Ammonia Loss from Surface-Applied Cattle Slurry

S. G. Sommer* and J. E. Olesen

ABSTRACT

Effects of increasing dry matter content in slurry on NH_3 loss was measured with a wind tunnel system, whereby parameters affecting the volatilization can be estimated under controlled conditions. The effect of dry matter content on NH_3 loss was measured using a slurry adjusted to different contents of dry matter. The slurry was prepared by mixing the fibrous and liquid fractions of a mechanically separated cattle slurry. Slurry was applied to a 5 cm high grass ley (*Lolium multiflorum* Lam.) and to barley (*Hordeum vulgare* L.) at a rate of 3 L m^{-2}. The content of dry matter varied from 0.9 to 22%, total N from 2.9 to 4.9 g N L^{-1}, TAN (NH_3 + NH_4^+) from 1.6 to 3.0 g N L^{-1} and pH from 7.0 to 7.9. The results indicated that NH_3 volatilization increased with increasing slurry dry matter content. The accumulated 6-d loss ranged from 19 to 100% of applied TAN from slurries having a dry matter content of 0.9 and 15.6%, respectively. The accumulated NH_3 loss after 6 h exposure was linearly related to dry matter content. In the periods of 6 to 12 h, 12 to 24 h and 24 h to 6 d the loss was nonlinearly related to dry matter content. If the results were adjusted for effects of pH and temperature, NH_3 loss tended to be sigmoidally related to content of dry matter in all four periods. Therefore, changes in slurry dry matter content on NH_3 loss seemed to be small if the dry matter content was higher than 12% or lower than 4%.

THE efficient use of inorganic N in animal manure is often neglected in agriculture. This can lead to great losses of N due to NH_3 volatilization from stables, manure storages, during application, and from applied manure (Kruse et al., 1989; Ryden et al., 1987). Ammonia lost by volatilization has to be compensated by N fertilizer, increasing the cost for plant production. Furthermore, deposition of NH_3 can be detrimental to natural ecosystems (van Dijk et al., 1990; Schulze et al., 1989).

Ammonia volatilization from surface-applied slurry can account for more than 50% of the NH_4^+ in manure (Lockyer et al., 1989; Thompsen et al., 1987). Within the first hours after application, a substantial loss of NH_3 can take place as a loss rate of 12 kg NH_3-N/ha per hour has been estimated (Pain et al., 1989). The loss can be reduced to less than 2.5% of the NH_4^+ content if the slurry is injected (Hoff et al., 1981) or NH_3 loss can be reduced by acidifying the slurry prior to application (Pain et al., 1989).

In agriculture the effort to reduce NH_3 loss should be weighed against the potential NH_3 loss rate from the slurry applied. It has been shown that pH of slurry affects NH_3 loss (Lauer et al., 1976) and that the loss rate is affected by climatic and soil conditions (Beauchamp et al., 1982; Holzer et al., 1988; Sommer et al., 1991). It has been proposed that the higher NH_3 loss from cattle, as compared to pig (*Sus scrofa domesticus*) slurry, was due to the higher dry matter content (Pain et al., 1990).

In this study NH_3 loss was related to dry matter content in cattle slurry, adjusted to different contents of dry matter. The slurry was prepared mixing the fibrous and liquid fraction of a mechanically separated slurry. The experiments were conducted from May 1989 to November 1989 giving a variation in climatic conditions.

MATERIALS AND METHODS

Wind Tunnel

Ammonia loss was measured using a wind tunnel system designed like the system described by Lockyer (1984). The four wind tunnels each consist of an inverted U-shaped transparent polycarbonate shell covering the experimental plot (2 m by 0.5 m = 1 m^2) and a circular steel duct housing a fan driven by an electric powered engine. The steel duct was 2 m long and had a diameter of 0.4 m, and the highest point of the transparent tunnel was 45 cm aboveground. The steel duct was equipped with a vane anemometer head, that measured wind speed within the tunnel. Signals from the four anemometers were scanned at 1 min intervals and stored as hourly means on a data logger.

After passing the experimental plot and the fan, the air stream was sampled near the outlet of the steel duct with a diaphragm suction pump. The pumps drew the air through 100-mL absorption flasks fitted with a sintered glass distribution tube. The flask contained 50 mL of 0.005 *M* H_3PO_4. Ammonia in the air was trapped in the phosphoric acid and subsequently determined colorimetrically with an indophenol reaction.

For each tunnel there was a gas-trapping unit consisting of four absorption flasks. A programmable magnetic valve control automatically switched each absorption flask on and off at preselected intervals. During the first 2 d after manure application NH_3 was collected for periods of 6 h; during the following 4 d NH_3 collection periods were 24 h long.

Meteorological Data

Air temperature was recorded at an automatic climate station at the research station Askov (55°28'N, 9°07'E), where the experiments were conducted. Air temperature was measured at a height of 2 m in a standard screen (Olesen, 1988).

Calculations of Ammonia Loss

Each experimental trial included one untreated reference plot (control) for measurements of background air NH_3 concentrations and two to three slurry-treated plots. For a given period, background NH_3 concentrations were subtracted from those obtained for treated plots:

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Published in J. Environ. Qual. 20:679-683 (1991).

$$J = A \times V \times 3600 \times (NH_{3e} - NH_{3r})$$

where:

J = NH_3 loss, g NH_3-N/h

A = area of steel duct, m^2

V = wind speed, m/s

NH_{3e} = NH_3 concentration in air from an experimental tunnel, g NH_3-N/m^3

NH_{3r} = NH_3 concentration in air from the reference tunnel, g NH_3-N/m^3

In an earlier experiment (Christensen and Sommer, 1989) it was found that mean recovery of NH_3 volatilized from animal slurry was 74% (CV = 9.7%). Therefore, results obtained by the wind tunnel system were corrected by the factor 100/74 to correct for recovery percentages.

Slurry Analysis

Total ammoniacal N (NH_3 + NH_4^+; TAN) content of the slurry was determined by direct distillation of the NH_3 with light MgO and $CuSO_4$, collection of NH_3 in boric acid–indicator solution, and titration with standard HCl solution.

Table 1. Characteristics of the slurries used in the experiments.

Exp. no.	Tunnel no.	Exp. period	Dry matter	Total N	TAN†	pH
			%	g N/L		
1	1	May–June 1989	22	4.9	1.6	7.0
1	2	May–June 1989	0.9	2.9	2.5	7.1
2	1	June 1989	0.9	2.9	2.5	7.0
2	2	June 1989	22	4.9	1.6	7.1
3	1	Aug. 1989	6.9	3.1	1.7	7.4
3	2	Aug. 1989	4.1	3.3	2.2	7.5
3	3	Aug. 1989	3.6	3.7	2.6	7.8
4	1	Oct. 1989	2.8	3.9	2.7	7.7
4	2	Oct. 1989	8.2	4.2	2.8	7.6
4	3	Oct. 1989	15.6	4.9	2.9	7.9
5	1	Oct.–Nov. 1989	2.8	3.9	2.7	7.7
5	2	Oct.–Nov. 1989	8.2	4.2	2.8	7.6
5	3	Oct.–Nov. 1989	15.6	4.9	2.9	7.9
6	1	Nov. 1989	5.2	4.4	3.0	7.7
6	2	Nov. 1989	6.0	4.3	2.9	7.7
6	3	Nov. 1989	10.0	4.6	2.9	7.6
7	1	Nov. 1989	5.2	4.4	3.0	7.7
7	2	Nov. 1989	6.0	4.3	2.9	7.7
7	3	Nov. 1989	10.0	4.6	2.9	7.6

† TAN: NH_3 + NH_4^+.

Table 2. Ammonia loss, wind speed, and mean climatic conditions during the experiments.

Exp. no.	Tunnel no.	Mean wind speed in tunnel	Air temp. 6 h	Air temp. 12 h	Air temp. 6 d	Accum. NH_3 loss 6 h	Accum. NH_3 loss 12 h	Accum. NH_3 loss 6 d
		m/s	°C			% of TAN		
1	1	3.4	9.9	9.3	9.7	58.6	68.0	97.4
1	2	3.4	9.9	9.3	9.7	4.5	5.4	19.0
2	1	3.6	15.0	12.9	13.1	4.8	6.6	26.3
2	2	3.8	15.0	12.9	13.1	31.0	37.3	72.5
3	1	3.2	19.6	17.6	15.9	23.8	30.1	56.5
3	2	2.8	19.6	17.6	15.9	15.3	18.5	42.0
3	3	2.8	19.6	17.6	15.9	6.8	11.1	29.6
4	1	3.6	11.7	11.7	10.5	1.6	4.6	25.1
4	2	3.7	11.7	11.7	10.5	2.5	12.3	38.0
4	3	3.4	11.7	11.7	10.5	19.0	31.1	80.5
5	1	3.6	10.3	8.5	7.9	12.9	18.6	39.9
5	2	3.7	10.3	8.5	7.9	18.5	27.3	64.2
5	3	3.4	10.3	8.5	7.9	35.9	51.2	111.4
6	1	3.3	7.5	6.0	1.5	9.7	15.1	38.4
6	2	3.1	7.5	6.0	1.5	10.7	17.9	44.0
6	3	3.2	7.5	6.0	1.5	24.7	39.3	86.8
7	1	3.3	1.9	1.4	0.5	7.1	13.3	40.7
7	2	3.1	1.9	1.4	0.5	6.3	12.7	45.5
7	3	3.2	1.9	1.4	0.5	13.3	25.0	71.1

Total N was analyzed using the Kjeldahl method and a Tecator Kjeltec Auto 1030 analyzer. Dry matter content was determined gravimetrically and slurry bulk pH with a standard electrode (Radiometer).

Slurries

Table 1 gives characteristics of the cattle slurries used in the study. The slurries were made by mixing the fibrous and liquid fractions of a mechanically separated cattle slurry in different proportions resulting in contents of dry matter ranging from 0.9 to 22%. In slurry, pH varied from 7.0 to 7.9, TAN concentrations from 1.6 to 3.0 g N L^{-1} and total N from 2.9 to 4.9 g N L^{-1}.

Nineteen experimental trials were conducted. The slurry was surface-applied at a rate of 3 L m^{-2} to the experimental plot having an area of 1 m^2. In the experiments during May and June slurries were applied to barley (*Hordeum vulgare* L.) (20 cm) and in the experiments during August to November, slurries were applied to a 5 cm high grass ley (*Lolium multiflorum* Lam.). The soil was a sandy loam with 10% clay and 2.7% organic matter.

RESULTS AND DISCUSSION

Ammonia Loss

The measured NH_3 losses, wind speed and the air temperatures during the experiments are listed in Table 2. It has been shown that differences in temperature measured inside the tunnel and ambient temperatures were less than 1 °C (Sommer et al., 1991; Ryden and Lockyer, 1985). Therefore, ambient temperatures can be used for the interpretation of the measured NH_3 loss.

Results from the experiments showed that more than half the total NH_3 loss from the cattle slurry occurred during the first day, which was similar to results reported elsewhere (Stevens and Logan, 1987; Thompson et al., 1987), and is illustrated in Figure 1 for Experiments 3 and 4. Volatilization of NH_3 were low from the slurries with a dry matter content of 2.8 and

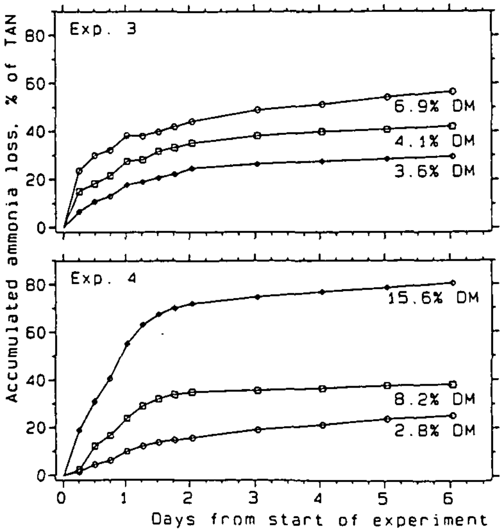

Fig. 1. Accumulated NH_3 loss in percent of applied TAN in slurry for Experiments 3 and 4.

8.2% in Experiment 4 during the first 6 h. This cannot be explained by low temperatures or the composition of the slurry, and is probably an effect of soil conditions.

Effect of Dry Matter Content

The effect of slurry dry matter content on NH_3 loss over four time periods is illustrated in Fig. 2. the accumulated NH_3 loss within the first 6 h seemed to increase linearly with increasing dry matter content. The scattering of the results was probably due to climatic conditions being important in this period (Sommer et al., 1991). After the first 6 h collection period and at low dry matter contents, there seemed to be a linear relationship between slurry dry matter content and accumulated NH_3 loss. At high dry matter contents the relationship seems to be nonlinear. Table 3 shows estimated first order and second order polynomials describing this relationship. The estimated curves are also shown in Fig. 2.

Ammonia loss during four periods were studied: 0 to 6 h, 6 to 12 h, 12 to 24 h, and 24 h to 6 d (Fig. 3). Ammonia loss (L) during these periods was first expressed as percent of initial TAN content in the slurry. This may, however, have introduced some errors for the later time periods, as some of the NH_3 had already been lost by volatilization in previous periods. Ammonia loss (L^*) during any period should be expressed as percent of the TAN content at the beginning of that period (Sommer et al., 1991). Using the measured loss rates in the preceding period for calculating the TAN content in slurry may, however, introduce some errors as the variability in measured NH_3 loss will increase with time. Such errors would be expected particularly at high dry matter contents, where only small amounts of TAN were left in the slurry after 24 h. The variability of estimates may be reduced—and the general validity of observations enhanced—if this analysis is based on all normalized data, which are summarized in Fig. 2 and represented by the equations for accumulated loss in Table 3. Using these equations to calculate cumulative percentage loss (L_a) up to the beginning of a given period, the NH_3 loss rate during the period (L^*) is then expressed as percent loss of TAN remaining at the beginning of each period:

$$L^* = 100\ L/(100 - L_a) \qquad [1]$$

where L^* is the calculated NH_3 loss rate in the period, L_a is the loss of NH_3 until the beginning of the period, and L is the NH_3 loss in the period.

The resulting estimates of L^* are related to slurry dry matter content (Fig. 3). The given figures are percent loss (in percent of initial TAN of the periods) over four time periods. During all four periods there is a significant effect ($P = 0.05$) of dry matter content. In the period 0 to 6 h there was a linear increase in the NH_3 loss when dry matter content was increased from 0.94 to 22%. There was no increase in NH_3 loss if dry matter content in the slurry was increased to above 10% for the periods 6 to 12 h and 24 h to 6 d and above 15% for the period 12 to 24 h.

Environmental Factors

The relationship between NH_3 loss and content of dry matter could perhaps be seen more clearly if effects

Table 3. Regression equations between accumulated NH_3 loss as percent of TAN in slurry (L_a) at different time intervals and slurry dry matter content (D); 19 observations.

Regression equation	R^2	RMSE
0 to 6 h: $L_a = 1.0 + 1.85D$	0.697	8.0
0 to 12 h: $L_a = 3.0 + 2.80D - 0.024D^2$	0.753	8.7
0 to 24 h: $L_a = 0.0 + 5.70D - 0.127D^2$	0.761	11.0
0 to 6 d: $L_a = 8.8 + 8.14D - 0.203D^2$	0.813	12.0

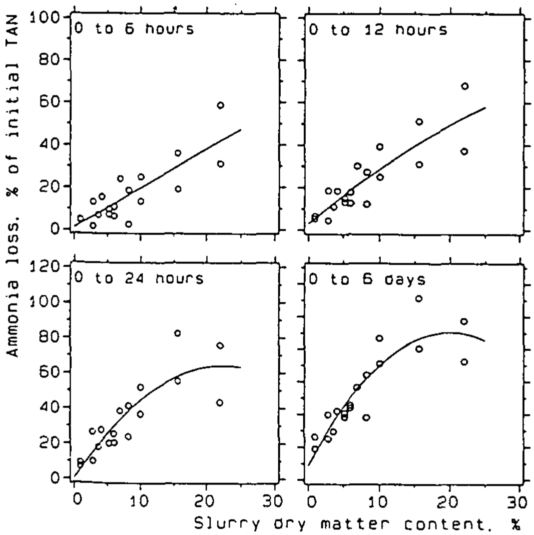

Fig. 2. Accumulated NH_3 loss in percent of TAN in applied cattle slurry related to slurry dry matter content for four time periods.

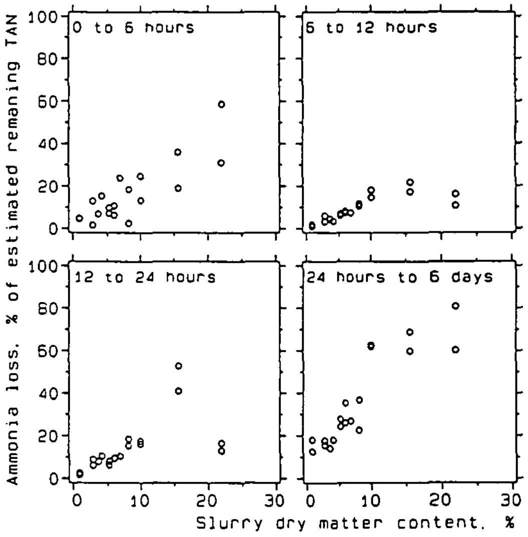

Fig. 3. Accumulated NH_3 loss related to dry matter content during four periods. The loss are expressed in percent of estimated TAN remaining in the slurry at the beginning of the period.

Table 4. Equations used for describing the relation between loss rate (L_c^*) and mean air temperature (T) during four time periods. Equations are adapted from Sommer et al. (1991).†

Equation	
0 to 6 h:	
$L^*_c = 13.0 + 0.031 \exp(0.375\ T)$	for $T < 15$ °C
$L^*_c = 0.5 + 1.68T$	for 15 °C $< T <$ 25 °C
6 to 12 h:	
$L^*_c = 5.2 + 0.712T$	
12 to 24 h:	
$L^*_c = -58.5 + 9.32\ \mathrm{pH} - 0.28T_e + 0.60T$	
24 h to 6 d:	
$L^*_c = 23.6 + 1.19T$	

† L^*_c = NH_3 volatilization rate in percent of slurry TAN content at the beginning of the period; T = the mean temperature during the period, °C; T_e = the mean temperature from start of the experiment until the beginning of the period.

of other factors of importance are eliminated. The dependence of NH_3 volatilization on air temperature and on the pH of the slurry has been expressed analytically for the four time periods, based on the analysis of earlier wind tunnel experiments by Sommer et al. (1991). These equations are shown in Table 4, and the effect of air humidity is not quantified because it has been shown to be of little importance compared with temperature and pH effects (Sommer et al., 1991). The equations for the period from 0 to 6 h do not match the equation presented by Sommer et al. (1991). At temperatures from 15 to 25 °C, a linear relationship between volatilization rate and temperature (Table 4) gives a better prediction, because there are small variations in the coefficient of inclination for the relation between NH_3 loss and temperature in this temperature interval.

With the assumption that effect of dry matter content (D) and environmental factors are multiplicative, the following relationship exists:

$$F = f(D) = L^*/L_c^* \qquad [2]$$

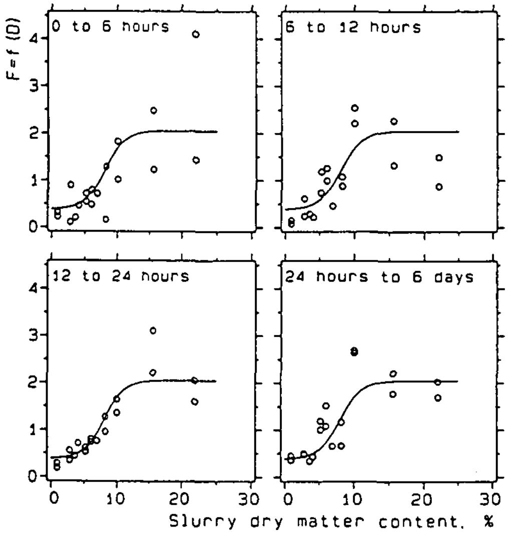

Fig. 4. Calculated dry matter factor (F) during four periods related to slurry dry matter content. F was calculated by dividing the observed loss rate by the loss rate estimated using the equations shown in Table 4, thereby correcting for climatic and pH effects.

The dry matter function (F) can be calculated by dividing the observed loss rates (L^*) by the loss rates (L_c^*) estimated using the equations in Table 4 whereby effect of temperature and pH was excluded. Figure 4 shows this estimated dry matter function vs. slurry dry matter content. Comparing Fig. 4 with Fig. 3, the variation in the observations was not reduced by corrections for temperature and pH effects. For the period from 12 to 24 h there is a less pronounced decrease in loss rate calculated with the dry matter function (Fig. 4), than the measured loss rate (Fig. 3) when slurry dry matter content increased from 15 to 22%. This was mainly due to the pH effect, which was included in the equation for L_c^* in this time period.

After having excluded effects of temperature and pH the estimated NH_3 loss expressed as F (Fig. 4) suggests the same sigmoidal relationship between loss rate and dry matter content, for all four time periods.

Observations from all four time periods were, therefore, pooled in the determination of a logistic type equation to describe the dry matter function. The parameters in the logistic equation were estimated using the NLIN procedure in the SAS statistical package (SAS Inst., 1988) resulting in the following equations:

$$F = 0.38 + 0.014/[0.0086 + 1.66 \exp(-0.654\ D)] \qquad [3]$$

where D is slurry dry matter content (in percent).

This estimated logistic function is shown in Fig. 4. It suggested that the main effect of dry matter content occurred in the interval from 4 to 12%. If dry matter content was high or low, variations in dry matter content resulted only in minor changes in NH_3 loss. This was probably due to small changes in water retention capacity of slurry at dry matter contents lower than 4% and higher than 12%. This will result in small changes in infiltration of TAN into the soil with changes in dry matter content in these intervals.

Equations [2] and [3] and the equations in Table 4

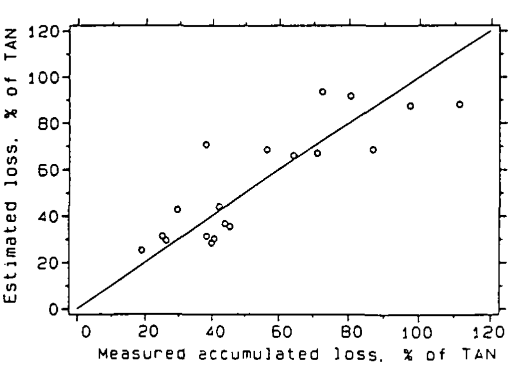

Fig. 5. Estimated compared with measured accumulated NH_3 loss during 6 d in percent of applied slurry TAN content. The estimated values were calculated using the equations shown in Table 4 and Eq. [2] and [3].

can be used to estimate the NH_3 loss during the entire period from 0 to 6 d. In Fig. 5 these estimated results are related to measured accumulated NH_3 loss. The estimated values explained 72% of the variation in the measurements, which was slightly less than the 81% obtained with the quadratic equation shown in Table 3. Taking the temperature and slurry pH into account did not improve the relationship between NH_3 loss and dry matter content.

CONCLUSION

Ammonia losses from 0 to 6 h, 0 to 12 h, 0 to 24 h, and 0 h to 6 d were studied. The NH_3 loss from 0 to 6 h was linearly related to content of dry matter, while the relationship in the following periods was nonlinear. The slurry with a high content of dry matter had a low pH, but interaction of acidity on NH_3 loss was only partly the reason for the nonlinear relationship.

The effect of temperature and pH was eliminated calculating a dry matter function, relating loss rate to content of dry matter in the periods 0 to 6 h, 6 to 12 h, 12 to 24 h, and 24 h to 6 d. The calculations included temperature from all four periods and pH in the period from 12 to 24 h. This transformation of data showed that NH_3 loss tended to be sigmoidally related to dry matter content in all four periods. This indicated that at low and high contents of dry matter, small changes in dry matter content had a limited influence on NH_3 loss. At dry matter contents from 4 to 12% NH_3 loss increased as dry matter content increased.

The accumulated loss over 6 d was predicted with two models calculating the NH_3 loss in four periods. With the model based on dry matter content, 81% of the variation in the NH_3 loss measured in the experiments was identified. With a model based on pH, temperature, and dry matter content, 72% of the measured NH_3 loss was identified. This shows that more work has to be done before the effect of interaction of climatic conditions and composition of slurry can be explained. The assumed simple multiplication of these two effects does not seem to be adequate in describing this interaction.

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Effects of temperature, wind speed and air humidity on ammonia volatilization from surface applied cattle slurry

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(*Revised MS received* 8 *November* 1990)

SUMMARY

Ammonia losses from surface-applied cattle slurry were measured under field conditions using a wind tunnel system that allows variables affecting ammonia loss to be examined under controlled conditions. The experiments were carried out on a sandy soil with seven different surface covers. This report considers the effect of wind speed, temperature and water vapour deficit on the ammonia loss over a series of 6-day periods. During October 1986 to November 1989 42 treatments were examined, using slurries taken from the same slurry tank to provide slurries of similar chemical composition.

When temperatures were near zero, the rate of ammonia loss was generally low. The accumulated loss over 6 days was high, however, because the rate of loss was constant throughout the period. In these experiments the soil was saturated with water and partly frozen, and the infiltration of slurry into the soil reduced. At 19 °C initial loss rates were high but, after 12 h, almost no further loss occurred. Apart from these extremes, the ammonia loss rates within the initial 24 h were significantly affected by temperature and wind speed.

Ammonia volatilization after 6 h was exponentially related to temperature ($r^2 = 0{\cdot}841$) but the correlation weakened with time after slurry application. An increase in ammonia volatilization with increasing water vapour pressure deficit was considered to be an effect of temperature.

The ammonia loss rate increased when wind speeds increased up to 2·5 m/s. No consistent increase in ammonia volatilization was found when the wind speed increased from 2·5 to 4 m/s. Ammonia loss after 24 h increased with increasing initial pH of the slurry.

A two-stage pattern for ammonia volatilization from slurry is proposed. During the first stage (the initial 24 h) ammonia loss rate is high due to an elevated pH at the slurry surface following application, and temperature significantly affects the loss rate. In the next stage, pH declines and the rate of ammonia volatilization decreases. During this stage other factors, including the dry matter content of the slurry, control the rate of ammonia loss.

INTRODUCTION

The gaseous loss of ammonia has direct implications for the efficient use of the nitrogen in animal manure. The emission of ammonia from animal manures represents the most important source of atmospheric ammonia in Europe (Buijsman *et al.* 1987), and deposition of ammonia may detrimentally affect nitrogen-limited natural ecosystems (Roelofs 1986). In Denmark, the use of animal manure has therefore been regulated by law. Slurry applied to bare soil has to be incorporated into the soil within 12 h, and storage facilities have to meet certain standards.

Early Danish research carried out during the 1920s and 1930s demonstrated significant loss of ammonia from animal manures left on the soil surface. Although the losses could be related to the general weather conditions, they were found to be highly variable due to interactions between the various climatic conditions, manure characteristics and manure handling (see review by Christensen 1986). Recent studies (e.g. Pain *et al.* 1989) have also shown that the proportion of ammonia lost from slurries within a few hours varies considerably.

To reduce ammonia losses from animal manures and to increase the predictability of the fertilizer equivalent of nitrogen applied in slurry, the effects of climate must be quantified. Consequently it is important to identify the most significant parameters and to establish general relationships between these

Table 1. *Soil cover and characteristics of cattle slurries used in experiments in Denmark in 1986–89*

Experiment	Experimental period	Total N (%)	TAN* (%)	pH	Dry matter (%)	Soil surface
1–3	Oct 1986	0·49	0·30	7·3	8·0	Stubble
4–5	Dec 1986	0·47	0·30	7·1	7·2	Clover-grass
6–10	Oct–Dec 1988	0·45	0·26	7·9	8·2	Grass
11–12	May 1989	0·44	0·26	7·5	7·0	Harrowed soil
13–14	May–Jun 1989	0·44	0·26	7·5	7·0	Spring barley
15–16	Sep 1989	0·44	0·26	7·5	7·0	Cultivated stubble
17–20	Oct–Nov 1989	0·44	0·26	7·5	7·0	Grass

* TAN = total ammoniacal nitrogen ($NH_4^+ + NH_3$).

and the loss of ammonia. Significant effects of temperature, wind speed and air humidity on ammonia loss rates have been demonstrated previously (Beauchamp *et al.* 1978, Brunke *et al.* 1988). The limited number of replicate experiments under different environmental regimes and differences in the origin and chemical composition of the slurries used has, however, prevented a thorough understanding of the results obtained.

In the present study, the ammonia loss from surface-applied slurry was examined in 42 treatments during the period from October 1986 to November 1989. Ammonia volatilization was determined by a wind tunnel system. Cattle slurry for all experiments was taken from the same slurry tank to provide as near identical slurries as possible, providing an opportunity to evaluate environmental effects on the loss of ammonia. The wind speed was adjusted to different levels in order to examine effects of wind speed on *in situ* ammonia loss rates.

MATERIALS AND METHODS

Wind tunnel unit

The basic design of the wind tunnel unit followed that described by Lockyer (1984). Each unit consisted of an inverted U-shaped tunnel made from transparent polycarbonate which covered the experimental plot (2·0 × 0·5 m), and a circular steel duct housing an electrically powered fan. In Expts 1–14 the fan was driven by an AC-powered motor. To be able to operate at reduced wind speeds, a DC-powered motor was used from Expt 15 onwards. The higher momentum of the DC-powered motor at low speeds produced more stable wind speeds.

The fan could produce tunnel wind speeds up to 5 m/s across the plot. The steel duct was 2 m long and had a diameter of 0·4 m. The highest point of the transparent tunnel was 0·45 m above the ground.

A vane anemometer head, housed in the steel duct, recorded the wind speed within the tunnel. Signals from the anemometer head were displayed and stored on a data logger. The anemometer was used to adjust tunnel wind speed to pre-selected levels by regulating fan speed, and subsequently for recording actual wind speeds during the experiments. There were four wind tunnel units of which one was used for reference (i.e. untreated plot at ambient ammonia levels).

During Expts 1–5, the data logger scanned the input channels every hour and stored the data. From Expt 6 onwards, input channels were scanned at 1 min intervals and data stored as hourly means.

Gas trapping unit

After passing over the experimental plot, the airstream was sampled near the outlet of the steel duct using a diaphragm suction pump. The pump drew an airstream (composed of air from six different sampling positions) at a rate of 5 litres/min through a 100 ml absorption flask fitted with a sintered gas distribution tube. The flask contained 50 ml of 0·005 M-H_3PO_4 and the air flow rate was checked by a flowmeter. Ammonia in the air was trapped in the orthophosphoric acid and subsequently determined in the laboratory by a Berthelot reaction (indophenol blue method).

Each gas trapping unit consisted of four absorption flasks. A programmable magnetic valve control automatically switched each absorption flask on and off at preselected intervals. During the first 2 days, absorption periods were 6 h; during the following four days absorption periods were 24 h.

Slurry analyses

Total ammoniacal nitrogen (ammonia plus ammonium, TAN) content of the slurry was determined by direct distillation with light MgO and $CuSO_4$, the ammonia being collected in boric acid-indicator solution and finally determined by titration with standard HCl. Total N was analysed using the Kjeldahl method and a Tecator Kjeltec Auto 1030 Analyser. Dry matter (DM) content was determined gravimetrically and slurry bulk pH with a standard electrode (Radiometer).

Table 2. *Ammonia loss (% of total ammoniacal N (TAN)), wind speed and mean climatic conditions during the experiments*

Experiment	Wind speed in tunnel (m/s)	Air temperature (°C)	Water vapour pressure deficit (Pa)	Accumulated ammonia loss
1	5·9	9·9	231	52·2
1	4·8	9·9	231	41·4
2	4·1	8·9	181	44·7
2	4·7	8·9	181	62·9
3	3·9	6·8	55	38·3
4	5·1	6·0	153	53·1
4	6·0	6·0	153	52·0
4	6·2	6·0	153	45·0
5	5·0	2·8	86	49·9
5	5·9	2·8	86	67·2
5	6·2	2·8	86	57·8
6	4·2	6·2	141	45·0
6	1·3	6·2	141	53·9
6	2·5	6·2	141	62·5
7	3·9	3·1	105	45·8
7	1·5	3·1	105	49·0
7	3·0	3·1	105	56·1
8	3·2	2·1	54	57·0
9	3·5	5·7	87	55·8
10	4·0	2·9	112	74·0
11	3·4*	13·6	564	74·6
12	3·3	14·5	1138	44·9
13	3·6	9·7	389	53·8
14	3·6	13·0	658	58·8
15	1·2	14·4	814	49·1
15	2·6	14·4	814	72·3
15	4·1	14·4	814	68·1
16	1·2	14·9	85	55·1
16	2·5	14·9	85	75·5
16	4·1	14·9	85	80·4
17	1·3	11·3	457	50·4
17	2·6	11·3	457	60·2
17	4·1	11·3	457	74·0
18	1·3*	8·9	314	42·4
18	2·5*	8·9	314	59·0
18	4·0*	8·9	314	82·9
19	3·5*	9·4	245	58·6
19	2·8*	9·4	245	65·1
19	4·0*	9·4	245	66·8
20	1·4	6·7	158	33·3
20	2·4	6·7	158	43·0
20	4·2	6·7	158	49·3

* Data measured manually as data logger was out of function.

Table 1 gives characteristics of the four cattle slurries used. Throughout the experiments slurry was taken from the same slurry tank to provide near identical slurries. Slurry bulk pH varied from 7·1 to 7·9, DM from 7·0 to 8·2 %, TAN content from 0·26 to 0·30 % and total-N from 0·44 to 0·49 %, showing that the chemical characteristics varied slightly.

Slurries and treatments

Twenty experiments, each covering a 6-day period, were carried out during October 1986 to November 1989. Each experiment included one to three treatments and one reference tunnel, giving a total of 42 treatments (Table 2). The slurries were applied at a rate of 3 litres/m^2 onto the surface of a sandy loam with 10% clay, 2·7% organic matter (OM), and pH 7·5. The slurry was left on the soil surface during the whole experimental period. Slurry was applied to bare, harrowed soil or to soil with six different covers (see Table 1 for details).

Plots were protected from rain during the experimental period, and irrigation treatments were not included in the present study. The slurry was therefore deliberately exposed to sustained drying conditions, created by the continuous airstream sweeping the plot surface.

Surface pH of applied slurry

In a separate experiment in 1989, changes in the pH at the surface of pig slurry applied at 3 litres/m^2 was followed over a period of 4 days after application. This slurry, having an initial bulk pH of 7·6, 0·52% total N, 0·37% TAN and 3·8% DM, was applied onto a tilled soil surface. pH at the surface was measured with a flat glass membrane Electrode (Radiometer).

Environmental data

For Expts 1–5, air temperature was recorded with thermocouple sensors situated in the steel duct of the tunnels. Temperature readings were stored on a data logger. In the following experiments, environmental data were taken as hourly mean values from the automatic climate station at Askov Experimental Station (55° 28′ N, 09° 07′ E) (Olesen 1988). Air temperature and relative humidity were measured at a height of 2 m in a standard screen, and air temperature was also recorded at a height of 0·20 m.

Tunnel temperatures were generally 1 °C lower than air temperatures at a height of 2 m measured at the weather station. The weather station was established after Expt 5, and tunnel air temperatures recorded in these experiments were adjusted for the difference of 1 °C.

For Expts 1–5 measurements of air relative humidity from the synoptic station at Billund (55° 44′ N, 9° 09′ E) were used. The relative humidity at Askov was approximately 3% higher than at Billund. A value of 3 was therefore added to the Billund figures, disallowing relative humidities higher than 100%.

Air temperature (T) and relative humidity (RH) were used to calculate water vapour pressure deficit (e_d), where $e_d = e_s - e_s\,\mathrm{RH}/100$, and e_s is saturated water vapour pressure (Pa) at temperature T.

Calculations of ammonia loss

For each absorption period, ambient ammonia concentrations were subtracted from concentrations obtained for treated plots and used to calculate ammonia loss, i.e.:

J (h) = $AV \times 3600\ (NH_{3e} - NH_{3r})$

J (h) : Ammonia loss, g NH_3–N/h.

A : Cross-section area of steel duct, m^2.

V : Wind speed, m/s.

NH_{3e} : Ammonia concentration in air from a tunnel with a treated plot, g NH_3–N/m^3.

NH_{3r} : Ammonia concentration in air from the reference tunnel (untreated plot), g NH_3–N/m^3.

Thus the values presented are net ammonia losses induced by the treatment. The results were finally corrected for wind tunnel system recovery of ammonia by multiplying by the factor 100/74 (Christensen & Sommer 1989).

RESULTS AND DISCUSSION

Surface pH of applied slurry

The rate of ammonia loss depends on the concentration of ammonia gas at the slurry surface:

$$NH_{3.l} \rightleftharpoons NH_{3.g}, \quad K_{HN} = [NH_{3.l}]/[NH_{3.g}] \qquad (1)$$

where K_{HN} is Henry's Law constant between $NH_{3.l}$ and $NH_{3.g}$, which is inversely related to proton activity:

$$NH_4^+ \rightleftharpoons NH_3 + H^+, \quad K_{N1} = [NH_3] \times [H^+]/[NH_4^+] \qquad (2)$$

where K_{N1} is the equilibrium constant for the dissociation of NH_4^+.

For ammonia loss to proceed, buffering substances must be present to neutralize the protons produced when ammonia volatilizes from the slurry. Fordham & Schwerdman (1977) demonstrated that bicarbonate ions are the dominating proton acceptors in slurry:

$$CO_2 + H_2O \rightleftharpoons HCO_3^- + H^+, \; K_{C2} = [HCO_3^-][H^+]/[CO_2] \qquad (3)$$

where K_{C2} is the equilibrium constant for the dissociation of HCO_3^-. The bicarbonate is the reaction product of the hydrolysis of urea and microbial conversion of organic matter. This is also assumed in the study of Stevens *et al.* (1989).

The dynamics of pH in the surface of applied pig slurry (Fig. 1) were similar to changes in soil surface pH observed after hydrolysis of urea in soil (Sherlock & Goh 1985; Rachpal-Singh & Nye 1986). Immediately following application, pH in the slurry surface rose to 8·4 (Fig. 1) as more carbon dioxide than ammonia was lost, because the water solubility of carbon dioxide is 200 times lower than the solubility of ammonia (Beutier & Renon 1978; Vlek & Stumpe 1978). Within 3–4 days, pH declined to 7·4 as ammonia volatilization produced a surplus of protons in the system.

Ammonia emission

Average climatic conditions during the experiments are shown in Table 2. Concentrations of ammonia in

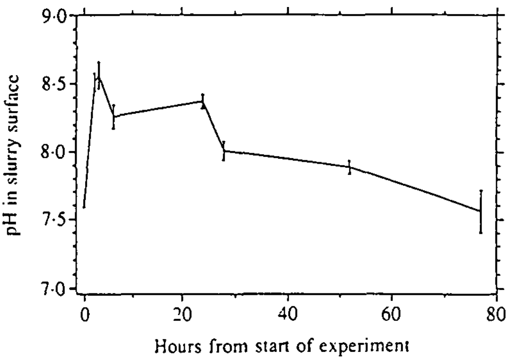

Fig. 1. pH in surface of pig slurry (initial pH 7·6) measured at intervals from start of application to soil surface. Bars indicate ±S.E.

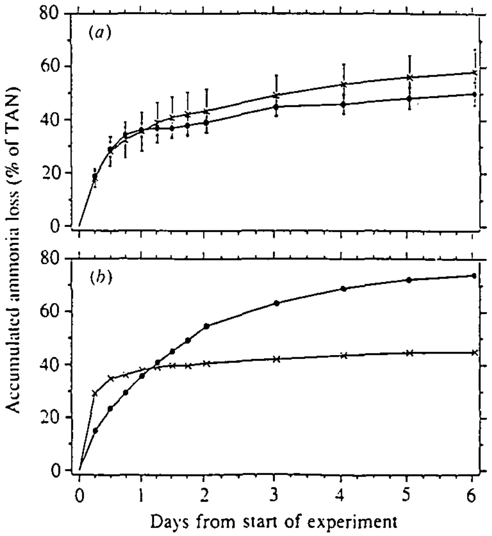

Fig. 2. Cumulative ammonia loss as a percentage of total ammoniacal N (TAN) applied in slurry, in (*a*) Expt 4 (●) and Expt 5 (×), *n* = 3, and (*b*) Expt 10 (●) and Expt 12 (×). Bars indicate ±S.E.

the air from the reference tunnels ranged from 0·3 to 36·2 μg N/m^3 and were in accordance with ammonia contents found in the ambient air of areas with livestock farming (Allen *et al.* 1988). It has been shown that differences between temperatures measured inside the tunnel and ambient temperatures are small (Ryden & Lockyer 1985), and ambient temperatures may therefore be used when interpreting the observed variations in ammonia loss.

The accumulated flux of ammonia is linearly related to the amount of TAN in the slurry (Brunke *et al.*

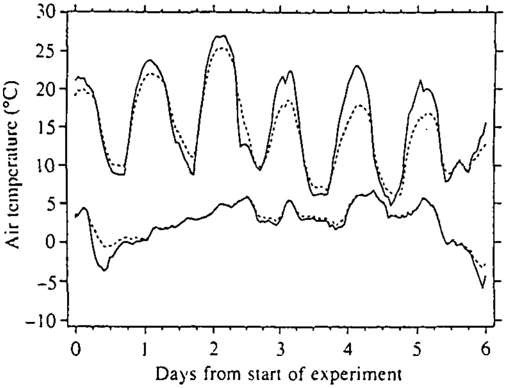

Fig. 3. Air temperature at a height of 2 m (---) and 20 cm (—) during Expts 10 (lower) and 12 (upper).

1988). Results on ammonia volatilization loss are therefore presented as a proportion of TAN in slurry, a procedure which eliminates small differences in the TAN content of the slurry. The variation in ammonia loss between wind tunnels with similar treatments was less than 25% (C.V.) (Fig. 2(*a*). In most of the experiments, more than half of the total loss occurring during the 6-day period took place within the first day, a pattern demonstrated in several other studies (Thompson *et al.* 1987; Pain *et al.* 1989). Proton activity had a substantial influence on the flux of ammonia from surface-applied slurry. After an initial period with a high loss rate (Fig. 2(*a*)), the ammonia volatilization potential will be reduced by acidification, decreasing concentrations of TAN and infiltration of TAN into the soil (Lauer *et al.* 1976; Beauchamp *et al.* 1982).

The ammonia loss pattern in most of the experiments followed that presented in Fig. 2(*a*). The two main exceptions were Expts 10 and 12 (Fig. 2(*b*)) for which temperatures are shown in Fig. 3. In Expt 10, freezing occurred during the first night of exposure. The subzero temperatures were most pronounced at ground level due to a temperature inversion. In Expt 12, air temperature was high and a marked diurnal fluctuation was observed. Furthermore the topsoil in Expt 12 was very dry due to a preceding period without precipitation and high evaporation potential.

A constant ammonia loss rate throughout Expt 10 caused a high cumulative loss of ammonia over 6 days despite low temperatures (Fig. 2(*b*)). The infiltration of TAN into the soil was reduced by a high content of water in the soil (Donovan & Logan 1983), and slow freezing during the nights may have created a concentrated TAN solution relative to the TAN-free ice (Lauer *et al.* 1976). Sustained ammonia losses during periods with near-zero temperatures have been observed in experiments with pig slurry (Sommer &

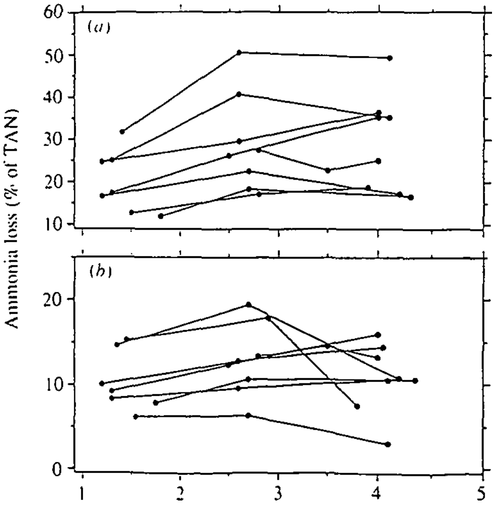

Fig. 4. Cumulative ammonia loss as a percentage of total ammoniacal N (TAN) during the periods (*a*) 0–12 h and (*b*) 12–24 h at different tunnel wind speeds. Expts 6–7 and 15–20. Observations from the same experiments are connected with lines.

Christensen 1989) and with cattle slurry (Thompson *et al.* 1987).

In Expt 12, high temperatures may have caused a rapid decrease in the rate of ammonia loss within a few hours of slurry application (Fig. 2(*b*)). Surface crusting of the slurry and rapid infiltration into the dry and recently tilled soil may have been responsible for the very low ammonia loss rate after 12 h.

Wind speed

The U-shaped tunnel was 2 m long, providing a relatively short travelling distance for the wind for the development of an equilibrium boundary layer. Using a wind tunnel with similar cross-section characteristics, Rasmussen & Mikkelsen (1988) found a boundary layer of less than 1 cm after a 3 m distance. Soil surface roughness is high compared to that of the tunnel walls. The soil surface will therefore dominate the momentum transfer. At high wind speeds, secondary motions with rotations about horizontal axes may occur (Rasmussen & Mikkelsen 1988).

These factors restrict somewhat the applicability of the wind tunnel system in studying the effect of wind speed on ammonia volatilization. Nevertheless, ammonia losses measured with a similar wind tunnel system were in accordance with losses obtained by a micrometeorological mass balance method, provided the wind speeds in the tunnels were adjusted to ambient wind speeds 0·25 m above the ground (Ryden & Lockyer 1985). This indicates that the wind tunnel system will give reliable ammonia loss estimates within a realistic range of wind speeds.

Wind speeds were recorded in the steel duct, which had an internal cross-section area of 1260 cm^2, while the cross-section area of the U-shaped tunnel was *c.* 1800 cm^2. Assuming homogeneous wind profiles, wind speeds over the plot surfaces will be *c.* 70% of the measured wind speeds. This correction has, however, not been applied in this study.

In Expts 6, 7 and 15–20, three different wind speeds were tested (Table 2). During 0–12 and 12–24 h, the ammonia loss increased when wind speed was increased from 1·5 to 2·5 m/s (Fig. 4). A further rise in wind speed to 4 m/s did not reveal a consistent relationship. In Expts 6 and 7 the ammonia loss rate during 12–24 h decreased when wind speed was increased from 2·5 to 4 m/s. These two experiments were carried out with the AC-powered fan, while Expts 15–20 were carried out with the DC-powered fan. Some of the discrepancy may be attributed to the less stable wind speeds obtained with the AC-powered fan. It should also be noted that the slurry used in these two experiments had a relatively high initial pH.

The rate of ammonia volatilization is controlled by chemical reaction rates, diffusive and convective transport in the slurry and by a gas phase resistance in the boundary layer above the slurry surface. At low wind speeds the volatilization rate will be small and the gas phase resistance dominates. When the wind speed is increased, the chemical resistance and liquid phase resistance will become more dominant while the gas phase resistance will be of less importance (Vlek & Craswell 1981). The shift from the dominance of gas phase to liquid phase resistance will cause a curvilinear relationship between the loss of ammonia from the slurry and the wind speed. If the chemical resistance is insignificant, the ammonia loss should be linearly related to wind speed (Vlek & Stumpe 1978).

During 0–12 h the ammonia loss rates increased with wind speeds up to 2·5 m/s (Fig. 4). In general, no further increase in loss rate was observed when the wind speed was increased to 4 m/s, indicating that the liquid phase resistance dominated at wind speeds between 2·5 and 4 m/s. Ammonia losses during 12–24 h were constant with increasing wind speed. Crust formation on the slurry surface probably increased the liquid phase resistance, inducing lower ammonia loss rates when wind speed was increased. Higher wind speeds will also cause higher water evaporation, inducing an accelerated crust formation. Water evaporation is, however, also dependent on other factors such as water vapour pressure deficit and temperature. There is no apparent relationship between the shape of the curves in Fig. 4 and these environmental factors.

Table 3. *Simple correlation coefficients between ammonia loss rates (% of total ammoniacal N (TAN)) and mean air temperature and water vapour pressure deficit during each period*

	Air temperature	Water vapour pressure deficit
Loss as percentage of TAN initially applied in slurry		
0–6 h	0·782	0·712
6–12 h	0·411	0·233
12–24 h	−0·054	0·222
24 h–6 d	0·261	0·034
Loss as percentage of remaining TAN in slurry at start of period		
0–6 h	0·782	0·712
6–12 h	0·724	0·485
12–24 h	0·155	0·329
24 h–6 d	0·547	0·385

Experiments 10 and 12 were excluded, giving a total of 18 observations.

The main reason for the small change in ammonia volatilization rate at higher wind speeds therefore seems to be a shift in dominance from gas phase resistance to liquid phase resistance.

Temperature

Because no clear effect of wind speed on ammonia loss could be detected at wind speeds $>2{\cdot}5$ m/s, data analysis was based on means of ammonia losses from each experiment in which wind speeds were $>2{\cdot}5$ m/s. The use of mean values was introduced to reduce intercorrelation in the data set.

Ammonia losses during four periods were analysed: 0–6 h, 6–12 h, 12–24 h and 24 h to 6 d. Ammonia losses (L) during these periods were first expressed as a percentage of initial TAN content in the slurry. However, this introduces some error for later periods because TAN is lost in preceding periods. Ammonia loss (L^*) expressed as a percentage of residual TAN content was therefore calculated as

$$L^* = 100\,L/(100-L_0)$$

where L_0 is the loss during the preceding periods as a percentage of initial slurry TAN content. For the initial time period, L and L^* are identical.

In most of the calculations Expts 10 and 12 were excluded because their loss patterns differed considerably from those in the other experiments.

Table 3 shows the correlation between air temperature and ammonia loss during the four periods. The relationship between temperature and ammonia loss is improved by expressing the loss as the percentage of TAN remaining in the slurry at the start of a given period, confirming that ammonia losses are linearly related to the content of TAN in slurry (Brunke *et al.* 1988). The highest correlation between ammonia loss and temperature was obtained during the initial 12 h period.

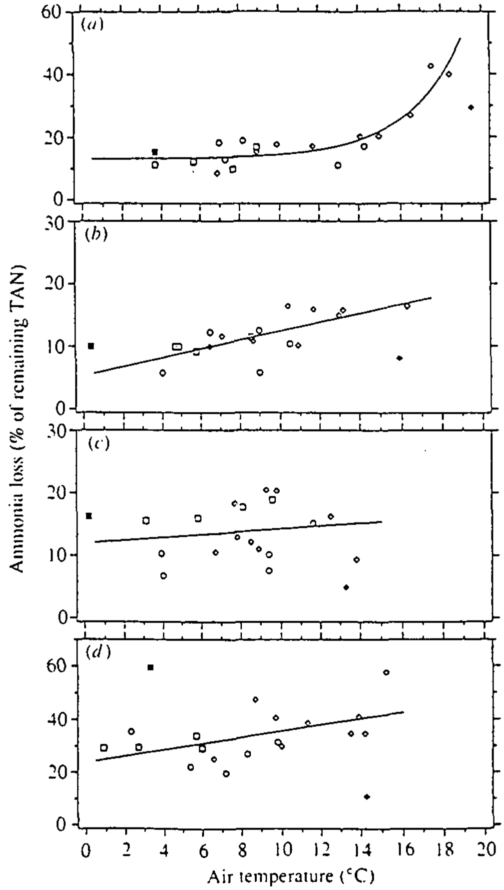

Fig. 5. Cumulative ammonia loss during the periods (*a*) 0–6 h, (*b*) 6–12 h, (*c*) 12–24 h and (*d*) 1–6 days as a percentage of total ammoniacal N (TAN) remaining in slurry at the start of a period in relation to mean air temperature during the period. Surface type: stubble (○), grass or clover-grass (□), harrowed soil or cultivated stubble (◇). Solid symbols indicate observations not included in estimation of the lines shown. The r^2 values for the fitted lines are (*a*) 0·841, (*b*) 0·524, (*c*) 0·024 and (*d*) 0·300.

The relationship between ammonia loss and temperature is shown in Fig. 5. The loss rate increased with temperature during all four periods. The effect was most pronounced during the first 6 h when an exponential relationship between loss rate and temperature was obtained. No such exponential re-

Table 4. *Equations derived for the relation between ammonia loss rate (L^*) and mean air temperature (T) during four experimental periods, where T_0 is mean temperature during the previous periods since the start of the experiment; pH is initial pH in slurry; ammonia loss is expressed as a percentage of slurry total ammoniacal N (TAN) remaining at start of a period. Experiments 10 and 12 were excluded, giving a total of 18 observations*

No.	Estimated equation	r^2	R.M.S.E.*
	0–6 h		
1	$L^* = 13{\cdot}0 + 0{\cdot}031 \exp(0{\cdot}375\ T)$	0·841	3·98
2	$L^* = 0{\cdot}5 + 1{\cdot}68\ T$	0·611	6·03
	6–12 h		
3	$L^* = 5{\cdot}2 + 0{\cdot}712\ T$	0·524	2·33
	12–24 h		
4	$L^* = 11{\cdot}9 + 0{\cdot}23\ T$	0·024	4·40
5	$L^* = 12{\cdot}7 - 0{\cdot}50\ T_0 + 0{\cdot}73\ T$	0·117	4·32
6	$L^* = -58{\cdot}4 + 9{\cdot}32\ pH - 0{\cdot}28\ T_0 + 0{\cdot}60\ T$	0·391	3·72
	24 h–6 d		
7	$L^* = 23{\cdot}6 + 1{\cdot}19\ T$	0·300	7·93

*R.M.S.E. = Root Mean Squared Error.

lationship was evident for the other periods. The equations describing the relationship are included in Table 4 and depicted as lines in Fig. 5. The equations were determined using linear and non-linear regression procedures in the SAS statistical package (SAS Institute 1988).

The reason for the correlation between loss rate and temperature is that equilibrium constants for Eqns 1, 2 and 3 increase with temperature (Beutier & Renon 1978). At a given concentration of TAN and total inorganic carbon (TIC), an increase in temperature will cause a higher NH_3 to NH_4^+ ratio. Furthermore, the solubility of ammonia falls with a rise in temperature. These effects cause the partial pressure of ammonia over a solution of TAN and TIC to increase exponentially with temperature (Vlek & Stumpe 1978). When pH is high, changes in temperature will significantly affect the ammonia volatilization as small changes in pH produce significant changes in the NH_3 to NH_4^+ ratio of the slurry.

It was only in a few experiments at temperatures > 16 °C that the exponential relationship in the period 0–6 h shown in Fig. 5 occurred. All these experiments were carried out on harrowed soil or cultivated stubble. Although soil tillage normally favours infiltration of TAN into the soil and thus reduces ammonia volatilization, the results show that this has not been an important process in the present study. A steep increase in ammonia volatilization rate from sewage sludge at temperatures > 15 °C was found also by Beauchamp *et al.* (1978).

No exponential relationship was found for the loss rate during 6–12 h. There was however a significant effect of temperature. The lack of an exponential relationship may partly be explained by the generally lower temperatures during this period. Other factors such as crust formation and TAN infiltration into the soil may also reduce losses at high temperatures. At 12–24 h there is a poor relationship between loss rate and temperature. This pattern could be an effect of temperature in the preceding period, as high temperature seems to limit ammonia loss in the following periods (Fig. 2(*b*)).

This assumption is supported by a negative correlation between ammonia loss from 12–24 h and mean temperature (T_0) during the preceding 0–12 h period. The parameter estimates of a multiple linear regression model including both the effect of temperature (T) during the period and T_0 is shown in Table 4. None of these effects are significant. The marked increase in r^2 by including T_0 does, however, indicate a possible effect.

Air humidity

Laboratory experiments have demonstrated a strong relationship between moisture loss and loss of ammonia from slurry (Molloy & Tunney 1983). Drying results in a higher concentration of ammonia in the slurry and an increased concentration of gaseous ammonia at the slurry surface.

Besides wind speed, evaporation of water in the field is often controlled by radiation balance, temperature, and water vapour pressure deficit, factors that are often highly correlated. It is assumed that, at the wind speeds applied in this study, water vapour pressure deficit is the major factor controlling water evaporation.

Experiment means of ammonia loss as described for the temperature analysis were also employed here. Experiments 10 and 12 were excluded from this analysis. Correlations between loss rates during the four experimental periods and water vapour pressure deficit are shown in Table 3.

Significant correlation between ammonia loss and vapour pressure deficit was obtained for the first two periods (Table 3). The correlations were, however, smaller than the corresponding correlations for temperature. Multiple linear regression analyses with both temperature and vapour pressure deficit as independent variables did not produce significant parameter estimates of the vapour pressure deficit component. The correlations shown in Fig. 6 are thus caused by correlation between temperature and vapour pressure deficit. The high correlation between vapour pressure deficit and ammonia volatilization suggested by Brunke *et al.* (1988) could not be

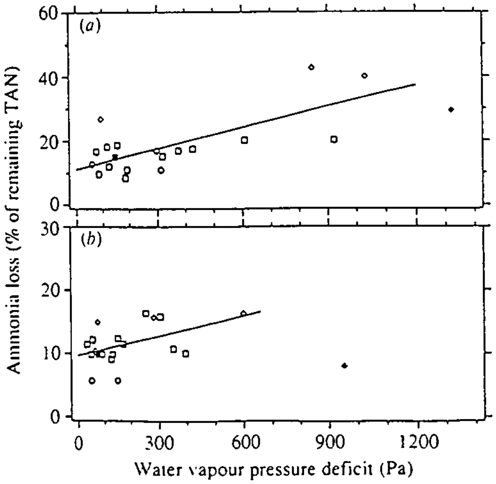

Fig. 6. Cumulative ammonia loss during the periods (*a*) 0–6 h, (*b*) 6–12 h as a percentage of total ammoniacal N (TAN) in slurry at the start of a period in relation to mean air water vapour pressure deficit during the period. Surface type: stubble (○), grass or clover-grass (□), harrowed soil or cultivated stubble (◇). Solid symbols indicate observations not included in estimation of the lines shown. The r^2 values for the fitted lines are (*a*) 0·507 and (*b*) 0·235.

confirmed. There may be several reasons for the lack of a consistent effect of water evaporation on ammonia volatilization. The effect may be insignificant compared to temperature and pH effects. Other effects of high water evaporation rates, e.g. an accelerated surface crusting, may increase resistances in the liquid phase. The different effects may also counteract each other, resulting in the lack of correlation between water evaporation and ammonia loss.

Effect of other factors and prediction of ammonia loss

Initial slurry pH affects ammonia loss. Figure 7 shows the residuals from the temperature-dependent models in Table 4 in relation to initial pH in the slurry. The relationship between residual ammonia loss and slurry pH is only significant at the 5% level for the period 12–24 h.

A model with both the temperature effect and the pH effect included is shown for this time period in Table 4. Only the pH effect is significant in this model at the 5% level.

The accumulated losses of ammonia for the 6-day periods were calculated by Eqns 1, 3, 6 and 7 in Table 4 for the time intervals 0–6 h, 6–12 h, 12–24 h and 1–6 days. Figure 8 shows calculated *v*. measured accumulated loss over 6 days. Losses for slurries applied to stubble are overestimated. For all experiments, 49% of the measured loss over 6 days was accounted for with the models.

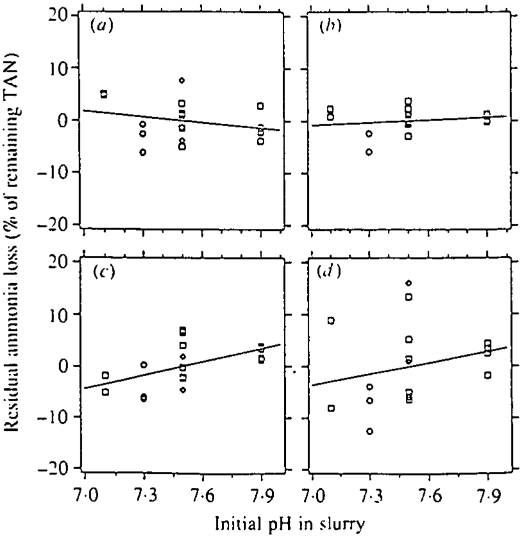

Fig. 7. Residual ammonia loss during the periods (*a*) 0–6 h, (*b*) 6–12 h, (*c*) 12–24 h and (*d*) 1–6 days as a percentage of total ammoniacal N (TAN) remaining in slurry at start of a period in relation to initial pH in slurry. The residual loss is the actual loss minus the estimated loss using the best temperature-dependent equations shown in Table 4. Surface types: stubble (○), grass or clover-grass (□), harrowed soil or cultivated stubble (◇). Experiments 10 and 12 are excluded.

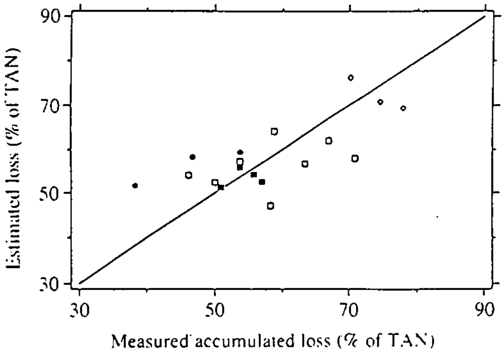

Fig. 8. Predicted versus measured cumulative ammonia loss during 6 days as a percentage of total ammoniacal N (TAN) in slurry. The predicted values are calculated using Eqns 1, 3, 6 and 7 in Table 4. Experiments 10 and 12 are excluded. Surface type: stubble (○), grass or clover-grass (□), harrowed soil or cultivated stubble (◇). Solid symbols indicate slurries with 8·0–8·2% DM and open symbols indicate slurries with 7·0–7·2% DM.

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Title: Ammonia Volatilization During Storage of Cattle and Pig Slurry: Effect of Surface Cover

Short title: Ammonia volatilization from stored slurry.

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Number of text pages: 12.
Number of tables: 4.
Number of figures: 3.

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SUMMARY

Gaseous NH_3 losses from pig and cattle slurry stored in eight storage tanks were measured simultaneously using wind-tunnels. The slurry was either stirred weekly (no cover), or was allowed to develop a natural surface crust. Oil, peat, chopped cereal straw, PVC-foil, leca® (Pebbles of burned montmorillonitic clay) and a lid were tested as additional covers. Convective transport of ammonium to the surface layers caused NH_3 volatilization losses of 3-5 g NH_3-N m^{-2} d^{-1} from stirred uncovered tanks. The loss of NH_3 from the weekly stirred slurry was related to air temperature. The development of a natural surface crust reduced losses of NH3 to 20% of those from stirred slurry. NH_3 losses from slurry not developing a natural surface crust layer and left undisturbed were similar to the losses from stirred slurry. A 15 cm layer of straw was as effective as a surface crust layer in reducing NH3 losses. In one experiment cracks developed in the oil cover, and losses were therefore only reduced to 50% compare to uncovered slurry. Apart from this experiment, NH_3 losses from slurry covered by oil, leca®, peat and floating foil were low.

INTRODUCTION

Large amounts of ammonium are lost by NH_3 volatilization from livestock farming. Animal production systems are recognised as the major source of atmospheric NH_3 in Europe (Buijsman et et al., 1987). Volatilization of NH_3 reduces the nutrient value of animal manure for plant production. In the atmosphere NH_3 is readily transformed to ammonium in acid cloud droplets. The emitted NH_3 is dry deposited near the source and at greater distances by dry or wet deposition of ammonium (Asman et al., 1991). Deposition of NH_3 and $NH^+{}_4$ may contribute to undesired changes in oligotrophic ecosystems (Schulze et al., 1989).

NH_3 volatilization related to livestock farming occurs from stables, manure storages, and during or after land spreading of manure (Jarvis and Pain, 1990). In Denmark more than fifty percent of the N in animal manure is collected and applied to fields in the form of cattle and pig slurry. Previous studies have provided a good understanding of NH_3 losses during and after field application of slurry (Christensen, 1986, Jarvis and Pain, 1990). Less is known about NH_3 loss rates from manure storages and how the losses may be reduced.

NH_3 losses from slurry storage tanks have been determined either as the difference in N content before and after a storage period (Dewes et al., 1990) or calculated by the use of models (Muck and Steenhuis, 1982). Estimating NH_3 losses by the recovery of ammonium is not feasible, because NH_4 is produced by net-mineralization during storage. Estimates of NH_3 loss by the differences in total-N of the stored slurry can give erroneous results due to sampling variability, denitrification and leaching losses. Inhomogenity in total-N is significant in stored slurry as the organic nitrogen precipitates or floats to the surface. Furthermore, the amount of NH_3 lost may be small compared to the amount of stored nitrogen. Recently, Bode (1991) has determined the NH_3 loss by drawing air at 1 m s^{-1} through enclosure placed on the top of pilot slurry tanks. It was shown that 10-20% of ammonium content of the slurry was lost from uncovered slurry tanks.

In the present study, NH_3 losses from pig and cattle slurry stored in 4.3 m^3 rectangular pilot-tanks were examined during the period February 1990 to June 1991 using a wind tunnel system. The effect of seven different surface covers were tested by comparing the NH_3 loss to the loss from a weekly stirred slurry.

MATERIALS AND METHODS

NH_3 loss from 8 pilot-slurry tanks was examined simultaneously by use of 8 wind-tunnel units. The slurry tanks were 90 cm wide, 289 cm long and 165 cm deep (surface area 2.60 m^2, volume 4.24 m^3). Loss of NH_3 from stored cattle slurry was measured during February-June 1990 (Exp. 1) and July-September 1990 (Exp. 2), from stored pig slurry during September-December 1990 (Exp. 3) and February-June 1991 (Exp. 4). Table 1 shows the characteristics of the slurries used in the 4 experimental periods.

Ammonia Loss Measurements

The NH_3 losses were measured using eight wind-tunnel units. Each unit consisted of an inverted box made from transparent polycarbonate (40 cm high, 100 cm wide and 310 cm long), which covered the slurry tank. At one end, the box was left open while the opposite end was attached to a circular metal duct (470 cm long and diameter 40 cm) housing a DC-powered fan. The metal duct was equipped with a vane anemometer head (Messtechnich Reinhard GMBH) measuring wind speed. Temperature was recorded in the metal ducts of two wind tunnels and at 10, 25, 50, 100 and 150 cm depth in two slurry tanks using thermocouple sensors. Signals from sensors and anemometers were scanned at 1 minute intervals and stored as hourly means on a data logger (Datataker 200). The wind speed within the metal duct could be adjusted, the signals being displayed on a personal computer.

After passing surface of the slurry tank and the vane anemometer, the air stream was sampled in front of the fan by use of suction pumps (ASF 7010 Z) and teflonpipes (FEP teflon). During February to March 1990, NH_3 -concentrations were measured with an NH_3 monitor (Thermo Electron Model 14 AA).

From April, the airstream was sampled at a rate of 4 litres min^{-1} and drawn through 250 ml gas washing bottles fitted with a sintered air distribution heads of glass. The flasks contained 100 ml of 0.01 $\underline{M}$ H_3PO_4. The air flow rate was checked by a flowmeter. NH_3 trapped in the orthophosphoric acid was subsequently determined colorimetrically by use of an autoanalyzer (Technicon autoanalyzer II, Segmented Flow Analytical Instruments) used essentially, as described by Crooke and Simpson (1971).

During February to May 1990, the NH_3 loss was determined from one slurry-tank per day. In the following periods, the NH_3 loss from the 8 slurry tanks were measured simultaneously. The concentration of NH_3 measured at the inlet of the wind tunnels was used as background concentration. NH_3-concentrations in air from the 8 wind-tunnels and background NH_3-concentrations were determined simultaneously using nine sets of acid traps and pumps. The acid traps were changed every 24 h during the first four days after stirring the uncovered slurry, during the next 3 days the absorption period was 72 h.

Treatments

Slurry thoroughly stirred once a week was considered to be an uncovered treatment (Table 2). One treatment was a crust layer which was applied onto the slurry (Exp. 2) or developed in the surface of the slurry (exp. 3 and 4). In the 6 other treatments, additional covers of oil, peat, straw, PVC-foil, leca® and a lid were placed on the surface crust (Tabel 2).

During Exp. 1 no surface crust developed on the unstirred cattle slurry. Therefore in Exp. 2, surface crust material was taken from a farm slurry tank and placed on the surface of the pilot slurry tank.

Slurry analyses

The amount of NH^+_4-N + NH_3 -N (Total Ammoniacal Nitrogen = TAN) in the slurry was determined by direct distillation with MgO, the NH_3 being collected in boric acid-indicator solution and titrated with standard HCl solution (Sommer et al. 1992). Total-N was analysed using Kjeldahl digestion and automatic distillation-titration on a Tecator Kjeltec Auto 1030 analyzer. Dry matter content (DM) was determined gravimetrically after oven drying at 80°C. Bulk pH of the slurry was determined with a standard electrode (Radiometer).

Calculations

For each absorption period, background atmospheric NH_3 -concentrations were subtracted from concentrations obtained from the wind tunnels, and the NH_3 loss for each period was calculated as follows:

$$J = A \times W \times (NH_{3e} - NH_{3b})$$

where:

J = NH_3 loss, g NH_3-N s^{-1}
A = area of steel duct, m^2
W = wind speed in the steel duct, m s^{-1}
NH_{3e} = NH_3 concentration in air from an experimental tunnel, g NH_3-N m^{-3}
NH_{3b} = NH_3 concentration in background air, g NH_3-N m^{-3}

RESULTS

Mean air temperatures were 7°C and 17°C during the experiments with cattle slurry and 7°C and 6°C in the experiments with pig slurry (Table 3). In the top layers of the slurry, the mean temperatures were 1 to 3°C higher than in the air, and temperatures did not increase further at greater depths. The mean wind speed recorded during the four periods ranged from 3.3 m s^{-1} to 4.4 m s^{-1} (Tabel 3).

During exp. 1, the NH_3-loss was measured periodically, therefore mean daily NH_3-loss rate are presented for each month in the period. Consequently, peaks in NH_3-loss rates due to stirring of the slurry do not appear in Figure 1. In the following experiments NH_3-loss rates increased two to three fold after stirring (Fig. 2). Two to four days after stirring, the loss rate approached the values determined before stirring.

In Exp. 1 the slurry did not develop surface crust and the NH_3-loss rate increased during the period (Fig. 1). After formation of a crust layer in Exp. 2 and , NH_3-loss rates decreased from cattle and pig slurry (Fig. 2). In Exp. 4, NH_3-losses from pig slurry with a surface crust were high during the first month, then loss rates decreased.

Additional surface covers of straw, oil, leca® and peat reduced the NH_3-loss rate compared to that from stirred slurry (Fig. 2). Generally, the loss rates were more or less constant or decreased slightly during the experiments. For the oil and peat cover, the NH_3-loss rate increased with time in Exp. 2 and 4, respectively, because cracks developed in the oil layer and along the sides of the peat layer. In all experiments, the NH_3-losses from slurry tanks covered with PVC-foil and a lid were small.

In order to compare the loss rates from the four experiments to values reported in the litterature mean daily NH_3-loss rates were calculated (Fig. 3). The reduction in NH_3 losses from covered slurry compared to losses from stirred slurry are presented in Table 4. Mean NH_3 loss rates from stirred slurry varied between 0.1 and 5.2 g NH_3-N m^{-2} d^{-1}. Surface coverings on the surface crust surface reduced NH_3 losses to less than 50% of that from the uncovered slurry.

DISCUSSION

The wind speed in the steel duct were preset to 3-4 m s^{-1}, because the mean yearly wind speed in Denmark is 4 m s^{-1}. At wind speeds higher than 3 m s^{-1}, NH_3 loss rate are not significantly affected by variations in wind speed (Olesen and Sommer, unpublished). Mainly because the gas phase resistance (boundary layer) becomes insignificant at higher wind speeds (Sommer et al., 1991). The losses determined in this study may therefore be compared without adjusting for the small differences in actual wind speed (Tabel 3).

Besides the effect of convective transport of atmospheric NH_3 from the slurry surface, the rate of NH_3-loss depends on the concentration of atmospheric NH_3 above the slurry surface. At constant pH and temperature, this concentration is linearly related to the TAN concentrations in the slurry surface (Vlek and Stumpe, 1978) and increases with pH and temperature.

Despite the higher concentrations of TAN in pig slurry than in cattle slurry (Table 1), NH_3 loss rates were similar for both slurries (Fig. 1 & 2). The losses from pig slurry were probably reduced by the development of a thick surface crust. In contrast, cattle slurry developed a thin or no surface crust (Table 2).

The NH_3 loss rates were high from stirred slurry (Fig. 2), because mixing increased the concentrations of TAN in the surface layer (data not shown). When slurry was stirred, NH_3-loss rates were generally high during the following 24-48 h period. Then loss rates decreased (Fig. 2), as TAN concentrations in the surface layer were reduced. Diffusive transport of TAN from deper layers to the surface was too slow to replace the volatilized NH_3 (see also Muck and Stenhuis, 1982). The results thus indicate that depletion of NH_3 at the slurry surface was the rate limiting factor for NH_3 losses from stored slurry.

No surface crust developed on the cattle slurry in Exp. 1. The NH_3 loss from the unstirred slurry was similar to that from slurry stirred once a week. Presumably because TAN was transported by convection to the surface layers as shown for NH_4-fertilized flooded rice paddies (Leuning et al., 1984). Furthermore no airfilled dry crust could reduce the transfer of atmospheric NH_3 from the slurry surface.

In contrast, a stagnant air layer was developed above the liquid fraction of slurry covered by crust, straw, peat, or leca®. Through this layer atmospheric NH_3 had to be transported by diffusion. This transport is slow and the concentration of atmospheric NH_3 at the slurry surface will increas, whereby at transfer of NH_3 from the slurry to the air layer above the slurry is reduced. The increasing thickness of the crust layer during the experiments reduced loss rates from the slurry storages with no additional cover. A similar gradual reduction in NH_3 losses was observed from slurry that developed a crust layer below the leca® and straw layers (Fig. 2). In Exp. 4, the crust did not dry up until April and the NH3 loss did not decline before the stagnant air layer developed. During the period when the crust surface was wet, TAN could be transported upwards as water evaporated from the surface.

NH3 loss rates from oil and peat covered storages were low. A surface layer of oil reduces NH3 volatilization because TAN is not soluble in oil. Peat creates a dense layer through which transport of atmospheric NH3 will be limited. During Exp. 1, gas bubbles penetrated the oil and some NH3 loss occured throughout this experiment (Fig. 2). Only small losses were determined in the experiments where pig slurry was covered with oil, indicating that the cattle slurry produced more gas (probably in form of methane) than the pig slurry (Hashimoto <u>et al.</u> 1980). During Exp. 2 cracks developed in the oil layer as the oil was partly absorbed by crust materials, and the crust dried up. As a consequence NH3 loss rates increased during the experimental period (Fig. 2). Cracks developed at the interface of the peat and the walls of the tank in the Exp. 4 and NH3 losses increased.

NH3 loss rates were small from slurry tanks covered with a lid or a PVC-foil. Gas was entrapped under the floating PVC-foil, which curved upward in the center. Thereby a slit was formed between the foil and the walls of the slurry tank, through which small amounts of NH3 was lost.

IWhen slurry was stirred weekly mean daily NH_3 loss from cattle slurry was 3.5 g NH3-N m-2 d^{-1} and 5.2 g NH_3-N m^{-2} d^{-1} in Exp. 1 and 2, respectively. In Exp. 3 and 4 with pig slurry, 3.9 g NH_3-N m^{-2} d^{-1} and 4.6 g NH_3-N m^{-2} d^{-1} was lost. For a summer and a winther period, Bode (1991) found higher NH_3 loss rates from pig slurry but similar rates for cattle slurry. The lower losses from pig slurry in the present study is ascribed to the development of a massive surface crust, which did not develop on the slurry studied by Bode (1991). Loss rates from slurry with surface covers were 1 to 60% of the loss rate from the stirred slurry (Table 4). Bode (1991) found that the NH_3 losses were reduced by 0-37%, when a natural crust was formed, and 63-79% when the crust was improved by addition of straw. Bode (1990) showed that roofings and floating covers could reduce losses of NH_3 with more than 80%.

Based on the results annual losses of NH_3 from stirred slurry is estimated to 1.6 and 1.5 kg NH_3-N m^{-2} from cattle and pig slurry, respectively. For a farm scale storage tank having a depth of 3 m, these losses correspond to 12% of the total-N and 21% of TAN in cattle slurry. Corresponding valued for pig slurry are 8% of total-N and 12% of TAN. These losses are considered to represent maximum values as the mixing intensity was high.

CONCLUSION

Mean daily NH_3 loss rate were between 3.5 g NH_3-N m^{-2} d^{-1} and 5.2 g NH_3-N m^{-2} d^{-1} from cattle and pig slurry being weekly stirred. From unstirred cattle slurry without a surface crust, similar NH_3 losses were obtained.

A 15 cm deep layer of straw was as effectively as a crust layer in reducing NH_3 losses from cattle slurry. When a crust layer was formed below the straw, NH_3 losses was reduced to 3-17% of losses from uncovered slurry.

Cracks may develop in oil layer used to cover slurry during storage. In one experiment with a perforated oil layer, NH_3 losses were only reduced to 50% of the losses from uncovered slurry.

Generally a natural crust, peat, leca, oil, PVC-foil or a lid will reduce NH_3 losses to between 0 and 30% of the losses found for stirred slurry.

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Legends to Figures.

Fig. 1. Mean daily NH_3 -loss rates during February -June 1990 (Exp. 1) from stored cattle slurry with eight different surface covers. NH_3 -concentrations were determined with an NH_3 -monitor during February and March and with gas washing bottles during April to June.

Fig. 2. Daily NH_3-loss rates from stored cattle and pig slurry with eight different surface coverings. The experiments were carried out during the following periods: Exp. 1, Dec. 1989-June 1990; Exp. 2, July-Sept. 1990; Exp. 3, Sept.-Dec. 1990; Exp. 4, Febr.-June 1990. Surface covers: ⊟-⊟, Oil; *-*-, Straw; △-△-, Crust; ●-●-, Uncovered; +-+-, Lid; #-#-, PVC-foil; ⊖-⊖-, Peat; ◇-◇-, Leca®.

Fig. 3. Mean daily NH_3-loss rates from stored cattle and pig slurry with eight different surface coverings. * Denotes that no surface crust was formed. The experiments were carried out during the following periods: Exp. 2, July-Sept. 1990; Exp. 3, Sept.-Dec. 1990; Exp. 4, Febr.-June 1990.

Table 1. Characteristics of the cattle and pig slurries.

Exp. no.	Experimental period	Type	Total-N g N l^{-1}	TAN[#] g N l^{-1}	pH	Dry matter %
1	21. Dec. 89- 15. Jun. 90	Cattle	5.2	2.5	7.5	5.9
2	6. Jul. 90- 2. Sep. 90	Cattle	4.1	2.6	7.7	5.9
3	18. Sep. 90- 10. Dec. 90	Pig	5.8	4.1	7.3	4.6
4	27. Feb. 91- 25. Jun. 91	Pig	6.1	4.2	7.4	7.4

[#] TAN = NH_3-N + NH_4^+-N.

Table 2. Thickness and dry matter content of the surface crust and characteristics of the additional cover.

Treatment	Description	Surface crust							
		Exp. 1		Exp. 2		Exp. 3		Exp. 4	
		Thickness cm	DM %	Thickness cm	DM %	Thickness cm	DM %	Thickness cm	DM %
Lid	Wodden cover (Width, length, and thickness; 950, 2950, 20 mm), fastened by screws to the slurry tank.	5	12	NSC	NSC	14	14	20	15
PVC-foil	Floating cover of polyester coated on both sides with PVC (thickness 2 mm), and boarded with an airfilled container. Inflatable Constructions, Esbjerg, Denmark.	NSC	NSC	NSC	NSC	10	15	30	18
Peat	Sphagnum peat cover (thickness 90 mm), pH 4-5, 1.6% content of ash, 2% sand. Pindstrup Mosebrug, Ryomgård, Denmark.	3	11	NSC	NSC	10	17	18	16
Leca	Cover of airfilled pebbles (thickness 90 mm) based on burned montmorillonitic clay, 10-20 mm, 215 kg m^{-3}. Danish Leca A/S, Copenhagen, Denmark.	NSC	NSC	NSC	NSC	15	18	20	21
Oil	Cover of unrefined oil (thickness 10 mm) from oil seed rape (COLZRO). Holes and cracks developed in the rape oil cover in Exp. 1 and 2. Aarhus Oliefabrik, Aarhus, Denmark.	4	15	2	20	10	19	16	21
Straw	Cover of chopped wheat straw (thickness 170 mm).	NSC	NSC	NSC	NSC	15	16	23	21
Crust	Cover of natural surface crust developed mainly of straw residues in the slurry. No surface crust developed in Exp. 1.	NSC	NSC	7	13	16	29	30	20
Uncovered	Slurry thoroughly stirred once a week. Within 1-2 days a cover of surface crust developed after stirring in Exp. 1, 3 and 4.	1	13	NSC	NSC	7	18	8	18

NSC : No surface crust was formed.

Table 3. Mean wind speed measured in the metal duct and mean air temperature during the experiments (SD in brackets).

Experiment No.	Duct wind speed m s^{-1}	Temperature					
			Depth in slurry tank				
		Air °C	10 cm	25 cm	40 cm °C	100 cm	160 cm
1	3.3 (0.7)	7[#] (4.2)					
2	3.5 (0.5)	17 (4.2)	18 (1.4)	18 (1.3)	18 (1.2)	17 (0.9)	6 (0.8)
3	4.4 (0.6)	7 (4.8)	10 (5.2)	10 (4.3)	10 (3.7)	9 (3.4)	10 (2.9)
4	4.0 (0.7)	6 (5.2)	8 (6.3)	7 (5.6)	7 (5.0)	7 (4.6)	6 (3.9)

[#] Measured at a nearby climate station (20 cm). Temperature measured occasionally in the tunnel was 1-2°C higher.

Table 4. Relative losses of NH_3 from covered slurry (% of loss from weekly stirred slurry.)

Surface covering	Cattle slurry Exp. 1 %	Cattle slurry Exp. 2 %	Pig slurry Exp. 3 %	Pig slurry Exp. 4 %
Lid	1	3	0	5
PVC-foil	26	7	2	9
Peat	19	1	16	32
Leca	17	14	5	12
Oil	27	48[##]	0	2
Straw	60	7	3	17
Crust[#]	105	13	8	24
Uncovered	100	100	100	100

[#] During the Exp. 1 no crust was developed.

[##] Cracks developed in the oil layer.

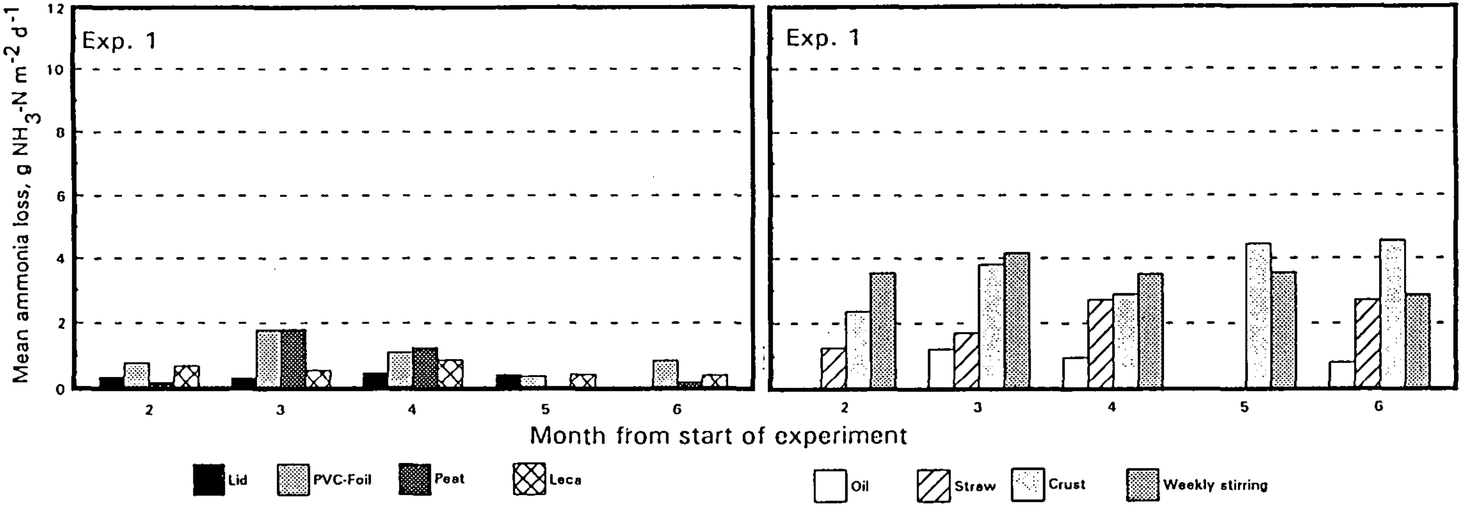
Exp. 1
Exp. 1
Mean ammonia loss, g NH_3-N m^{-2} d^{-1}
0
2
4
6
8
10
12
2
3
4
5
6
Month from start of experiment
Lid
PVC-Foil
Peat
Leca
Oil
Straw
Crust
Weekly stirring

Fig 1 Sommer et al 1992

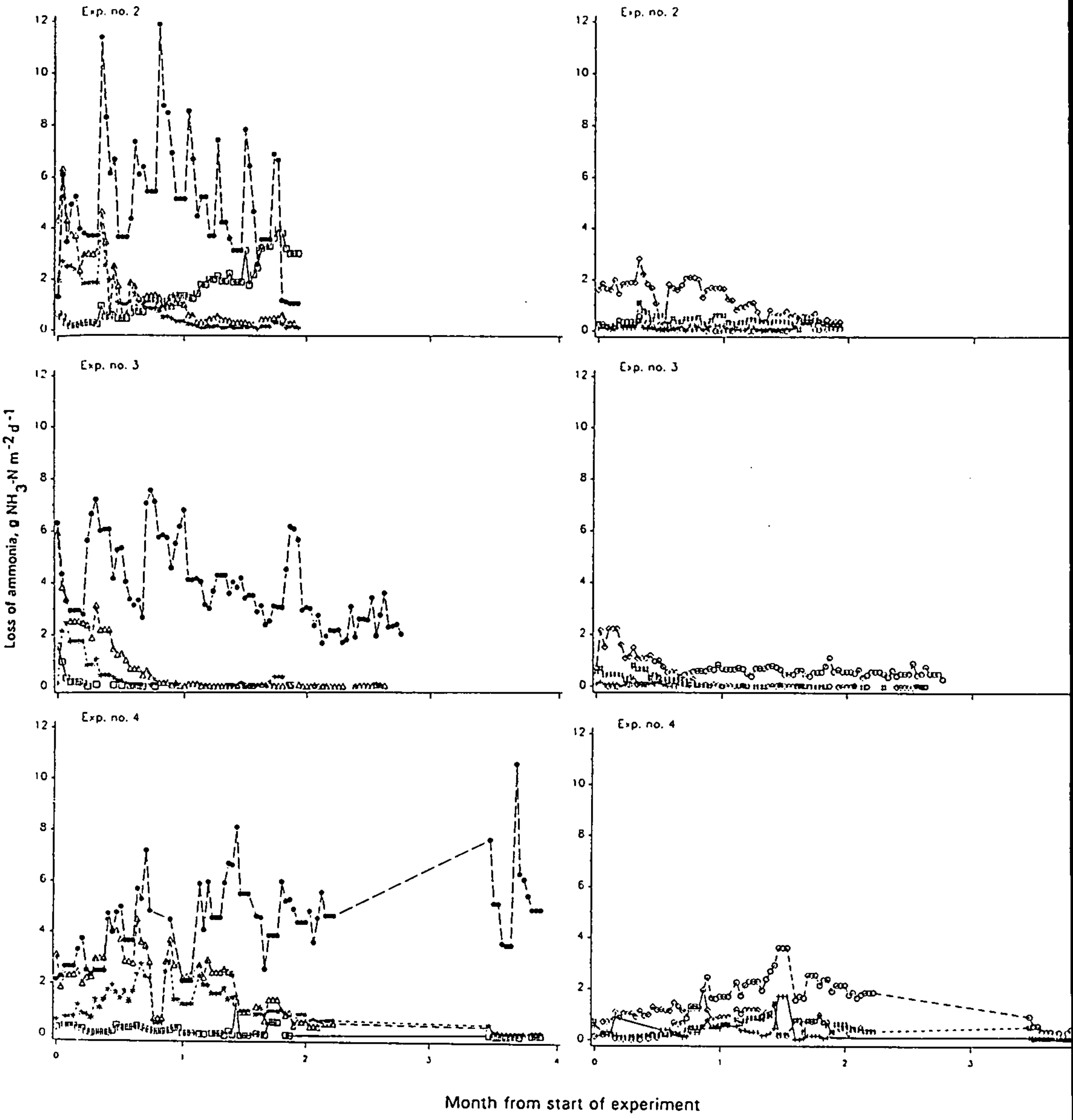

Fig 2
Sommer et al. 199

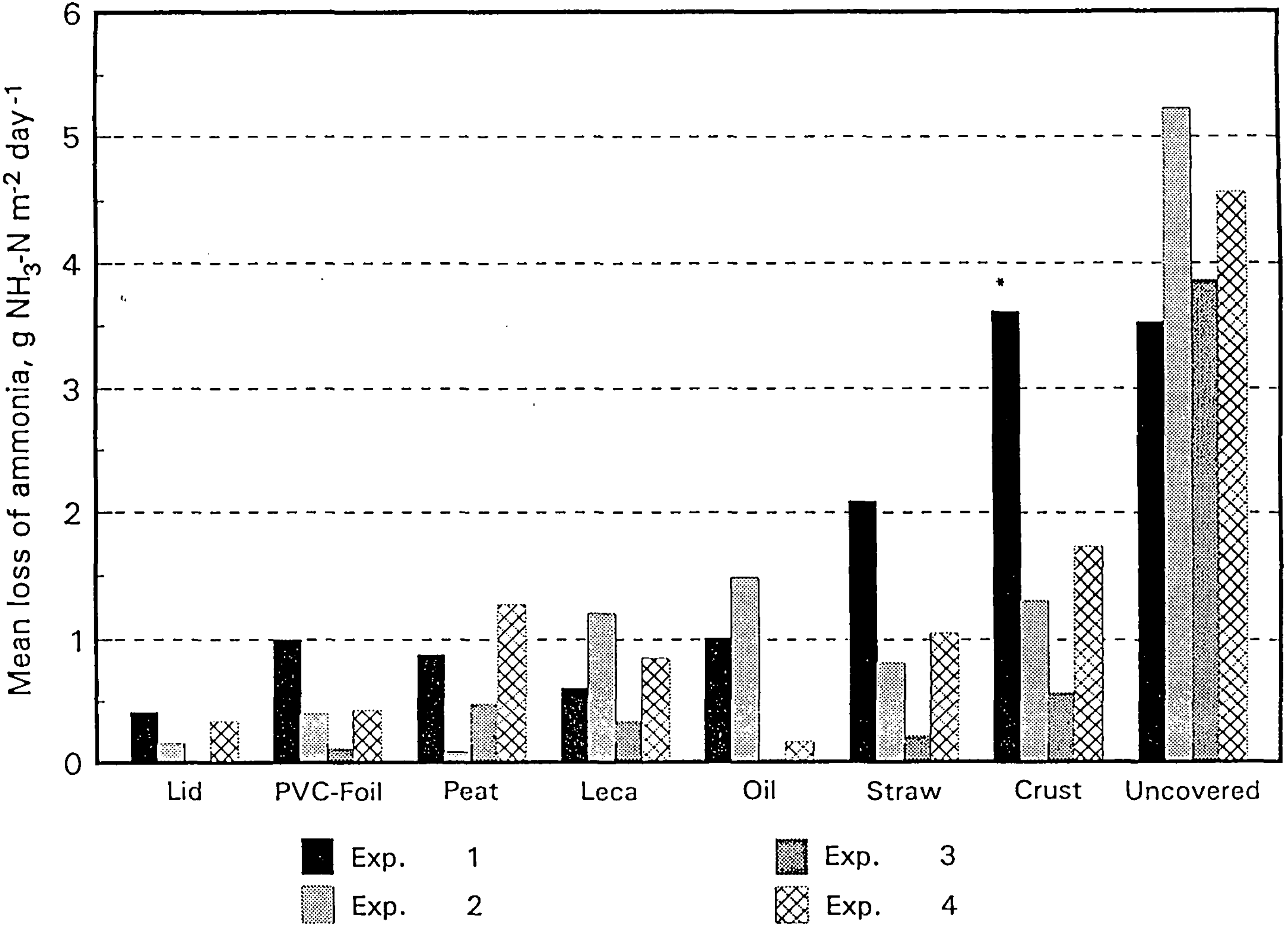

Fig. 3
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COMMISSION OF THE EUROPEAN COMMUNITIES
Directorate-General for Science, Research and Development
Environment Research Programme

Air Pollution Research Report 39

Joint Workshop COST 611/Working Party 3 and EUROTRAC

I. Field measurements and interpretation of species related to photo-oxidants and acid deposition

II. Exchange of Nitrogen Compounds (BIATEX)

III. Ammonia emission

October 28-30, 1991
TNO, Delft, The Netherlands

Edited by
G. Angeletti, S. Beilke and J. Slanina

LEAF ABSORPTION OF GASEOUS AMMONIA AFTER APPLICATION OF PIG SLURRY ON SAND BETWEEN ROWS OF WINTER WHEAT

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Summary

Application of slurry to the soil between rows of crops reduces ammonia losses, compared to slurry applied onto crops by splash plates. In the present investigation the effect of wind reduction by a winter wheat crop and the leaf absorption of volatilized ammonia after application of slurry to the soil between rows of wheat was studied. The ammonium in the slurry was labelled with ^{15}N. Gaseous N loss from the slurry varied from 6.9 g N m^{-2} to 11.1 g N m^{-2}. At 5 cm height the wheat crop did not influence the ammonia loss from the slurry, while a 43 cm high crop reduced the ammonia volatilization from 98% to 90% of applied ammonium, showing that crop height had an influence on the amount of ammonia lost from the applied slurry. The 5 cm and the 43 cm high wheat crop absorbed 2.2% and 3.3% of the lost ammonium, respectively.

Introduction

Large amounts of ammonium in surface applied slurry are lost by ammonia volatilization (Jarvis and Pain, 1990), thereby reducing the nutrient efficiency of the slurry. Ammonia volatilization from slurry can be reduced by incorporation or injection of the slurry into the soil (Thompson et al., 1987). Recently it has been shown that trail hose application of slurry on the soil between rows of a crop may reduce ammonia volatilization (Bless et al., 1991).

The reduced ammonia volatilization from slurry applied on the soil between plant rows may be due to absorption of ammonia by the leaves of the crop (Sommer and Jensen, 1991; Whitehead and Lockyer, 1987), or to a reduction in wind speed within the crop (Denmead et al., 1982). A reduced wind speed within the crop will increase the ammonia concentration above the slurry, and thus reduce the transport of ammonia from the slurry to the air. Furthermore absorption of ammonia will increase with increasing atmospheric ammonia concentrations (Whitehead and Lockyer, 1987).

In this study, we examined to what extent absorption of ammonia by plant leaves reduces ammonia volatilization losses from slurry applied on the soil between rows of wheat. Slurry enriched with ^{15}N-ammonium was spread to sand placed in trays on the soil surface between the rows of winter-wheat (Triticum aestivum, Lam). By this procedure the volatilized ammonia could be traced in the plants when harvested.

Material and methods

Ammonia losses from pig slurry applied to a bare soil and to a winter wheat crop (Triticum aestivum, Lam) were determined in the field. Two experiments were carried out during the periods 24.4.91-1.5.91 (April experiment) and 28.5.91-4.6.91 (May experiment). Transparent roofs of PVC were placed on the plots during rain.

To each plot was applied 2.9 to 3.1 kg m^{-2} of pig slurry corresponding to 7.5 to 14.4 g NH^{+}_{4}-N m^{-2}. The slurry was poured onto 1.6 to 2.0 kg nitrogen free sand placed on trays (50 cm by 7 cm) located between the rows of winter wheat and on trays placed on an uncropped soil. In the spring 120 kg N/ha in 21:4:10 NPK-fertilizer was broadcast to the wheat, in rows with a space of 11 cm in between. Three trays with 7 cm in between were placed in each plot, covering a total area of 0.25 m^2. Leaf area, plant height and plant age characterized by Feeke's scale were determined.

To the slurry was added 0.4 g NH_4^+-N in $(NH_4)_2SO_4$ (60 atom % ^{15}N excess) per L of slurry. Microbial activity in the slurry was inhibited by addition of 1.75 ml of a solution containing 25 g $HgCl_2$ per L.

At the beginning of the experiments 100 g slurry samples were taken and stored at -18°C. After seven days of exposure, the sand and slurry mixture from the three trays in a plot was collected in jars, which were sealed weighed and stored at -18°C. The sand and slurry mixture was homogenized in a mortar and 5 samples per jar were collected for analysis. Plant tops were harvested at the soil surface. Roots were isolated by randomly taking three 4.5 cm diameter soil cores to 50 cm depth in each plot, and gently washing the soil of the roots. The plant material was oven-dried at 80°C for 24 hours, weighed and ground.

Total-N in the sand and slurry mixture and slurry was determined by the use of a Kjeldahl-digestion followed by distillation with NaOH and titration with a Kjeltec Auto 1030 Analyzer (Tecator). Ammonium content was determined by distillation with MgO and titration with an Kjeltec Auto 1030 Analyzer (Tecator). Ammonium in the distillate was diffused to an acid impregnated filter for determination of ^{15}N enrichment. Total-N and ^{15}N enrichment in the dried and finely ground plant material and ^{15}N enrichment in the acid impregnated filters were determined by an elemental analyzer (Carlo Erba NA 1500), interfaced to an isotope ratio mass spectrometer (Delta, Finnigan MAT) (Jensen, 1991).

Results and Discussion

The last four days of each experiment, the plots were sheltered from rain by PVC roofs. The roof absorbed 20-30 % of the photosynthetic light. This may have reduced the uptake of ammonia by the leaves (Rogers and Aneja, 1980). In April, the wheat was low due to a cold spring and the leaf area was small (Table 1). A few weeks before the May experiment started, temperatures had increased. Consequently the plants grew vigorously, and height

Table I. Mean air temperature, plant height, stage on Feekes scale and leaf area index in the two experimental periods.

	Experimental period	
	April	May
Air temperature °C	5.2	9.6
Plant height, cm	5	43
Feekes scale	4	7
LAI index	0.68	4.83

and leaf area increased considerably relative to the April experiment.

The gaseous N loss from the trays varied from 6.9 g N m^{-2} to 11.1 g N m^{-2}, as determined by the difference in total-N at the beginning of the experiments and at the end (Table 2). The greatest loss was from the plot with 5 cm high wheat plants in the April experiment. The smallest loss of N was from the plot of 43 cm high wheat plants in the May experiment. A substantial part of the ammonium added was lost (Table 2), probably due to the low cation exchange capacity of the sand and the sustained drying conditions. The higher losses of applied ammonium in the May experiment was probably due to a higher temperature (Sommer _et al._ 1991). There was no significant reduction in losses of ammonia from slurry applied to the plot with low wheat plants, but the ammonia loss was reduced from 98 % to 90 % in the experiment with high wheat plants (Table 2), indicating that the reduction of wind speed in the canopy reduced the transfer of ammonia from the slurry to the atmosphere, compared to the uncropped plot.

In the April and May experiment the wheat plants absorbed 0.24 g NH_3-N m^{-2} and 0.23 g NH_3-N m^{-2}, respectively (Table 3). A

Table II. Loss of ammonium from the surface applied pig slurry.

Period	Surface Caracteristic	Ammount of NH_4^+ added g NH_4^+-N m^{-2}	Gaseous loss of N g N m^{-2}	 % of NH_4^+-N added
April	Uncropped	14.16	10.8	79
	Wheat, 5 cm	14.36	11.1	77
May	Uncropped	7.47	7.3	98
	Wheat, 43 cm	7.66	6.9	90

Table III. Total-N content and absorption by wheat leaves of gaseous ammonia volatilized from the surface applied pig slurry.

	Wheat top		Wheat root		Uptake of
	N-total $g\ N\ m^{-2}$	Labelled NH_3 $g\ N\ m^{-2}$	N-total $g\ N\ m^{-2}$	Labelled NH_3 $g\ N\ m^{-2}$	Labelled NH_3 $g\ N\ m^{-2}$
April	4.98	0.22	1.89	0.02	0.24
May	14.24	0.22	3.14	0.01	0.23

similar uptake of ammonia in the two periods was not expected, as uptake is related to leaf area. However high concentrations of gaseous ammonia, due to a high emission of ammonia may have provided a high absorption of ammonia by the wheat plant with a small leaf area in the April experiment. In May the ammonia loss was much smaller and the absorption of ammonia by the wheat plants may have been restricted by lower concentrations of gaseous ammonia. However the more efficient uptake of ammonia by a greater plant canopy resulted in a 3.3% uptake of lost ammonia in May compared to 2.2% in April.

Application of slurry on the soil between rows of winter wheat reduced the loss of ammonia, due to absorption of ammonia by plant leaves and a reduced loss of ammonia from the slurry. From the plot with a 5 cm high wheat crop, ammonia loss from the top of the canopy was only reduced by uptake of ammonia by the leaves, while the reduced loss from a 43 cm high crop was due to both a reduced ammonia volatilization from the slurry and to uptake of gaseous ammonia by the plants. Due to plant uptake and reduced ammonia volatilization from the slurry in the 43 cm high wheat crop, the ammonia loss was reduced with 9%, compared to the loss from slurry applied to an uncropped soil.

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Udspredning af gylle: Fordampning af ammoniak og fordeling af udbragt gylle

Spreading of slurry: Volatilization of ammonia and distribution of applied slurry

SVEN G. SOMMER

Resumé

Fordelingen af gylle fra to gyllespredere med en højt- og en lavtsiddende central sprede plade samt en spreder med spredebom og seks sprede plader var stærkt påvirket af sidevind. Med centralt placeret sprede plade fordeltes gyllen ujævnt på tværs af kørselsretningen. Der blev målt de mindste mængder midt for og de største i siderne af spredefeltet.

Ammoniak-tabet blev bestemt som forskellen i ammonium-indholdet i gylle før og efter udspredning. Tabet var mindre end 4 pct. af den udbragte ammonium, uanset om der blev anvendt en gyllespreder med en lavtsiddende sprede plade og et stort spredefelt eller en højtsiddende sprede plade og et lille spredefelt. Der var ingen målelig forskel i ammoniak-tabet ved anvendelsen af de to gyllespredere.

På grund af ammoniak-fordampning kunne indholdet af ammonium i gylleprøverne ændres væsentligt under opbevaring, såfremt prøvebeholderen ikke var helt fyldt og forsynet med tætsluttende låg.

Nøgleord: Ammoniakfordampning, ammonium, gylle, udspredning, spredefelt og gyllespreder.

Summary

Two slurry-spreaders equipped with a central sprinkler-plate situated one and two metres above the ground respectively, and one slurry-spreader with a spreading bar having six sprinkler-plates were included in this study. Wind across the driving direction caused an uneven spreading of the slurry. The two spreaders with central sprinkler-plates produced the highest slurry application rate in the sides and the lowest rate in the center of the spreading fan.

The ammonia loss was determined as the difference in the ammonium content in samples taken from the tank of the spreader and collected during spreading in containers placed on the soil surface. Losses during spreading represented less than 4 per cent of the amount of ammonium applied. Similar losses were found for both spreaders with central sprinkler-plates.

Unless sample containers were filled completely and closed with an airtight lid, a substancial loss of ammonium took place during storage of slurry samples.

Key words: Ammonia volatilization, ammonium, slurry, spreading-fan, spreading machine.

Indledning

Der findes ingen danske og kun enkelte udenlandske undersøgelser af NH_3-fordampningen ved udspredning af gylle, dvs. tab af NH_3 fra gyllen forlader sprederen, til den rammer jorden. Resultaterne af de udenlandske undersøgelser er meget forskellige. *Besson et al.* (1) fandt tab på 10–14 pct. af gyllens NH_4^+-indhold under udspredning, mens *Pain et al.* (3) fandt tab på mindre end én pct.

Der er derfor behov for målinger af NH_3-fordampningen ved udspredning af gylle. Foruden et bedre kendskab til tabets størrelse, vil det være af interesse at få kendskab til, om tabet varierer med maskintype, idet nye gyllespredere bl.a. udvikles med henblik på at forbedre udnyttelsen af kvælstofindholdet i gylle.

For at sikre det fulde udbytte af den udbragte gylle er en jævn fordeling nødvendig. Som led i undersøgelsen blev fordelingen af gylle med tre forskellige maskintyper derfor undersøgt, herunder indflydelse af vinddrift.

Metode

NH_3-tabet blev bestemt som forskellen i NH_4^+-indholdet i gylle før og efter udspredning, da en reduktion i gyllens NH_4^+-indhold antages at hidrøre fra NH_3-fordampningen i forbindelse med udspredningen.

NH_4^+-indholdet i gyllen før udspredning blev bestemt i prøver udtaget fra gyllesprederens tank før og efter udspredning. For hvert forsøg blev gyllen i tanken omhyggeligt blandet.

Den udspredte gylle blev opsamlet i 6 l opsamlingsbeholdere opstillet i tre rækker på tværs af kørselsretningen (tabel 1). Afstanden mellem opsamlingsbeholderne blev afpasset efter spredebredden. I de første tre forsøg blev der på opsamlingsbeholderen sat tætsluttende låg umiddelbart efter opsamling af den udspredte gylle, og gyllen blev opbevaret heri i et uopvarmet rum indtil analyse. I de efterfølgende forsøg blev en del af gyllen straks overført til lufttætte bægre (200 ml), der indtil analyse blev opbevaret i køleskab. Bægrene blev fyldt, så de ikke indeholdt luft.

Analyse

Umiddelbart efter spredning blev mængden af opsamlet gylle bestemt ved vejning.

Forud for analyse blev opsamlingsbeholderne indeholdende gylle opbevaret i 2 til 6 uger i en kølig gang. Bægrene blev opbevaret maksimalt tre dage i køleskab. Gyllens pH blev bestemt med pH elektrode (Radiometer). NH_4^+-indholdet blev bestemt ved destillation efter tilsætning af MgO og $CuSO_4$, og NH_3 blev opsamlet i et forlag indeholdende borsyre og A. C. Andersen indikator. Derpå bestemtes det opsamlede NH_4^+ ved titrering med HCl.

Opbevaring af gylleprøver

Opbevaringens indflydelse på NH_4^+-indholdet i gylleprøver blev bestemt ved at udtage 300 ml gylle fra gyllesprederens tank og opbevare prøverne i seks opsamlingsbeholdere (volumen 6 l) med tætsluttende låg, som beskrevet ovenfor. Ved

Tabel 1. Dimensioner af spredefelt og afstand mellem opsamlingsbeholderne.
Geometry of slurry fan and distance between the colletors.

Gyllespreder *Slurry-spreader* nr.	Sprede-aggregat *Application device*	Aggregat højde *Height* m	Sprede bredde *Width of fan* m	Sprede længde *Length of fan* m	Afstand mellem *Distance between* række af opsamlingsbeholdere *rows of collectors* m	 opsamlingsbeholdere i rækkerne *collectors in rows* m
1	Central spredeplade *Central sprinkler-plate*	1	11	9.5	6	1.3
2	Central spredeplade *Central sprinkler-plate*	2	6	4.2	6	0.8
3	Spredebom med seks spredeplader *Bar with six sprinkler-plates*	1	12	0	6	1.5

denne opbevaringsmetode indeholdt beholderne udover gyllen også 5.7 l luft. Fra de seks opsamlingsbeholdere blev gylle fra to beholdere udtaget til analyse efter henholdsvis 4. 72. 144 timers opbevaring.

Tab af NH_4^+ ved opbevaring af gylle i 200 ml bægre blev undersøgt ved at opbevare gyllen i 13 helt fyldte bægre med låg. Fem bægre blev tilsat svovlsyre. Indholdet af NH_4^+ blev efter tre døgns opbevaring sammenlignet med indholdet i gylle opbevaret i bægre uden tilsætning af syre. Den forsurede gylles pH var mindre end seks, hvilket hindrer NH_3-fordampning.

Tab og fordeling ved udspredning

I perioden 16. november 1987 til 13. juni 1989 blev der gennemført 15 undersøgelser af ammoniakfordampningen ved udspredning af gylle. Undersøgelserne gennemførtes på ni forskellige forsøgsdage (tabel 2). Temperaturen varierede mellem −1.0°C og 23.2°C og vindhastigheden mellem 0.6 og 6.7 m/s.

Tre forskellige typer af gyllespredere blev anvendt (tabel 1). Der blev i ét forsøg d. 16. november 1987 anvendt svinegylle. I de øvrige forsøg anvendtes kvæggylle. pH i gyllen var mellem 7.4 og 8.0 før udspredning. Der blev udspredt mængder svarende til mellem 10 og 41 t/ha.

Beregninger

NH_3-fordampningen for hver række af opsamlingsbeholdere blev bestemt som forskellen mellem gennemsnittet af den opsamlede gylles NH_4^+-koncentration og koncentrationen i gylle udtaget i gyllesprederens tank. I de forsøg, hvor gylleprøvernes vægt blev bestemt, blev der for hver række beregnet et vægtet gennemsnit af NH_4^+-koncentrationerne. Derved blev der kompenseret for en ujævn fordeling af gyllen på tværs af kørselsretningen. Tabet blev beregnet på følgende måde:

$$NH_3(tab).r = NH_4^+(tank) - \frac{\sum_{i=1..7} NH_4^+.r.i * M.r.i}{\sum_{i=1..7} M.r.i}$$

NH_3(tab). r:	Ammoniaktab i række r.
NH_4^+. r.i:	NH_4^+ koncentrationen i række r. og opsamlingsbeholder nr. i.
M. r.i:	Opsamlet mængde gylle pr. spand i række r. og opsamlingsbeholder nr. i.
NH_4^+ (tank):	Det gennemsnitlige NH_4^+-indhold i gylle udtaget i tanken.

Tabel 2. Gyllespreder, gylletype, mængde af udbragt gylle og vejrforhold i løbet af forsøgene.
Slurry spreader, type of slurry, amount of applied slurry and climatic conditions during experiments.

Dato *Date*	Gyllespreder *Slurry-spreader* nr.	Udbragt mængde *Amount* t/ha	Gyllens pH *Slurry pH*	NH_4^+ *NH_4^+* pct.	Gylletype* *Slurry type*	Vindhastighed *Wind speed* m/s	Vindretning grader *Wind direction* degrees	Kørselsretning grader *Driving direction* degrees	Temperatur *Temperature* °C
16.11.87	1	20	7.6	0.298	Sg	5.1	195	360	7.5
	2	40	7.6	0.298	Sg	5.1	195	360	7.5
08.12.87	1	23	7.9	0.300	Kg	0,6	287	360	−1.0
	2	30	7.9	0.300	Kg	0.6	287	360	−1.0
22.02.88	1	10	8.0	0.276	Kg	3.0	259	360	5.9
	2	56	8.0	0.276	Kg	3.0	259	360	5.9
	3	33	8.0	0.276	Kg	3.0	259	360	5.9
26.08.88	1	27	7.9	0.222	Kg	2.4	130	360	13.7
	2	31	7.9	0.222	Kg	2.4	130	360	13.7
12.10.88	1	28	7.9	0.226	Kg	6.7	92	90	9.6
	2	27	7.9	0.226	Kg	6.7	92	90	9.6
14.12.88	1	29	7.4	0.245	Kg	3.5	330	360	3.9
17.02.89	2	38	7.6	0.257	Kg	2.5	231	180	2.5
10.05.89	2	41	7.7	0.259	Kg	2.6	282	270	11.2
13.06.89	2	41	7.8	0.255	Kg	3.5	99	180	23.2

* Sg Svinegylle, *Pig slurry.*
Kg Kvæggylle, *Cattle slurry.*

NH_3-tabet pr. række er en observation for en maskine en bestemt dag. Middelværdi og spredning for NH_3 tabet ved udspredning blev beregnet med SAS proc. glm. procedure (4). NH_3-tabet er derpå beregnet som pct. af den udbragte mængde NH_4^+.

pH i gyllen efter spredning blev beregnet ved at omregne pH til hydrogenionkoncentration. Gennemsnittet af hydrogenionkoncentrationen blev beregnet og omregnet til pH.

Resultater og diskussion

Ammoniaktab ved opbevaring af gylleprøver

Såfremt gylleproven kun optager en lille del af provebeholderens volumen, vil der kunne ske en netto-fordampning af NH_3, indtil der opstår ligevægt mellem gyllens og luftens indhold af NH_3. Da opsamlingsbeholdernes volume var 6 l og gyllen kun optog 200 ml af dette volumen, kunne en del af NH_4^+-indholdet tabes fra proven under opbevaringen.

Indholdet af NH_4^+ faldt over seks døgn (tabel 3). Faldet i NH_4^+-koncentrationen modsvarer en netto-fordampning, der kan mætte luften i beholderen med NH_3. Derimod var der efter tre døgns opbevaring i bægre ingen signifikant forskel mellem indholdet af NH_4^+ i ubehandlet gylle og i forsuret gylle. Opbevaring af gylle i fyldte bægre uden indhold af luft hindrer således NH_4^+-tab under opbevaring i op til tre døgn, dvs. den maksimale tid disse prover blev opbevaret indtil analyse.

Ammoniaktab ved udspredning af gylle

NH_3-fordampningen bestemt ved differensmetoden består af tabet under selve udspredningen og tabet, mens gyllen ligger i opsamlingsbeholderen. Eventuelle tab ved vinddrift af aerosoler bestemmes ikke med differensmetoden. I forsogene, hvor den opsamlede gylle straks blev hældt over i bægre, var det målte tab mellem 1 og 4 pct. af den udbragte NH_4^+ (tabel 4). Der var ikke væsentlig forskel på fordampningen ved de to beregningsmetoder. Tabene var uafhængige af temperatur og af de to maskintyper. Dette forhold tilskrives, at gyllens opholdstid i luften er så kortvarig, at eventuelle forskelle i fordampningen ikke er målelige med den her anvendte metode. De målte forskelle i NH_3-fordampningen skyldes antagelig forskelle i den tid, der er forlobet, inden proverne blev overført fra opsamlingsbeholdere til bægre.

I de forsog, hvor gyllen efter opsamlingen blev opbevaret i opsamlingsbeholdere (luftvolumen 5.7 l), fandtes der NH_3-tab på mellem 7 og 40 pct. af gyllens NH_4^+-indhold (tabel 5). De storre tab må tilskrives, at der med denne fremgangsmåde efter udspredning skete tab af ammoniak ved opbevaring og håndtering af gylleproverne.

Tabel 3. Ændringer i gyllens indhold af NH_4^+ ved opbevaring i opsamlingsbeholdere med låg (300 ml i 6 l beholdere) og i fyldte 200 ml bægre med og uden syretilsætning.
Change in concentrations of NH_4^+ in slurry stored in collectors (300 ml slurry in 6 l collectors) with lids and in boxes (0.200 l) with untreated and acidified slurry.

NH_4^+ i gylle opbevaret i opsamlingsbeholdere (6 l).
NH_4^+ in slurry stored in collectors.

Tid, timer *Time hours*	4	72	144
NH_4^+	0.234 (±0)	0.229 (±0.003)	0.222 (±0.004)

NH_4^+ i gylle opbevaret i lufttætte bægre.
NH_4^+ in slurry stored in airtight boxes.

Forsuret gylle.. *Acidified slurry*	pct. NH_4^+	$x = 0.222^*$	S = 0.005	n = 5
Ubehandlet gylle. *Untreated slurry*	pct. NH_4^+	$x = 0.226^*$	S = 0.005	n = 8

* Ikke signifikant forskel, 5 pct. niveau.
* *No significant difference, 5 per cent level.*

Tabel 4. Ammoniaktab og ændringer i gyllens pH ved udspredning af gylle. Gylleprøver opbevaret i 200 ml bægre uden luftvolumen.

Loss of ammonia and change in slurry pH during application of slurry. Samples were stored in 200 ml boxes without air-filled headspace.

Dato *Date*	Gylle-spreder *Slurry-spreader*	Start pH *Start pH*	Slut pH *Final pH*	NH_4^+ forskel pct. *NH_4^+ difference %* Simpelt gns. (1) *Average (1)*		Mængdevægtet gns. (2) *Weighted average (2)*		NH_4^+ tab i pct. af udbragt NH_4^+ *NH_4^+ loss in % of NH_4^+ applied*	
				$\bar{X}$	S	$\bar{X}$	S	1*	2*
12.10.88	1	7.9	8.0	–0.006	0.001	–0.006	0.002	3	3
	2	7.9	8.0	–0.009	0.001	–0.006	0.001	4	4
14.12.88	1	7.4	7.6	–0.003	0.002	–0.003	0.002	1	1
17.02.89	2	7.6	7.9	–0.005	0.002	–0.005	0.003	2	2
10.05.89	2	7.7	7.7	–0.011	0.001			4	
13.06.89	2	7.8	7.9	–0.004	0.002	–0.005	0.002	2	2

* 1. Beregnet som et simplet gennemsnit. *Calculated as a simple average.*

* 2. Beregnet som et vægtet gennemsnit. *Calculated as weighted average.*

Det målte tab var lavt ved forsøget udført d. 13. juni 1989 selv om lufttemperaturen var høj (23.2°C). Dette skyldes sandsynligvis, at overførslen af gyllen til bægrene skete hurtigere end i de øvrige forsøg. En varieret henliggetid i opsamlingsbeholderen kan medføre en variation i størrelsen af ammoniaktabet. Direkte målinger af NH_3-fordampningen støtter denne antagelse (3), idet der med en meteorologisk massebalancemetode blev målt tab på mindre end 1 pct. af den udbragte gylle.

Besson et al. (1) undersøgte tabet af NH_4^+ ved differensmetoden i forsøg, hvor gyllen blev opsamlet på bakker og lå i 20 minutter før prøvetagning. Resultatet viste, at NH_3-tabet umiddelbart efter udbringning kan være betydeligt, hvis et tyndt lag gylle henligger på jordoverfladen kort tid. Det samme ses af undersøgelser af ammoni-

Tabel 5. Ammoniaktab og ændringer i gyllens pH ved udspredning og opbevaring af gylle. Gylleprøver opbevaret i 6 l opsamlingsbeholdere med 5.7 l luftvolume.

Loss of ammonia and change in slurry pH during application and storage of slurry. Samples were stored in 6 l containers with air-filled headspace (5.7 l).

Dato *Date*	Gylle-spreder *Slurry-spreader*	Start pH *Start pH*	Slut pH *Final pH*	NH_4^+ forskel pct. *NH_4^+ difference %* Simpelt gns. (1) *Average (1)*		Mængdevægtet gns. (2) *Weighted average (2)*		NH_4^+ tab i pct. af udbragt NH_4^+ *NH_4^+ loss in % of content of NH_4^+*	
				$\bar{X}$	S	$\bar{X}$	S	1*	2*
16.11.87	1	7.6	7.1	–0.12	0.011			40	
	2	7.6	9.9	–0.05	0.036			17	
08.12.87	1	7.9	7.3	–0.06	0.022			20	
	2	7.9	7.4	–0.06	0.015			20	
22.02.88	1	8.0	8.4	–0.03	0.006	–0.02	0.003	11	7
	2	8.0	8.4	–0.03	0.001	–0.02	0.001	7	7
	3	8.0	8.5	–0.03	0.002	–0.03	0.002	11	11
26.08.88	1	7.9	–	–0.03	0.007	–0.03	0.006	14	14
	2	7.9	–	–0.02	0.006	–0.03	0.004	9	14

* 1. Beregnet som et simplet gennemsnit. *Calculated as a simple average.*

2. Beregnet som et vægtet gennemsnit. *Calculated as weighted average.*

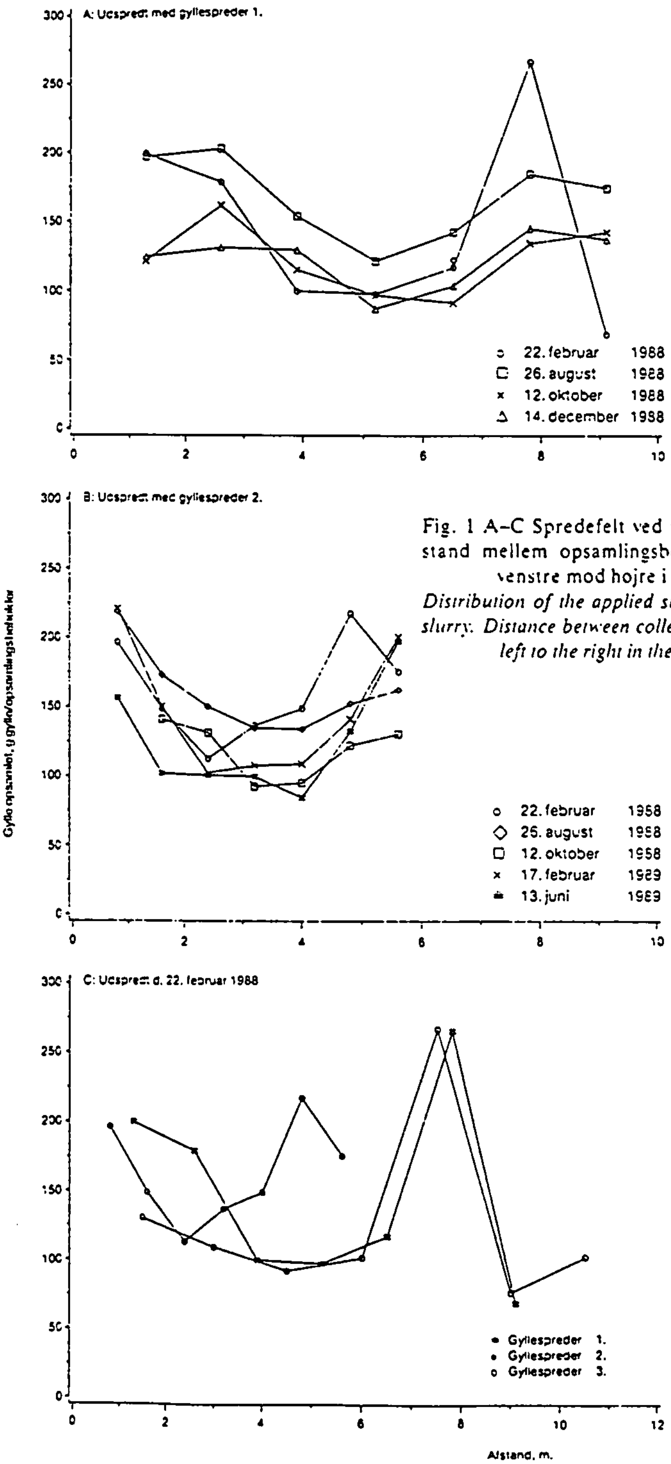

Fig. 1 A–C Spredefelt ved udsprojtning af gylle. Afstand mellem opsamlingsbeholderne er opmålt fra venstre mod hojre i korselsretningen.

Distribution of the applied slurry during application of slurry. Distance between collectors is measured from the left to the right in the driving direction.

akfordampningen fra gylle på jordoverfladen (2, 5), idet der er målt tabshastigheder på 12,1 kg NH_3-N/ha pr. time umiddelbart efter udbringning af gylle (3).

Gyllens pH påvirkes af NH_3-fordampning og af omsætning af organisk materiale i gyllen. I de forsøg, hvor gyllen blev opbevaret kort tid i køleskab, har omsætning næppe haft indflydelse på gyllens pH. Den målte stigning i gyllens pH i disse forsøg (tabel 4) må derfor antages at være forårsaget af en større fordampning af CO_2 end af NH_3 (6). I forsøgene udført i perioden 16. november 1987 – 26. august 1988 (tabel 5), er pH i de tre forsøg faldet og i fire forsøg steget. Dette kan skyldes såvel fordampning af CO_2 og NH_3 som omsætning af organisk materiale, idet gyllen i disse forsøg blev opbevaret i op til seks uger før analyse.

Fordeling af udspredt gylle

Med de tre gyllespredere blev gyllen spredt ujævnt på tværs af kørselsretningen. Gyllesprederne med centralt placeret spredeplade bragte mere gylle ud i siderne end centralt i spredefeltet (fig. 1A og 1B). En ujævn fordeling kan modvirkes, såfremt spredepladernes indstilling justeres.

Forskellen i spredefeltet mellem forsøgsdage skyldes forskelle i vindpåvirkning. Når vindretningen var vinkelret på kørselsretningen, blev spredefeltet påvirket ved vindhastigheder på 2 til 3 m/s (fig. 1A, 1B og 1C), uanset om gyllen blev udspredt med spredebom eller med central spredeplade.

Af de to gyllespredere med centralt placeret spredeplade var gyllesprederen med størst spredefelt mest følsom over for sidevind. Ved en vindhastighed på 5 m/s og vindretning på langs ad kørselsretning blev spredefeltet ikke påvirket. Spredefeltet fra gyllesprederen med spredebom blev også påvirket af sidevind.

Konklusion

Med de her anvendte gyllespredere var NH_3-fordampningen ved udspredningen af gylle relativt lille sammenholdt med de øvrige ammoniaktab ved husdyrgødningens håndtering. Resultaterne viser, at fordampningen er af samme størrelse, uanset om gyllen udbringes med gyllespreder med 6 eller 11 m spredebredde.

Fordeling af gylle var meget ujævn ved udspredning af gylle med tre forskellige gyllespredere. Dels varierede mængden af gylle udbragt på tværs af kørselsretningen, dels var spredefeltet meget følsomt over for sidevind. Gyllespredere med bedre fordeling og mindre vindfølsomhed bør udvikles. Placering af gyllen tæt ved jordoverfladen vil bidrage til, at vindeffekten begrænses.

NH_3-tabet umiddelbart efter udbringning kan være betydeligt. Ved udbringning af gylle i vækstsæsonen kan udlægning af gylle under vegetationen medvirke til en nedsat NH_3-fordampning og bevirke en mindre vindfølsom og mere ensartet fordeling af gylle på tværs af kørselsretningen. Direkte nedfældning af gylle vil eliminere såvel udbringningstabet som det tab, der finder sted mellem udspredning og nedbringning.

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Manuskript modtaget den 1. december 1989.

IX.

Statens Planteavlsforsøg
Landbrugscentret
Afdeling for Landbrugsplanternes Ernæring, Askov
6600 Vejen

Beretning nr. 2001

Fordampning af ammoniak fra udbragt gødning. Metode og ammoniaktab fra urea og urea-ammonium-nitrat

Volatilization of ammonia from fertilizers and manure. Methodology and loss of ammonia from urea and urea-ammonium-nitrate

BENT T. CHRISTENSEN og SVEN G. SOMMER

Resumé

Til bestemmelse af fordampningstabet af ammoniak fra udbragt handels- og husdyrgødning blev opbygget et vindtunnelsystem bestående af fire tunnelenheder, en dataopsamlingsenhed og et system af gasvaskeflasker til opsamling af ammoniak i luft. Vindtunnelsystemet muliggør en direkte bestemmelse af ammoniakindholdet i den luft, der forlader det gødede areal. Desuden kan vindhastighed og nedbør styres. Med systemet kan der i hvert forsøg undersøges op til fire behandlinger samtidigt.

Hver tunnelenhed består af en omvendt U-formet polycarbonatplade, der dækker forsøgsarealet (0,5 × 2 m), og et 2,3 m langt metalrør monteret med en regulerbar ventilator, der skaber en luftstrøm hen over forsøgsarealet. Hastigheden af luftstrømmen gennem metalrøret, lufttemperaturen, og jordtemperaturen (2 cm dybde) under polycarbonattunnelen registreres hver time. Før luftstrømmen forlader metalrøret, indsamles delprøver af luftstrømmen. Luften ledes gennem en gasvaskeflaske med en fosforsyreopløsning, som binder ammoniakken i luften. Et programmerbart styresystem tilkoblet magnetventiler skifter automatisk mellem fire gasvaskeflasker pr. tunnelenhed. Ammoniakindholdet i gasvaskeflaskerne bestemmes efterfølgende ved en Berthelot reaktion.

Den gennemsnitlige genfindelse af ammoniak fordampet fra gylle blev i fire forsøg bestemt til 74 pct. (CV, 9,7 pct.). De efterfølgende bestemmelser af tabet af ammoniak korrigeres med faktoren 100/74 for at beregne det totale fordampningstab. Den i tunnelen målte lufttemperatur var i overensstemmelse med temperaturdata fra en nærliggende klimastation (1,8 m's højde).

Tre gange i perioden 5. maj – 23. juni 1987 og fire gange i perioden 11. februar – 8. marts 1988 blev der gennemført undersøgelser af ammoniaktabet fra overfladeudbragt urea. Undersøgelserne blev foretaget i rug og hvede samt græs. Flydende urea-ammonium-nitrat blev medtaget i to forsøg. I alt blev undersøgt 20 behandlinger af hver seks døgns varighed.

Tabet af ammoniak fra urea over seks døgn var 20–30 pct. i sommerperioden, mens det tilsvarende tab i vinterperioden var 3–10 pct. Tabet fra urea-ammonium-nitrat var mindre end tabet fra urea. Såfremt udbringningen af urea skete under tørre forhold, hæmmedes fordampningen i det første døgn efter udbringningen sammenlignet med udbringning under mere fugtige forhold. Vanding med 5 til 10 mm reducerede fordampning, men bragte den ikke til ophør.

Nøgleord: Ammoniakfordampning, vindtunnelsystem, urea, urea-ammonium-nitrat, vanding, atmosfærisk ammoniakindhold, rug, hvede, slætgræs.

Summary

A wind tunnel system was constructed in order to measure the ammonia volatilization loss from mineral fertilizers and animal manure. The system consists of four wind tunnels, a data monitoring unit and a gas trapping unit. The concentration of ammonia in the air leaving the fertilized plot is measured directly, and wind speed and precipitation can be controlled. Four treatments may be examined simultaneously.

The wind tunnel unit consists of an inverted U-shaped tunnel made from transparent polycarbonate and covering the experimental area (0.5 × 2 m), and a circular steel duct housing an electrically powered fan. The fan draws an airstream across the experimental area and is controlled to produce different wind speeds. The steel duct is 2.3 m long and has a diameter of 0.4 m. The steel duct is equipped with a vane anemometer. Air and soil (2 cm depth) temperatures, and the wind speed in the duct are recorded every hour.

The air stream leaving the steel duct is sampled at 6 different points by using a diaphragm suction pump (5 l per min). The air is drawn through a 100 ml absorption flask fitted with a sintered gas distribution tube and containing 50 ml of 0.005 M orthophosphoric acid. The ammonia is trapped in the acid and subsequently determined in the laboratory by a Berthelot reaction.

At preselected intervals, a programable magnetic valve control automatically switch among the four flasks of each tunnel unit.

Mean recovery of ammonia volatilized from animal slurry was in four experiments found to be 74% (CV 9.7%). Results obtained by the wind tunnel system is corrected by the factor 100/74 in order to correct for recovery percentages. The air temperature under the transparent tunnel was in accordance with the temperatures measured in a climatic station nearby.

The ammonia loss from surface-applied urea was determined in three experiments during 5 May – 23 June 1987 and in four experiments during 11 February – 8 March 1988. Liquid urea-ammonium-nitrate was included in two experiments. The crops were winterrye and winter wheat, and grass cut for silage in one experiment. Totally, 20 treatments were included in the study. The ammonia loss was measured over a period of six days.

The volatilization loss of ammonia from urea was 20–30% during the summer period and 3–10% during winter. The loss from ureaammoniumnitrate was lower than that from urea. When the application of urea took place under dry conditions, the ammonia volatilization loss during the first day was lower than that found under more humid conditions. Irrigation treatments with 5–10 mm reduced the volatilization loss.

Key words: Ammonia volatilization, wind tunnel system, urea, urea-ammonium-nitrate, irrigation, atmospheric ammonia concentration, winterrye, winterwheat, cut grass.

Indledning

I NPO-redegørelsen (26) skønnes ammoniakfordampningen på landsplan at være omkring 130.000 tons NH_3-N pr. år. Mere end 75 pct. af tabet tilskrives håndtering af husdyrgødning, mens der antageligt fordamper væsentlig mindre mængder ammoniak fra ammoniak/ammonium-holdige handelsgødninger. *Buijsmann et al.* (3) og *Meeus – Verdinne et al.* (23) har i tilsvarende opgørelser for Holland og Belgien fundet samme tendenser.

Ammoniaktab fra håndtering af husdyrgødning kan ske 1) fra stalde, 2) fra gødningsoplag, 3) ved udspredning af gødning og 4) fra gødning udbragt på jordoverfladen. Den her beskrevne metode sigter alene på bestemmelse af ammoniaktab fra udbragt gødning.

Et større kendskab til ammoniaktabets størrelse og til mulighederne for at reducere dette kan øge udnyttelsen af den udbragte gødning. Samtidig kan den samlede reelle N-tilførsel til afgrøderne beregnes. Afsætning af ammoniak kan have en uønsket effekt på næringssaltbegrænsede natursystemer, hvorfor en reduktion i ammoniakfordampningen både vil forbedre udnyttelsen af gødning og have en positiv effekt på det omgivende miljø.

Ammoniakfordampning fra husdyrgødning er tidligere undersøgt i udbytteforsøg (12, 13, 17, 18, 24), ved bestemmelse af ammoniaktabet fra gødning anbragt udendørs på bakker (9, 20), og i laboratoriet ved analyse for indhold af ammoniak i luft, der har passeret gennem flasker indeholdende gødningsprøver (14). Disse undersøgelser viste, at fordampningen af ammoniak kan begrænses ved udbringning af husdyrgødning i koldt og fugtigt vejr, ved direkte nedfældning eller ved nedbringning umiddelbart efter udbringningen.

Når ammoniakfordampningen bestemmes med indirekte metoder, kan resultaterne påvirkes af denitrifikation, N-mineralisering/immobilisering og udvaskning. I bakkeforsøgene indgår ikke vekselvirkning mellem jord og gødning, og resultater fra laboratorieforsøg kan ikke umiddelbart overføres til markforhold. En sammenligning af resultater fra ammoniakfordampning bestemt ved forskellige metoder har vist, at ammoniaktab bestemt ved indirekte målinger synes at være dobbelt så store som tab bestemt ved direkte målinger (4).

På denne baggrund påbegyndtes i 1985 opbygningen af et vindtunnelsystem til direkte bestemmelse af ammoniakindholdet i luft, der har passeret et gødet areal. Metoden skulle give mulighed for, 1) at kontrollere lufthastigheden i et interval svarende til naturligt forekommende vindhastigheder, 2) at kunne styre nedbøren (vanding), og 3) at kunne medtage gentagelser under identiske klimaforhold. Endelig skulle metoden give mulighed for, at et større antal undersøgelser kunne gennemføres uden brug af store forsøgsarealer eller stor ressourceindsats.

Nærværende beretning beskriver det opbyggede vindtunnelsystem samt en afprøvning af systemet. Endvidere præsenteres undersøgelser over ammoniakfordampningen fra overfladeudbragt urea og flydende urea-ammonium-nitrat (UAN). Efterfølgende beretninger vil præsentere undersøgelser af ammoniakfordampningen fra husdyrgødning.

Materialer og metoder

Fig. 1 viser vindtunnelsystemet under måling i marken, og fig. 2 giver en skematisk fremstilling af systemets opbygning. Systemet består af fire vindtunnelenheder, en dataopsamlingsenhed og et system af gasvaskeflasker til opsamling af ammoniak i luft. En skurvogn forsynet med 380 V/220 V tjener som feltlaboratorium og huser en del af instrumenteringen.

Vindtunnelenhed

Udformningen af vindtunnelenheden følger stort set *Lockyer's* (21) beskrivelse. Fig. 3 viser et tværsnit af den her anvendte tunnelenhed.

Vindtunnelen består af en omvendt U-formet polycarbonatplade, der holdes i facon af en metalramme med en 5 cm kant. Kanten kan presses ned i den underliggende jord. På det højeste sted er tunnelen 50 cm, og den afgrænser et forsøgsareal på 0,5 × 2 m. Inden for metalrammen er placeret en 0,5 × 2 m metalramme ligeledes med en kant på 5 cm. Den indre ramme afgrænser forsøgsarealet, der behandles inden polycarbonattunnelen placeres. Rammen sikrer desuden, at flydende gødninger selv ved store doseringer holdes inden for forsøgsarealet.

I forlængelse af polycarbonattunnelen er placeret et 2,3 m langt metalrør med en indre diameter på 40,2 cm. Overgangen mellem de to tunneldele udgøres af et tragtformet metalrør med en 5 cm kant, der kan forankres i jorden.

I modsatte ende af tilslutningen til polycarbonattunnelen er metalrøret monteret med en ventilator, hvis hastighed kan reguleres i området 4 til 9 m pr. sek. (3-faset axialmotor). Denne motortype er senere udskiftet med en jævnstrømsmotor, der tillader vindhastigheder ned til ca. 1 m/s. Med ventilatoren skabes en vindstrøm hen over forsøgsarealet.

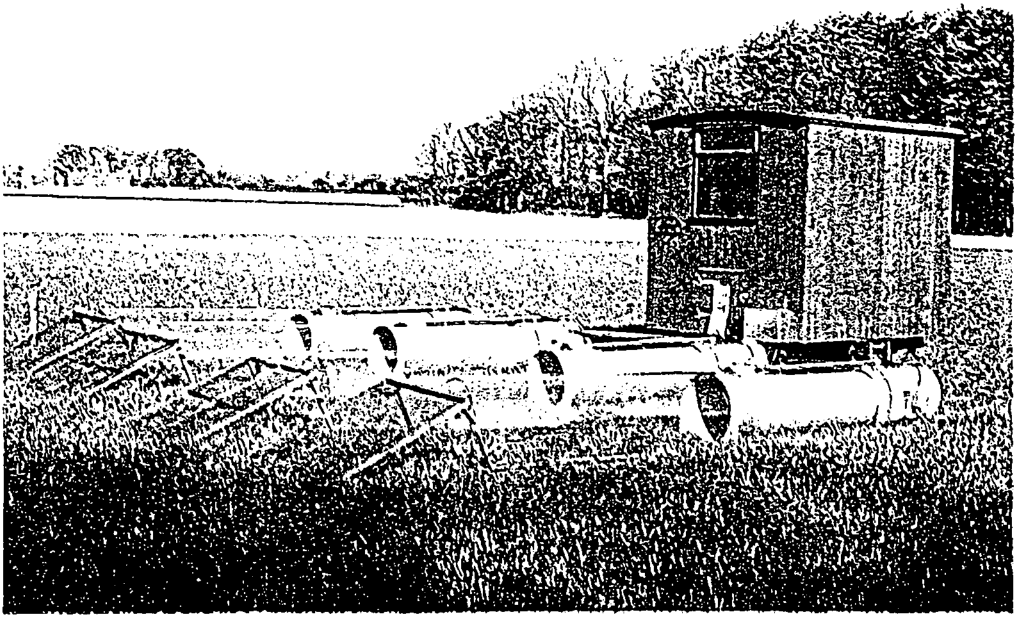

Fig. 1. Vindtunnelsystemet opstillet til måling af NH_3-fordampning fra urea udbragt d. 5. maj 1987 til vinterhvede (Askov).
The wind tunnel system in position for measuring the ammonia loss from urea applied to winter wheat on the 5 May 1987 (Askov).

Dataopsamlingsenhed
Metalrøret er udstyret med et turbineanemometer, der anvendes ved indstilling til ønsket vindhastighed, og som efterfølgende aflæses for at følge udviklingen i luftstrømmens hastighed gennem tunnelen. Signalerne fra anemometeret ledes til signalkonverteringsenhed (EDRA 5, Airflow Developments) og derfra videre til datalogger (Minilogger MLX-20, A. D. Data Systems). Luftstrømmens hastighed aflæses hver time. Værdier for jord- og lufttemperatur (Comark Thermocouple) aflæses med tilsvarende intervaller. Jordtemperaturen bestemmes i 2 cm dybde under polycarbonattunnelen, og lufttemperaturen måles i metalrøret.

De opsamlede data overføres automatisk til hulstrimmel (GNT-3401 Perforator, GNT Automatic).

Nedbør (vanding)
Idet vindtunnelen afskærmer forsøgsarealet mod nedbør, kan denne indgå som forsøgsvariabel. Nedbør simuleres ved vanding med 5 mm i en eller flere omgange uden flytning af vindtunnel. Vandingsaggregatet består af et 2,5 m langt rør, der fungerer som håndtag, og som leder vandingsvandet frem til et tværgående rør, hvis længde svarer til bredden af forsøgsarealet. Det tværgående rør er på undersiden perforeret, således at vandingsvandet fordeles jævnt på tværs af forsøgsarealet. Vandingsaggregatet er via en plastslange fra håndtaget tilsluttet et 5 l reservoir. Ved at føre vandingsaggregatet frem og tilbage i forsøgsarealets længde tildeles 5 mm nedbør pr. vanding.

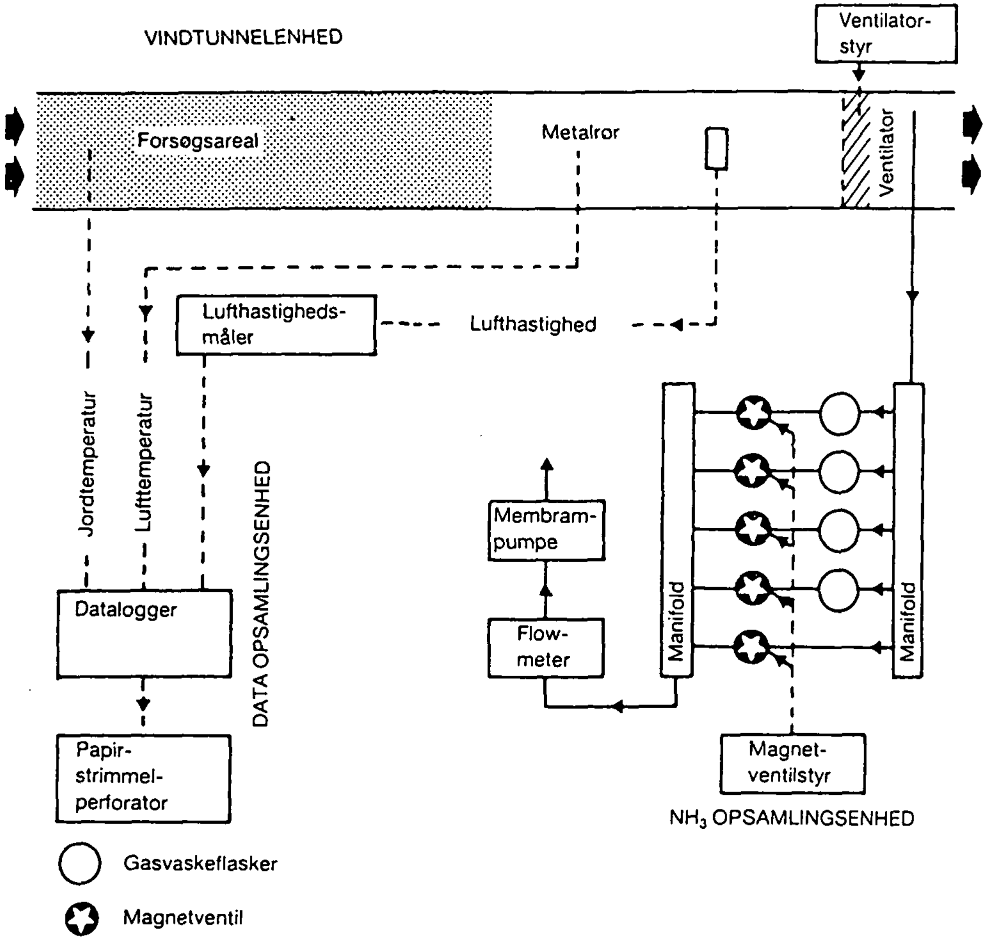

Fig. 2. Skematisk fremstilling af det anvendte vindtunnelsystem. Der benyttes fire vindtunnelenheder til hvert forsøg.
Outline of the wind tunnel system. Four tunnels were used for each experiment.

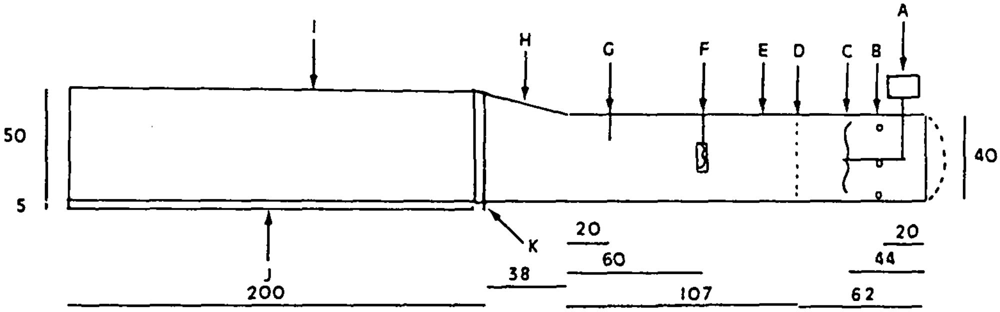

Fig. 3. Tværsnit af en vindtunnelenhed med dimensioner angivet i cm.
A, motor; B, udtag for luft til ammoniakanalyse; C, ventilator; D, net; E, metalrør; F, lufthastighedsmåler; G, temperaturføler; H, metaltragt; I, tunnel af polycarbonat; J, metalramme; K, kant på undersiden af metalrøret.
Cross section of one wind tunnel unit with dimensions given in cm.
A, motor; B, air sampling points; C, fan; D, steel-net; E, steel duct; F, vane-anemometer head; G, temperaturesensor; H, steel-funnel; I, tunnel of polycarbonate; J, metal frame; K, spade-edge.

Ammoniakopsamling

Efter ventilatoren, men inden luftstrømmen forlader metalrøret, udtages seks steder en delprøve af luften med en membranpumpe (ASF 7010 Z). Pumpen er placeret i skurvognen og arbejder med et flow på 5 l pr. min. Flowet kontrolleres med et Dweyer flowmeter (RMA-21-SSV). Fra de seks indsamlingssteder ledes luften via PVC slanger til en manifold og herfra til en 100 ml gasvaskeflaske indeholdende 50 ml 0,005 M orthofosforsyre. Gasvaskeflaskerne er placeret i kasser nær metalrøret, således at slangelængden fra indsamlingsstederne til gasvaskeflasken er ca. 2 m. Til hver vindtunnelenhed er knyttet fire flasker. Ved hjælp af magnetventiler og et programmerbart styresystem (Martonair) kan der på forud fastsatte tidspunkter skiftes mellem de fire flasker.

Indholdet af ammonium i fosforsyreopløsningen bestemmes spektrofotometrisk ved en Berthelot reaktion (salicylat-dichloroisocyanat, ni-

Tabel 1. Oversigt over gennemførte forsøg med urea og urea ammonium nitrat.
Summary of experiments with urea and urea-ammonium-nitrate.

Forsøgsperiode *Experimental period*	Tilført gødning *Fertilizer applied*		Tidspunkt for vanding vandingsmængde *Time for irrigation and amount of water*			Jordtype og afgrøde (cm plante højde) *Soil type and crop (cm plant height)*
	Type *Type*	Mængde *Amount* g N/m²	0 timer *hours* mm	24 timer *hours* mm	48 timer *hours* mm	
5.–11. maj 87	urea	10,12	0	0	0	JB 5
	urea	10,12	0	0	0	Vinterhvede
	urea	10,12	0	0	0	*Winterwheat*
						(30 cm)
12.–18. maj 87	urea	10,12	0	10	0	JB 5
	urea	10,12	0	10	0	Vinterhvede
	urea	10,12	0	10	0	*Winterwheat*
						(35 cm)
17.–23. juni 87	urea	15,18	0	0	0	JB 5
	urea	15,18	5	5	0	Græs efter slæt
	urea	15,18	5	5	5	*Cut grass*
11.–17. feb. 88	urea	10,12	0	0	0	JB 1
	urea	10,12	0	0	0	Vinterrug
	urea	10,12	0	0	0	*Winterrye*
						(<10 cm)
17.–23. feb. 88	urea	10,12	0	0	0	JB 1
	urea	10,12	5	5	0	Vinterrug
						Winterrye
						(<10 cm)
24. feb.– 1. marts 88	urea	10,12	5	0	0	JB 1
	UAN*	3,76	5	0	0	Vinterrug
	UAN	3,76	5	5	0	*Winterrye*
						(<10 cm)
2.–8. marts 88	urea	10,12	5	5	0	JB 1
	UAN	3,42	5	5	0	Vinterrug
	UAN	3,42	5	0	0	*Winterrye*
						(<15 cm)

* UAN = urea ammonium nitrat opløsning (30 pct. N)
urea-ammonium-nitrate solution (30 p.c. N)

troprussid katalysator). Metoden er beskrevet af *Crooke* og *Simpson* (5), *Krom* (16) og *Searle* (28).

Total-N i gødning bestemmes ved Kjeldahl nedbrydning og destillation/titrering (Kjeltec Auto 1030 Analyzer). Ammonium/ammoniak-indholdet i gødning bestemmes ved makrodestillation med MgO og $CuSO_4$ og efterfølgende titrering.

Beregning af ammoniaktab (vindtunnelsystem)
Fordampningstabet af ammoniak beregnes på grundlag af luftmængden, der har passeret forsøgsarealet i et givent tidsrum (metalrørets tværsnitsareal × de aflæste lufthastigheder × tidsrum). Luftmængden for et givent tidsrum (fx 6 timer) multipliceres med koncentrationen af ammoniak i luften i samme tidsrum efter at ammoniakkoncentrationen i luften fra den ubehandlede reference-vindtunnel er trukket fra. Herved fås den fordampede ammoniakmængde. Denne sammenholdes med forsøgsarealets størrelse (1 m^2) og den udbragte gødningsmængde. Endelig korrigeres for genfindelsesprocenten (se senere).

Kalibrering og genfindelsesprocent
Reproducerbarheden af resultater opnået med vindtunnelsystemet og genfindelsen af ammoniak blev undersøgt ved at placere gylleprøver på 3 til 5 kg på plastfolie eller i PVC bakker under polycarbonattunnelen. Ved hvert forsøg indgik en tunnel som reference (ubehandlet). Efter placering af gylleprøverne, blev repræsentative delprøver straks udtaget til analyse for indholdet af ammonium/ammoniak. Umiddelbart herefter blev vindtunnelsystemet sat igang. Undersøgelserne forløb over 24 eller 48 timer, hvorefter der atter blev udtaget gylleprøver til analyse. Prøverne blev opbevaret lufttæt ved 4°C indtil analyse.

Ammoniaktabet beregnet som differencen mellem ammoniak/ammonium-indholdet i gyllen før og efter forsøget blev sammenholdt med tabet bestemt med vindtunnelsystemet. Genfindelsesprocenten er beregnet som tabet bestemt ved vindtunnelsystem divideret med tabet bestemt ved differencemåling og multipliceret med 100.

Ammoniaktab fra urea og urea-ammonium-nitrat
Tabel 1 giver en oversigt over de gennemførte forsøg til belysning af ammoniaktabet fra urea og urea-ammonium-nitrat. I hvert forsøg indgik tre behandlinger, mens en vindtunnel blev medtaget som ubehandlet reference. Ved forsøget påbegyndt d. 17. februar 1988 medtoges kun to behandlinger. Forsøgene blev i 1987 gennemført ved Askov forsøgsstation i vinterhvede (maj) og efter græsslæt (juni). I 1988 gennemførtes forsøgene ved Lundgård forsøgsstation i vinterrug.

Den faste gødning urea blev udstrøet på jordoverfladen, mens den vandige opløsning af urea-ammoniumnitrat blev tilført med vandkande. De første to døgn efter gødningstilførslen blev ammoniakfordampningen bestemt over seks timers intervaller, mens der de følgende fire døgn blev anvendt 24 timers intervaller.

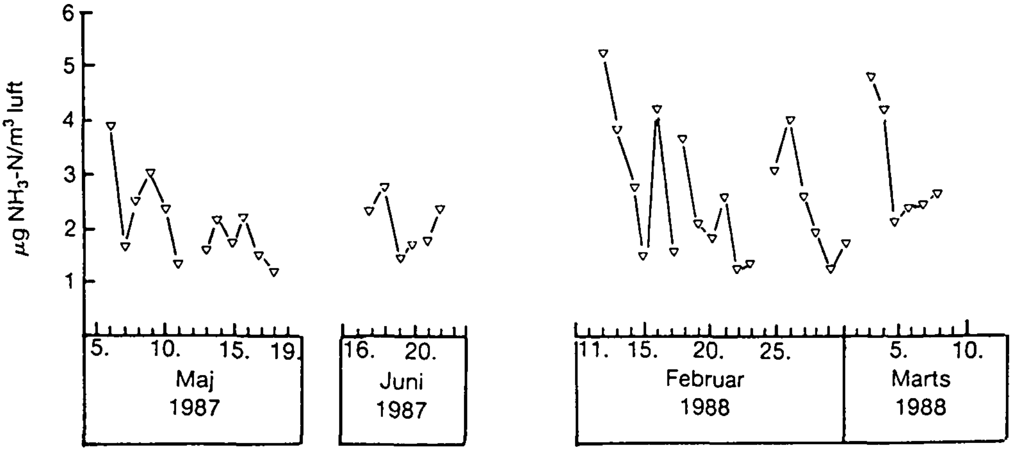

Fig. 4. Ammoniak indholdet i luft fra ubehandlet referencetunnel.
The ammonia content in air leaving the untreated reference tunnel.

Resultater og diskussion

Fig. 4 viser ammoniakindholdet i luft, der har passeret det ubehandlede forsøgsareal (referencetunnel). Indholdet varierede mellem 1 og 5 μg NH_3-N pr. m^3 luft og udviste ikke systematiske forskelle mellem de forskellige forsøgsperioder. Der fandtes en tendens til højere indhold af ammoniak i luften i begyndelsen af de enkelte forsøgsperioder. Den målte ammoniakkoncentration i luften fra det ubehandlede areal (baggrundsværdier) er i overensstemmelse med værdier rapporteret af *Ferm et al.* (7), *Jørgensen* (15) og *Söderlund* og *Svensson* (30).

Luft- og jordtemperaturerne afveg ikke væsentligt mellem de fire vindtunneler (fig. 5). Lufttemperaturen bestemt i vindtunnelerne var i overensstemmelse med lufttemperaturen målt ved en nærliggende klimastation (1,8 m højde). Med de her valgte lufthastigheder er luftskiftet i vindtunnelerne 30–40 gange pr. min. *Ryden* og *Lockyer* (27) fandt ved luftskifte mellem 4 og 17 gange pr. min. samme lufttemperatur i vindtunnel og udenfor.

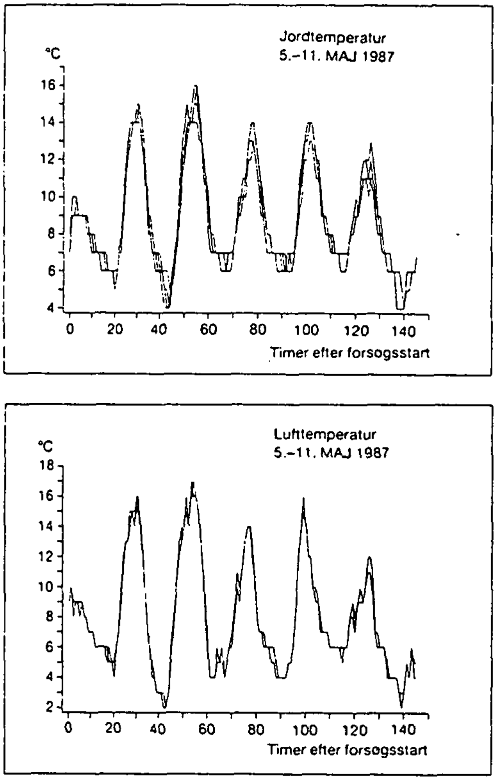

Fig. 5. Jordtemperatur (øverst) og lufttemperatur (nederst) målt i de fire vindtunneler i perioden 5.-11. maj 1987.

Soil (upper part) and air (lower part) temperature measured in the 4 wind tunnels during 5-11 maj 1987.

Kalibrering og genfindelsesprocent

Resultater fra sammenligningen af ammoniakfordampningen fra gylle (udlagt i vindtunnel på plastfolie eller PVC bakker) bestemt med vindtunnelsystemet og ved analyse af ammoniakindholdet i gyllen før og efter forsøgsperioden er vist i tabel 2. Når tabet bestemt med vindtunnelsystemet udtrykkes som procent af tabet bestemt ved analyse af gylleprøver (differensmetoden) fås genfindelsesprocenten. Denne varierede i de 8 forsøg mellem 66 og 85 pct. (gennemsnit 74 pct., variationskoefficient CV 9,7 pct.). Idet det antages, at tabet bestemt ved differensmetoden angiver det absolutte ammoniaktab, er de efterfølgende bestemmelser af ammoniaktab med vindtunnelsystemet korrigeret med faktoren 100/74.

Ryden og *Lockyer* (27) har sammenlignet resultater for ammoniakfordampning fra urea bestemt ved en mikrometerorologisk massebalancemetode og ved anvendelse af et vindtunnelsystem. I perioder uden nedbør, og når lufthastigheden i vindtunnelerne løbende justeredes til den omgivende vindhastighed, blev der med de to metoder fundet overensstemmende ammoniaktab.

Ammoniakfordampning fra urea og urea-ammoniumnitrat

Middel-, maksimum- og minimumsværdier for luft og jordtemperatur i de forskellige forsøgsperioder er angivet i tabel 3. Desuden er medtaget den forud indstillede lufthastighed og variationer (minimum- og maksimum-værdier) for de efterfølgende aflæste timeværdier. Der registreredes nogen variation i lufthastigheden i løbet af forsøgsperioderne. Dette skyldes, at der med de 3-fasede axialmotorer ikke overførtes tilstrækkelig moment til ventilatorerne ved lave omdrejningstal, hvorfor lufthastigheden i vindtunnelen blev påvirket af den omgivende vindhastighed, især når den var høj i forhold til lufthastigheden i vindtunnelen. Motorerne er derfor senere udskiftet med 220 V jævnstrømsmotorer, hvis hastighedsregulering sikrer, at der overføres fuldt moment ved alle omdrejningstal.

Tabel 2. Fordampningstab af ammoniak fra gylle bestemt med vindtunnelsystem og ved analyse af ammoniakindhold i delprøve udtaget før og efter forsøgsperiode (differensmetode). Gyllen blev udlagt i PVC bakker eller på plastfolie. Genfindelsesprocenten er tab bestemt ved vindtunnelsystem udtrykt som procent af tab ved differensmetode.
Volatilization loss of ammonia from animal slurry determined with the wind tunnel system and by analysing for ammonia content in subsamples collected before and after the experimental period (difference method). The slurry was exposed on PVC trays or foil. Recovery is the loss determined with the wind tunnel system expressed as a percentage of the loss determined by the difference method.

Forsøgsperiode, time *Experimental period, hours*	Ammoniaktab, g N *Ammonia loss, g N*		Genfindelse, pct. *Recovery, %*
	Vindtunnel *Wind tunnel*	Differensmetode *Difference method*	
24	2,02	2,37	85
24	2,19	2,85	77
24	2,35	2,85	82
48	3,01	4,02	75
48	2,94	4,06	72
48	5,95	8,89	67
48	5,52	8,37	66
48	5,97	8,93	67
Gns. *Mean*			74 (CV 9,7 pct.)

Tabel 3. Middelværdier for luft- og jordtemperaturer samt indstillet lufthastighed (aflæst maksimum- og minimumværdier i parentes).
Average air and soil temperature during the experiment and humidity of the surface before beginning of an experiment and adjusted wind speed (in brackets readings during experiments).

Forsøgsperiode *Experimental period*	Tunnel nr. *Tunnel no.*	Luft temp. °C *Air temp. °C*			Jord temp. °C *Soil temp. °C*			Lufthastighed m/sek.[1] *Wind speed* m/sec.	Jordens fugtighed ved periodens begyndelse *Soil humidity at the start of the period*
		middel *mean*	maks. *max.*	min. *min.*	middel *mean*	maks. *max.*	min. *min.*		
5.–11. maj 87	1	8,1	17,0	2,0	9,0	16,0	4,0	4,5	Tør[2]
	2	7,9	16,0	2,0	8,7	15,0	4,0	(3,6-5,0)	*Dry*
	3	8,1	17,0	2,0	8,8	14,0	4,0		
12.–18. maj 87	1	6,5	12,0	2,0	6,9	10,0	5,0	4,5	Fugtig
	2	6,4	12,0	2,0	7,2	11,0	5,0	(3,8–4,9)	*Humid*
	3	6,5	12,0	3,0	7,1	10,0	5,0		
17.–23. juni 87	1	8,5	14,0	3,0	9.1	12,0	7,0	4,3	Tør
	2	8,6	14,0	3,0	9,5	13,0	7,0	(2,8–4,9)	*Dry*
	3	8,5	14,0	3,0	9,3	13,0	7,0		
11.–17. feb. 87		2,8[3]	5	0,8				6,4 (4,8–7,4)	Fugtig *Humid*
17.–23. feb. 88		2,9	4,9	0,2				6,5 (5,3–6,9)	Fugtig *Humid*
24. feb.–1. marts 88		0,0	2,7	1,6				5,5 (4,8–6,7)	Fugtig *Humid*
2.–8. marts 88		1,3	2,9	1,0				5,5 (3,7–6,2)	Fugtig *Humid*

[1] Indstillet lufthastighed i metalrørstunnel. Min. og maks. hastighed registreret i måleperioden anført i parentes.
[2] Fugtig, hvis det har regnet samme dag eller dagen før ellers tør.
[3] For målinger efter 11. feb. 1988 er anvendt temperaturdata fra nærliggende engelsk vejrhytte (1,8 m højde).

På grund af svigt af datalogger er lufttemperaturen for forsøgene gennemført februar/marts 1988 taget fra klimastation. Som nævnt ovenfor blev der ved de her benyttede lufthastigheder fundet god overensstemmelse mellem lufttemperaturer målt i vindtunneler og ved klimastation.

Standard-afvigelsen på værdier fra ammoniakfordampning fra urea var 20–30 pct. af middelværdien (fig. 6). Variationen antages primært at hidrøre fra forskelle i hydrolysehastigheden af urea som følge af forskelle i krystallernes kontakt med jord og planter, og fra forskelle i fugtighedsforhold.

I de første 12 timer efter forsøgsstart var ammoniakfordampningen ofte lav, hvorfor ammoniakindholdet i luften fra de gødede arealer kun afveg lidt fra indholdet i luften fra den ubehandlede tunnel. Derfor kan variationen på disse målinger være betydelig. I vinterperioden fandtes ofte lave indhold af ammoniak i luften.

Alt andet lige er ammoniakfordampningen fra hydrolyseret urea en funktion af pH. Fordampningen begynder, når ureakrystallerne i tilstedeværelse af vand hydrolyseres til NH_3 og CO_2, og der dannes NH_4 og HCO_3. Dette medfører, at pH stiger. Ved fordampningen afgives imidlertid protoner, og pH falder, hvorved CO_2 fordamper under forbrug af de frigjorte protoner. I denne fase sker der en samtidig fordampning af CO_2 og NH_3 med det resultat, at pH holdes konstant. Når den dannede CO_2 er fordampet, vil den fortsatte fordampning af NH_3 medføre faldende pH. Slutteligt bliver pH så lavt i jordoverfladen, at fordampningen af ammoniak stort set ophører (14, 29).

Fig. 6A viser et sådant forløb. Fordampningshastigheden er lav i starten, men stiger efter et døgn for derefter at være konstant. Efter 5 døgn ses et begyndende fald i fordampningen.

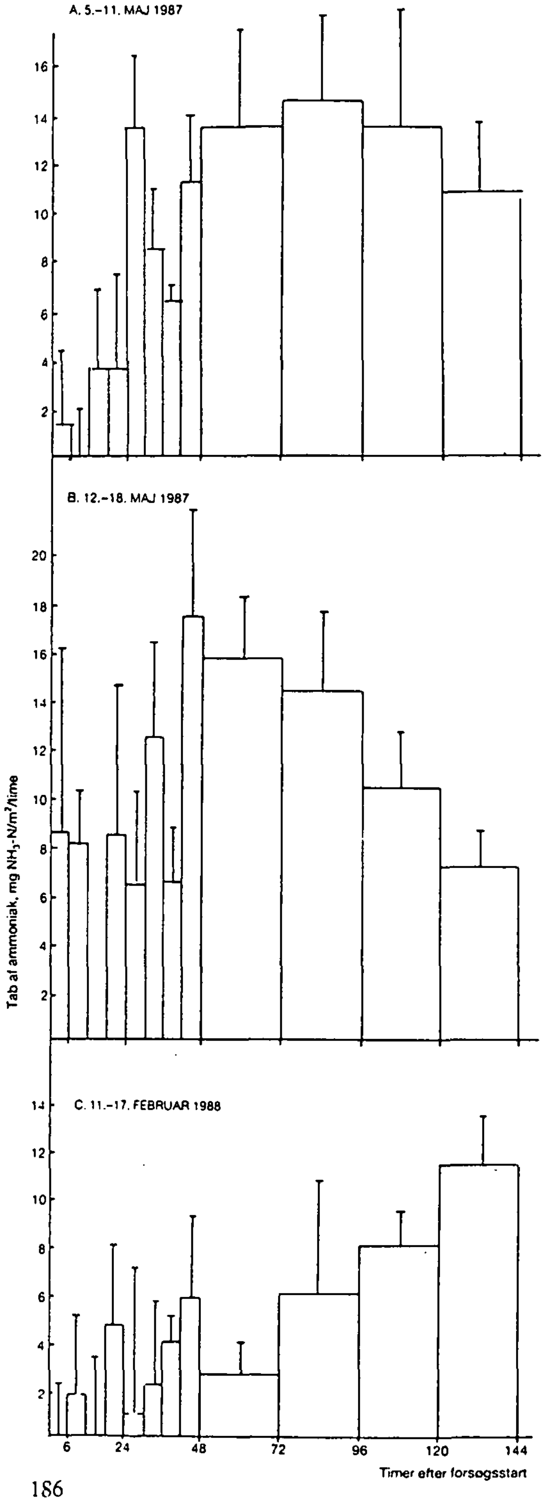

Fig. 6. Fordampning af ammoniak fra urea (10 g N/m²). I de tre undersøgelser blev urea udbragt: A. d. 5. maj 1987 (kl. 10.15) på 30 cm høj vinterhvede; B. d. 12. maj 1987 (kl. 10.15) på 35 cm høj vinterhvede; og C. d. 11. februar 1988 (kl. 13.30) på <10 cm høj vinterrug. Forsøget påbegyndt d. 12. maj blev vandet med 10 mm efter 24 timer. Lodrette pinde angiver 1 s.d. (n = 3).
Volatilization of ammonia from urea (10 g N/m²) applied on A. 5 May 1987 (10,15) to winterwheat (plant height 30 cm). B. 12 May 1987 (10,15) to winterwheat (plant height 35 cm) and C. 11 February 1988 (13,30) to winterrye (plant height <10 cm). The experiment initiated on 12 May was irrigated with 10 mm after 24 hours. Bars indicate 1 s.d. (n = 3).

Når urea blev udbragt på tør jord og ikke blev udsat for nedbør (fig. 6A), var ammoniak-fordampningen lav ved forsøgets start, sammenholdt med forsøg under lignende temperaturforhold, men hvor jord og planter ved forsøgets start var fugtige (fig. 6B). Tilsvarende sammenhæng mellem overfladens fugtighed og ammoniak-fordampning fra urea er vist af *Milchunas et al.* (25) og *Hoult* og *McGarity* (11). *McInnes et al.* (22) fandt, at den begrænsede ammoniak-fordampning fra tør jord skyldes en hæmning af hydrolysen af urea. I forsøget d. 5. maj (fig. 6A) var luftfugtigheden høj i døgnene efter forsøgets start, hvilket formentlig har igangsat hydrolysen af urea og dermed også fordampningen af ammoniak.

Hydrolysen af urea og fordampningen af ammoniak påvirkes også af temperatur (10). Den største fordampningshastighed optræder derfor på et senere tidspunkt ved udbringning om vinteren end ved udbringning om sommeren. Ligeledes vil fordampningen begynde at aftage på et senere tidspunkt efter udbringning om vinteren sammenlignet med sommerudbringning (fig. 6C).

I nogle forsøg (fig. 6A og 6C) var der en tendens til døgnvariation i ammoniakfordampningen, idet de største fordampningshastigheder registreredes midt på dagen, hvor temperaturen var betydeligt højere end om natten. Om vinteren var fordampningen generelt lav (fig. 7 og 8). I forsøget påbegyndt d. 2. marts 1988 kunne der ikke registreres fordampning af ammoniak fra urea og UAN.

Vanding af arealer tilført urea kan fremme hydrolysen af urea, såfremt lokaliteten er tør. Derved kan fordampningen af ammoniak også fremmes i forhold til uvandede arealer. I denne undersøgelse blev de fleste forsøg gennemført under forhold, hvor jord og luft var fugtige ved forsøgsstart (tabel 3). Vanding ved forsøgsstart (fig. 7 og

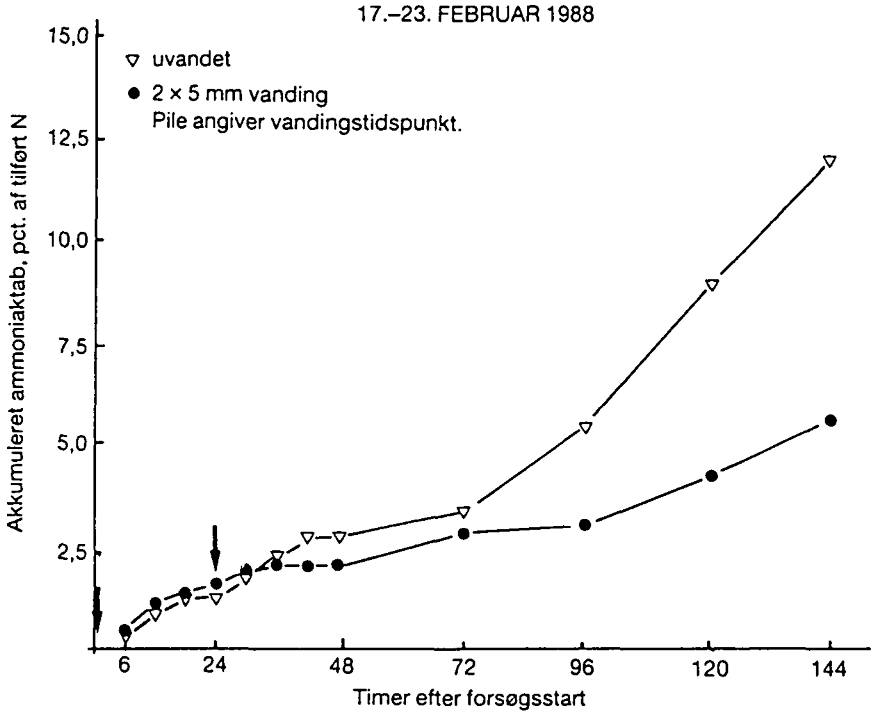

Fig. 7. Akkumuleret ammoniaktab fra urea (10 g N/m^2) udbragt d. 17. februar 1988 (kl. 14.50) på vinterrug (10 cm høj).

Cumulated loss of ammonia from urea (10 g N/m^2) applied on 17 february 1988 (14,50) to winterrye (plant height, <10 cm).

9) har derfor næppe øget hastigheden af urea-hydrolysen og på den vis næppe påvirket fordampningen af ammoniak i forhold til uvandet.

Vanding kan imidlertid påvirke fordampningen af ammoniak ved, at urea og ammoniak/ammonium vaskes ned i jorden, hvorved fordampning mindskes (fig. 7 og 9). Ved de her anvendte vandingsmængder på 5 og 10 mm (fig. 7, 8 og 9) blev fordampningen nedsat, men vandingsmængden har ikke været tilstrækkelig til at bringe fordampningen til ophør.

Efter vanding med mindre vandmængder kan fordampningen fortsætte, idet der ved en efterfølgende udtørring fortsat vil kunne finde fordampning af ammoniak sted, fordi nedvaskningen har været ubetydelig. (8, 19). *Bouwmeester et al.* (2) og *Ferguson et al.* (6) fandt, at fordampningen af ammoniak fra urea ophørte ved nedbørs- eller vandingsmængder på over 20 mm.

Den akkumulerede fordampning af ammoniak fra urea efter 6 døgn var af samme størrelse, uanset om der blev vandet med 10 mm efter et døgn, eller vandingen blev gennemført ad to gange med 5 mm ved forsøgets start og 5 mm efter et døgn (fig. 9). Der var kun mindre forskelle i temperaturen i de pågældende forsøg.

Fordampningen fra UAN (urea-ammonium-nitrat) var lavere end fra urea (fig. 8). Tilstedeværelsen af nitrat i UAN-gødningen medfører, at pH falder til lavere niveauer som følge af salpetersyredannelsen (1, 14), og carbonat-afgasningen får mindre betydning. Endelig blev UAN tilført som væske i modsætning til urea, der fandtes på fast form. Kvælstofindholdet i UAN fordeler sig i forholdet 2:1:1 mellem henholdsvis urea, ammonium og nitrat.

Ved udbringning af urea i februar/marts var tabet af ammoniak ved fordampning på 3 pct. til 10 pct. af den tilførte N-mængde, når gødningen ikke udsattes for nedbør. Vanding med mere end 5 mm de første døgn efter udbringning kan begrænse fordampningen. Temperaturen har betydning for ammoniaktabets størrelse, idet både hydrolysen og fordampningen af ammoniak øges ved stigende temperatur. I maj/juni måltes ammoniaktab på 20 til 30 pct. af N-indholdet i den tilførte urea, såfremt nedbøren var mindre end 10 mm inden for de første døgn.

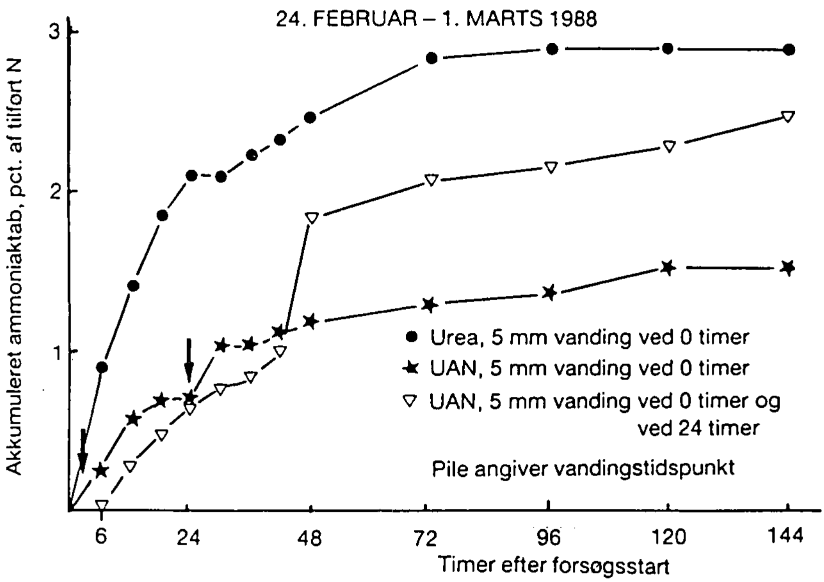

Fig. 8. Akkumuleret ammoniaktab fra urea (10 g N/m^2 og ureaammoniumnitrat (3.8 g N/m^2) udbragt d. 24. februar 1988 (kl. 12.55) på vinterrug (<10 cm høj).

Cumulated loss of ammonia from urea (10 g N/m^2) and urea-ammonium-nitrate (3.8 g N/m^2) applied on 24 February 1988 (12,55) to winterrye (plant height, <10 cm).

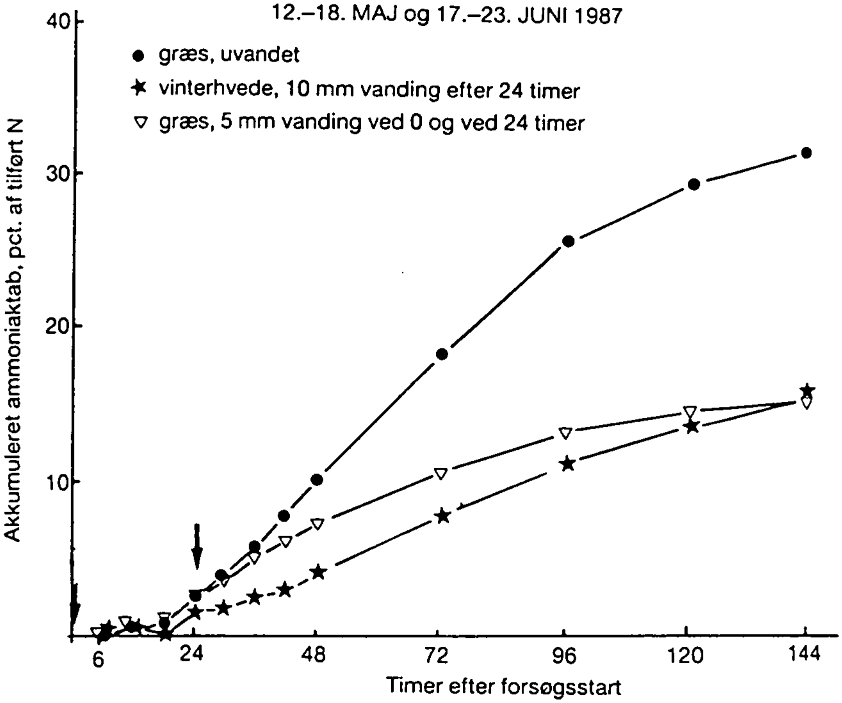

Fig. 9. Akkumuleret ammoniaktab fra urea udbragt d. 12. maj 1987 (kl. 10.15) med 10 g N/m² til vinterhvede (35 cm høj) og d. 17. juni 1987 (kl. 10.50) med 15 g N/m² til græs efter slæt.
Cumulated loss of ammonia from urea applied 12 May (10,15) to winter wheat (plant height, 35 cm) at a rate of 10 g N/m² and on 17 June 1987 (10,50) to cut grass at a rate of 15 g N/m².

Erkendtlighed

Forsøgsteknisk Værksted, Årslev, har medvirket ved opbygning af vindtunnelsystemet, og *Kirsten Vang* har varetaget den tekniske gennemførelse af forsøgene.

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Manuskript modtaget den 26. maj 1989.

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6600 Vejen

Beretning nr. 2023

Fordampning af ammoniak fra svinegylle udbragt på jordoverfladen

Volatilization of ammonia from surface-applied pig slurry

SVEN G. SOMMER og BENT T. CHRISTENSEN

Resumé

Ammoniaktabet fra svinegylle udbragt på jordfladen blev bestemt med et mobilt vindtunnelsystem, hvorved ammoniakfordampningen fra gødede arealer bestemtes direkte.

Fra oktober 1986 til juni 1988 blev der gennemført 39 forsøg (hver af seks døgns varighed) med forskellige typer af svinegylle udbragt på grov sandblandet lerjord (JB5) og grovsandet jord (JB1). Jordoverfladen var enten fræset stub eller ubehandlet stub, græs efter slæt, vinterhvede, rug eller majs. Forsøgsarealet var afskærmet mod nedbør, men vanding indgik i tre forsøg.

Fordampningen af ammoniak varierede med pH, temperatur og tørstofindhold, og der fandtes en betydelig vekselvirkning mellem disse faktorer. Den akkumulerede ammoniakfordampning over seks døgn varierede fra 10 til 60 pct. af ammoniumindholdet i den udbragte gylle.

De største tab fandt sted, når temperaturen var over 13°C og i frostvejr, hvor gyllens flydende fraktion ikke kunne sive ned i jorden. Ammoniakfordampningen var mindst ved temperaturer mellem 0°C og 7°C med gennemsnitlige ammoniaktab over seks døgn på mindre end 30 pct. af gyllens ammoniumindhold.

Ved tørstofindhold lavere end 1,5 pct. var ammoniakfordampningen lav uanset gyllens pH–værdi. Effekten af vanding på ammoniaktabet var ikke målelig, fordi der i de gennemførte vandingsforsøg blev anvendt gylle med lavt tørstofindhold.

Fra gylle med pH lavere end 6,8 fordampede i løbet af seks døgn mindre end 12 pct. af ammoniumindholdet. Ved pH 7,5 – 7,7 varierede ammoniakfordampningen over 24 timer fra 7 til 48 pct. af ammoniumindholdet. De lave tab blev fundet ved udbringning af gylle med lavt tørstofindhold (<1,5 pct.) og ved temperaturer omkring 5°C.

Såfremt forårsudbragt gylle nedbringes i jorden inden 12 timer efter udbringningen, vil ammoniaktabet være mindre end 10 pct. af ammoniumindholdet. Om sommeren vil tabet over en tilsvarende periode være cirka dobbelt så stort.

Idet forsøgsarealerne var afskærmet mod nedbør i forsøgsperioden, vil der under almindelige markforhold forekomme lavere ammoniaktab end de her målte, såfremt det gødede areal udsættes for større mængde nedbør.

Nøgleord: Ammoniakfordampning, vindtunnelsystem, svinegylle, atmosfærisk ammoniakindhold, ammonium, stub, rug, hvede, slætgræs, majs og vanding.

Tidsskr. Planteavl 93 (1989), 307-321.

Summary

A mobile wind tunnel system was used to determine the ammonia volatilization from surface-applied pig slurry under field conditions.

The ammonia loss from different types of pig slurry was measured in 39 experiments carried out from October 1986 to June 1988 on a sandy loam (JB5) and a coarse sand soil (JB1). The soil was rotavated or covered by intact stubble, grass cut for silage, winter wheat, rye or maize. The experimental area was not exposed to precipitation, but irrigation was included in three experiments. In each experiment, the ammonia loss was determined over a six day period.

Volatilization loss from pig slurry depended on pH, temperature and content of dry matter. The interaction between these parameters was strong. The cumulated loss of ammonia over six days varied from 10 to 60 per cent of the ammonium applied in slurry. The greatest loss was found in periods with frozen soil where the liquid fraction could not infiltrate the soil. The loss was also high during periods with temperatures above 13°C. The lowest volatilization loss of ammonia was found when temperatures were between 0°C and 7°C. Under these temperature regimes, the average loss of ammonia over six days accounted for less than 30 per cent of the ammonium applied.

When the dry matter content was less than 1.5 per cent, the loss of ammonia was small regardless of pH. Due to the low content of dry matter, irrigation did not reduce the loss of ammonia.

The cumulated loss of ammonia during six days was less than 12 per cent for slurries with pH lower than 6.8. With pH of 7.5 – 7.7, the ammonia loss during 24 hours varied from 7 to 48 per cent of the ammonium applied. The lowest loss was found for slurries with low contents of dry matter (< 1.5 per cent) and slurry applied in periods with temperatures around 5°C.

When slurry is surface-applied in spring and incorporated into the soil within 12 hours, the loss of ammonia will be less than 10 per cent of the ammonium applied. The corresponding loss during the summer period will be twice as high.

Key words: Volatilization of ammonia, wind tunnel system, pig slurry, atmospheric ammonia, ammonium, stubble, rye, winter wheat, grass cut for silage, maize, irrigation.

Indledning

I 1986 blev det ved bekendtgørelser fastsat, at flydende husdyrgødning udbragt på ubevokset jord skal nedbringes inden 24 timer (12). Dette krav er siden skærpet til nedbringning inden 12 timer (13) og i den seneste bekendtgørelse på området (14) kombineret med krav om 6 – 9 mdr's opbevaringskapacitet for gylle, samt forbud mod udbringning på ubevoksede arealer mellem høst og 1. november.

Hensigten med disse krav er blandt andet at opnå en forbedret udnyttelse af kvælstofindholdet i gylle, så indkøb af handelsgødning kan nedsættes og næringsstoftab til det omgivende miljø begrænses.

I denne sammenhæng spiller ammoniaktabet ved håndteringen af gylle en vigtig rolle. Tidligere undersøgelser af ammoniakfordampning fra fast husdyrgødning og ajle har vist, at størrelsen af og variationen i tabet af ammoniak kan være betydeligt (3). Samtidigt viste en sammenligning af resultater for ammoniaktab opnået med forskellige metoder, at tab bestemt ved indirekte metoder (fx udbyttebestemmelser) synes at være betydeligt større end tab bestemt ved direkte målinger af ammoniakindhold i luft, der har passeret det gødede areal.

For at kunne kvantificere betydningen af de førnævnte krav i relation til tabet af ammoniak til omgivelserne, og for at kunne tilskrive gyllen en mere korrekt gødningsværdi, kræves mere detaljerede undersøgelser af størrelsen af ammoniakfordampningen fra gylle.

Det er blandt andet væsentligt, at kunne identificere parametre af overordnet betydning for ammoniaktabet, idet det vides, at tidsfaktoren ikke alene er bestemmende for tabets størrelse.

Ved Askov forsøgsstation er det siden 20'erne blevet undersøgt, hvorledes størrelsen af NH_3-fordampningen fra ajle og fast staldgødning afhænger af håndteringen, herunder nedbringningstidspunktet. I 1985 indledtes undersøgelser af NH_3-fordampningen fra gylle udspredt på jordoverfladen. Til disse undersøgelser blev udviklet et vindtunnelsystem (4).

Denne beretning omhandler ammoniakfordampning fra en række forskellige typer af svinegylle, der blev overfladeudbragt på forskellige årstider.

Fordampningen fra gylle blev bestemt på to jordtyper med og uden afgrøde. Fordampningen fra stigende mængder af gylle pr. arealenhed blev undersøgt, og der blev benyttet gylle med forskelligt pH og tørstofindhold. Endvidere blev effekten af nedbør inddraget ved hjælp af vanding, idet forsøgsarealet under vindtunnelerne ikke blev udsat for nedbør i forsøgsperioden.

Materialer og metoder

Vindtunnel

Der benyttes fire vindtunneler (4) til måling af NH_3-fordampningen. Heraf benyttes én til måling af NH_3-koncentrationen i luft fra et ubehandlet areal og de tre øvrige til måling af forsøgsbehandlinger. Hver vindtunnel består af et metalrør med en ventilator, der skaber en luftstrøm gennem en omvendt u-formet tunnelenhed. Sidstnævnte er udført i klar polycarbonatplade og dækker selve forsøgsarealet (0,5 × 2 m). I luftafkastet måles NH_3-koncentrationen.

NH_3-målinger

Efter ventilatoren, men inden luften forlader metalrøret, udtages i seks punkter delprøver af luftstrømmen med membranpumpe. Luften suges gennem en 100 ml gasvaskeflaske (5 l/min) indeholdende 50 ml 0,005 M H_3PO_4, hvori NH_3 absorberes. NH_4^+-koncentrationen i H_3PO_4-opløsningen bestemmes ved en Berthelot reaktion og spektrofotometri. Hver tunnel er udstyret med fire gasvaskeflasker. Med et programmerbart magnetventilsystem skiftes automatisk mellem gasvaskeflaskerne, der derved opsamler NH_3 i fire forud fastlagte tidsrum.

Vindhastighed og temperaturmålinger

I metalrøret måles vindhastigheden med vindturbine og lufttemperatur med termoelement. Jordtemperatur måles med termoelement anbragt 2 cm under jordoverfladen i tunnelenheden. Signalerne fra temperaturføleren og vindhastighedsmåleren lagres hver time i datalogger.

Forsøgsplan

Tabel 1 giver en beskrivelse af de anvendte typer af svinegylle. Der blev anvendt gylle med pH varierende fra 6,4 til 7,7, med tørstofindhold fra 0,70 til 7,87 pct., og med indhold af ammoniak og ammonium (herefter kaldet NH_4^+) varierende fra 0,18 til 0,56 pct. Total N-indholdet varierede fra 0,25 til 0,76 pct.

Der blev som regel tilført gylle svarende til 30 t pr. ha. I tre forsøg blev der tilført gylle svarende til 10, 20 og 30 t pr. ha, og i et enkelt forsøg mængder svarende til 30, 60 og 90 t pr. ha. Forsøgene blev gennemført i perioden oktober 1986 til juni 1988.

Gyllen blev udbragt på bar jord, ubehandlet stubmark, fræset stub, græs efter slæt, på hvede og rug i forskellige vækststadier eller på majs. Forsøgene blev gennemført på JB1 og JB5 jorde.

Nedbør blev simuleret ved vanding i tre forsøg (tabel 1). Den anvendte metode er beskrevet tidligere (4).

Lufthastigheden i vindtunnelerne var i forsøget indstillet til mellem 4,0 og 6,3 m/s (tabel 2). Der blev under målingerne registreret lufttemperaturer fra −6,0°C til 28,0°C og jordtemperaturer fra −2,0°C til 24,8°C.

NH_3-fordampningen blev de første to døgn målt i tidsrum af seks timers varighed og af 24 timers varighed de efterfølgende fire døgn.

Beregninger

Fordampningen af ammoniak blev beregnet ud fra følgende ligning:

$J\,(\text{time}) = K \times A \times U \times (NH_3\,\text{fs.} - NH_3\,\text{ref.})$, hvor

J (time) = NH_3-fordampning, g NH_3-N/time.
K = Omregningskonstant, 3600 s/time.
A = Afkastets tværsnitsareal, m^2.
U = Vindhastighed, m/s.
NH_3 fs. = NH_3 koncentration i luftafkast fra forsøgsareal, g NH_3-N/m^3.
NH_3 ref. = NH_3 koncentration i luftafkast fra ubehandlet areal (reference), g NH_3-N/m^3.

Ved denne beregning fratrækkes NH_3-indholdet i luft fra ubehandlet areal (referencetunnel), hvorved netto-fordampningen fra de behandlede forsøgsarealer bestemmes.

Fordampningen er opgjort som NH_3-N fordampet i procent af den udbragte mængde NH_4^+-N. Derved muliggøres en sammenligning af NH_3-tabet fra forskellige gylletyper uden hensyntagen til

Tabel 1. Kemisk sammensætning og mængde af den anvendte gylle, vanding, jordbundstype og overflade af forsøgsareal.

Chemical composition and amount of added slurry, irrigation, soil type and surface of experimental area.

Forsøgs-Periode *Eksperimental period*	Gylle t/ha *Slurry t/ha*	Total-N pct. *Total-N %*	NH_4^{+*} pct. *NH_4^{+*} %*	pH	Tørstof pct. *Dry matter %*	Vanding mm *Irrigation mm*	Overflade *Soil surface*	Jordbunds typer *Soil type*
1986							Stub	JB 5
08.10–14.10	30	0.55	0.37	7,2	4.46	0	*Stubble*	–
1986							Stub	JB 5
14.10–20.10	30	0,55	0.37	7,2	4.46	0	*Stubble*	–
1986	90	0.55	0.37	7,2	4,46	0	Stub	JB 5
30.10–04.11	60	–	–	–	–	0	*Stubble*	–
	30	–	–	–	–	0		–
1986	30	0,27	0,23	7,7	1,20	0	Stub	JB 5
11.11–17.11	30	0,45	0,35	7,2	2,44	0	*Stubble*	–
	30	0,42	0,33	7,0	3,17	0	–	–
1986	30	0.53	0.38	6,9	4,42	0	Vinter hvede	JB 5
18.11–25.11	30	0,27	0,23	7,7	1,20	0	*Winter wheat*	–
	30	0.53	0,38	6,9	4,42	0	(<10 cm)	–
1986	30	0,53	0,38	6,9	4,42	0	Vinter hvede	JB 5
25.11–01.12	30	0,27	0,23	7,7	1,20	0	*Winter wheat*	–
	30	0,53	0.38	6,9	4,42	0	(<10 cm)	–
1987	30	0.27	0,18	6,4	3.34	0	Græs	JB 5
09.04–15.04	30	0.68	0.56	7,4	4.37	0	*Grass*	–
1987	30	0.30	0,21	6,4	3,65	0	Græs JB 5	
22.04–28.04	30	0,76	0,56	7,1	7,40	0	*Grass*	–
	30	0.54	0.39	6.8	3.81	0		
1987	30	0,43	0.25	7,0	7,87	0	Vinter hvede	JB 5
19.05–25.05	30	0.34	0,29	7,0	1,15	5	*Winter wheat*	–
	30	0.25	0,23	7,4	0.70	5	(< 35 cm)	–
1987	30	0,28	0,24	7,5	1,02	0	Græs efter slæt	JB 5
10.06–16.06	30	0.28	0,24	7,5	1.02	10	*Cut grass*	–
1987	30	0,42	0,30	6,8	2.58	0	Græs efter slæt	JB 5
25.08–31.08	30	0,33	0.25	6,9	1,92	0	*Cut grass*	–
	30	0,25	0,23	7,4	0,70	0		
1987	10	0,48	0,32	7,5	5,60	0	Fræset	JB 5
24.11–30.11	20	0,48	0,32	7,5	5,60	0	*Rotavated*	–
	30	0,48	0.32	7,5	5,60	0		
1987	10	0,48	0,32	7,5	5,60	0	Stub	JB 5
02.12–08.12	20	0,48	0,32	7,5	5,60	0	*Stubble*	–
	30	0,48	0,32	7,5	5,60	0		
1987	10	0,48	0,32	7,5	5,60	0	Stub	JB 5
10.12–16.12	20	0,48	0,32	7,5	5,60	0	*Stubble*	–
	30	0,48	0.32	7,5	5,60	0		
1988							Rug (<10 cm)	JB 1
17.05–23.05	30	0,43	0.38	7,5	3,10	0	*Rye*	–
1988	30	0,43	0,38	7,5	3,10	0	Majs (<5-10cm)	JB 1
25.05–31.05	30	0,43	0,38	7,5	3,10	0	*Maize*	–

*$(NH_3+NH_4^+)$-N

Tabel 2. Middelværdier for luft- og jordtemperaturer, samt indstillet lufthastighed (aflæst maksimum og minimumsværdier i parentes).

Average air and soil temperature during the experiments and wind speed settings (maximum and minimum readings during experiments in brackets).

Forsøgs- periode *Eksperimental* *period*	Luft temp. °C *Air temp. °C*			Jord temp. °C *Soil temp.°C*			Lufthastighed m/sek. *Wind speed m/sec.*	
	middel *mean*	min. *min.*	maks. *max.*	middel *mean*	min. *min.*	maks. *max.*		
1986 08.10–14.10	9.0	1.0	19.0	10.0	7.0	13.0	4.0	(3.5–9.0)
1986 14.10–20.10	8,0	2,0	17,0	9,0	4,0	13,0	4,0–4,5	(4,0–7,0)
1986 30.10–04.11	4.6	0.2	8.9	5.2	2.1	8.0	4,0–4.5	(3,8–7,0)
1986 11.11–17.11	6,0	0,2	10,0	6,0	4,1	8,0	4,0	(2,9–7,3)
1986 18.11–25.11	3.7	0.2	9.5	3,7	2,1	8.5	4.5	(4.0–7,5)
1986 25.11–01.12	7,0	3,0	10,0	7.0	4,1	8,0	4,3	(4,0–9,5)
1987 09.04–15.04	3.0	0.0	6.0	3.2	1.1	6.5	5.0	(4,5–6,0)
1987 22.04–28.04	8,9	0,0	19,0	8,1	4,0	14,0	4,5	(3.8–6,0)
1987 19.05–25.05	8.6	3.1	21.0	7.8	4.1	15.0	4.5	(3.3–5.5)
1987 10.06–16.06	9.0	3,0	18,0	9,0	7,1	17,0	4,5	(3,8–5,2)
1987 25.08–31.09	12.8	7.1	19.0	13.4	10,0	18.5	4.1–4.7	(3.8–5.2)
1987 24.11–30.11	3,7	−1,0	8,0	4,3	3,0	6,0	4,8–5,5	(4,7–5,9)
1987 0.2.12–08.12	−2.0	−6.0	0.0	−1.0	−2.0	0.0	5,8–6,2	(4,3–7.2)
1987 10.12–16.12	−1,2	−4,0	5,0	−1,0	2,0	2.0	5,8–6,3	(3,3–7,5)
1988 17.05–23.05	7.0	−2.0	14.0	8.0	5.0	13.0	4.5–5.4	(3.5–7.6)
1988 25.05–31.05	16,0	12.0	28,0	16.0	14,0	24,8	4,8–5,5	(3,4–8,0)

forskelle i NH_4^+-indholdet (se også senere). Da genfindelsesprocenten ved målingerne er 74 pct., er de målte værdier justeret med en faktor 100/74 (4).

Ammoniakfordampningen efter henholdsvis 12 timer og 24 timer blev analyseret med procedure regression i Statistical Analysis System (SAS). Det blev undersøgt, om der var sammenhæng mellem NH_3-fordampningen, den gennemsnitlige jordtemperatur, lufttemperatur, hydrogenionkoncentration og tørstofindhold. For sammenhængen mellem NH_3-fordampningen efter 24 timer og hydrogenionkoncentrationen var korrelationen r = 0,2. For de øvrige var den lineære korrelation lavere.

Ved præsentation af jord- og lufttemperatur benyttes et gennemsnit af målinger i de fire tunneler, idet spredningen i temperaturen mellem tunnellerne var ubetydelige (C.V. < 5 pct.). I de forsøg, hvor der ikke blev lagret klimadata, er benyttet gennemsnitlige døgnværdier målt på Askov klimastation.

Resultater og diskussion

De atmosfæriske NH_3-koncentrationer varierede mellem 0,2μg NH_3-N/m^3 og 14,0 μg NH_3-N/m^3 (fig. 1). Koncentrationerne er i overensstemmelse med tidligere målinger (4).

NH_3-fordampningen er som følge af de kemiske processer ligefrem proportional med indholdet af NH_4^+ i gyllen. Ved anvendelse af massebalancemålinger fandt *Brunke et al.* (2), at der var en lineær sammenhæng mellem NH_4^+-indholdet i gylle og NH_3-fordampningen. Ved at præsentere NH_3-fordampningen i procent af NH_4^+-indholdet kan forskellige forsøg derfor sammenlignes uden hensyntagen til eventuelle forskelle i NH_4^+-indhold.

I forsøgene begyndt d. 8., d. 14. og d. 30. oktober 1986 blev NH_3-fordampningen fra samme type gylle undersøgt. Forskellen på resultaterne fra målingerne i de tre forsøg var lille (fig. 2A). De små forskelle i forløbet af NH_3-fordampningen over tid skyldes formentlig forskelle i lufttemperaturen, der ved forsøgenes start var 8-10°C for derefter at vise forskelle over døgnene for de tre perioder.

Gyllens pH

I fig. 3 er NH_3-tabet afsat som funktion af hydrogenionkoncentrationen i gylle. Den negative logaritme til hydrogenionkoncentrationen er gyllens pH. Ved faldende hydrogenionkoncentration (stigende pH) øges NH_3-fordampningen. I denne undersøgelse viser fordampningen efter 24 timer ringe sammenhæng med hydrogenionkoncentrationen (r = 0,2), hvilket må skyldes andre faktorers indflydelse på fordampningen. Muligvis sker der efter udbringningen en ændring i gyllens pH som følge af fordampning af flygtige syrer og omsætning af fedtsyrer, således at måling af gyllens pH forud for udbringning ikke er repræsentativ for pH i den udbragte gylle.

Forsøgene med de forskellige gylletyper er gennemført på forskellige tider af året. Temperaturforskelle har derfor haft indflydelse på den ringe korrelation mellem NH_3-fordampning og hydrogenionkoncentration. NH_3-tabene efter 24 timer varierede således fra 7 pct. til 48 pct. af NH_4^+-indholdet i gylle, der havde pH 7,5 svarende til en hydrogenionkoncentration på 0,31 × 10^{-7} (fig. 3). De store tab på 48 pct. af NH_4^+-indholdet fandt sted ved temperaturer på omkring 16°C og fra en gylle med et tørstofindhold på 3,1 pct. De laveste tab på 8 – 10 pct. af NH_4^+-indholdet i gylle fandt sted ved temperaturer på omkring 4°C og fra en gylle med et tørstofindhold på 5,6 pct.

Ved pH lavere end 7,0 vil kun få promille af NH_4^+-indholdet findes som NH_3. Derfor vil NH_3-fordampningshastigheden være lav, når gyllens pH er under dette niveau. For gylle med pH 6,4, henholdsvis 6,8, blev der således også fundet relativ lav NH_3-fordampning (fig. 2B).

Fig. 2C viser NH_3-fordampningen fra gylle med pH 7,4 og et lavt tørstofindhold (0,7 pct.), og fra to typer gylle med pH 6,8 – 6,9 og to til tre gange højere tørstofindhold. NH_3-fordampningen er to-tre gange større fra gyllen med det høje pH, uanset at et lavt tørstofindhold alt andet lige vil begrænse NH_3-tabet.

Fig. 4 viser den gennemsnitlige, akkumulerede NH_3-fordampning fra gylle med pH i intervallerne 6,4 – 7,0, 7,1 – 7,4 og 7,5 – 7,7. Da de afsatte værdier er gennemsnit af alle forsøg, er spredningen stor, hvilket tilskrives vekselvirkning med bl.a. temperatur og tørstofindhold. Det fremgår imidlertid, at NH_3-fordampningen er væsentlig lavere fra gylle med lavt pH end fra gylle med højt pH, og at den relative forskel på fordampningen er af samme størrelsesorden 6 og 145 timer efter udbringning.

Temperatur

Ved stigende temperatur øges hastigheden af de processer, der har indflydelse på fordampningen af NH_3, hvorfor fordampningen stiger ved stigende temperaturer. Af ligningerne, der beskriver processerne, fremgår det, at fordampningen stiger kraftigt ved temperaturer omkring 17°C (7). Endvidere udtørres gyllen hurtigere ved høje temperaturer, hvilket medfører et øget NH_4^+-tab fra gyllen (15 og 11).

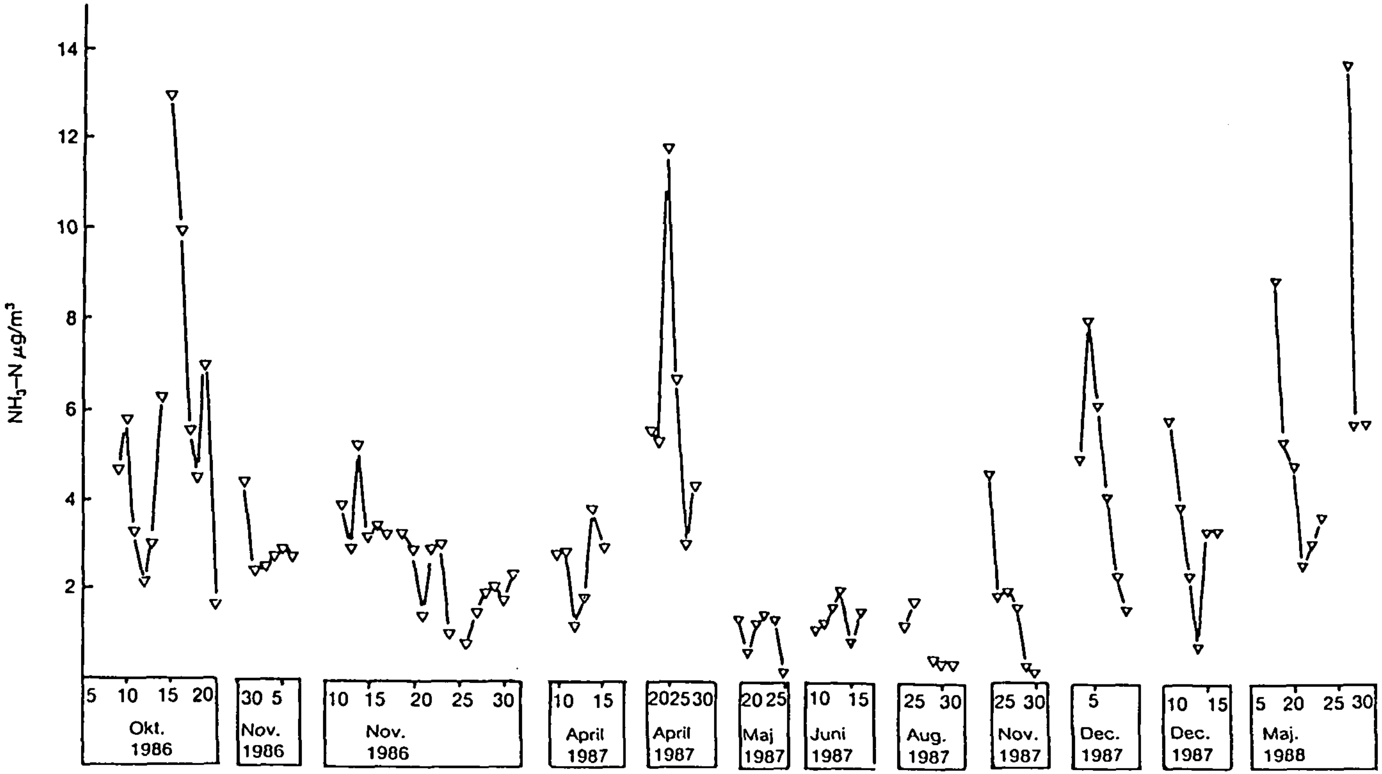

Fig. 1. Atmosfærisk koncentration af ammoniak målt i referencetunnelen.
Atmospheric concentration of ammonia measured in the reference tunnel.

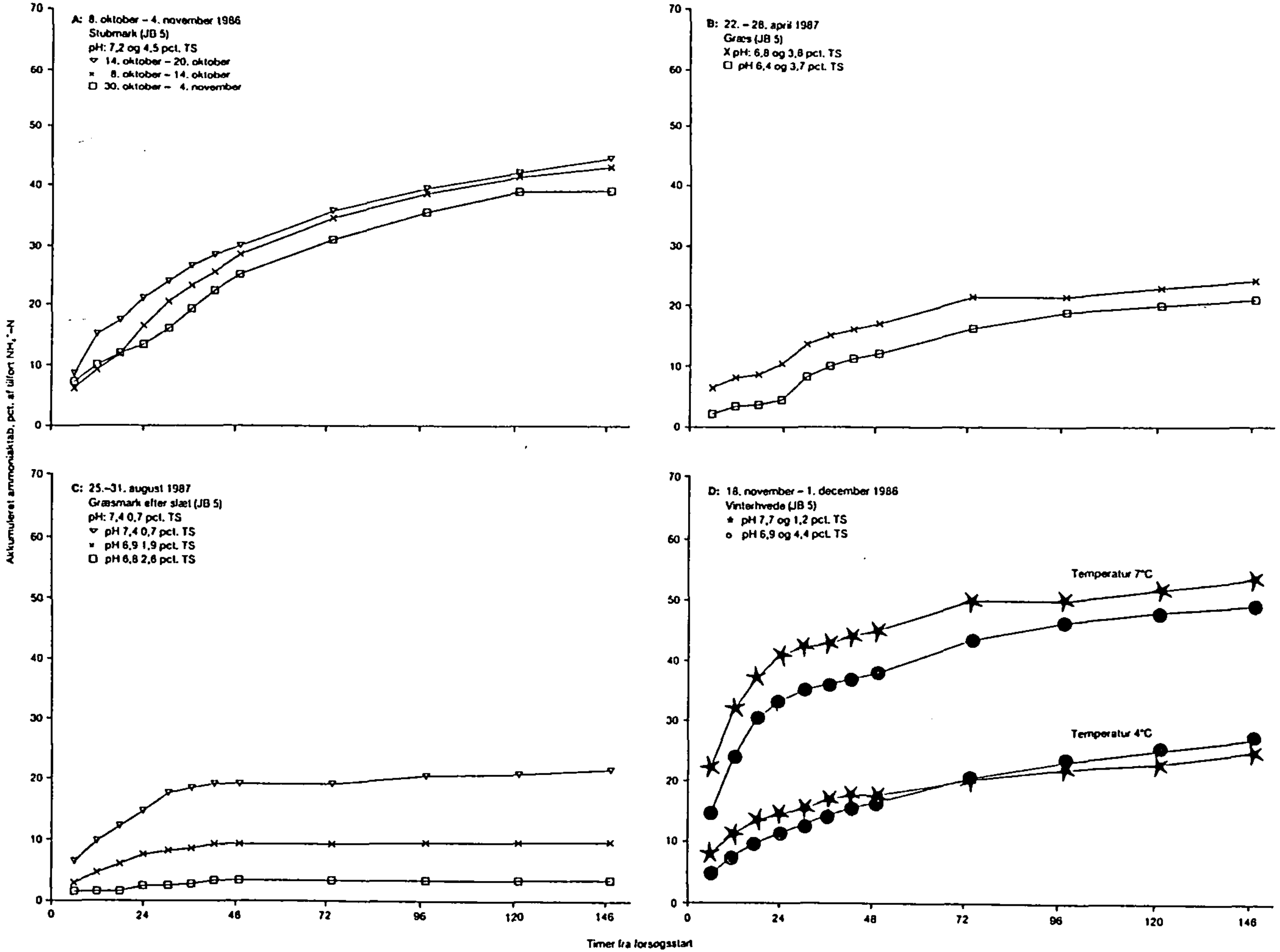

Fig. 2. Akkumuleret ammoniaktab fra svinegylle (30 t pr. ha)

Cumulated loss of ammonia from pig slurries (30 t per ha).

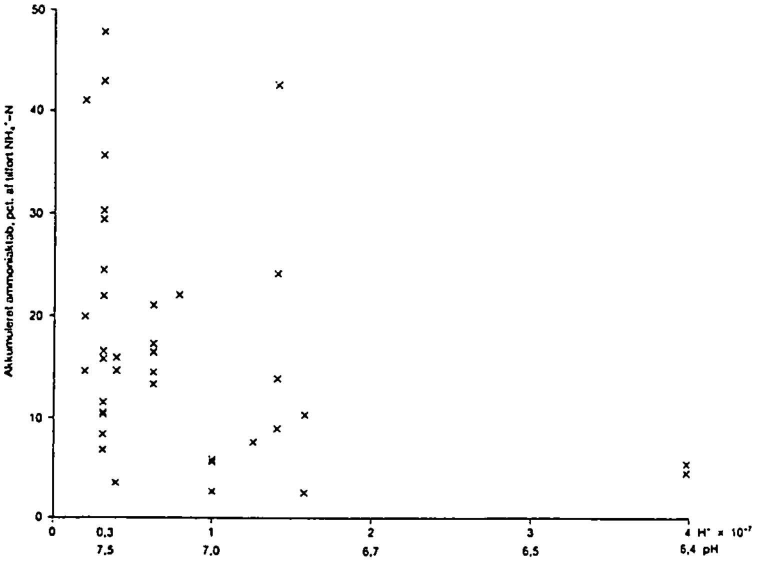

Fig. 3 Akkumuleret ammoniaktab fra svinegylle (30 t pr. ha) efter 24 timer ved stigende hydrogenionkoncentration (H^+)

Cumulated loss of ammonia from pig slurry (30 t per ha) related to the concentration of the hydrogen ion (H^+).

Målingerne af NH_3-fordampningen fandt sted ved temperaturer mellem -2°C og 16°C, og det blev derfor undersøgt, om fordampning i dette interval steg lineært med temperaturen. NH_3-fordampningen efter 12 timer og efter 24 timer var hverken korreleret med luft- eller jordtemperaturen, hvilket må skyldes effekter af tørstofindhold og pH, samt vekselvirkning mellem disse og temperaturen. Vekselvirkningen vil blive eksemplificeret i det følgende.

I de tre forsøg udført mellem d. 8. oktober og d. 4. november 1986 (fig. 2A) var forskellen på gennemsnitstemperaturen i de enkelte forsøgsperioder 3–4°C. Dette medførte ikke en forskel i fordampningen i de tre forsøg, hvor samme gødningstyper blev benyttet.

NH_3-fordampningen fra samme gylletype var to–tre gange større (fig. 2D) ved ca. dobbelt så høje temperaturer i forsøg begyndt d. 25. november som i forsøget startet d. 18. november 1986. Ved den høje temperatur var NH_3-tabet fra gylle med pH 7,7 og 1,2 pct. tørstof større end fra gylle med pH 6,9 og tørstofindhold på 4,4 pct. Denne forskel fandtes ikke ved lave temperaturer. Her var tabene af samme størrelse uanset forskelle i pH og tørstofindhold.

Ved temperaturer under 0°C var NH_3-fordampningen høj (fig. 5A) sammenlignet med fordampningen fra en tilsvarende gylle ved temperaturer lige over frysepunktet. I frostvejr var NH_3-fordampningen efter 24 timer på niveau med fordampningen om sommeren. Årsagen hertil er muligvis, at NH_4^+ ikke kan sive ned i den frosne jord og derfor ikke adsorberes. Langsom dannelse af is i gyllen kan endvidere medføre en opkoncentrering af salte i den ikke frosne fraktion. Dette vil fremme NH_3-fordampningen fra den udbragte gylle (11).

Der kan således finde et betydeligt NH_3-tab sted i frostvejr. Selv om NH_3-fordampningshastigheden var lav ved de lave temperaturer, blev det akkumulerede tab efter seks døgn betydeligt.

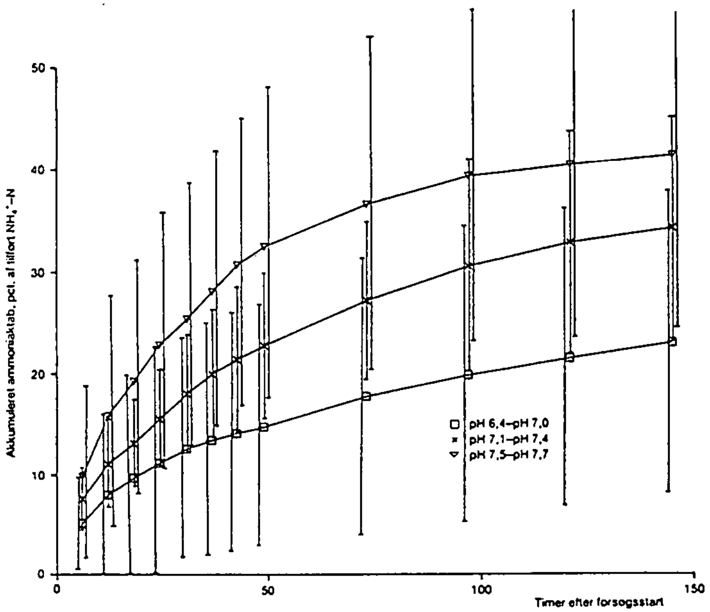

Fig. 4. Gennemsnitligt akkumuleret ammoniaktab fra svinegylle (30 t pr. ha) med pH i intervaller 6.6–7.0. 7.1–7.4 og 7.5–7.7.

Average cumulated loss of ammonia from pig slurry (30 t per ha) with pH in the intervals 6.6–7.0, 7.1–7.4 and 7.5–7.7.

Thompson et al. (18) fandt, at der i løbet af 12 døgn fordampede 74 pct. af NH_4^+-indholdet fra gylle udbragt i frostvejr og 48 pct. af gyllens NH_4^+-indhold ved udbringning om foråret.

I fig. 6 er gennemsnittet af den akkummulerede NH_3-fordampning i temperaturintervallerne -2,0°C – -1,2°C, 3,4°C – 6,9°C og 7,0°C – 16,0°C afbildet. Den store spredning skyldes effekten af forskelle i pH og tørstofindhold af de anvendte gylletyper. Ved temperaturer omkring 0°C, hvor jorden har været frossen, finder som nævnt de største tab sted, idet tabene dog indledningsvis er lavere end i forsøgene ved 7°C til 16°C, formentlig som følge af den langsommere hastighed af de kemiske processer ved lave temperaturer. Ved temperaturer fra 3,4°C til 6,9°C ses de laveste tab. Ved disse temperaturer kan gyllens flydende fraktion sive ned i jorden, og fordampningshastigheden er ringe.

Tørstofindhold

Pain et al. (16) fandt, at NH_3-fordampningen var 3–5 gange større fra gylle med et tørstofindhold på 14 – 18 pct. sammenlignet med gylle med 4,6 – 4,7 pct. tørstof. Dette bekræftes af nærværende undersøgelse, idet NH_3-fordampningen er 2–3 gange større fra en gylle med 7,4 pct. tørstof end fra gylle med et tørstofindhold på 3,2 pct. (fig. 5B). De to gylletyper havde samme pH og blev udbragt ved samme temperatur. Gyllen med højt tørstofindhold blev udbragt på græs, og gyllen med lavt tørstofindhold blev udbragt på en stubmark.

Vekselvirkningen mellem tørstofindhold og pH fremgår af resultater vist i fig. 2D. Fordampningen af NH_3 fra gylle med 4,4 pct. tørstof og pH 6,9 var i dette forsøg af samme størrelsesorden som fra gylle med pH 7,7 og et tørstofindhold på 1,2 pct. På trods af at pH var en enhed lavere og

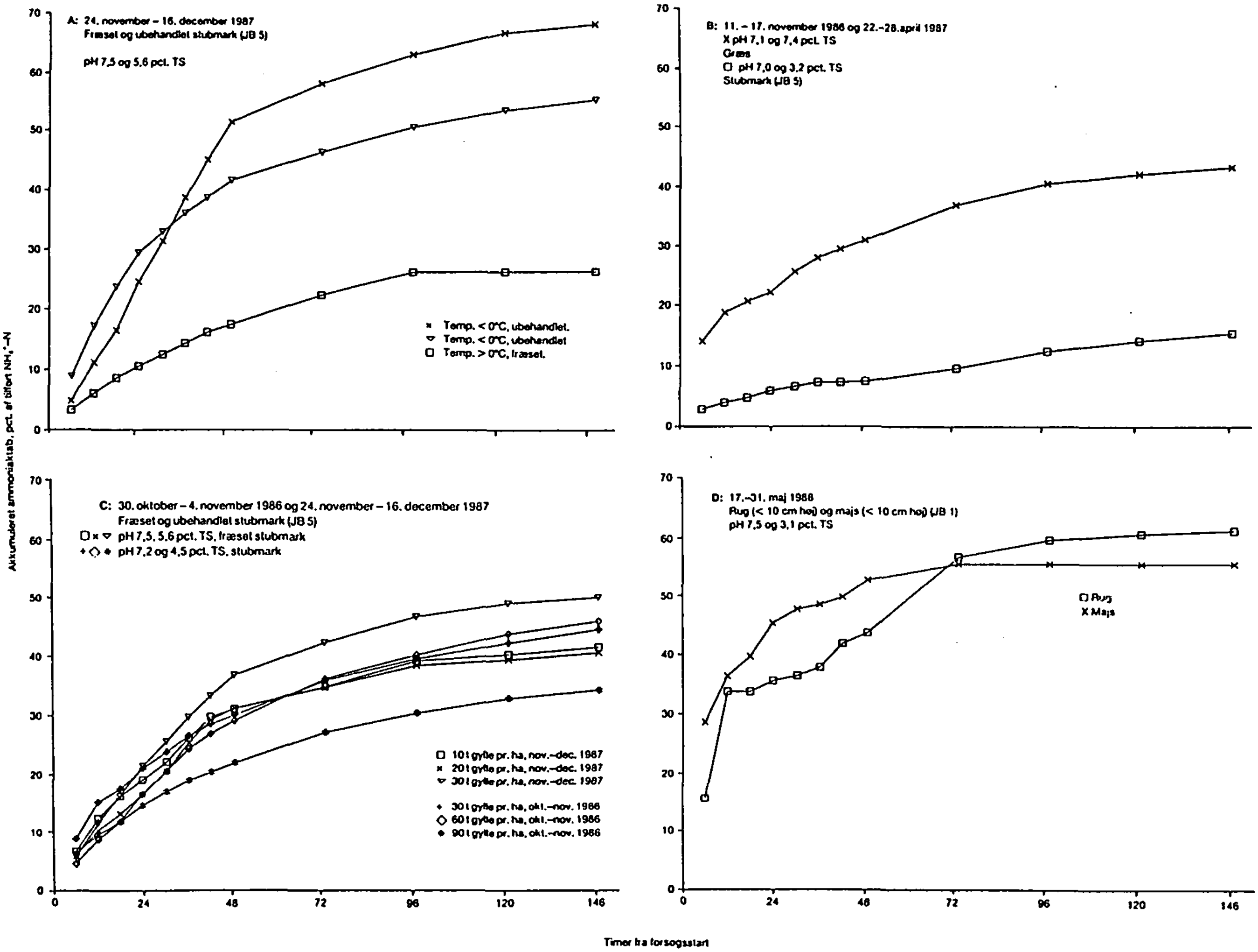

Fig. 5. Akkumuleret ammoniakfordampning fra svinegylle (30 t pr. ha).
Cumulated loss of ammonia from pig slurry (30 t per ha).

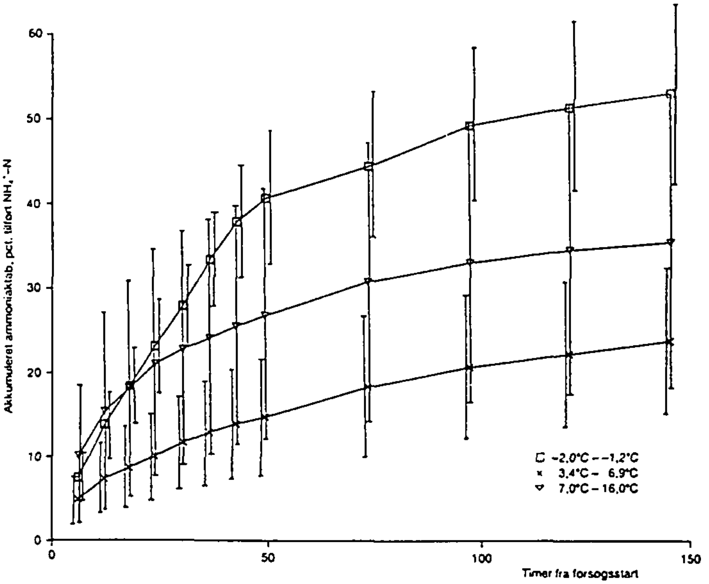

Fig. 6. Gennemsnitlig akkumuleret ammoniakfordampning fra svinegylle (30 t pr. ha)udbragt i perioder, hvor gennemsnitstemperaturen var i intervallerne −2,0°C– −1,2°C,3,4°C–6,9°C og 7°C–16°C.
Average cumulated loss of ammonia from pig slurry (30 t pr. ha) spread in periods with average temperatures within the interval of −2.0°C – −1.2°C, 3.4°C–6.9°C and 7°C–16°C.

hydrogenionkoncentrationen derfor 10 gange højere i forstnævnte gylle, har det lave tørstofindhold begrænset den høje fordampning et højt pH ellers kan medføre.

Årsagen til, at NH_3-fordampningen er stor ved høje tørstofindhold er formentlig, at nedsivningen af NH_4^+ i jorden bliver hæmmet. I jorden fastholdes NH_4^+, hvorved NH_3-fordampningen mindskes. Når gyllens NH_4^+ forbliver på overfladen af jord og planter, vil fordampningen af vand medføre en opkoncentrering af NH_4^+, hvorved fordampningen af NH_3 fremmes. *Donovan* og *Logan* (6) viste, at denne effekt især er markant, når gylle udbringes på vegetationen, idet partiklerne klæber til bladenes overflade, hvorfra fordampningen af NH_3 finder sted.

I fig. 7 er den gennemsnitlige akkumlerede NH_3-fordampning fra gylle med tørstofindhold i intervallerne 0,7 – 3,8 pct. og 4,4 – 7,9 pct. afbildet. NH_3-fordampningen er lavest fra gylle med lavt tørstofindhold, men spredningen er stor. Ved højt tørstofindhold er spredningen mindre, fordi effekter og vekselvirkning af pH og temperatur formodentlig overskygges af det høje tørstofindhold.

Vanding

Ved vanding eller ved nedbør kan indholdet af NH_4^+ i gylle vaskes ned i jorden, hvor NH_4^+ adsoberes. Fortynding som følge af vanding medfører endvidere i sig selv en mindsket NH_3-fordampning.

NH_3-fordampningen fra gylle med lavt tørstofindhold (1,0 pct.) påvirkedes ikke ved vanding. Når gyllens tørstofindhold var 0,7 til 1,0 pct., og der blev vandet med 5 mm, var NH_3-tabet over seks døgn mellem 5 og 10 pct. af gyllens NH_4^+-indhold.

Tilførsel af stigende mængder gylle

Ved tilførsel af stigende mængder gylle pr. ha var det relative NH_3-tab stort set ens efter udbringning af op til 60 t gylle pr. ha (fig. 5C). Ved udbringning af 90 t gylle pr. ha var det procentiske NH_3-tab 2–6 døgn efter udbringningen lavere end ved udbringning af 30 og 60 t gylle pr. ha (fig. 5C).

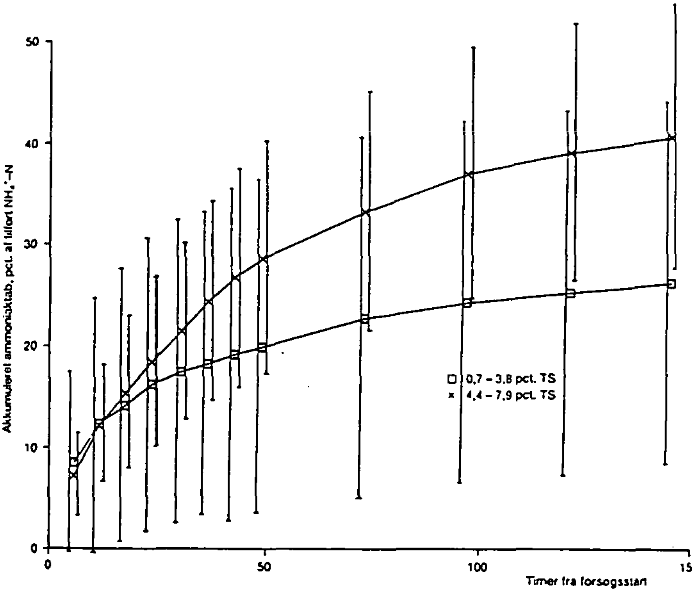

Fig. 7. Gennemsnitligt akkumuleret ammoniakfordampning fra svinegylle (30 t pr. ha) med tørstofindhold i intervaller 0,7–3,8 pct. og 4,4–7,9 pct.
Average cumulated loss of ammonia from pig slurry (30 t pr. ha) with a content of dry matter within the intervals 0.7–3.8% and 4.4–7.9%.

I de første to døgn var der ingen målelig forskel i det relative NH$_3$-tab fra gyllemængder på mellem 10 og 90 t pr. ha.

I de her gennemførte forsøg var tørstofindholdet 4,5 pct. og 5,6 pct. Ved stigende tørstofindhold tilbageholdes NH$_4^+$ i højere grad i gyllen på overfladen af jord og planter. Ved udbringning af gylle med lavt tørstofindhold må det antages, at det relative NH$_3$-tab vil være mindre ved tilførsel af store gyllemængder, idet en større del af NH$_4^+$-indholdet vil kunne sive ned i jorden. *Hoff et al.* (10) fandt, at den relative NH$_3$-fordampning fra svinegylle i løbet af 3 1/2 døgn var ca. 10 pct. lavere ved tilførsel af 130 og 180 t pr. ha end ved tilførsel af 90 t pr. ha. I en senere undersøgelse over syv døgn fandtes ikke signifikant forskel på det relative NH$_3$-tab ved stigende tilførsel af gylle.

Ved udbringning af 35 t og 200 t fast husdyrgødning pr. ha fandt *Lauer et al.* (11), at der ved den lave dosering fordampede en større del af NH$_4^+$-indholdet end ved den høje. Nedsivningen af NH$_4^+$ var ubetydelig ved den lave dosering, mens nedsivning af NH$_4^+$ androg 15–25 pct. ved høj dosering, hvilket medvirkede til begrænsningen af NH$_3$-fordampningen.

Overfladens indflydelse på NH$_3$-fordampningen
I det grænselag, der dannes umiddelbart over gylleoverfladen, vil den atmosfæriske koncentration af NH$_3$ være høj. Grænselagets størrelse og transporten af NH$_3$ væk fra gylleoverfladen er afhængig af overfladens aerodynamiske ruhed (17), turbulens og vindhastighed (19). Ved lave vindhastigheder vil grænselaget være betydeligt og NH$_3$-transporten begrænset af diffusionsprocessen i grænselaget. Transporten af NH$_3$ stiger ved stigende vindhastigheder (9 og 8) indtil et niveau, hvorefter grænselaget er uden betydning for hastigheden af NH$_3$-fordampningen (19). Endvidere øges udtørringen af gylle ved stigende vindhastigheder, hvilket også fremmer NH$_3$-fordampning.

Ved jordoverfladen vil vindhastigheden i en korn- eller stubmark være lavere end over bar jord, hvorfor grænselagsmodstanden må formodes at være større end over bar jord. Det var derfor at forvente, at NH_3-fordampningen ville være mindre ved udbringning af gylle på jorden i en korn- eller stubmark end på bar jord alt andet lige.

De i fig 5A viste forskelle i NH_3-tab fra fræset og ubehandlet stub kan imidlertid, som tidligere anført, hovedsageligt tilskrives forskelle i temperaturen. I undersøgelserne november–december 1987 fandtes der ikke betydende forskelle mellem de to jordbehandlinger. Den manglende effekt kan skyldes, at vindhastigheden i alle de her gennemførte forsøg har været så høj (indstillet vindhastighed>4,0 m/s, tabel 2), at grænselagets beskaffenhed har været uden væsentlig betydning for fordampningshastigheden. Eventuelt har fræsning af jorden bevirket en større nedsivningshastighed for gyllens indhold af ammonium.

I et forsøg blev gyllen udlagt på jorden i en 10 cm høj majsmark (fig. 5D), vindtunnelen var placeret parallelt med majsrækken. Fordampningen var af samme størrelse som fra gylle udspredt i 10 cm høj rug. Majsplanterne har ved denne opstilling ikke givet læ, hvorfor vindhastigheden har været høj hen over gyllen. Grænselagsmodstanden har således næppe haft nævneværdig indflydelse på fordampninghastigheden.

Indflydelsen af afgrødens højde på NH_3-fordampningen fra NH_4^+-holdig handelsgødning i afgrøden er påvist af *Denmead et al.* (5). Det blev fundet, at ammoniakfordampningen ved furevanding med NH_4^+-beriget vand var 7 pct. i en 0,9 m høj majsafgrøde og 1 pct. i en 2,1 m høj majsafgrøde.

Konklusion

Halvdelen af NH_3-fordampningen fra overfladeudbragt svinegylle fandt sted inden for det første 1 –1 1/2 døgn efter udbringningen. Det samme er vist ved massebalancemålinger (1) og vindtunnelforsøg (18). Tabet af NH_3 varierer med temperaturen. Om sommeren ved høje temperaturer vil halvdelen af den NH_3, der fordamper i løbet af seks døgn, tabes inden for de første 18 timer (tabel 3). Om foråret og efteråret ved lavere temperaturer er halvdelen af den NH_3, der fordamper i løbet af seks døgn, tabt inden for 36 timer.

Den målte akkumulerede NH_3-fordampning over seks døgn var 50 pct. af NH_4^+-indholdet, når gyllen blev udbragt på frossen jord. Tilsvarende høje tab blev fundet ved temperaturer over 13 °C om sommeren. De laveste tab blev målt ved temperaturer mellem 0°C og 7°C.

NH_3-fordampningen falder ved faldende pH. Ved pH 6,4 og 6,8 var den akkumulerede fordampning efter seks døgn mindre end 12 pct. af NH_4^+-indholdet i gyllen. Til sammenligning varierede NH_3-fordampningen efter 12 timer fra 11

Tabel 3. Ammoniaktab fra gylle (30 t pr. ha) på jordoverfladen, udbragt ved temperaturer fra 7,0°C–16,0°C og 3,4–6,9°C. Gennemsnit af samtlige forsøg (n = 29).
Volatilization of ammonia (30 t per ha) from surface-applied slurry at temperatures from 7.0°C–16.0°C and 3.4°C–6.9°C. Average values of all experiments (n = 29).

	Temperatur					
	3,4°C–6,9°C			7,0°C–16,0°C		
Tidsrum	Ammoniaktab, *loss of ammonia*			Ammoniaktab, *loss of ammonia*		
	Pct.*)	CV	Andel**)	Pct.*)	CV	Andel**)
6 timer. *h*	5	67	0,2	11	84	0,3
12 timer	7	61	0,3	16	79	0,5
18 timer	9	60	0,4	19	72	0,5
1 døgn. *d*	10	55	0,4	22	66	0,6
1,5 døgn	13	52	0,5	24	61	0,7
2 døgn	14	51	0,6	27	59	0,8
6 døgn	23	37	1,0	35	53	1,0

*) Ammoniaktab i pct. af ammoniumindholdet i gylle.
Ammonia loss, per cent of added ammonium.

**) Andel af ammoniaktab i forhold til det samlede tab af ammoniak i 6 døgn.
Part of the cumulated loss during 6 days.

pct. til 31 pct. af NH_4^+-indholdet fra en gylle med pH 7,7.

Fra gylle med lavt tørstofindhold er ammoniakfordampningen ringe. Således er ammoniakfordampningen selv ved pH større end 7,5 lav fra gylle med tørstofindhold lavere end 1,5 pct. I vandingsforsøgene blev en tynd gylle anvendt, derfor var der en begrænset reduktion i NH_3-fordampningen ved vanding.

Det er vist, at NH_3-fordampningen ved nedfældning mindskes til mindre end 2 pct. af NH_4^+-indholdet (10 og 18). Udbringes gylle om foråret, vil nedbringning i løbet af det første døgn derfor begrænse NH_3-tabet til mellem 5 og 15 pct. af gyllens NH_4^+-indhold. Udbringes gyllen om sommeren, skal den nedfældes eller nedbringes umiddelbart efter udbringning, hvis NH_3-fordampningen ønskes begrænset til et tilsvarende niveau.

I de her gennemførte undersøgelser var forsøgsarealerne afskærmet mod nedbør i forsøgsperioden. De opnåede resultater relaterer derfor til fordampning fra gylle, der henligger på jordoverfladen under udtørrende forhold. Tabet af ammoniak fra gylle vil være lavere, såfremt den udsættes for større mængder nedbør.

Erkendtlighed

Undersøgelserne er gennemført med økonomisk støtte fra Miljøstyrelsens NPO-forskningsprogram.

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Manuskript modtaget den 13. september 1989.

Ammoniakfordampning fra svinegylle på nykalket jord

Ved fordampning af ammoniak fra husdyrgødning tabes kvælstof på plantetilgængelig form, der skal erstattes ved tilførsel af handelsgødning.

I forbindelse med tilførsel af jordbrugskalk forud for såning af såvel vårsæd som vintersæd udbringes undertiden gylle på den nykalkede jord inden pløjning. Ved kalkning øges jordens pH. Størrelsen og hastigheden af ammoniakfordampning fra gylle afhænger blandt mange faktorer af pH. Virkningen af samtidig kalkning og gylletilførsel i praksis er ikke undersøgt. Først på efteråret blev der derfor gennemført 4 forsøg med gylle på nykalket jord og 2 forsøg med gylle på ukalket jord. Der blev bragt svinegylle og jordbrugskalk ud i mængder svarende til henholdsvis 30 t/ha og 5 t/ha. Fordampningen af ammoniak blev undersøgt med et vindtunnelsystem (forsidebilledet).

Forsøgene viste, at der fra ukalket jord fordampede 19-25 pct. af det udbragte ammonium i løbet af 6 døgn (tabel 1). Ammoniakfordampningen øgedes med 21-28 pct. af denne værdi, hvis gyllen blev bragt ud på nykalket jord. I perioder med mindst risiko for fordampning af ammoniak er virkningen af kalk mindst.

Ved udbringning af gylle på nykalket jord øges således tabet af plantetilgængeligt kvælstof.

TABEL 1. **Samlet ammoniaktab efter 6 timer, 12 timer, 1 døgn og 6 døgn fra svinegylle bragt ud på nykalket og ukalket jord.**

Antal timer eller døgn efter forsøgsstart	**Periode A** 29. august - 4. september			**Periode B** 5. - 11. september		
	Ammoniaktab, pct. af udbragt ammonium			**Ammoniaktab, pct. af udbragt ammonium**		
	Ukalket jord	Nykalket jord	Stigning som følge af kalk	Ukalket jord	Nykalket jord	Stigning som følge af kalk
6 timer	9	12	33	7	9	29
12 timer	11	15	36	10	12	20
1 døgn	14	21	50	13	17	30
6 døgn	25	32	28	19	23	21

Forsidebilledet:

Bestemmelse af ammoniakfordampning

Ammoniakfordampning fra gylle bragt ud på jordoverfladen bestemmes med et vindtunnelsystem. Gødningen udlægges på et 2 m x 0,5 m forsøgsareal, der er dækket af en lysgennemtrængelig U-formet tunnel. I forlængelse af tunnelen findes et metalrør med en regulerbar ventilator, der suger luft gennem tunnelen med en forud bestemt vindhastighed. Efter ventilatoren måles luftens indhold af ammoniak. Det målte indhold trækkes fra indholdet af ammoniak målt i en tunnel, hvor der ikke er bragt gylle ud. Ved at gange det herved fremkomne indhold af ammoniak med luftmængden, der passerer tunnelen i det givne tidsrum, kan ammoniakfordampningen beregnes.

Forsøgsplan

Forsøgssted: Afdeling for Planteernæring og -fysiologi, Askov.
Pløjet og harvet.
Jordtype: JB 4
Vandindhold i jord: Periode A, 15,7 pct.
Periode B, 13,5 pct.

Tidspunkt for forsøg
Periode A: 29. august - 4. september 1989,
2 forsøg på nykalket jord
1 forsøg på ukalket jord
Periode B: 5. september - 11. september 1989,
2 forsøg på nykalket jord
1 forsøg på ukalket jord

Gylle og kalk
Svinegylle: Mængde 30 t/ha
pH 7,6
Total-N 0,52 pct.
NH_4^+-N 0,37 pct.
Tørstof 3,82 pct.
Jordbrugskalk: Mængde 5 t/ha
Sigteanalyse:
<0,2mm: 17 pct.
0,2-0,5 mm: 11 pct.
0,5-2,0 mm: 24 pct.
>2,0 mm: 48 pct.

Klimaforhold målt ved klimastation og i tunnelen, døgngennemsnit.

Forsøgs-periode	Dag fra forsøgsstart	I tunnelen		Klimastation	
		Temperatur °C	Vindhastighed m/s	Temperatur °C	Luftfugtighed pct.
A	1		2,9	12	77
	2		2,9	15	85
	1-6		2,9	13	81
B	1	13	3,0	14	87
	2	14	2,9	15	84
	1-6	15	2,7	14	85

Denne praksis kan derfor ikke anbefales, medmindre gyllen nedbringes umiddelbart efter udspredningen. I øvrigt har gyllen tilført før såning af vintersæd en meget lille gødningsvirkning, og tilførsel af gylle på dette tidspunkt kan ikke anbefales.

Klimaforhold

Forsøgene blev gennemført ved vindhastigheder 2,7-3,0 m/s. Temperaturen varierede mellem 12°C og 15°C i tunnelen. Som gennemsnit var lufttemperaturen 18°C, og den relative fugtighed 77-87 pct. på klimastationen på afdelingen i Askov.

Ammoniak-fordampning

Fordampningen af ammoniak var stor de første et til to døgn efter gylleudbringning, for derpå at aftage betydeligt (fig. 1). Dette er i overensstemmelse med tidligere undersøgelser, der viste, at halvdelen af ammoniakfordampningen fandt sted inden for dette tidsrum. I periode A var fordampningen større end i forsø-

røn viden

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et fra perioden B. Dagen før
arten af forsøgene i periode A
ldt 4 mm nedbør, mens det i
en efterfølgende periode B, ikke
avde regnet 4 dage før forsø-
ets start. Et højt vandindhold i
rden kan begrænse nedsiv-
ingen af ammonium fra gyllen
l jorden og dermed fremme
etingelserne for ammoniak-
rdampningen. Luftens relati-
e fugtighed var lavere de før-
e 2 døgn i periode A end i
eriode B, hvilket også kan frem-
e ammoniakfordampningen.

Efter de to første døgn var
mmoniakfordampningen fra
ylle udbragt på nykalket jord
1 pct. og 28 pct. større end fra
kalket jord (fig.1). Herefter var
er ikke forskel i fordampningen
a nykalket og ukalket jord,
vilket ses af, at kurverne i fig. 1
rløber parallelt. I periode B var
rskellen på ammoniakfor-
ampningen fra gylle på nykal-
et og ukalket jord mindre end i
eriode A. Dette tyder på, at i
erioder, hvor der er gunstige
etingelser for ammoniakfor-
ampning, vil virkningen af
amtidig tilførsel af gylle og kalk
ære størst.

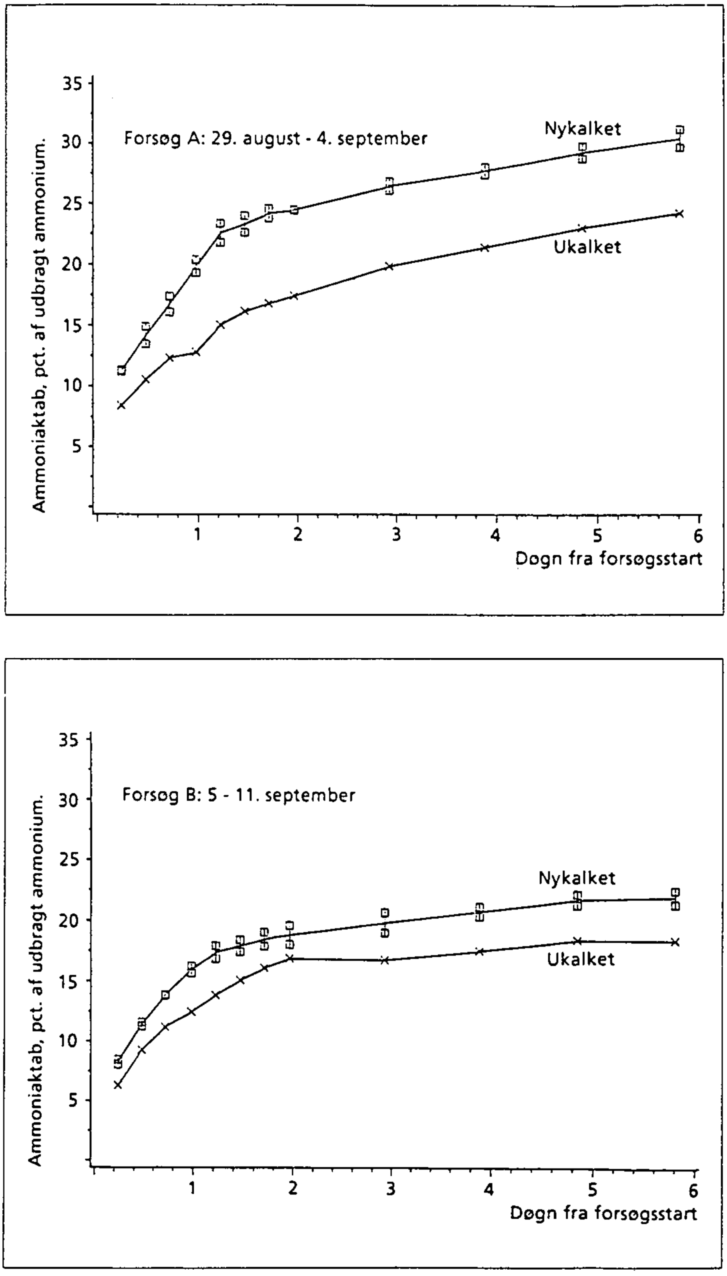

Fig. 1. Fordampning af ammoniak fra svinegylle (30 t/ha) bragt ud på nykalket (5 t/ha) og ukalket jord.

Statens Planteavlsforsøg
Landbrugscentret
Afdeling for Planteernæring og -fysiologi, Askov
6600 Vejen

Beretning nr. 2090

Ammoniakfordampning fra fast husdyrgødning samt ubehandlet, afgasset og filtreret gylle efter overfladeudbringning, nedfældning, nedharvning og vanding

Ammonia volatilization from solid manure and raw, fermented and separated slurry after surface application, injection, incorporation into the soil and irrigation

SVEN G. SOMMER og BENT T. CHRISTENSEN

Resumé

Ammoniakfordampning fra ubehandlet hønse-, kvæg- og svinegylle, væske- og fiberfraktion af mekanisk filtreret gylle, afgasset gylle fra biogasanlæg, samt fast kvæg- og svinegødning blev bestemt med et vindtunnelsystem. For fast gødning blev virkningen af nedharvning og vanding undersøgt, mens betydningen af direkte nedfældning blev belyst for gylle.

Ubehandlet og afgasset gylle gav anledning til ammoniakfordampning af samme størrelse. Ammoniaktabet fra væskefraktionen af ubehandlet og afgasset gylle var ligeledes af samme størrelse, formentlig fordi gyllens pH og tørstofindhold ikke ændredes ved afgasningen.

Inden for samme gødningskategori (fx gylle, fast gødning og ajle) kan ammoniaktabet generelt set forudsiges ud fra kendskab til tørstofindhold, pH og klimaforhold.

Fra væskefraktionen (0,9 pct. TS) var ammoniaktabet efter 6 døgn mindre end 23 pct. af ammoniumindholdet. Fra fiberfraktionen (22 pct. TS) fordampede mere end 66 pct. I perioder med frost øgedes tabet af ammoniak fra fiberfraktionen, men ikke fra væskefraktionen. Ved tilførsel af stigende mængder fiberfraktion fordampede en stigende andel af den udbragte ammonium.

Nedfældning i tør jord begrænsede ammoniaktabet efter 6 døgn til under 17 pct. af ammoniumindholdet, hvorimod fordampningen efter nedfældning i jord med højt vandindhold var ca. 50 pct. Nedharvning af fast svinegødning mindskede ammoniaktabet til 39 og 93 pct. af tabet fra gødning på jordoverfladen.

Vanding med 5 og 10 mm i forbindelse med udbringning af fast svinegødning og efter 1, 2 og 3 døgn begrænsede ammoniaktabet. I de første 2 døgn havde vanding med 4 × 10 mm størst effekt, men herefter øgedes tabshastigheden. Efter 6 døgn fandtes samme tab ved de to vandingsniveauer.

I vindtunnelen er forsøgsarealerne afskærmet mod nedbør, ammoniaktabet bestemmes derfor under udtørrende forhold. Tabet af ammoniak vil være lavere, såfremt den udbragte gødning udsættes for nedbør.

Nøgleord: Ammoniakfordampning, vindtunnelsystem, gylle, fast gødning, behandlet gylle, nedbringning, vanding, nedfældning.

Summary

A wind tunnel system was used to determine the ammonia volatilization loss from surface applied and incorporated animal manure, and from injected slurry. The ammonia loss from solid manure, cattle, pig and poultry slurry, fermented slurry, and the liquid and fibrous fraction of mechanically separated slurry was examined.

Fermentation of slurry had no effect on the ammonia loss following landspreading. The loss from the liquid fraction of fermented slurry did not differ from that of the liquid fraction of untreated slurry, probably reflecting that fermentation did not change slurry pH and dry matter content.

Within the same category of manure (e. g. slurries, farmyard manure or urine), the loss of ammonia may be predicted from dry matter content, pH and climatic conditions.

After six days the ammonia loss from the liquid fraction (0.9 per cent DM) was less than 23 per cent of the applied ammonium. From the fibrous fraction (22 per cent DM) more than 66 per cent of the applied ammonium was lost. At temperatures below 0°C ammonia loss increased from the fibrous fraction but not from the liquid fraction. The proportion of ammonia lost from 80 and 120 t/ha of fibrous fraction left on the soil surface was higher than from 40 t per ha.

Injection into a dry soil reduced the ammonia loss to less than 17 per cent of the applied ammonium, whereas 50 per cent of the injected ammonium was lost when the soil was wet. Shallow incorporation of pig manure by harrowing reduced ammonia loss to 39 and 93 per cent of the loss from manure left on the soil surface.

Irrigation at 5 and 10 mm at application of pig solid manure and after 1, 2 and 3 days reduced the ammonia loss. Irrigation at 10 mm had greatest effect during the first two days, thereafter the rate of ammonia loss increased. After six days of exposure the ammonia loss did not differ between the two treatments.

In the wind tunnels the experimental area is protected against rain and the experiments are run under drying conditions. The loss of ammonia will be lower if the manure is exposed to precipitation.

Key words: Volatilization of ammonia, wind tunnel system, animal slurry, solid manure, treated slurry, incorporation, irrigation, injection.

Indledning

Ammoniakfordampning fra husdyrgødning mindsker gødningsværdien og medfører en uønsket påvirkning af miljøet. Tabet af ammoniak fra gylle på jordoverfladen udgør ofte mere end 50 pct. af det udbragte ammonium (13). I den første time efter udbringning af gylle er der målt tab på 12,1 kg NH_3-N pr. ha (8).

Den stadigt stigende opmærksomhed omkring en mere optimal anvendelse af specielt gylle har blandt andet medført interesse for at forarbejde gyllen, inden den anvendes som gødning på markerne. Således anvendes gylle som grundlag for biogasfremstilling. Gyllens store vandindhold har medført interesse for at separere gylle i en fiberrig fraktion, der kan håndteres som fast gødning, og en tyndtflydende og mere homogen væskefraktion, der er lettere at håndtere end ubehandlet gylle (lettere doserbar, mindre tilstopningsrisiko i udbringningsudstyr).

Det er ikke muligt at forudse, hvilke nye behandlingsformer for husdyrgødning, der vil blive udviklet. Det er derfor vigtigt at øge kendskabet til de faktorer i gødningen, der har størst betydning for ammoniaktabet. Derved kan behovet for supplerende undersøgelser i forbindelse med nye typer af behandlet gylle mindskes.

Gyllens ammoniumindhold, pH og tørstofindhold er af stor betydning for ammoniaktabet fra gylle (3, 11, 12). Ammoniaktabet fra afgasset gylle, fiber- og væskefraktionen af gylle og fra fast gødning blev derfor undersøgt i relation til gødningstypen, dens pH og tørstofindhold samt klimaforhold.

Materialer og metoder

Bestemmelse af ammoniakfordampning

Fordampningen af ammoniak blev bestemt ved hjælp af et vindtunnelsystem som tidligere beskrevet af *Christensen* og *Sommer* (4). Ved denne metode bestemmes ammoniakindholdet i den

Tabel 1. Kemisk sammensætning og mængde af den anvendte gødning, behandlinger, jordbundstyper og overflade af forsøgsarealet.
Chemical composition and amount of added manure, treatments, soil type and surface of experimental area.

nr. *no.*	Forsøgsperiode *Experiment period*	Gødning, *Manure*						Behandling *Treatments*	Jordtype *Soil type*	Overflade *Soil surface*
		Type**) *type*	Mængde t/ha *amount t/ha*	Total-N pct. *Total-N %*	NH_4**) pct. *NH_4^+ %*	pH *pH*	Tørstof pct. *Dry matter %*			
1.	1987	Svg	30	0,27	0,18	6,4	3,3	Overflade	JB 5	Græs 5 cm, *grass 5 cm*
	09.04–15.04	Svg	30	0.68	0,56	7,4	4,4	-	JB 5	- -- - --
		Hg	25	0,80	0,61	6.9	9,5	-	JB 5	- -- - --
2.	1987	Kg	30	0,44	0,25	7.8	7,5	Nedfældet	JB 5	Græs efter slæt, *cut grass*
	02.06–08.06	Kg	30	0,44	0,25	7.8	7,5	-	JB 5	- - - - -
		Kg	30	0,44	0,25	7.8	7,5	-	JB 5	- - - - -
3.	1987							Overflade		
	15.09–21.09	Svf	30	0,92	0,56	7.7	20.4	- 5 mm***)	JB 5	Stub, *stubble*
		Svf	30	0.92	0.56	7,7	20,4	- 10 mm***)	JB 5	- -
4.	1987	Svf	30	0,92	0,56	7,7	20,4	Nedharvet	JB 5	Fræset stub, *rotavated stubble*
	24.09–30.09	Svf	30	0.92	0,56	7,7	20,4	-	JB 5	- - - -
		Svf	30	0,92	0,56	7.7	20,4	Overflade	JB 5	Stub, *stubble*
5.	1987	Kf	30	0.37	0,11	7,8	19.8	Overflade	JB 5	Fræset jord. *rotavated soil*
	30.09–06.10	Kf	30	0.37	0.11	7,8	19,8	-	JB 5	- - - -
		Kf	30	0.37	0,11	7,8	19,8	-	JB 5	- - - -
6.	1987	Kf	30	0.37	0,11	7,8	19.8	Overflade	JB 5	Fræset jord, *rotaved soil*
	17.11–23.11	Kf	30	0.37	0.11	7.8	19,8	-	JB 5	- - - -
7.	1988	Svgv	30	0.55	0.50	7,9	2,1	Overflade	JB 1	Rug < 10 cm. *Rye < 10 cm*
	09.03–15.03	Svgav	30	0.56	0.50	8,1	1,9	-	JB 1	- - - -
		Svgav	30	0.56	0.50	8,1	1,9	-	JB 1	- - - -
8.	1988	Svgv	30	0.55	0.50	7,9	2,1	Overflade	JB 1	Rug < 10 cm, *Rye < 10 cm*
	16.03–22.03	Svgv	30	0.55	0,50	7,9	2,1	-	JB 1	- - - -
		Svgav	30	0.56	0.50	8,1	1,9	-	JB 1	- - - -
9.	1988	Svgv	30	0.55	0.50	7,9	2,1	Overflade	JB 1	Rug < 10 cm. *Rye < 10 cm*
	23.03–29.03	Svgav	30	0.56	0.50	8,1	1,9	-	JB 1	- - - -
		Svgav	30	0.56	0.50	8.1	1,9	-	JB 1	- - - -
10.	1988	Svgv	30	0.55	0,50	7,9	2,1	Overflade	JB 1	Rug < 20 cm. *Rye < 20 cm*
	05.04–11.04	Svgv	30	0.55	0,50	7,9	2,1	-	JB 1	- - - -
		Svgav	30	0.56	0.50	8,1	1,9	-	JB 1	- - - -
11.	1988	Svg	30	0,43	0.38	7,5	3,1	Overflade	JB 1	Rug < 30 cm. *Rye < 30 cm*
	17.05–23.05	Svga	30	0,44	0,37	7,8	2,7	-	JB 1	- - - -
		Svga	30	0,44	0,37	7,8	2,7	-	JB 1	- - - -
12.	1988	Svg	30	0,43	0,38	7,5	3,1	Overflade	JB 1	Majs < 10 cm, *Maize < 10 cm*
	25.05–31.05	Svg	30	0.43	0,38	7,5	3.1	-	JB 1	- - - -
		Svga	30	0,44	0.37	7.8	2,7	-	JB 1	- - - -
13.	1988	Kgf	120	0.40	0,16	8,1	19,9	Overflade	JB 1	Majs < 20 cm, *Maize < 20 cm*
	31.05–06.06	Kgf	80	0.40	0.16	8,1	19,9	-	JB 1	- - - -
		Kgf	40	0,40	0.16	8,1	19.9	-	JB 1	- - - -
14.	1988	Kg	30	0,45	0.26	7,9	8.2	Overflade	JB 5	Græs < 5 cm. *Grass < 5 cm*
	16.11–22.11	Svgv	30	0.29	0.23	7,5	1,1	-	JB 5	- - - -
		Svgf	30	0,46	0.20	8,6	19,6	-	JB 5	- - - -

(fortsætter)

Tabel 1. (Fortsat).

nr. *no.*	Forsøgsperiode *Experiment period*	Godning, *Manure*						Behandling *Treatments*	Jordtype *Soil type*	Overflade *Soil surface*
		Type**) *type*	Mængde t/ha *amount t/ha*	Total-N pct. *Total-N %*	NH_4^+*) pct. *NH_4^+ %*	pH *pH*	Tørstof pct. *Dry matter %*			
15.	1988 23.11–29.11	Kg	30	0,45	0.26	7,9	8.2	Overflade	JB 5	Græs < 5 cm. *grass < 5 cm*
		Svgv	30	0.29	0.23	7.5	1,1	–	JB 5	– – – –
		Svgf	30	0,46	0,20	8,6	19,6	–	JB 5	– – – –
16.	1988 14.12–20.12	Kg	30	0,45	0,26	7,9	8,2	Overflade	JB 5	Græs < 5 cm. *grass < 5 cm*
		Svgv	30	0,29	0,23	7,5	1,1	–	JB 5	– – – –
		Svgf	30	0,46	0.20	8.6	19.6	–	JB 5	– – – –
17.	1989 25.04–01.05	Bga	40	0.61	0.37	7.2	8.1	Nedfældet	JB 5	Byg < 10 cm. *Barley < 10 cm*
		Bga	40	0,61	0,37	7,2	8,1	–	JB 5	– – – –
		Bga	40	0.61	0.37	7,2	8,1	–	JB 5	– – – –
18.	1989 31.05–06.06	Bgf	30	0,49	0.16	7,0	22.0	Overflade	JB 5	Byg < 20 cm. *Barley < 20 cm*
		Bgv	30	0,29	0,25	7,1	0,9	–	JB 5	– – – –
		Kg	30	0.44	0.26	7.5	6.5	–	JB 5	– – – –
19.	1989 07.06–13.06	Bgf	30	0,49	0.16	7.0	22,0	Overflade	JB 5	Byg < 30 cm. *Barley < 30 cm*
		Bgv	30	0.29	0,25	7.1	0,9	–	JB 5	– – – –
		Kg	30	0.44	0.26	7.5	6,5	–	JB 5	– – – –

*) $NH_4^+ = (NH_3 + NH_4^+)$

**) Gødningstype:
Kg : Kvæggylle
Kf : Fast Kvæggødning
Svf : Fast Svinegødning
Svg : Svinegylle
Hg : Hønsegylle
Bgf : Blandet gylle, fiberfraktion
Bgv : Blandet gylle, væskefraktion
Bga : Blandet gylle, afgasset
Kgf : Kvæggylle, fiberfraktion
Svga : Svinegylle, afgasset
Svgv : Svinegylle, væskefraktion
Svgf : Svinegylle, fiberfraktion
Svgav : Svinegylle, afgasset væskefraktion

***) Vandet efter udbringning samt 24, 48 og 72 timer efter udbringning i alt tilført henholdsvis 20 og 40 mm.

luft, der forlader det gødede areal. Der anvendes i alt fire vindtunneler, der hver dækker et forsøgsareal på 0.5 gange 2 m. Én vindtunnel benyttes til bestemmelse af ammoniakindholdet i luften fra et ubehandlet areal (referenceareal), mens de tre øvrige anvendes til måling af forsøgsbehandlinger.

Lufthastigheden i vindtunnelerne kan indstilles til forud fastlagte niveauer. I måleperioden (6 døgn) aflæses aktuel vindhastighed og lufttemperatur i vindtunnelerne, og disse værdier lagres på datalogger som timemiddelværdier.

Ammoniakken i luftafkastet fra vindtunnelerne opsamles i en fosforsyreopløsning og bestemmes efterfølgende ved spektrofotometri (Berthelot reaktion). I de to første døgn efter forsøgsstart opsamles den fordampede ammoniak over 6 timers intervaller, mens der de sidste fire døgn opsamles over 24 timers intervaller.

De registrerede ammoniaktab korrigeres for ammoniaktab fra referenceareal og for genfindelsesprocent (4).

Fordampningen er opgjort som ammoniak fordampet i procent af udbragt ammonium. Derved muliggøres en sammenligning af ammoniaktabet fra forskellige gødningstyper uden hensyntagen til forskelle i ammoniumindholdet.

Forsøgsplan

Tabel 1 giver en karakterisering af de anvendte gødningstyper. Der blev benyttet væske- og fiberfraktionen af mekanisk filtreret og afgasset gylle, afgasset gylle, hønsegylle, kvæggylle og svinegylle, samt fast kvæg- og svinegødning. Den udbragte gødning havde pH fra 6,4 til 8,6, tørstof fra 0,9 til 22 pct. og fra 0,27 til 0,92 pct. total-N. Ammoniak- og ammoniumindholdet (herefter benævnt ammonium) varierede fra 0,11 til 0,61 pct.

Tabel 2. Middelværdi for lufttemperatur i tunnel, vanddampsdeficit målt på klimastation, samt aflæst vindhastighed i stålrøret (I parentes standardafvigelser).

Average air temperature during experiments, watervapour deficit measured at climate station, and average of measured wind speed in steel ducts (standard deviation in brackets).

nr. *no.*	Forsøgsperiode *Experiment period*		Luft temp. °C *Air temp. °C*	Vanddamps deficit, mbar *Watervapour pressure deficit, mbar*	Vindhastighed m/s *Windspeed m/s*	Akkumuleret NH_3 tab, pct. af NH_4^+ *Cumulated NH_3 loss, p.c. of NH_4^+*		
						6 timer *6 hours*	12 timer *12 hours*	6 dage *6 days*
1.	1988	Svg	3,0 (1,0)	0,6 (0,5)	5,2 (0,2)	2.8	3.8	15,8
	09.04–15.04	Svg				10,1	13,2	27,9
		Hg				5,2	7,2	23,1
2.	1987	Kg	10.3 (1,9)	2,3 (1,4)	4.6 (0,1)	1,2	3.1	16.7
	02.06–08.06	Kg				1,5	3.1	14.5
		Kg				0,4	1.3	12.1
3.	1987	Svf	10,3 (1,5)	2,0 (1,3)	4,8 (0,5)	7.6	11.2	17.5
	15.09–21.09	Svf				5.1	6.8	21.4
4.	1987	Svf	7,7 (2,0)	1,8 (0,9)	5,1 (0,3)	4.8	8.1	17.8
	24.09–30.09	Svf				7.3	11.9	42.2
		Svf				11.0	16.3	45.4
5.	1987	Kf	5.5 (3,4)	2,5 (1,8)	5.0 (0.3)	31.0	31.0	42,4
	30.09–06.10	Kf				30.2	30.2	48.0
		Kf				22.7	22.7	45.2
6.	1987	Kf	6.5 (1.8)	0,7 (0.3)	5.5 (0.2)	6.2	22.5	30.0
	17.11–23.11	Kf				15.1	21.4	44.0
7.	1988	Svgv	1,6* (1.9)	0,8 (0,5)	4,6 (0,3)	5.1	8.4	29.9
	09.03–15.03	Svgav				5.9	10.3	26.2
		Svgav				4.9	8.8	25.5
8.	1988	Svgv	2,0 (1.1)	1,0 (0,6)	4,5 (0,2)	5.5	8,2	33.2
	16.03–22.03	Svgv				6.5	9.0	32.6
		Svgav				6.5	9.2	30.9
9.	1988	Svgv	2.7 (1,2)	0,7 (0,3)	4,7 (0,3)	4.1	7.2	18.7
	23.03–29.03	Svgav				9.9	14.8	17.8
		Svgav				8.0	12.0	25.2
10.	1988	Svgv	4,6* (3.2)	2,0 (1,4)	4,6 (0,3)	12,2	15.6	48.4
	05.04–11.04	Svgv				13,4	17.0	54,1
		Svgav				17.6	23.3	46.1
11.	1988	Svg	8,1* (2.3)	2,7 (1.3)	5,0 (0,3)	15.6	33.8	61,3
	17.05–23.05	Svga				24.5	34,4	47,9
		Svga				32.9	44.3	58.0
12.	1988	Svg	17,4 (0,2)	5.8 (2.7)	5,1 (0,3)	26.7	34.1	54.4
	25.05–31.05	Svg				30,5	38.7	56.8
		Svga				44.1	51.9	67.2
13.	1988	Kgf	11,9* (1,2)	2,2 (1,1)	4.3 (0,1)	40,6	48.1	72.6
	31.05–06.06	Kgf				45,7	52.1	64,7
		Kgf				25,1	26.9	33,1

(fortsætter)

Tabel 2. (Fortsat).

nr. *no.*	Forsøgsperiode *Experiment period*		Luft temp. °C *Air temp. °C*	Vanddamps deficit, mbar *Watervapour pressure deficit, mbar*	Vindhastighed m/s *Windspeed m/s*	Akkumuleret NH_3 tab. pct. af NH_4^+ *Cumulated NH_3 loss, p.c. of NH_4^+*		
						6 timer *6 hours*	12 timer *12 hours*	6 dage *6 days*
14.	1988	Kg	3,2 (4,7)	0,7 (0,3)	3,3 (0,1)	16,8	16,8	47.3
	16.11–22.11	Svgv				3,8	5,2	15,6
		Svgf				21,8	36,3	66,1
15.	1988	Kg	5.5 (1,6)	0,7 (0,3)	3,5 (0.2)	12,0	20.7	55.8
	23.11–29.11	Svgv				3.1	4,7	18,1
		Svgf				16,7	33,9	73.5
16.	1988	Kg	1.3 (1,8)	0,7 (0,5)	3,8 (0.2)	15.1	23.5	74,0
	14.12–20.12	Svgv				2,1	3.1	10,3
		Svgf				36.2	51.9	100.0
17.	1989	Bga	5,7* (1,9)	2,2 (1,4)	3,7 (0,1)	1,5	3.8	52.5
	25.04–01.05	Bga				2,2	4,5	48,7
		Bga				2,7	6,4	50.3
18.	1989	Bgf	8,7 (2,0)	2,7 (1,6)	3,4 (0.1)	58,6	68,0	97,4
	31.05–06.06	Bgv				4,5	5,4	19.0
		Kg				17.6	26.4	53.8
19.	1989	Bgv	11,4 (3.5)	4,2 (2,6)	3,7 (0.1)	1,6	3.5	23.1
	07.06–13.06	Bgf				26,1	32,4	67.6
		Kg				20.2	28.2	58.8

* Målt på klimastation.

Svinegyllen er afgasset i et anaerobt, fikseret biofilter med gennemsnitlig opholdstid på ca. 7 døgn. En gyllenedfælder med arbejdsbredde på 2 m svarende til forsøgsarealets længde blev benyttet til nedfældning af gyllen i 15 cm dybde.

Forsøgene blev gennemført fra d. 9. april 1987 til d. 13. juni 1989. Der blev som regel tilført gylle svarende til 30 t pr. ha. I forsøget med hønsegylle blev der tilført mængder svarende til 25 t pr. ha, og i et forsøg med fiberfraktionen af filtreret kvæggylle tilførtes 40, 80 og 120 t pr. ha.

Gyllen blev udbragt på fræset bar jord, fræset stub, ubehandlet stub, græs efter slæt, samt rug, majs og byg i forskellige vækststadier. Forsøgene blev gennemført på JB1 og JB5. Gyllen blev i seks forsøg nedfældet direkte, og fast gødning blev i to forsøg nedharvet. I to forsøg blev der vandet med henholdsvis 5 eller 10 mm vand 0, 1, 2 og 3 døgn efter udbringning af fast gødning svarende til i alt 20 og 40 mm.

Resultater og diskussion

Vindhastigheden målt i metalrøret var i forsøgene mellem 3,3 og 5,5 m/s (tabel 2), og der blev registreret middellufttemperaturer fra 1.3 til 17,4°C og vanddampsdeficit fra 0,6 til 5,8 mbar. Der er benyttet vanddampsdeficit bestemt fra målinger på klimastationen på Askov forsøgsstation. Målinger af lufttemperaturen på klimastationen er benyttet i de forsøg, hvor der ikke er målt lufttemperatur i vindtunnelen. Det er påvist, at der er lille forskel på temperaturen målt uden for og inde i vindtunnelen (9).

For gødning på jordoverfladen fandtes de største ammoniaktabshastigheder inden for det første døgn efter udbringningen, hvorefter tabshastigheden mindskedes. Således udgjorde ammoniaktabet inden for det første døgn typisk halvdelen af det samlede tab over 6 døgns perioden. Det samme mønster er fundet af *Pain et al.* (8) og *Thompsen et al.* (13). De høje tab fra gylle i det første døgn efter udbringningen skyldes formentlig, at der i forbindelse med udbringningen sker en pH stigning i gyllens overflade (10). Efterfølgende falder pH som følge af ammoniakfordampningen. Dette fald, samt nedsivning af ammonium i jorden og udtørring af gødningen med skorpedannelse til følge medfører, at der med tiden sker en reduktion i hastigheden af ammoniaktabet (10, 13).

Fast kvæggødning og hønsegylle

Ammoniaktabet fra fast kvæggødning på jordoverfladen viste et eksponentielt forløb svarende til tabet fra gylle (fig. 1A). Af den tilførte ammonium fordampede i gennemsnit 45 pct. i oktober og 37 pct. i november 1987 (tabel 2). Især de første 6 timer efter udbringning var ammoniakfordampningen i november lavere end i det forudgående forsøg. Da der ikke var stor forskel på temperaturen i de to forsøg, er det formentligt den lavere luftfugtighed i oktober, der har medført de større ammoniaktab (10). Med vindtunnelmetoden er der målt dobbelt så store tab af ammoniak i løbet af seks døgn fra filtreret kvæggylle med samme pH og justeret til samme tørstofindhold (12).

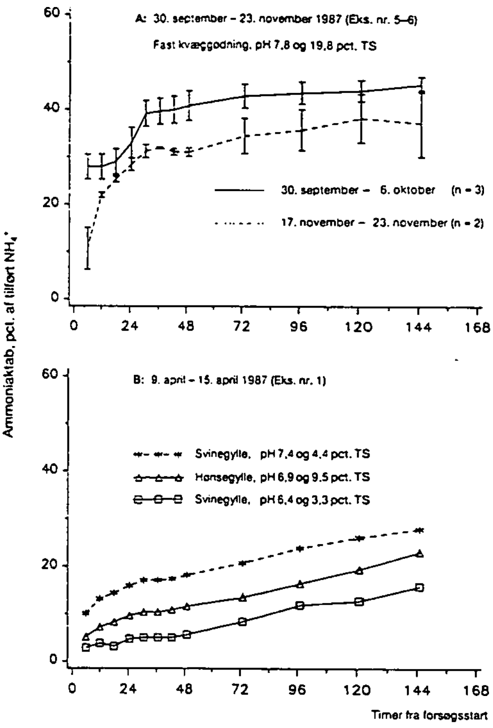

Fig. 1. Akkumuleret ammoniakfordampning fra fast kvæggodning (30 t pr. ha), svinegylle (30 t pr. ha) og hønsegylle (25 t pr. ha). TS = tørstof. Lodrette pinde angiver 1 s. d.

Cumulated loss of ammonia from solid cattle manure (30 t per ha), pig slurry (30 t per ha) and poultry slurry (25 t per ha). TS = dry matter. Bars indicate 1 s. d.

Ammoniaktabet fra hønsegylle blev sammenlignet med tabet fra to forskellige typer af svinegylle (fig. 1B). Fra de to typer svinegylle var ammoniaktabet i løbet af 6 døgn fra 15,8 til 27,9 pct. af den udbragte ammonium (tabel 2). Ammoniaktabet fra hønsegyllen var på et niveau mellem tabet fra de to typer svinegylle. Det laveste tab stammer fra svinegyllen med lavere tørstofindhold og et pH væsentlig lavere som i hønsegyllen. Det største tab er fra svinegyllen med lavt tørstofindhold, men med højt pH. Ammoniakfordampningen var generelt lav i dette forsøg som følge af lave temperaturer (uden frost) og en høj luftfugtighed.

Ammoniaktabet fra hønsegylle er således på niveau med tabet fra svinegylle. Eventuelle forskelle skyldes forskelle i gyllens pH, tørstof og ammoniumindhold. Lignende konklusioner kan drages af forsøg af *Lockyer et al.* (6). Disse har endvidere vist, at tørring kort efter produktion af hønsegylle kan begrænse ammoniaktabet i stalden og ved efterfølgende udbringning. Dette tilskrives, at tørring har begrænset hydrolysen af urinsyre og derved begrænset indholdet af ammonium i hønsegødning.

Afgasset gylle

Ammoniakfordampningen fra afgasset og ubehandlet svinegylle blev undersøgt i to på hinanden følgende perioder i maj 1988 (fig. 2A, tabel 2). Der blev ikke fundet forskel på ammoniakfordampningen fra de to typer af svinegylle. Indholdet af ammonium og total-N var ens for de to gylletyper, mens pH i den ubehandlede svinegylle var en smule lavere og tørstofindholdet en smule højere end i den afgassede svinegylle.

Ammoniakfordampningen fra væskefraktionen af filtreret, afgasset og ubehandlet svinegylle blev undersøgt i 12 forsog over fire på hinanden følgende perioder i marts og april 1988 (fig. 2B). Der var ikke forskel på fordampningen af ammoniak fra de to typer af væskefraktioner, hverken på gennemsnittet af det akkumulerede ammoniaktab for de 4 perioder (fig. 2B) eller for

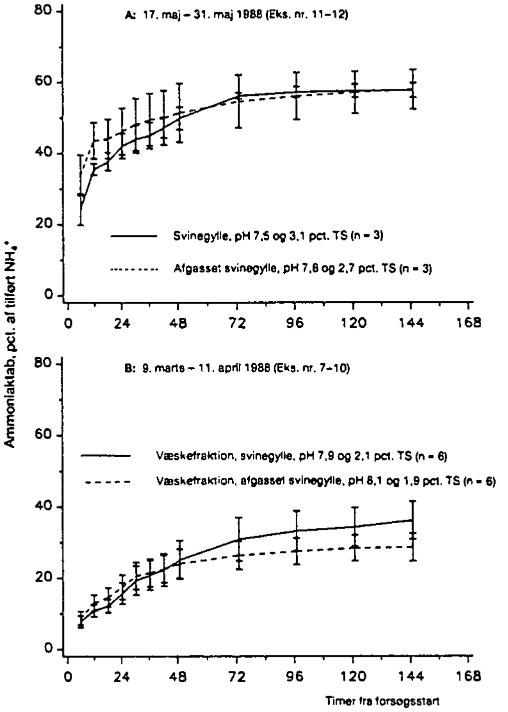

Fig. 2. Akkumuleret ammoniakfordampning fra svinegylle og afgasset svinegylle samt væskefraktionen af svinegylle og afgasset svinegylle (30 t pr. ha). TS = tørstof. Lodrette pinde angiver 1 s. d.

Cumulated loss of ammonia from pig slurry and fermented pig slurry, and from the liquid fraction of pig slurry and fermented slurry (30 t per ha). TS = dry matter. Bars indicate 1 s. d.

de enkelte perioder (tabel 2). Det lidt højere pH i væskefraktionen af den afgassede gylle modvirkes af et lavere tørstofindhold.

Tabene i perioden fra 5.–11. april 1988 var væsentlig større end i de foregående forsøg (tabel 2), hvilket har bevirket den store standardafvigelse på middelværdierne for alle forsøgene. I denne periode var temperaturen højere og vanddampsdeficit væsentlig større end i de forgående forsøg. Ved stigende temperatur og øget vanddampsdeficit øges ammoniakfordampningen (10).

Omsætning af organiske forbindelser ved afgasning af gylle i biogasanlæg påvirker således ikke ammoniakfordampningen efter udbringning. Behandling i form af filtrering har imidlertid en effekt på ammoniakfordampningen, idet tabet fra væskefraktionen er mindre end fra den ubehandlede gylle (fig. 2A og 2B).

Væske- og fiberfraktion af filtreret, almindelig gylle

Ammoniaktabet fra væske- og fiberfraktionen af almindelig gylle blev sammenlignet med tabet fra ubehandlet kvæggylle. Fordampningen i forsøgene gennemført i vinteren 1988 og i sommeren 1989 var på samme niveau (fig. 3). De høje tab fra fiberfraktionen af svinegyllen samt kvæggyllen udbragt i vinteren 1988 skyldes formentlig både effekten af et højt tørstofindhold og et hojt pH. De første timer efter udbringning af fiberfraktionen og kvæggyllen var tabet større i sommeren 1989 end i vinteren 1988 (fig. 3A og B). De høje

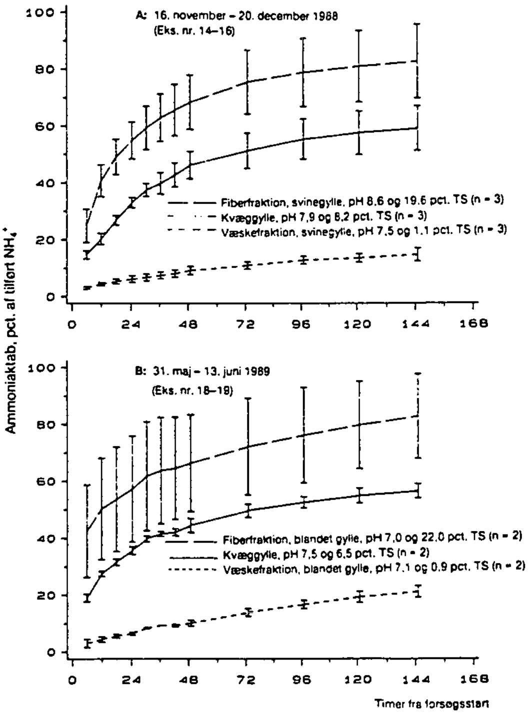

Fig. 3. Akkumuleret ammoniakfordampning fra kvæggylle, fiber- og væskefraktionen af svinegylle og blandet gylle (30 t pr. ha). TS = tørstof. Lodrette pinde angiver 1 s. d.

Cumulated loss of ammonia from cattle slurry, the fibrous and liquid fractions of pig slurry and mixed slurry (30 t per ha). TS = dry matter. Bars indicate 1 s. d.

temperaturer om sommeren har således medført høje tabshastigheder inden for de første 12 timer. Det akkumulerede tab efter seks døgn er det samme som i vinterperioden, hvor tabshastigheden efter de første 12 timer ikke aftager i samme grad som om sommeren. Lufttemperaturen var lav under forsøgene i vinteren 1988 (tabel 2), og der har været perioder med frost, hvilket kan have medvirket til de store tab fra fiberfraktionen og kvæggyllen. Frostperioder har ikke haft samme indvirkning på tabet fra væskefraktionen, sandsynligvis fordi væskefraktionen i dagtimerne efter udbringningen har kunnet sive ned i jorden.

Efter seks døgn var ammoniaktabet fra væskefraktionen 10–20 pct. af ammoniumindholdet ved udbringning i vinteren 1988 og 19–23 pct. ved udbringning i sommeren 1989 (tabel 2). Fra fiberfraktionen var tabene henholdsvis 66–100 pct. og 68–97 pct. Ammoniaktabet fra fiberfraktionen var i begge perioder større end tabet fra kvæggyllen, mens tabet fra væskefraktionen var mindre. Undersøgelsen bekræfter således, at ammoniaktabet er stort, hvis gødningen har højt tørstofindhold, og at tabet fra gødning med lavt tørstofindhold er ringe. Det er tidligere vist, at ammoniaktabet stiger lineært med tørstofindholdet i gylle (12).

Ved udbringning af 80 og 120 t fiberfraktion pr. ha var tabet ca. 65 og 73 pct. af den udbragte ammonium (tabel 2). Dette er mere end dobbelt så meget som ved udbringning af 40 t pr. ha (fig. 4). Tabet ved de to høje tilførsler var efter 6 timer væsentligt større end ved udbringning af 40 t pr. ha. I dette forsøg har udbringning af stigende mængder fiberfraktion således øget det relative ammoniaktab. Dette er i modsætning til resultaterne ved udbringning af stigende mængder af gylle, hvor det blev vist, at det procentiske ammoniaktab reduceres ved udbringning af mere end 60 t svinegylle pr. ha (6, 11).

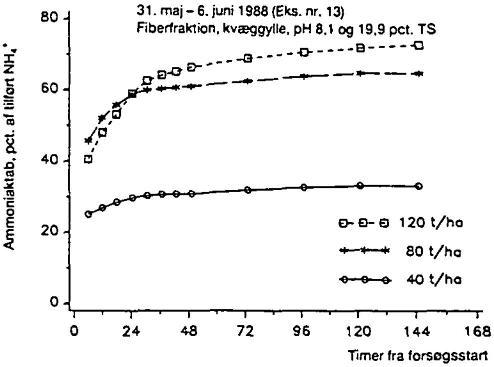

Fig. 4. Akkumuleret ammoniakfordampning fra fiberfraktionen af kvæggylle (40, 80 eller 120 t pr. ha). TS = tørstof.

Cumulated loss of ammonia from fibrous fraction of cattle slurry (40, 80 or 120 t per ha). TS = dry matter.

Direkte nedfældning og nedharvning

Seks døgn efter nedfældning af kvæggylle var ammoniaktabet i sommeren 1987 mindre end 17 pct. af den udbragte ammonium. I et tilsvarende forsøg med biogasgylle i forsommeren 1989 var tabet 49–53 pct. I begge forsøg var tabet lavt ved forsøgets start, hvorefter det akkumulerede tab steg lineært med tiden (fig. 5). Dette forløb afviger væsentligt fra det normale tabsmønster efter udbringning af ubehandlet gylle på jordoverfladen.

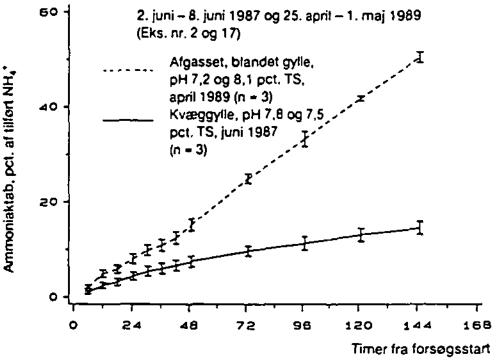

Fig. 5. Akkumuleret ammoniakfordampning fra direkte nedfældet kvæggylle (30 t pr. ha) og afgasset, blandet gylle (40 t pr. ha). TS = tørstof. Lodrette pinde angiver 1 s. d.

Cumulated loss of ammonia from injected cattle slurry (30 t per ha) and fermented mixed slurry (40 t per ha). TS = dry matter. Bars indicate 1 s. d.

I forsommeren 1989 blev gyllen nedfældet i jord med højt vandindhold efter en lang periode med megen nedbør. Dette er formentlig årsagen til det store tab af ammoniak efter seks døgn. Ammoniaktabet fra jord med højt vandindhold er korreleret til fordampningen af vand fra jorden, idet det nedfældede ammonium følger den opadgående vandbevægelse under udtørring (1, 7). I sommeren 1987 var jorden udtørret, idet der kun var faldet 22 mm nedbør i de 2 uger forud for forsøget.

I en undersøgelse af nedfældning gennemført af *Thompson et al.* (13) blev gyllen placeret i 35 cm dybde i furer lavet med en plov. Ved denne dybe nedfældning var ammoniaktabet i løbet af 12 døgn ca. 2 kg NH_3-N pr. ha ved nedfældning af 104–110 kg NH_4^+-N pr. ha.

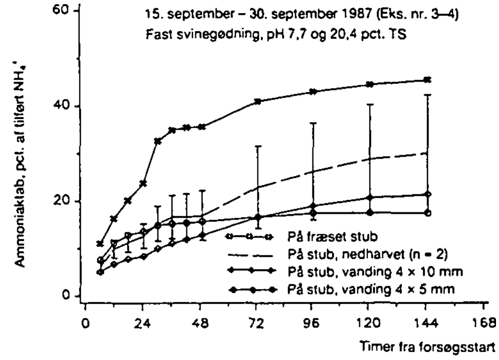

Fig. 6. Akkumuleret ammoniakfordampning fra vandet eller nedharvet fast svinegødning (30 t pr. ha). TS = tørstof. Lodrette pinde angiver 1 s. d.

Cumulated loss of ammonia from the irrigated or incorporated solid pig manure (30 t per ha). TS = dry matter. Bars indicate 1 s. d.

Harvning af jorden umiddelbart efter udbringning af fast svinegødning begrænsede ammoniaktabet efter seks døgn til 39 og 93 pct. af fordampningen fra gødning efterladt på overfladen (tabel 2). Det gennemsnitlige akkumulerede ammoniaktab var jævnt stigende gennem hele forsøgsperioden (fig. 6). Forløbet svarer til ammoniakfordampningen fra gylle nedfældet i våd jord. Adsorption af ammonium til jorden er den faktor, der begrænser ammoniaktabet ved nedharvning. Forskellen i effekten af nedharvning skyldes derfor sandsynligvis en ringere opblanding af svinegødning og jord i forsøget, hvor der blev målt store tab af ammoniak efter nedharvning.

Nedbør

Nedbør har halveret ammoniakfordampningen fra fast svinegødning på jordoverfladen (tabel 2). Der blev vandet umiddelbart efter udbringningen og derpå efter hvert af de efterfølgende tre døgn. I de tre døgn, hvor der blev vandet, var ammoniaktabet mindre ved vanding med 10 mm end med 5 mm pr. gang (fig. 6). Efter seks døgn var tabet ved de to behandlinger imidlertid det samme.

Vanding eller nedbør mindsker således ammoniakfordampningen uden at bringe den til ophør. Efter nedbørsperioder er et lignende forløb af ammoniaktabet fra gylle udbragt på jord blevet målt med meteorologiske massebalancemetoder (2). *Beauchamp et al.* (2) antog, at fordampningen af vand efter nedbørsperioder ledsages af ammoniakfordampning.

Konklusion

Der er ikke forskel på ammoniaktabet fra afgasset og almindelig gylle. Videre forarbejdning af disse gylletyper ændrer ikke på dette forhold, idet der ikke var forskel på ammoniaktabet fra væskefraktionen af almindelig og afgasset gylle. Der var ubetydelig forskel på de to gylletypers sammensætning. Under ens klimaforhold og ved samme udbringningsteknik vil forskelle i ammoniakfordampning hovedsageligt skyldes forskelle i pH, tørstofindhold og ammoniumindhold.

Ammoniaktabet fra hønsegylle var på niveau med tabet fra svinegylle. Disse resultater, samt undersøgelser af fiber- og væskefraktioner af gylle antyder således, at inden for samme gødningskategori som fx gylle, ajle eller fast gødning, kan fordampningen relateres til gyllens pH og tørstofindhold. Dette er ikke tilfældet imellem gødningskategorier.

Fordampningen af ammoniak fra væskefraktionen var mindre end 20 pct. og fra fiberfraktionen større end 66 pct. af ammoniumindholdet. Til sammenligning var fordampningen fra kvæggylle ca. 50 pct. i samme forsøgsperioder. Ved udbringning af stigende mængder fiberfraktion pr. ha fordampede en stigende andel af det udbragte ammonium. Perioder med frost medførte øget ammoniaktab fra fiberfraktionen, men ikke fra væskefraktionen. Væskefraktionen har øjensynligt infiltreret jorden i dagtimerne efter udbringning, hvorved adsorption af ammonium til jorden har begrænset effekten af frost.

Ved nedfældning af gylle i en ikke vandmættet jord var ammoniaktabet efter seks døgn mindre end 17 pct. af ammoniumindholdet. Blev gyllen nedfældet i fugtig jord, var tabet ca. 50 pct. Harvning efter udbringning af fast svinegødning begrænsede ammoniaktabet til 39 og 93 pct. af tabet fra gødning på jordoverfladen. Forskellen mellem de to forsøg kan tilskrives varierende opblandingsgrad af jord og gødning.

Vanding med 5 og 10 mm ved udbringningen og 24, 48 og 72 timer efter udbringning af fast svinegødning begrænsede ammoniaktabet i perioden, hvor der blev vandet. I de første tre døgn havde tilførsel af 4 × 10 mm størst effekt, men efter seks døgn var tabet ved de to vandingsniveauer det samme.

I vindtunnelen er forsøgsarealerne afskærmet mod nedbør. Undersøgelserne fandt derfor sted under udtørrende forhold. Perioder med nedbør vil medføre et reduceret tab af ammoniak fra husdyrgødning.

Erkendtlighed

Undersøgelserne er gennemført med økonomisk støtte fra Miljøstyrelsens NPO-forskningsprogram.

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Manuskript modtaget den 30. juli 1990.

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