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# AMMONIA EMISSIONS FROM SLURRY APPLICATIONS TO LAND

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University of Plymouth

# AMMONIA EMISSIONS FROM SLURRY APPLICATIONS TO LAND

by

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## List of published works


Paper 1 Misselbrook, T.H., T.J. van der Weerden, B.F. Pain, S.C. Jarvis, B.J. Chambers, K.A. Smith, V.R. Phillips, and T.G.M. Demmers. (2000). Ammonia emission factors for UK agriculture. *Atmospheric Environment* **34**, 871-880.

Paper 2 Webb, J., and T.H. Misselbrook. (2004). A mass-flow model of ammonia emissions from UK livestock production. *Atmospheric Environment* **38**, 2163-2176.

Paper 3 Misselbrook, T.H., and M.N. Hansen. (2001). Field evaluation of the equilibrium concentration technique (JTI method) for measuring ammonia emission from land spread manure or fertiliser. *Atmospheric Environment* **35**, 3761-3768.

Paper 4 Misselbrook, T.H., F.A. Nicholson, B.J. Chambers and R.A. Johnson. (2005). Measuring ammonia emissions from land applied manure: an intercomparison of commonly-used samplers and techniques. *Environmental Pollution* **135**, 389-397.

Paper 5 Misselbrook, T.H., F.A. Nicholson, and B.J. Chambers. (2005). Predicting ammonia losses following the application of livestock manure to land. *Bioresource Technology* **96**, 159-168.

Paper 6 Misselbrook, T.H., D. Scholefield and R. Parkinson. (2005). Using time domain reflectometry to characterise cattle and pig slurry infiltration into soil. Soil Use and Management 21, 167-172.

Paper 7 Smith, K.A., D.R. Jackson, T.H. Misselbrook, B.F. Pain, and R.A. Johnson. (2000). Reduction of ammonia emission by slurry application techniques. Journal of Agricultural Engineering Research 77, 277-287.

Paper 8 Misselbrook, T.H., K.A. Smith, R.A. Johnson, and B.F. Pain. (2002). Slurry application techniques to reduce ammonia emissions: Results of some UK field-scale experiments. Biosystems Engineering 81, 313-321.

Paper 9 Misselbrook, T.H., D.R. Chadwick, B.F. Pain, and D.M. Headon. (1998). Dietary manipulation as a means of decreasing N losses and methane emissions and improving herbage N uptake following application of pig slurry to grassland. Journal of Agricultural Science 130, 183-191.

Paper 10 Misselbrook, T.H., Powell, J.M., Broderick, G.A. and Grabber, J.H. 2005. Dietary manipulation in dairy cattle – laboratory experiments to assess the influence on ammonia emissions. Journal of Dairy Science 88, 1765-1777.

**Declaration**

The research contributing to the published works listed above was undertaken during the period 1995 to 2004 at which time TH Misselbrook was employed at the Institute of Grassland and Environmental Research (IGER).

Papers 1 and 2 detail the developments in methodology for national ammonia inventory emission models. Paper 1 involved collaboration between IGER, ADAS and Silsoe Research Institute (SRI), with TH Misselbrook responsible for collating emissions data for the whole range of agricultural sources to produce an inventory, highlighting the major sources and areas of greatest uncertainty. Paper 2 involved collaboration between ADAS and IGER in which the inventory model as presented in paper 1, which modelled emissions discretely from individual sources, was modified to become a nitrogen mass-flow model with linkages between related sources to allow for realistic scenario testing (e.g. implementation of potential abatement strategies).

Paper 3 involved collaboration between IGER and the Danish Institute of Agricultural Sciences, with field experimentation being conducted at both sites (Bygholm Research Station in Denmark) between 1998 and 2000. A recently developed method for measuring ammonia emissions was validated against an established micrometeorological technique and its use for measuring emissions from manure applications to land was discussed. Paper 4, a collaborative effort between IGER and ADAS conducted between 1996 and 1999, details the commonly used measurement techniques with field work conducted to assess the variability in each when employed to measure emissions from manure applications and controlled chamber studies used to assess variability in specific sampler types. Paper 5 details research conducted at a number of IGER and ADAS field sites between 1997 and

2001 during which a large number of individual small plot experiments were conducted to assess the influence of a range of factors on ammonia emissions from manure applications to land with the aim of producing a predictive model. Paper 6 describes a laboratory study conducted at IGER North Wyke during 2003-2004 in which methodology to measure slurry infiltration into soil was developed so that this process could be characterised and fully incorporated into process-based models.

Papers 7 and 8 describe research in which a number of slurry application techniques were assessed in terms of their effectiveness at reducing ammonia emissions. The research described in paper 7 was a collaborative effort between ADAS and IGER and was conducted between 1995 and 1997 at a number of experimental field stations in England. The application techniques were assessed at a small plot scale using a specially constructed small-plot applicator. Paper 8, a collaborative study between IGER and ADAS, describes the research which scaled up that described in paper 7 such that the application techniques were used at field scale employing commercially available equipment and using micrometeorological measurement techniques. Again, this was conducted at a number of experimental research stations in addition to some commercial farm sites across England. Papers 9 and 10 describe research on dietary manipulation. The research conducted in paper 9 was conducted by IGER at North Wyke from 1995-1996 aimed at assessing the impact of reducing the crude protein content of pigs diets on subsequent nitrogen losses from the slurry applications to land. Paper 10 details laboratory studies conducted in collaboration with the USDA Dairy Forage Research Center in Madison, Wisconsin, during 2004, in which the influence of protein content and form in the diet of dairy cattle on nitrogen excretion and subsequent ammonia volatilisation was studied.

Misselbrook input (%) to the publications:

| Paper | Initiation | Execution | Writing |
|---|---|---|---|
| 1 | 20 | 30 | 60 |
| 2 | 40 | 40 | 35 |
| 3 | 50 | 60 | 75 |
| 4 | 50 | 40 | 75 |
| 5 | 30 | 35 | 80 |
| 6 | 70 | 100 | 80 |
| 7 | 15 | 25 | 25 |
| 8 | 40 | 30 | 70 |
| 9 | 20 | 30 | 60 |
| 10 | 65 | 80 | 80 |

11/1/2006.

**Abstract**

Over the last 10-15 years there has been increasing concern within Europe as to the effects of ammonia emission and subsequent deposition to sensitive ecosystems, causing eutrophication and soil acidification. Transboundary transport of emissions has led to legislation at EC level with member states being given emission ceiling targets. Research has therefore aimed at quantifying national emissions, modelling emission processes and developing mitigation strategies. Agriculture accounts for >80% of total UK ammonia emission, therefore an accurate and robust model is required to estimate emissions from this sector. National inventory methodology has improved as the database of emission measurements and survey data has grown and as models have evolved from discrete empirical calculations for individual sources to linked nitrogen flow models incorporating more process-based algorithms.

Ammonia emissions from agriculture derive mainly from livestock manures (primarily from the urea content of urine) and land application of manures represents a major emission source. Research in this area has therefore aimed to improve our ability to predict losses, taking into account the major influencing factors, in order to improve inventory estimates, improve manure management decision support models for farmers and advisers and to highlight potential mitigation strategies. This requires the ability to make precise, accurate measurements and measurement technology has been developed for a range of scales. A key factor influencing ammonia emissions following applications of livestock slurries to soil is the rate and extent to which slurry infiltrates into the soil, where it will be largely protected from volatilisation. This has not previously been fully incorporated into process-based models and research presented here has provided a mechanism describing the infitration process

in which the slurry dry matter concentration and the nature of that dry matter are among the important influencing factors.

Measures aimed at reducing emissions from land spreading are generally regarded as the most cost-effective means of reducing emissions from agriculture. A number of slurry application techniques aimed at reducing emissions have been developed and assessed against the conventional method of surface broadcasting. These new techniques rely on either reducing the exposed slurry surface area from which emission occurs, reducing the air flow and temperature at the emitting surface (thereby increasing the resistance to ammonia transport from the emitting surface to the free atmosphere) or increasing the contact between slurry and soil. A more holistic approach to reducing emissions is via dietary manipulation, with the aim of reducing both the amount and form of nitrogen excreted by livestock. This can result in lower ammonia emissions at all stages of manure management i.e. livestock housing, manure storage and application to land.

# 1. Critical Appraisal

## 1.1 Background

"He who is within the sphere of the scent of a dunghill, smells that which his crop would have eaten, if he would have permitted it. Instead of manuring his land, he manures the atmosphere; and before his dunghill has finished turning, he has manured another parish, perhaps another county."

(Young, quoted by Potts (1807)).

As early as two hundred years ago it had already been recognised that gaseous emissions from manures represented a loss of nutrients available for crop uptake. Prior to the advent of mass produced inorganic fertilisers, recycling of livestock manures to agricultural land was the major source of nutrients for crop growth. However, nitrogen (N) in particular, may follow pathways other than directly from manure to plant uptake. The N content of manures will consist of organic N, ammonium-N ($NH_4^+$-N), deriving primarily from the hydrolysis of urea excreted by livestock, and possibly a small amount of nitrate-N ($NO_3^-$-N). During and after application, $NH_4^+$-N can be lost to the atmosphere through ammonia ($NH_3$) volatilisation. Ammonium-N may be lost readily via $NH_3$ volatilisation, may be nitrified to nitrate (which may be taken up by the growing crop, or lost via nitrate leaching or denitrification) by the soil microbial community, may be immobilised by the soil microbial community, may be bound on the soil cation exchange surfaces, may be lost directly to water ways via run-off or leaching or may be taken up directly (to a small extent) by plants. Losses to the atmosphere via $NH_3$ volatilisation can be significant following slurry applications to land, often being a major factor in the unpredictability of yield response, and their quantification, prediction and minimisation form the focus of this thesis.

Research in the early 20$^{th}$ century showed that $NH_3$ volatilisation could account for up to half of the manure N being lost via this pathway following application to land (Heck, 1931b). It was also shown that weather conditions greatly affected the extent of the loss and that losses could be reduced by incorporating manure into the soil (Heck, 1931a; Heck, 1931b). The production of low cost synthetic fertilisers, with more predictable yield response, led to manure applications becoming a disposal operation for a majority of farmers with little account being taken of the agronomic benefits. To a certain extent this still remains true today, but increasing emphasis on reducing the environmental impact of agriculture has led to research aimed at increasing recycling of nutrients from manures within agriculture and minimising losses to the environment. For $NH_3$ emissions in particular, concern has been expressed as to the damaging effect that increased deposition of $NH_3$ can have on natural ecosystems (e.g. ApSimon *et al.*, 1987) and in Europe, agriculture is the major source of atmospheric $NH_3$ (Buijsman *et al.*, 1987). There are benefits therefore, both agronomically (with a reduced requirement for inorganic fertiliser) and to the wider environment, in ensuring that $NH_3$ emissions following manure application to land are minimised. In order to achieve this, a clear understanding of the volatilisation process and the factors governing it is required.

The following chapters detail the research efforts to quantify $NH_3$ emissions from UK agriculture, highlighting the importance of manure application to land as a source, to gain a better understanding of process leading to emissions and to develop strategies for reducing emissions from land application of manures.

**1.2 Inventory of ammonia emissions from UK agriculture (Papers 1 & 2)**

Concerns at a European level about $NH_3$, among other gases, and its role in eutrophication and acidification led to the drafting of EC legislation (National Emissions Ceilings Directive, 2000). Member states were set internationally agreed ceiling targets to be achieved by 2010. This led to the requirement of an inventory of $NH_3$ emissions for each member state. Paper 1 describes the development of the first detailed inventory of $NH_3$ emissions from UK agriculture, giving the derivation of empirical emission factors, largely from UK measurements. Agricultural sources were estimated to account for 80% of total UK $NH_3$ emissions, with the remainder from a large number of minor sources (Sutton *et al.*, 2000). The development of a detailed emissions inventory structure is therefore of major importance in assessing the UK position in relation to the internationally agreed emission ceiling (EC National Emissions Ceiling Directive, 2000) and the model presented in Paper 1 is used to derive the official UK total emission from agricultural sources for annual reporting under NECD requirements. The detailed breakdown of both livestock classes and farm management practices, each associated with emission factors, represented a major step forward in increasing the accuracy of the inventory compared with other, less detailed, models (e.g. ECETOC, 1994; McInnes, 1996). The total emission from agriculture estimated in Paper 1 (274 kt $NH_3$) combined with that from non-agricultural sources (66 kt $NH_3$, Sutton *et al.*, 2000) showed that reductions in emission would be required for the UK to meet its 2010 ceiling target of 297 kt $NH_3$.

While the inventory model presented in Paper 1 provides a robust estimate of total national $NH_3$ emissions from agriculture, the model structure does not lend itself to scenario testing. In addition, atmospheric transport and deposition models require much finer temporal and spatial resolution than mean national emission estimates. To address these requirements, a mass-flow, GIS-based model, the National Ammonia Reduction Strategy Evaluation System (NARSES) was developed (Webb *et al.*, 2002). Paper 2 details the mass-flow approach for emissions from livestock production. Using an approach first described by Cowell and ApSimon (1998), $NH_3$ is emitted from a pool of total ammoniacal nitrogen (TAN) in livestock excreta. This pool is not added to during manure management, but is depleted by losses at each stage, with the remaining TAN being passed on to the next stage. The linking of emission sources in this way, as compared to estimating emissions from each source discretely and independently, enables rapid and easy estimation of the consequences of abatement at one stage of manure management on losses at later stages. This model facilitates scenario analysis of potential mitigation strategies including cost curve production and is being used for policy development.

Application of slurry to land was identified in the national inventory as a major emission source but also the source with the greatest potential for cost-effective abatement. The remainder of the published works presented here focus on this source.

### 1.3 Techniques for measuring emissions from land sources (Papers 3 & 4)

Various techniques have been developed for the measurement of $NH_3$ emissions from land sources (McGinn and Janzen, 1998). For absolute measurements of emission, micrometeorological techniques are preferred as they do not interfere with the emitting surface. However, the large land areas required by these techniques make it impractical to conduct replicated multi-factorial experiments, so small plot studies are more often employed. Svensson (1994) developed the equilibrium concentration technique, essentially a micrometeorological technique but suitable for use on small plots, described as being both practical and inexpensive. Prior to widespread adoption, a validation of the accuracy of the technique was required. Paper 3 describes a field evaluation in which the equilibrium concentration technique was compared against a robust micrometeorological mass balance technique for measuring emissions from urea fertiliser, cattle slurry and pig FYM. Emission rates measured by the two techniques were not significantly different. However, the comparison highlighted some shortcomings of the equilibrium concentration technique and the importance of good sampler preparation, adequate replication of emission measurements (increasing labour requirements) and appropriate choice of sampler exposure period, with much narrower margins of error for the equilibrium concentration technique. The method has since been used successfully to measure emissions from outdoor concrete yards used by livestock (Misselbrook *et al.*, 2001) but has been used less successfully in measuring emissions from slurry applications to land (e.g. Misselbrook *et al.*, 2004a), largely due to the difficulties in estimating appropriate sampler exposure duration.

A wider comparison of samplers and measurement techniques is given in Paper 4. This produced coefficient of variation for commonly-used samplers and measurement techniques. Such information is rarely reported and is of importance when designing experiment in order to estimate the likely replication required to show significant differences at given levels between treatments. This study again highlighted the practical problems associated with the equilibrium concentration technique. Conclusions from the study were that for measurements of absolute emission the integrated horizontal flux mass balance technique should be used, while for small plot comparative studies wind tunnels were preferred to the equilibrium concentration technique.

### 1.4 Modelling emissions following slurry applications to land (Papers 5 & 6)

Ammonia emissions following slurry application to land can be influenced by a large number of manure, weather, soil, crop and management variables, resulting in large variation in the magnitude of emission and therefore large uncertainty as to the fertiliser replacement value of the applied slurry. Mechanistic models attempt to mathematically describe the physical, chemical and biological processes and interactions leading to $NH_3$ emission (e.g. Genermont and Cellier, 1997; van der Molen *et al.*, 1990), but they are often difficult to validate and can be too complex for use in farmer/advisor orientated decision support systems. The objectives of the study reported in Paper 5 were to increase our understanding of the variables influencing $NH_3$ emission following slurry application to land and to develop a simple empirical model which might be used in such decision support systems. Field measurements were made at a small plot scale using the wind tunnel technique. Michaelis-Menten type curves were fitted to the cumulative emission measurements within each experiment giving model parameters which could be compared across experiments and used in multiple linear regression analysis. Fitted linear regression models accounted for 70-90% of the variation within the observations. Model validation against independent data sets, derived from micrometeorological mass balance measurements, showed the models to overestimate emission rates. This was most probably due to the inherent differences in the measurement techniques used; wind tunnels may overestimate emissions by as much as 50-75% compared with larger plot measurements (Genermont and Cellier, 1997).

Key variables influencing emission were wind speed and slurry dry matter (DM) content. Slurry DM content has previously been reported as an important influencing variable (e.g. Sommer and Olesen, 1991) with the suggestion that the DM impedes slurry infiltration into the soil, where the TAN content will be largely protected from volatilisation. Paper 5 is the first to suggest that the nature of the slurry DM may be an important variable, showing different relationships between emission and DM for pig and cattle slurries. The DM of cattle slurry was described as being more fibrous and it was suggested this impeded infiltration more than the 'gravelly-natured' DM content of the pig slurry. Algorithms derived from the study reported in Paper 5 have been incorporated in a revised version of the MANNER model (Chambers *et al.*, 1999) for prediction of manure nitrogen value to crops following application.

The rate and extent to which slurry infiltrates into the soil after application is, therefore, one of the key factors determining the rate and extent of subsequent $NH_3$ emission. However, while reducing $NH_3$ emissions, increasing the infiltration of slurry may result in increased denitrification rates, nitrous oxide emissions and leaching losses. A better characterisation of slurry infiltration into soil is therefore required both to improve current predictive $NH_3$ emission models and also to link $NH_3$ emission models with other nitrogen transformations and pathways which may occur once slurry is in the soil matrix. Current mechanistic models of $NH_3$ emission following slurry application do not adequately describe slurry infiltration. Misselbrook *et al.* (2005) proposed a model whereby the hydraulic conductivity of the top soil layer is progressively decreased as slurry infiltrates, due to the clogging effect and water retaining characteristics of the slurry DM. Paper 6 describes the development of a laboratory system which will enable the generation of continuous data for slurry infiltration in a non-destructive manner, using time domain reflectometry, for the parameterisation and validation of the proposed model. The advantage of using time domain reflectometry as opposed to destructive sampling (e.g.

Sommer *et al.*, 2004; Sommer and Jacobsen, 1999) is the greatly improved time resolution of the data, particularly important for the time period immediately following slurry application when the changes in infiltration rate are greatest. Preliminary results given in Paper 6 again showed important differences in the infiltration behaviour of cattle and pig slurries, with slurry DM content having most influence on infiltration rate for cattle slurries whereas soil type was more important for pig slurries. Further measurements using the described system will give an empirical assessment of the importance of a range of variables (slurry type, DM content, soil type, soil water tension) on slurry infiltration and enable the development of a process-based model.

### 1.5 Abatement strategies

#### 1.5.1 Novel slurry application techniques (Papers 7 & 8)

Slurry in the UK is almost entirely surface broadcast to land. Research elsewhere in Europe has demonstrated the potential of careful placement of slurry in bands or into injection slots in the soil at reducing $NH_3$ emissions, with reductions of up to 90% compared with surface broadcast application being reported (e.g. Frost, 1994; Huijsmans *et al.*, 1997). However, the few data available from UK measurements suggested much poorer abatement efficiencies for shallow injection (Misselbrook *et al.*, 1996). It was therefore important to derive robust emission reduction efficiency factors for alternate application methods as used under UK conditions for use in policy support scenario analyses.

Paper 7 reports a trial comparing the novel application techniques (band spreading, trailing shoe and shallow injection) with surface broadcast application at a small plot scale, using a specially designed small plot applicator. Measurements were conducted at a range of sites across England at several times of year, using the wind tunnel system. Mean abatement efficiencies were 39, 43 and 57% for band spreading, trailing shoe and shallow injection, respectively. Shallow injection was more effective at reducing emissions on grassland under moist, rather than dry, soil conditions. Paper 8 compares the same application techniques but at a larger scale, using commercially available application machinery and the micrometeorological mass balance measurement technique. Mean abatement efficiencies on grassland were 26, 57 and 73% and on arable land were 27, 38 and 23% for band spreading, trailing shoe and shallow injection, respectively. The UK-specific abatement efficiencies from Papers 7 and 8 are lower than those previously reported for elsewhere in Europe, particularly for shallow injection and trailing shoe, highlighting the importance of deriving country-specific emission factors for use in policy development. The reasons for lower abatement efficiencies may be several, including differences in machinery configuration, operator skill, slurry composition and soil, crop and weather variables. There is some evidence that the earlier quoted abatement efficiencies for the Netherlands (Huijsmans *et al.*, 1997) are not achieved in practice on commercial farms and this is believed to be a contributing factor in the discrepancy between the modelled and measured reductions in atmospheric $NH_3$ concentrations (Erisman *et al.*, 1998; Erisman and Monteny, 1998).

**1.5.2 Dietary manipulation (Papers 9 & 10)**

Manipulating the diet of livestock to achieve a reduction in the total amount and/or a change in the forms of N excretion represents a more holistic approach to reducing $NH_3$ emissions from livestock production than measures targeted at a specific source. Paper 9 assesses the influence of reducing the crude protein (CP) content in the diet of finishing pigs on subsequent $NH_3$ (and nitrous oxide and methane) emissions following slurry application to grassland. Reducing the CP content of the diet resulted in slurry with lower total nitrogen and TAN content and also a lower slurry pH. This led to greater than expected reductions in $NH_3$ emission following slurry application. Importantly, Paper 9 demonstrated the improved utilisation of the applied slurry nitrogen by the crop as a result of reducing $NH_3$ and denitrification losses.

For ruminants, reducing the CP content of the diet also results in lower nitrogen excretion, as has been fairly widely reported (e.g. Broderick, 2003; Krober *et al.*, 2000). However, as observed with the pig slurry in Paper 9, reducing the CP content in the diet of lactating dairy cows also resulted in greater than expected reductions in $NH_3$ emission from slurries applied to soil (at a laboratory scale), again, due to the resultant lower slurry pH for the lower CP diet. For ruminants, an additional strategy to improve N utilisation by the animal is to protect a proportion of the protein in the diet of the animal from rumen degradation. Paper 10 describes how this was achieved by the inclusion in the diet of forages with significant condensed tannin content. This resulted in a shift in N excretion from urine to faecal N which, being less labile, resulted in lower $NH_3$ emissions following application of the slurries to soil.

### 1.6 Key scientific achievements

The body of research detailed in Papers 1-10 has been important in addressing two key objectives: 1) Providing policy makers with tools and information to assist with their decision making processes in relation to the NECD 2010 target; 2) Improving the recycling of nitrogen within the agricultural system and minimising losses to the environment. Key scientific achievements include:

- Development of a robust inventory of $NH_3$ emissions from UK agriculture
- Development of a mass-flow model for $NH_3$ reduction strategy evaluation
- Comparison of commonly used $NH_3$ emission measurement samplers and techniques, establishing coefficients of variation and developing criteria for choice of technique
- An improved understanding of the variables influencing $NH_3$ emission following slurry application to land and the development of an empirical predictive model
- Development of methodology to enable continuous, non-destructive measurement of slurry infiltration into soil
- Establishment of UK-applicable abatement efficiencies for novel slurry application techniques
- Demonstration of the potential of dietary manipulation to reduce $NH_3$ emissions following slurry application to land for both finishing pigs and lactating dairy cows

Key areas in which the research can be progressed include the development of process-based emission factors (e.g. Misselbrook *et al.*, 2004b) for national inventory and farm-level scenario modelling, further optimisation of alternative slurry application techniques to maximise emission abatement efficiencies and an integrated research effort by emission specialists, nutritionist, plant breeders and grazing behaviour specialists to develop practical and cost-effective mitigation measures through livestock diet manipulation.

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# 2. Published works

## 2.1 Paper 1

Misselbrook, T.H., T.J. van der Weerden, B.F. Pain, S.C. Jarvis, B.J. Chambers, K.A. Smith, V.R. Phillips, and T.G.M. Demmers. (2000). Ammonia emission factors for UK agriculture. *Atmospheric Environment* **34**, 871-880.

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# Ammonia emission factors for UK agriculture

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**Abstract**

Ammonia ($NH_3$) emission inventories are required for modelling atmospheric $NH_3$ transport and estimating downwind deposition. A recent inventory for UK agriculture, estimating emission as 197 kt $NH_3$–N $yr^{-1}$, was constructed using 1993 statistical and census data for the UK. This paper describes the derivation of the UK-based emission factors used in the calculation of that emission for a range of livestock classes, farm practices and fertiliser applications to agricultural land. Some emission factors have been updated where more recent information has become available. Some of the largest emission factors derived for each farming practice include 16.9 g $NH_3$–N dairy $cow^{-1}$ $d^{-1}$ for grazing, 148.8 g $NH_3$–N liveweight $unit^{-1}$ $yr^{-1}$ for housed broilers and 4.8 g $NH_3$–N $m^{-2}$ $d^{-1}$ for storage of solid pig and poultry waste as manure heaps. Emissions for land spreading of all livestock waste were 59% of the total ammoniacal nitrogen (TAN) applied as a high dry matter content slurry and 76% of TAN applied as farm yard manure. An updated estimate of emission from UK agriculture, using updated emission factors together with 1997 statistical and census data, is presented, giving a total of 226 kt $NH_3$–N per year. 

*Keywords:* Ammonia; Inventory; Agriculture; Emission factors

## 1. Introduction

Atmospheric ammonia ($NH_3$) transport models and derived estimates of deposition rely on emission data which are often assembled as inventories. Previous $NH_3$ emission inventories from several countries, including the UK, have shown that agriculture produces approximately 90% of the total emission of $NH_3$ to the atmosphere. Earlier estimates for the UK suggest that emissions from agriculture range from 186 to 405 kt $NH_3$–N $yr^{-1}$ (Buijsman et al., 1987; Ryden et al., 1987; Kruse et al., 1989; Jarvis and Pain, 1990; Asman, 1992; Eggleston, 1992; Klaassen, 1992; Sutton et al., 1995). Such a large range in emissions from this major source suggests there are large differences in the emission factors used for each source of $NH_3$. Unfortunately, in a number of published inventories it has not always been obvious how some emission factors were established. Similarly, the use of average values, or those inappropriate for UK agriculture, may give unreliable estimations.

A recent, detailed inventory for UK agriculture, which estimated $NH_3$ loss to be 197 kt $NH_3$–N per year (Pain et al., 1998), was based on emission factors derived primarily from measurements in the UK and, where these were not available, on best estimates from the literature, with, again, UK literature being used wherever possible. This inventory, constructed on a computer spreadsheet, calculated the emission by combining the estimated contribution of each livestock class, farming practice and fertiliser applications. The present paper describes how the emission factors were derived and

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gives details of the statistical and census data, experimental results and assumptions used in the construction of the inventory. Recent experimental data have been included in the estimate of emission factors in this paper, some of which differed from those used in the inventory of Pain et al. (1998).

## 2. Derivation of emission factors

The construction of the inventory is illustrated in Fig. 1, which shows the main components of UK agriculture for which census or survey data and emission factors were required. The emission factors used in the inventory are given in Table 1. Values used for each livestock type and for fertiliser applications are discussed below.

### *2.1. Emission factors for cattle*

Cattle were split into four sub-classes to include dairy cows, beef cattle, bulls and others less than 2 years of age, which were further sub-divided to reflect the availability of census data.

#### *2.1.1. Outdoor cattle emissions*

Ammonia emissions from grazing cattle are known to be related to inorganic N input to the grassland (Jarvis and Bussink, 1990). An updated version of this relationship was used in which emission estimates from complete grazing seasons in the UK (Jarvis et al., 1989; van der Weerden, unpublished), the Netherlands (Bussink, 1992,1994) and New Zealand (Ledgard, 1996) were incorporated (Fig. 2). A linear relationship was fitted between $NH_3$–N loss, expressed as g per liveweight unit per day (where a liveweight unit, or lu, is equivalent to 500 kg) and inorganic fertiliser N input (kg $ha^{-1}$ $yr^{-1}$)

$$\text{Nloss} = 2.27 + (0.0683 \times \text{Ninput})$$

with an $r^2$ value of 0.63. All measurements were made directly using the micrometeorological mass balance technique (Jarvis et al., 1989). The most recent measurements in the UK (van der Weerden, unpublished) were

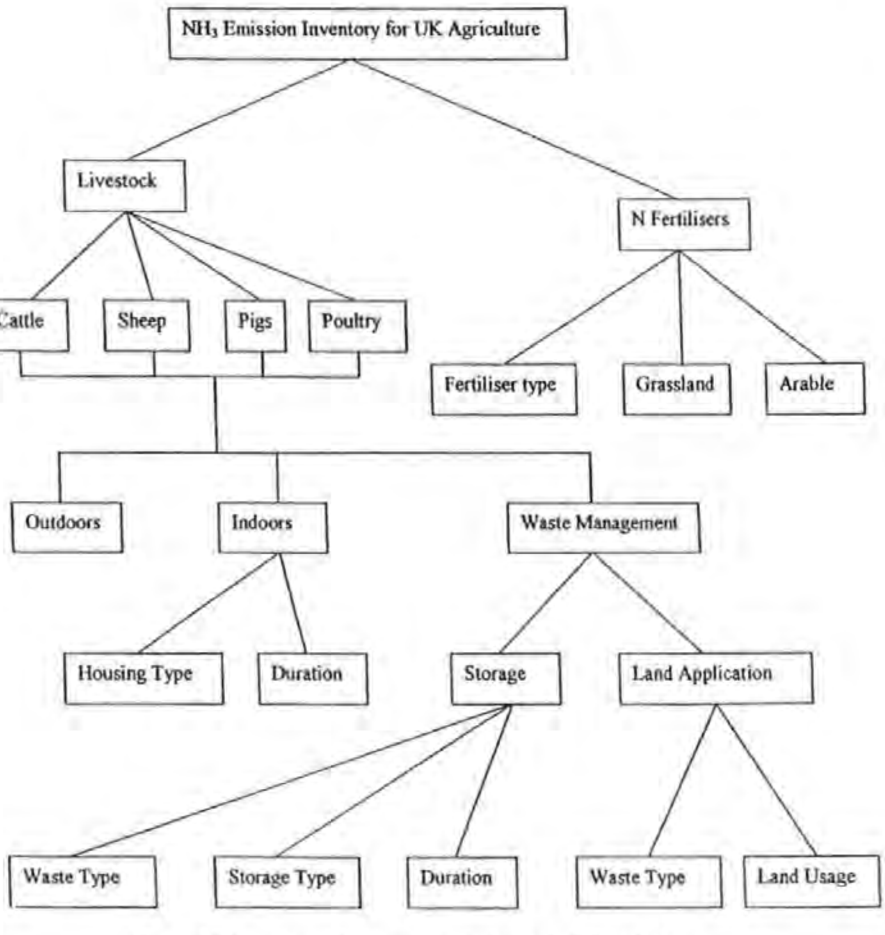


Fig. 1. Main sources of ammonia emission included in the inventory.

Table 1
Emission factors for livestock

| Livestock class | Grazing/Outdoor emission factor ($g\ N\ animal^{-1}\ d^{-1}$) | Housing emission factor[a] ($g\ N\ lu^{-1}\ d^{-1}$) | | Waste storage emission factor ($g\ N\ m^{-2}\ d^{-1}$) | | Land spreading emission factor[b] (% of TAN applied) | |
|---|---|---|---|---|---|---|---|
| *Cattle* | | | | | | | |
| Dairy cows and heifers | 16.9 | Dairy-cubicles | 34.3 | Slurry: | | Slurry (based on %DM): | |
| | | -litter | 17.2 | Circular stores/Lagoons: | | Aug–Apr < 4% | 15% |
| Heifers in calf | 12.3 | | | Crusted | 2.1 | 4–8% | 37% |
| | | | | Not crusted | 4.4 | > 8% | 59% |
| | | Beef-cubicles | 34.3 | Weeping walls | 2.1 | May–Jul all DMs | 60% |
| Beef cattle | 4.7 | -litter | 17.2 | Solid manure | 2.5 | Solid manure | 76% |
| Calves | 1.9 | Calves-litter | 10.6 | Dirty water | 0.4 | Dirty water | 15% |
| | | | | Yard emission (dairy) | 8.3 $g\ N\ animal^{-1}\ d^{-1}$ | | |
| *Pigs* | | | | | | | |
| Dry sows | 8.0 | Slatted | 17.0 | Slurry: | | Slurry (based on %DM): | |
| | | Straw bedded | 19.7 | Circular stores | 4.3 | < 4% | 15% |
| Farrowers | 8.0 | Slatted | 29.5 | Lagoons | 2.4 | 4–8% | 37% |
| | | Straw bedded | 34.1 | | | > 8% | 59% |
| Boars | 8.0 | Straw bedded | 17.0 | Solid manure | 4.8 | | |
| Fatteners < 20 kg lw | 0.9 | Slatted | 27.8 | | | Solid manure | 76% |
| | | Straw bedded | 45.6 | | | | |
| 20–110 kg lw | N/A[c] | Slatted | 79.2 | | | | |
| | | Straw bedded | 45.6 | | | | |
| > 110 kg lw | N/A | Slatted | 79.2 | | | | |
| | | Straw bedded | 45.6 | | | | |
| *Poultry* | | | | | | | |
| Layers | 0.5 | Perchery | 146.4 | All as solid manure heaps: | | All poultry[d] | 45% |
| | | Cages | 132.0 | Litter/manure | 4.8 | | |
| Broilers | N/A | Litter | 148.8 | | | | |
| Pullets | 0.3 | Manure | 148.8 | | | | |
| | | Litter | 148.8 | | | | |
| Other Hens | 0.5 | Manure | 148.8 | | | | |
| | | Litter | 148.8 | | | | |
| Other poultry | 0.7 | Litter | 148.8 | | | | |
| *Sheep* | | | | | | | |
| Lowland-sheep | 2.0 | Sheep barn | 3.0 $g\ N\ animal^{-1}\ d^{-1}$ | Solid manure: | 2.5 | Solid manure: | 76% |
| -lambs | 1.0 | | | | | | |
| Upland-sheep | 0.6 | | | | | | |
| -lambs | 0.3 | | | | | | |
| *Deer* | | | | | | | |
| Deer | 2.0 | Deer barn | 3.0 $g\ N\ animal^{-1}\ d^{-1}$ | Solid manure: | 2.0 | Solid manure: | 76% |

[a] lu is equivalent to 500 kg liveweight.
[b] TAN content = total ammoniacal nitrogen content.
[c] N/A = not applicable.
[d] For poultry waste, TAN also includes uric acid nitrogen.

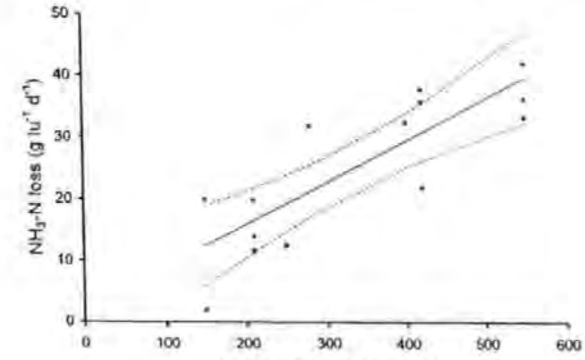


Fig. 2. Ammonia emission from grazing cattle related to annual inorganic N input to pasture being grazed. Fitted line ($y = 2.27 + 0.0683x$) together with 95% confidence intervals. Data from Jarvis et al. (1989) (♦), Bussink (1992) ( + ), Bussink (1994) (▲), Ledgard (1996) (■) and IGER unpublished ( × ).

from 1 year old steers continuously grazing a ryegrass sward receiving 280 kg inorganic N as fertiliser, with emissions from week-long monitoring periods throughout two grazing seasons ranging from 0.8 to 124 g $NH_3$–N $lu^{-1}$ $d^{-1}$ in 1992 and 14 to 74 g $NH_3$–N $lu^{-1}$ $d^{-1}$ in 1993.

For the UK, N fertiliser inputs onto grazed pasture for dairy cattle and all other cattle average 192 and 67 kg N $ha^{-1}$, respectively (Burnhill et al., 1998). Emission factors for the different sub-classes of cattle were based on these N inputs and standard liveweights of 550 kg for a milking dairy cow, 400 kg for an in-calf heifer, 140 kg for a calf up to 1 year old and 340 kg for all other sub-classes. Data from the ADAS Surveys of Animal Manure Practices in the Dairy and Beef Industries (ADAS, unpublished) were used to estimate the number of days spent grazing by each sub-class of cattle. For dairy cattle 190 days are spent grazing, 183 for beef cattle and 200 for calves $< 1$ year old.

### 2.1.2. Housing emissions

Dairy cattle housing was considered to be either in cubicles or on litter-based systems, beef cattle on slurry or litter-based systems whilst calves were assumed to be all housed on litter. The proportion of cattle housed under each system, as well as mean housing periods, were derived from ADAS Surveys of Animal Manure Practices in the Dairy and Beef Industries (ADAS, unpublished). The emission factors for dairy cattle in cubicle housing and beef cattle on straw were obtained from recent experimental work (Demmers, 1997; Demmers et al., 1997. There is some evidence from recent work (Phillips et al., 1998) that emissions from dairy cattle housing during the summer, accounted for in the inventory by increasing the housing period by 24 d (3 h per day during the summer months) to account for time spent by milking dairy cattle being milked each day, have been underestimated. The emission factor for beef cattle housed in slurry-based systems was assumed to be the same as that for dairy cattle housed in cubicles and that for dairy cattle on litter to be the same as for beef cattle on litter. The emission factor for calves was estimated from recent measurements by Groot Koerkamp et al. (1998). Emissions from concrete collecting yards used by dairy cattle prior to milking were estimated as 8.31 g $animal^{-1}$ $d^{-1}$ from recent measurements by Misselbrook et al. (1998).

### 2.1.3. Waste management: storage emissions

Emissions from storage were primarily based on estimates of the total surface area of each type of waste in storage each year. Storage of waste from dairy cows and beef cattle was sub-divided into the type of waste (i.e. slurry, farm yard manure (FYM), dirty water) and the type of storage facility used (e.g. for slurry: circular stores, lagoons and weeping walls; for FYM: concrete pads and field heaps). Estimates of the total surface area for each of these divisions were obtained from Nicholson and Brewer (1997) and Baines et al. (1997). Emission factors, expressed as g $NH_3$–N $m^{-2}$ $d^{-1}$, were based on Danish data for slurry stores (Sommer et al., 1993) (Table 1). It was assumed that circular stores and lagoons which are stirred frequently (data from ADAS Surveys of Animal Manure Practices in the Dairy and Beef Industries (ADAS, unpublished)) would not develop a crust whereas those stirred infrequently or not at all would develop a crust and have a lower emission factor. The emission factor for weeping wall stores was assumed to be the same as that for crusted stores. Emission factors for stored FYM were based on work conducted by IGER (unpublished data). No data on $NH_3$ emissions from stored dirty water were available, therefore an emission factor of 10% of that used for slurry storage was used, since the ammoniacal-N content of dirty water was approximately 10% of that of slurry.

The proportion of the year for which $NH_3$ loss occurs from stores will vary with the type of waste and store, together with management practice. It was assumed that slurry storage systems and dirty water tanks will always contain some waste, and so will emit $NH_3$ throughout the year. Solid manure is normally stored for 1 month to 2 years, so a weighted average of 6 months was used.

### 2.1.4. Waste management: land application emissions

The quantity of waste applied to land as slurry and FYM was calculated from quantities of waste excreted by the different classes of livestock (Smith, 1996). The quantity of FYM produced was estimated by increasing the excretal output by 1.3 to allow for the addition of straw. The quantity of dirty water applied to land was obtained from estimates of the volumes of water stored by farmers (Nicholson and Brewer, 1997). The proportions of waste applied to grassland and arable land, the timing of applications, the proportion applied by shallow injection and the proportion applied to arable land which was subsequently incorporated within 1 day or 1 week were derived from the ADAS Surveys of Animal Manure Practices in the Dairy and Beef Industries (ADAS, unpublished). It was assumed that all dirty water is applied to grassland.

Ammonia emissions from slurry applied to the land surface are known to be linearly related to the dry matter content of the slurry (Smith and Chambers, 1995). This relationship was used to calculate emission factors for a range of dry matter contents, viz. $< 4\%$, between 4 and 8%, and $> 8\%$, for slurry applied to land between August and April. Emission factors were expressed as $NH_3$ lost as a percentage of the total ammoniacal nitrogen (TAN) applied and ranged from 15 to 59% (Table 1). For slurry applied to land during the period May to July a constant emission factor of 60% was used, irrespective of slurry dry matter content. The TAN contents used for dairy cows and all other cattle were 2.25 and 1.75 kg TAN $m^{-3}$ slurry, respectively (MAFF, 1995). An emission factor of 76% of the applied TAN for FYM applications to grassland and arable land was based on results from field experiments (Chambers et al., 1997; IGER unpublished data). An emission factor of 15% of the applied N, as used for slurry with a low dry matter content, was used for dirty water applications to grassland. Emission from slurry applied by shallow injection was assumed to be 80% less than for surface applied slurry. Reduction in emission following incorporation of slurry into arable land were 30 and 10% for incorporation after 1 day and 1 week respectively, compared to slurry which was left on the surface. Respective reductions applied to incorporation of FYM were 55 and 25%.

### 2.2. Emission factors for pigs

Pigs were divided into three main classes, breeding sows, boars and fatteners, with further division of sows to dry sows and farrowers. Fatteners were separated into three sub-classes on a weight basis, viz. $< 20$ kg liveweight (lw), 20–110 kg lw, and $> 110$ kg lw.

#### 2.2.1. Outdoor pig emissions

The number of pigs kept outdoors in 1996 was estimated to be 25% sows, 25% boars and 10% of fatteners $< 20$ kg (Sheppard, 1998). From measurements of emissions from outdoor sows (unpublished data) an emission factor of 8 g $NH_3$–N $animal^{-1}$ $d^{-1}$ was derived. The same emission factor was used for boars kept outdoors and the emission factor for fatteners $< 20$ kg was based on the ratio of excretal outputs for sows and $< 20$ kg fatteners.

#### 2.2.2. Housing emissions

Each pig class was split into appropriate housing categories, based on data from the MLC Pig Yearbook (1995) and Sheppard (1998). Emission factors, expressed as g $NH_3$–N $lu^{-1}$ $d^{-1}$, were estimated from several recent studies (Groot Koerkamp et al., 1998; Demmers et al., 1997; Peirson, 1995; Phillips, unpublished) and pigs were assumed to be indoors for 365 days per year.

#### 2.2.3. Waste management: storage emissions

Emission factors for stored pig waste were estimated in a similar way to that described for cattle using data on stored surface areas (Nicholson and Brewer, 1997), Danish emission data for circular slurry stores (Sommer et al., 1993) and recent UK data for slurry lagoons (Phillips et al., 1997). Phillips et al. (1997) give a mean emission factor of 18 g $NH_3$–N $m^{-2}$ $d^{-1}$ for stored pig FYM. Recent measurements (Williams, unpublished) give an emission factor for stored pig FYM of 4.8 g $NH_3$–N $m^{-2}$ $d^{-1}$. Slurry and dirty water emissions were assumed to occur throughout the year and those from solid manure for 6 months.

#### 2.2.4. Waste management: land spreading emissions

The amount and type of stored waste applied to grassland and arable land, and the associated emission factors, were estimated in a similar way to that for cattle. The proportions of waste applied to grassland and arable land, the timing of applications, the proportion applied by shallow injection and the proportion applied to arable land which was subsequently incorporated within 1 day or 1 week were derived from the ADAS Survey of Animal Manure Practices in the Pig Industry (ADAS, unpublished). Emissions factors for land application of slurry and FYM were the same as those used for cattle, as they were derived from experiments involving both cattle and pig manure. Reductions in emission for applications by shallow injection and for slurry or FYM incorporated within 1 day or 1 week were also as for cattle manure.

### 2.3. Emission factors for poultry

#### 2.3.1. Outdoor poultry emissions

Poultry were divided into laying hens, broilers, pullets, other hens and other poultry (including turkeys, ducks, geese, ostriches and Guinea fowl). Numbers of free-range were estimated at 6% of layers and 10% of pullets, other hens and other poultry (S. Tucker, pers. comm.). However, it has been estimated that only 12% of the excreta is dropped outside by free-range poultry (A. Fuller, pers. comm.), the remainder being dropped in the house and therefore subject to the housing, storage and landspreading emission factors of housed poultry. The emission factor for excreta dropped outside by free-range poultry was estimated as 35% of excretal ammoniacal and uric acid N (AUN) output.

*2.3.2. Housed emissions*

The number of housed layers were sub-divided into perchery (32%) and cages (68%) according to data from the ADAS Survey of Animal Manure Practices in the Poultry Industry (ADAS, unpublished). Pullets and other hens were split on a 50 : 50 basis into manure and litter based housing, and all the other poultry types kept indoors were assumed to be on litter (Mercer, 1993). Emission factors were expressed as g $NH_3$-N $lu^{-1}$ $d^{-1}$ and were estimated from several recent studies (Groot Koerkamp et al., 1998; Demmers, 1997; Peirson, 1995). Building occupancy was assumed to be 100% as measurements reflected periods when occupancy was less than this.

*2.3.3. Waste management: storage emissions*

All poultry waste was considered to be stored as solid manure in field heaps after removal from the buildings. The surface area of broiler litter field heaps is more than twice that from layer manure field heaps (Nicholson and Brewer, 1997). The emission factor for manure was assumed to be the same as for pig FYM. The storage period for the field heaps was derived as 120 days from the ADAS Survey of Animal Manure Practices in the Poultry Industry (ADAS, unpublished).

*2.3.4. Waste management: land spreading emissions*

The quantity of manure spread onto land was estimated from poultry excretal output (Smith, 1996). Approximately 335 kt, representing 16%, of UK broiler and turkey litter is presently combusted annually for electricity generation, thus removing this fraction as a source of $NH_3$ emission.

Ammonia emissions from poultry manure spread onto land can persist for many weeks because of the slow conversion of uric acid to urea. An emission factor of 45% of AUN content of the poultry manure was estimated from the results of field experiments (Chambers et al., 1997). The average AUN content varies according to poultry type and was obtained from Nicholson et al. (1996).

*2.4. Emission factors for sheep*

The number of sheep was divided into adult sheep and lambs, with a split of approximately 50 : 50 between upland and lowland areas. The small population of farmed goats was included with sheep because liveweights are similar.

*2.4.1. Outdoor sheep emissions*

Emission factors for sheep grazing were estimated from measurements made by Jarvis et al. (1991) and some more recent measurements made at IGER (unpublished data). For upland sheep, emission factor was based on measurements made from sheep grazing grass/clover and grass swards receiving no inorganic N. Sheep were considered to graze outdoors year-round in upland areas, but to spend 30 days per year indoors during lambing in lowland areas.

*2.4.2. Housing and waste management emissions*

No information exists for indoor sheep and so the emission factor for ewes during lambing was obtained from the ratio of excretal outputs of sheep and beef cattle, multiplied by the emission factor for beef cattle housed on straw (converted to per animal per day). The small quantity of FYM produced by indoor ewes was assumed to be stored as field heaps and the same emission factor as for cattle FYM was used. Prior to land spreading, sheep FYM contains approximately 0.6 kg TAN $t^{-1}$ and it was assumed that, as for cattle FYM, 76% of this was lost as $NH_3$.

*2.5. Emission factors for deer*

Although the contribution from deer to the total $NH_3$ emission is very small, it has been included in the calculation for completeness. Deer numbers were divided into stags, hinds and calves, with stags being outdoors all year round and hinds and calves being outdoors for 75% of the year (MAFF, 1994). Emission factors for grazing, housing, storage and landspreading were estimated using emission factors for sheep because of the similar body weights, output and N content of excreta.

*2.6. Emission factors for inorganic N fertiliser applications to land*

Nitrogen fertiliser applications to agricultural land were divided into grassland and arable land. The fertiliser types included urea, ammonium nitrate and other, with the quantity applied being estimated from the Survey of Fertiliser Practice (Burnhill et al., 1998) and the Statistical Review of Northern Ireland Agriculture (DANI, 1997). Emission factors used in this inventory for urea, ammonium nitrate and other were 23.0, 1.6 and 1.6% of the applied N, respectively, for grassland applications, and 11.5, 0.8 and 0.8% of the applied N, respectively, for arable land applications. The estimation of these values are fully discussed by van der Weerden and Jarvis (1997), in which an emission of 32.7 kt $NH_3$-N per year from N fertiliser applied to agricultural land in the UK was calculated. This value includes emissions from fertiliser applied to grazed grassland, whereas the inventory separates emissions from this source from other fertiliser applications because losses from applications to grazed pasture are included in direct losses from grazing for each livestock type. So losses from fertiliser applications in the inventory include only those from grassland used for silage and hay production and from arable crops. The inventory has been calculated in this manner to eliminate any risk of double-counting.

## 3. Updating the $NH_3$ emission inventory for 1997

Since the publication of the $NH_3$ emission inventory for UK agriculture of Pain et al. (1998), additional data have become available from more recent studies which has led to a revision of some emission factors. The emission factors presented in this paper incorporate these newly available data, so some differ from those used by Pain et al. (1998) in their estimate of $NH_3$ emission from UK agriculture in 1993. Using the revised emission factors together with census and statistical data for 1997 (HMSO, 1997; Burnhill et al., 1997; DANI, 1997) gives an increased estimate of $NH_3$ emission from UK agriculture (for 1997) of 229 kt $NH_3$-N (Table 2) compared with 197 kt $NH_3$-N for the earlier version (Pain et al., 1998).

## 4. Comparison with other studies

Details of emission factors used in compiling previous inventory estimates are not always given. Lee and Dollard (1994) compared emission factors for livestock classes derived from some of the earlier inventories, which show great variation, but give no detail as to emission factors from each stage of the production cycle (housing, storage, etc.). Much of the data used for these inventories has also been used for estimates made for countries within Western Europe by the European Centre for Ecotoxicology and Toxicology of Chemicals (ECETOC, 1994) and, more recently, within the EMEP/CORINAIR Atmospheric Emission Inventory Guidebook (McInnes, 1996) which gives default emission factor values for use by European countries in calculating national emission inventories. ECETOC tends to use largely Dutch or German data where national data are missing, adjusted to account for differences in excretion rates in some cases. EMEP/CORINAIR uses largely

Table 2
Inventory for ammonia emission from UK agriculture, 1997

| | Source | Amount of $NH_3$-N lost (kt $NH_3$-N per year) | Percentage of total |
|---|---|---|---|
| *Cattle* | | | |
| | Housing | 42.0 | 18.6 |
| | Storage | 15.7 | 7.0 |
| | Land spreading | 45.1 | 20.0 |
| | Grazing | 15.2 | 6.7 |
| | Total | 118.0 | 52.3 |
| *Sheep* | | | |
| | Housing/storage | 1.1 | 0.5 |
| | Land spreading | 0.8 | 0.4 |
| | Upland grazing | 2.7 | 1.2 |
| | Lowland grazing | 9.5 | 4.2 |
| | Total | 14.2 | 6.3 |
| *Pigs* | | | |
| | Housing | 16.2 | 7.2 |
| | Storage | 2.8 | 1.2 |
| | Land spreading | 7.0 | 3.1 |
| | Outdoors | 0.9 | 0.4 |
| | Total | 27.0 | 12.0 |
| *Poultry* | | | |
| | Housing | 27.5 | 12.2 |
| | Storage | 0.3 | 0.1 |
| | Land spreading | 14.1 | 6.3 |
| | Outdoors | 1.0 | 0.4 |
| | Total | 43.0 | 19.1 |
| *Deer* | Total | 0.04 | < 0.1 |
| *Conserved grassland* | Total | 11.1 | 4.9 |
| *Tillage crops* | Total | 12.3 | 5.5 |
| **Grand Total** | | **225.6** | **100** |

Table 3
Estimates of N excretion (kg N animal$^{-1}$ yr$^{-1}$) and emission of $NH_3$–N (as % total N excretion) for different livestock types from ECETOC (1994), EMEP/CORINAIR (McInnes, 1996), FAL/IUL/FAT (1998)[a] and this paper

| Livestock type | ECETOC UK values | | EMEP/CORINAIR default values | | FAL/IUL/FAT Switzerland | This paper | |
|---|---|---|---|---|---|---|---|
| | N Excretion | $NH_3$–N Emission | N Excretion | $NH_3$–N Emission | $NH_3$–N Emission | N Excretion | $NH_3$–N Emission |
| Dairy cow | 122 | 27 | 100 | 24 | 32 | 104 | 21 |
| Other cattle | | | 50 | 24 | 37 | 51 | 11 |
| Sow | 33 | 30 | 36 | 38 | | 33 | 13 |
| Finishing pig | 13 | 30 | 14 | 38 | 46 | 11 | 36 |
| Laying hen | 0.8 | 43 | 0.8 | 39 | 54 | 0.8 | 46 |
| Broiler | 0.3 | 22 | 0.6 | 37 | 48 | 0.8 | 24 |
| Sheep | 23 | 7 | 20 | 6 | 14 | 12 | 5 |

[a]No details of N excretion given by FAL/IUL/FAT (1998).

Dutch and UK data, with default values being agreed by a panel of experts representing 17 European countries. Emission factors for calculating ammonia emission from animal husbandry in Switzerland have also been recently published (FAL/IUL/FAT, 1998). Emission factors for each livestock type from these studies are compared with those derived from the emission factors presented in this paper in Table 3, with values expressed as a proportion of N excretion. Values given for Switzerland (FAL/IUL/FAT, 1998) are greater for all livestock types, but this may relate to differences in N excretion estimates, which are not given. Emission factors presented in this paper are lower for other cattle and sows than those given by ECETOC or EMEP/CORINAIR.

Emission factors for each of the production stages are given for each livestock type by ECETOC and EMEP/CORINAIR, although not to the level of detail given in this paper (with only one emission factor being given for each stage and no distinction between, e.g. housing type, manure type at land spreading, etc.). For cattle grazing, both ECETOC and EMEP/CORINAIR give the emission factor as 8% of the total N excreted by cattle during grazing, giving an emission factor of c. 30 g N animal$^{-1}$ d$^{-1}$ for dairy cattle, much greater than the value derived from the relationship between emission and inorganic N input to the pasture. The ECETOC emission factor for cattle ($>$ 2 years) housing of c. 50 g N lu$^{-1}$ d$^{-1}$ is much greater than that presented here for dairy or other cattle, whereas the value given by EMEP/CORINAIR for dairy cattle is similar to that presented here for cattle in cubicles and that for other cattle similar to that presented here for cattle housed on litter. Housing emission factors presented here for sows are lower than those quoted elsewhere, and those given here for poultry housing are lower than those given by ECETOC, but otherwise, housing emission factors are broadly similar. Emissions from manure storage are included within the housing emission factor for ECETOC values. EMEP/CORINAIR storage emission factors are given as a proportion of total N in the manure stored (6% for cattle and pigs, 4% for laying hens and 3% for broilers), rather than an emission factor for manure surface area, with no distinction between manure type or storage method. For manure spreading, ECETOC and EMEP/CORINAIR give emission factors as proportion of total N applied and do not distinguish between slurry and solid manure. ECETOC give 28.5% of total N for cattle manure, 5.35% for pig manure (very low in comparison with others), 37.6% for laying hens and 7.2% for broilers. EMEP/CORINAIR give 20% of total N for manure from all livestock types. Emission factors for fertiliser applications are given as 15 and 2% for urea and ammonium nitrate respectively.

Groot Koerkamp et al. (1998) conducted a series of measurements comparing $NH_3$ emissions from livestock buildings in Northern Europe from which emissions from much of the UK animal housing tended to be lower than those from the Netherlands, Denmark and Germany. It is not surprising therefore that default values, often based on research in the Netherlands or Germany, are greater than emission factors based on actual measurements in the UK. The inventory of Pain et al. (1998), updated in this paper, is derived from many more recent UK-specific data than were previously available, providing more robust estimates of emission factors to give a more accurate estimate of the total emission of $NH_3$ from UK agriculture. Also, emission factors specific to particular production systems are presented which, when combined with survey information, further improve the accuracy of the estimate as well as allowing for simpler updating of the inventory in the light of new surveys and scenario testing to assess the effect of changes in practice.

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## 2.2 Paper 2

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# A mass-flow model of ammonia emissions from UK livestock production

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**Abstract**

This paper describes a mass-flow approach to estimating ammonia ($NH_3$) emissions from livestock production at the national scale. $NH_3$ is emitted from a pool of ammoniacal-N (TAN) in livestock excreta. This pool is not added to during manure management, but is depleted by losses as gaseous emissions and leachate and by immobilization in litter. At each stage of manure management, a proportion of TAN will be lost, mainly as $NH_3$, and the rest passed on to the next stage. This approach enables rapid and easy estimation of the consequences of abatement at one stage of manure management (upstream) on $NH_3$ losses at later stages of manure management (downstream). Such a model facilitates scenario analysis of abatement options and cost-curve production. Model output is most sensitive to variation in estimates of the length of the housing period for cattle. Thus, the collation of accurate data on factors such as the length of the housing period and other 'activity' data, are as important in compiling accurate inventories of national emissions as improving the accuracy of emission factors. Priorities for research should be to accurately quantify the relationship between $NH_3$ emissions from livestock buildings and the proportion of the day those buildings are occupied, and to characterize and quantify the transformations of N that take place during storage of litter-based manures.


*Keywords:* Ammonia; Emissions; Inventory; Abatement; Model

## 1. Introduction

Accurate inventories of gaseous emissions are required to calculate total national emissions, identify the major sources and hence to develop effective abatement policies. The first inventories of ammonia ($NH_3$) emissions from livestock production were calculated by multiplying livestock numbers by emission factors (EFs) per animal (e.g. Buijsman et al., 1987). This approach did not allow for significant differences in the potential for $NH_3$ emissions due to differences in diet and hence N excretion, or differences in livestock and manure management between countries and regions. More recent inventories have replaced EFs per animal with specific EFs for the different phases of manure management, i.e. during animal housing, during manure storage, after manure spreading, and for different housing, storage or spreading systems, etc. (e.g. Pain et al., 1998; Misselbrook et al., 2000). However, increasing the number of EFs to account for emissions at each stage of manure management and discriminating between systems and abatement measures, makes the calculation of the interactions between abatement measures complicated. In particular, such an approach may fail to recognise that introducing abatement at an early stage of manure management, e.g. housing, will, by conserving $NH_3$-N, increase the potential size of $NH_3$ emissions later, i.e. during storage or after spreading. Thus a mass-flow approach is needed, and is particularly important when attempting to rank the costs of introducing measures to reduce $NH_3$ emissions. Such an approach was first introduced in the MARACCAS

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Table 1
Estimates of total $NH_3$-N abatement from a livestock production system using an additive approach and the TAN-flow method

| Emission source | Unabated | | | Abated | | |
|---|---|---|---|---|---|---|
| | | | | Addition approach | TAN flow approach | |
| | % loss of TAN | kg $NH_3$-N | Abatement (%) | loss (kg $NH_3$-N) | TAN before $NH_3$ emission (kg) | $NH_3$-N loss (kg) |
| Housing | 30 | 300 | 30 | 210 | 1000 | 210 |
| Storage | 20 | 140 | 80 | 28 | 790 | 32 |
| Spreading | 40 | 250 | 70 | 67 | 758 | 91 |
| Total | | 690 | | 305 | | 333 |

model (Cowell and ApSimon, 1998) in which $NH_3$ emissions originate only from the pool of total ammoniacal-N (TAN) in livestock excreta. This paper reports the development of this concept into a system to estimate $NH_3$ emissions from UK livestock production as part of a broader development of a system to estimate UK $NH_3$ emissions, the National Ammonia Reduction Strategy Evaluation System (NARSES) (Webb and Anthony, 2002). In NARSES the $NH_3$ emissions model described here (NARSES_EM) is integrated with a custom-built spatial information system that will provide data on model inputs, including animal numbers and regional differences in manure management. This will enable account to be taken of local variability of farm practice and environment in developing national emission reduction policies. The objective of NARSES is to develop a national-scale model to estimate the magnitude, spatial distribution and time course of agricultural $NH_3$ emissions and the potential applicability of abatement measures with the associated costs. The end product will be a GIS-based model that policy-makers can use to investigate cost-effective implementation of strategies for $NH_3$ abatement at national and other scales, and to estimate the impact of independent developments on emissions of $NH_3$. A copy of the model can be obtained from the first author.

## 2. Approach

$NH_3$ emissions from livestock farming are estimated using a simple mass-flow model, in which $NH_3$ emissions originate from the pool of TAN in livestock excreta. $NH_3$ may be volatilized from this pool of TAN at any stage of manure management. This concept of a TAN pool, from which $NH_3$ may be successively lost, but to which no newly generated TAN is added, allows calculation of the consequences of reducing $NH_3$ emissions at one stage of manure management (upstream) on emissions at later stages of manure management (downstream) and represents the major advantage of this model over the previous UK $NH_3$ emission inventory model (Pain et al., 1998; Misselbrook et al., 2000). For example, consider a livestock system in which 1000 kg of TAN are excreted annually. Unabated losses during housing, storage and spreading are 300, 140 and 224 kg $NH_3$-N, respectively, giving a cumulative loss of 664 kg $NH_3$-N (Table 1). Abatement measures are introduced to this system that reduce emissions from buildings, from stores and following spreading by 20%, 80% and 70%, respectively. Using a simple additive approach, total emissions of $NH_3$-N following adoption of all three abatement measures are estimated as 305 kg per year, a reduction of 359 kg $NH_3$-N (Table 1). However, this approach underestimates abated losses by 28 kg $NH_3$-N as it fails to recognise that conserving $NH_3$-N in the building or in the store will increase the potential for loss of $NH_3$-N later. This approach is needed when ranking the costs of different measures to reduce $NH_3$ emissions at the national scale. Cowell and ApSimon (1998) recognised that the emission reduction achieved by the implementation of a particular measure will depend on which other measures are implemented. It was therefore necessary to adopt this approach to optimize the ranking of the cost-effectiveness of abatement measures.

### 2.1. Dependence of $NH_3$ emissions on TAN excreted

For each livestock class, the amount of TAN in the excreta is considered to determine the potential for $NH_3$ loss at all stages of manure management. More than half of the N excreted by mammalian livestock is in the urine, and between 65% and 85% of urine-N is in the form of urea (Jarvis et al., 1989). Urea is rapidly hydrolyzed by the extracellular enzyme urease to ammonium carbonate ($(NH_4)_2CO_3$) thus providing the main source of $NH_3$. Urease is widespread in soils and faeces and, in consequence, hydrolysis of urea is usually complete within a few days (Whitehead, 1990). As well as urea, urine also contains compounds such as allantoin which may also be broken down to release $NH_3$ (Whitehead et al., 1989). Poultry do not produce urine. A major constituent of poultry faeces is uric acid and this, together with some other labile compounds, may be degraded to $NH_4^+$ after hydrolysis to urea (Groot Koerkamp, 1994). In the model described here, the total quantity of compounds with the potential to break down to $NH_3$ is referred to as TAN. In contrast, the majority of N in livestock *faeces* is not readily degradable (Van Fassen and Van Dijk, 1987). Only a small percentage of this N is urea or $NH_4^+$ (Ettala and Kreula, 1979) suggesting a limited $NH_3$ volatilization potential for faecal-N. In a field study Petersen et al. (1998b) found $NH_3$ losses from dung to be negligible.

Published studies have confirmed the relationship between $NH_3$ emissions and TAN. For example, Kellems et al. (1979) demonstrated that the initial rate of $NH_3$ volatilization was positively correlated with the urea and volatile amine content and specific gravity of cattle urine. Together, urea- and volatile amine-N were described as volatile-N. Paul et al. (1998), James et al. (1999) and Smits et al. (1995) found $NH_3$ volatilization decreased in proportion to the decrease in crude protein (cp) in the diet fed to dairy cows, N and TAN excreted. Latimier and Dourmad (1993), Kay and Lee (1997) and Cahn et al. (1998) reported that $NH_3$ emissions from pig production decreased with reductions in TAN excreted, while $NH_3$ emission as a proportion of TAN excreted remained fairly constant.

Clearly other factors, such as temperature, pH, wind speed and the surface area of fresh urine or slurry exposed to the air, influence $NH_3$ emissions. Surface area effects are taken into account in estimating emissions from storage facilities. However, the objectives of NARSES are to first, estimate the potential for $NH_3$ abatement and second, estimate changes in national $NH_3$ emissions due to unrelated developments within livestock farming. The estimate of annual variability due to changes in weather is not part of the current remit. In consequence, environmental effects are considered to be constant between years. However, it is envisaged that future development of the model will enable annual variation in some of these factors to be taken into account in order to model the consequences of climate change on national emissions of $NH_3$. The calculation of $NH_3$ emission by NARSES_EM is based on the same body of data as was used to derive the EFs used in the Inventory of Ammonia Emission for the UK (IAEUK, Misselbrook et al., 2000).

### 2.2. Model structure

The model begins with the estimate of annual N excretion and the proportion of N in the form of TAN for each class of livestock (Table 2). Combining this with estimates of livestock numbers in each class gives the initial size of the TAN pool. The flow of this TAN pool is then modelled through the various livestock and manure management stages (livestock grazing/outdoors, livestock housing, manure storage, manure applications to land: Fig. 1). Estimates of $NH_3$ emission are made from each stage, with EFs based on those given by Misselbrook et al. (2000), but expressed as a proportion of the available TAN pool. Estimated emissions are subtracted from the TAN pool which then flows to the next manure management stage (e.g. $NH_3$ emissions from livestock housing reduce the size of the TAN pool within manure storage). Estimates are made, based on survey data (e.g. Smith et al., 2000b; 2001a, b), of the proportion of TAN flow associated with different management practices (e.g. slurry vs. litter-based livestock housing, different manure storage types) to which specific EFs can be applied. A detailed example of the calculations of TAN flow and $NH_3$ emission specifically for dairy cattle on slurry systems is given in Appendix A.

Table 2
Estimates of annual N excretion, used in NARSES_EM, per animal based on dietary N balance

| Livestock class | | Annual N excretion (kg) | % TAN |
|---|---|---|---|
| Dairy cows | | 106 | 60 |
| Dairy heifers | | 48 | 60 |
| Beef cows | | 61 | 60 |
| Beef heifers | | 46 | 60 |
| Bulls | | 84 | 60 |
| Beef >2 years | | 58 | 60 |
| Beef 1–2 years | | 56 | 60 |
| Calves <12 months | | 29 | 60 |
| Ewes | | 11 | 60 |
| Lambs | | 1.7 | 60 |
| Sows and litters to 7 kg | | 30 | 70 |
| Weaners 7–20 kg | | 2.3 | 70 |
| Fattening pigs 20–130 kg | | 15.6 | 70 |
| Gilts and boars | | 15.6 | 70 |
| Laying hens | (000) | 850 | 70 |
| Broilers | (000) | 600 | 70 |
| Breeding hens | (000) | 1100 | 70 |
| Pullets | (000) | 400 | 70 |
| Turkeys | | | |
| Male | (000) | 1880 | 70 |
| Female | (000) | 1000 | 70 |
| Ducks | (000) | 1200 | 70 |

Taken from Webb (2000).

### 2.3. Expressing EFs as a proportion of TAN

In the IAEUK, $NH_3$ EFs for $NH_3$ emissions during housing are expressed as g per livestock unit (LU) $d^{-1}$. A LU is defined as 500 kg liveweight. Emissions expressed as g $LU^{-1} d^{-1}$, may be converted to a proportion of TAN excreted using data on the average weight of each livestock class, the number of days each class is housed, and the annual TAN excretion by the livestock class (Eq. (1)). Estimates of total N excretion and percentage

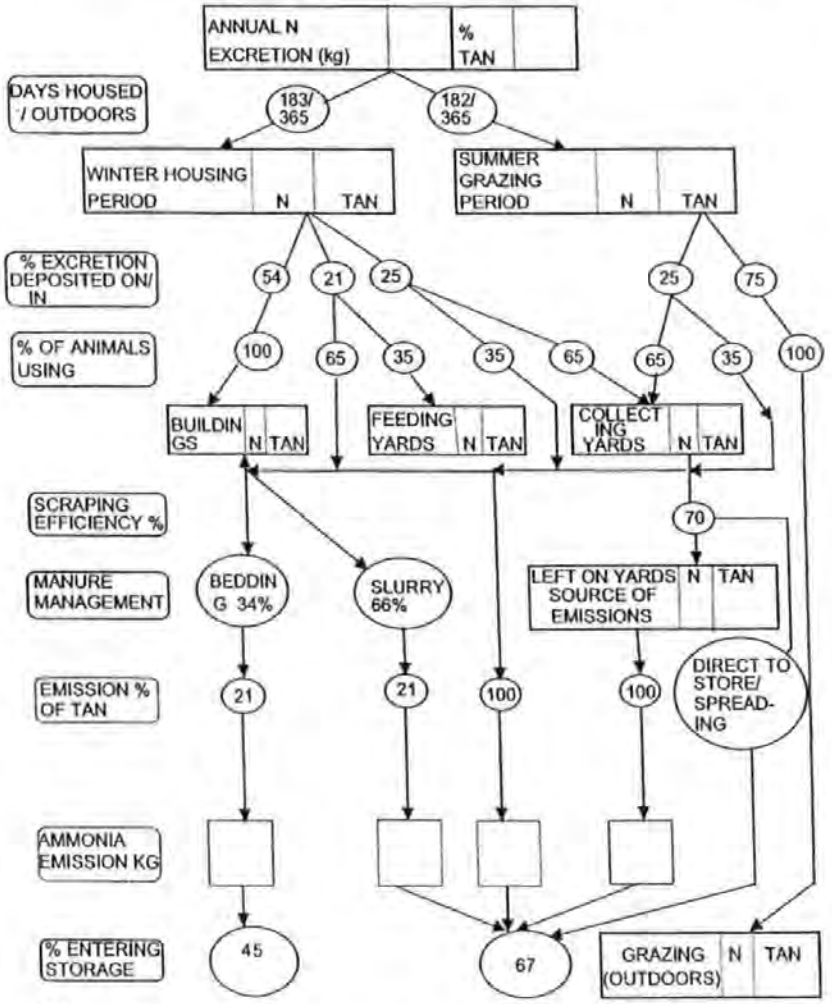
TAN are given in Table 2 for each livestock class in the UK June Agricultural Census:

$$EF_{\%TAN} = \frac{EF_{LU}}{1000} \times \frac{X}{500} \times d \times \frac{100}{TAN}, \qquad (1)$$

where $EF_{\%TAN}$ is the emission factor expressed as a percentage of the TAN pool, $EF_{LU}$ is the emission factor in g $LU^{-1}$ $d^{-1}$, $X$ is the mean weight per animal (kg) for the livestock class, $d$ is the number of days housed and TAN is the annual TAN excretion per animal (kg).

Measurements of $NH_3$ emission from buildings housing cattle have been made in the UK for three classes: dairy cows, beef heifers and calves. In consequence, for all housed cattle where manure is collected as slurry, an average EF (as a proportion of TAN) is used in the calculations. For cattle housed on straw, an average loss of TAN is used for all classes except calves, for which separate data exist. Results are given in Table 3.

In the IAEUK, $NH_3$ emissions from hardstandings (i.e. outdoor concrete yards) are expressed as g $m^{-2}$ $h^{-1}$ (Misselbrook et al., 2001). Nitrogen and TAN deposited to hardstandings were estimated by NARSES_EM by combining observations of the proportions of urination and defecation events occurring on such areas (Jackson, pers. comm.) with data on the percentage of animals using each type of hardstanding and the frequency of cleaning/scraping (Webb et al., 2001). While dairy cow collecting yards were typically scraped clean at least once a day, other yards were cleaned much less frequently. For all types of hardstanding areas, except dairy cow collecting yards, it is assumed that, because of the infrequent cleaning, all the TAN deposited is lost as $NH_3$. This approximation produces an estimate similar to that calculated by the IAEUK. For dairy cow




(a)

Fig. 1.

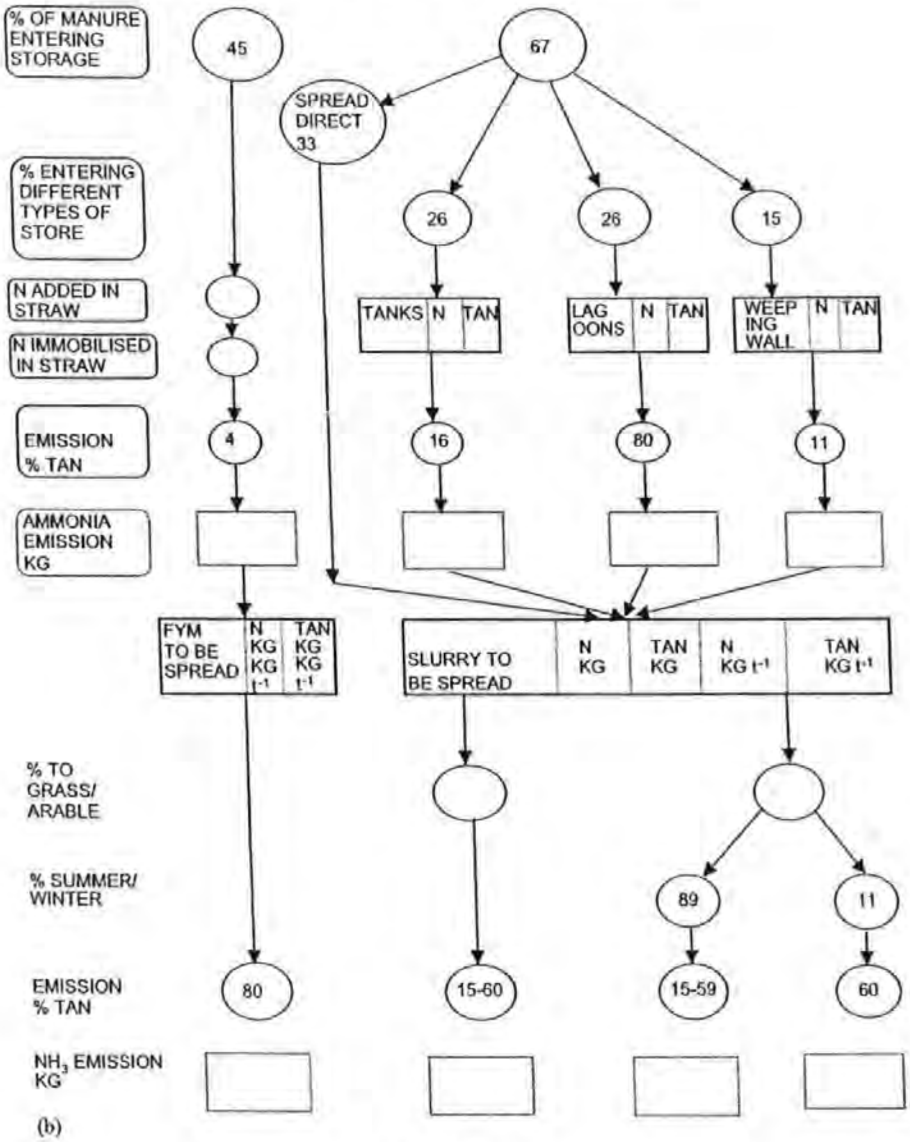



Fig. 1 (*continued*).

collecting yards a scraping efficiency of 80% is assumed. All the TAN remaining after scraping is assumed to be subsequently lost as $NH_3$. All the N (and TAN in the case of dairy cow collecting yards) removed by scraping all types of yard, is added to the N remaining within buildings after $NH_3$ emissions. These totals are then transferred into store or spread direct to land.

$NH_3$ emissions from stored manures are expressed in the IAEUK, as $g\,m^{-2}\,d^{-1}$, with the proviso that emission from stored farmyard manure only takes place for the first 30 days of storage. $NH_3$ emissions are calculated as the product of EFs and the total area of each type of store. Taking these estimates, together with the NARSES_EM output of the amounts of N and TAN remaining in manures to be put into storage after losses and immobilization from buildings and hardstandings, emissions as a proportion of TAN entering the store may be determined (Table 4).

$NH_3$ emissions following spreading of manures to land are calculated as a proportion of TAN in the applied manures in the AEIUK. The current values are given in Table 5 and are the ones used in NARSES_EM.

### 2.4. Other gaseous N losses and TAN immobilizaton

In order to fully account for changes in TAN during manure management, estimates need to be made of other gaseous emissions and, for litter-based manures,

Table 3
Percent of N and TAN emitted as ammonia in livestock buildings used in NARSES_EM

| Livestock | Manure/ housing | Ammonia emissions as % | |
|---|---|---|---|
| | | N | TAN |
| All cattle | Slurry | 18.5 | 31.0 |
| Except calves | FYM | 12.5 | 21.0 |
| Calves | FYM | 3.5 | 6.0 |
| Sheep | FYM | 13.5 | 22.5 |
| All pigs except weaners | Slurry | 18.0 | 25.5 |
| Weaners | Slurry | 10.5 | 15.0 |
| Sows and boars | FYM | 16.5 | 23.5 |
| Fatteners and weaners | FYM | 24.0 | 34.0 |
| Laying Hens | Manure | 29.5 | 37.0 |
| Pullets | Manure | 19.5 | 24.5 |
| | Litter | 21.0 | 26.5 |
| Breeders | Manure | 19.5 | 24.5 |
| | Litter | 21.0 | 26.5 |
| Broilers and turkeys | Litter | 21.0 | 26.5 |

Table 4
Percent N and TAN emitted as $NH_3$ from manure stores used in NARSES_EM

| Livestock | Manure | Store | Ammonia emission as | |
|---|---|---|---|---|
| | | | % N | % TAN |
| Cattle | Slurry | Circular tank | 8.3 | 15.8 |
| | | Weeping wall | 5.6 | 10.8 |
| | | Lagoon | 41.7 | 79.9 |
| | FYM | | 1.1 | 4.2 |
| Pigs | Slurry | Circular tank | 2.7 | 3.8 |
| | | Lagoon | 19.5 | 28.1 |
| | FYM | | 2.3 | 4.6 |
| Poultry | Layer manure | | 2.3 | 3.7 |
| | Broiler litter | | 0.5 | 0.8 |

immobilization. For livestock housing, the UK Inventory of $N_2O$ emissions from farmed livestock (Chadwick et al., 1999) estimates significant losses by denitrification from poultry housing only. Losses of $N_2O$ from poultry manure were calculated, as a proportion of TAN excreted, using these data. Emissions of $N_2O$ from stored FYM and poultry manure, based on the results of Chadwick et al. (1999), were estimated as 7.5% of TAN lost as $N_2O$. The IPCC default EF for $N_2O$ of stored FYM is 2% of N (IPCC/OECD, 1997), which for manures with ca. 25% TAN, equates to an EF of ca. 8% TAN.

When conditions favourable to both nitrification and denitrification are created, as is the case in aerated slurry stores and in FYM heaps, $N_2$ emissions may take place. Studies in which $NH_3$ and other N losses (e.g. leaching from FYM stores) are measured, allow an estimate to be made of $N_2$ emissions from calculations of total N in the manure at the beginning and the end of storage (N balance studies). Petersen et al. (1998a) concluded that between 13% and 33% of N was lost by denitrification (including $N_2O$) emissions from cattle and pig FYM during storage. In contrast Sommer (2001) estimated only 1% of total N was lost as $N_2$ (with $N_2O$-N emissions of ca. 0.1–0.3% N). The difference in results between these two studies may be due to the greater C:N ratio (20:1) in the manure used by Sommer (2001) compared to that used by Petersen et al. (1998a) of 8:1–10:1, with wider C:N ratios favouring immobilization of TAN. Eghball et al. (1997) estimated maximum total denitrification losses as 7%. It is difficult to draw accurate conclusions from such scant data, but as a first approximation, emissions of $N_2$ may be estimated as 3-times those of $N_2O$. This multiplier has also been used by other workers (Jarvis and Pain, 1994).

Estimates of the total N put into store lost by leaching are given in Table 6. From these data an average of 12% of TAN leached would be a reasonable overall estimate, based on TAN as 25% of total N at the beginning of storage (Anon., 2000).

Table 5
Losses of TAN following spreading of livestock manures to land used in NARSES_EM

| Manure type | | % TAN emitted | |
|---|---|---|---|
| | | 'Summer' June–August | 'Winter' September–May |
| Cattle and pig slurry | <4% DM | 60 | 15 |
| Cattle and pig slurry | 4–8% DM | 60 | 37 |
| Cattle and pig slurry | >8% DM | 60 | 59 |
| Cattle, pig and sheep FYM | | 81 | 81 |
| Layer manure | | 63 | 63 |
| Broiler and turkey litter | | 63 | 63 |

DM = dry matter.
FYM = farm yard manure.

Table 6
Estimates of N losses by leaching from stored FYM used in NARSES_EM

| Author | Manure | % lost by leaching | |
|---|---|---|---|
| | | N | TAN[a] |
| Amon et al. (1997) | Cattle | 2–4 | [8–16] |
| Eghball et al. (1997) | Beef cattle | 3 | [12] |
| Petersen et al. (1998a) | Cattle and Pig | 2–4 | [4–16] |
| Sommer (2001) | | 2–4 | [8–16] |

[a] Estimated assuming TAN in fresh FYM is 25% of total N.

The immobilization of TAN in litter is calculated as 1 kg N per 150 kg straw added, in the middle of the range of immobilization reported by Kirchmann and Witter (1989) for C:N ratios of between 18 and 36:1. Cattle manure in the UK typically has a C:N ratio of ca. 20, at which immobilization was considered likely to occur by Petersen et al. (1998a). Moreover, since straw has a C:N ratio of ca. 100, and mixing of straw and excreta is poor, then some of the TAN in urine is likely to be immobilized where it is voided to fresh straw. These calculations are, however, based on limited data and emphasize the need for work to establish more precisely the processes taking place in litter-based manures.

### 2.5. Uncertainty analysis

Uncertainty analysis was conducted using @RISK software (Palisade Europe, London), in which a distribution was attached to each of the model inputs (activity or emission factor data), based on the distribution of raw data or, where no or only single estimates exist, on expert assumptions. A large number of model runs (2000) were then conducted in which input values were selected at random from within the given distribution (Latin hypercube sampling) and an uncertainty limit produced for each of the model outputs.

## 3. Results

### 3.1. Total $NH_3$ emissions from UK livestock and comparison of NARSES_EM output with other estimates of manure-N

Estimated annual emissions of $NH_3$ from UK livestock are given in Table 7, together with estimates from the AEIUK. Agreement is generally very good, but cannot be used as validation of the NARSES_EM output, since the emission estimates were based on the same data as those of the AEIUK. A better basis for comparison is between NARSES_EM estimates of total N and TAN in livestock manures prior to storage and at the time of spreading, with data available from measurements. Such comparisons are possible in respect of both total amounts of N and TAN and of TAN expressed as a proportion of total N. Results are presented in Table 8. Typical manure analyses are given in RB209 (Anon., 2000), albeit these are an amalgam of the analyses of manures that have been stored as well as those fresh from buildings, while estimates of total manure-N outputs are provided by Smith and Frost (2000) and Smith et al. (2000a). There is generally good agreement with these independent estimates of N and TAN available for storage and spreading, within the 95% CI of those values calculated by NARSES_EM, except for some of the poultry manure estimates. For cattle slurry and FYM there is good agreement for the amounts of N and TAN going into store. The data in RB209 are a mixture of stored and fresh analyses, and so will overestimate N and TAN at spreading. At present, NARSES_EM appears to be underestimating housing losses/immobilization of pig FYM and poultry litter.

## 4. Discussion

### 4.1. Comparison with estimates of N excretion and EFs from other European data

The annual N excretion data used in NARSES_EM for cattle, poultry and sows and litters are similar to those quoted for Denmark by Hutchings et al. (2001). However, the estimates of N excretion by weaner and fattening pigs used in NARSES_EM (2.3 and 15.6 $kg\,yr^{-1}$, respectively) are much greater than those used by Hutchings et al. (2001). In recent years diets have been adopted by pig producers in Denmark to carefully match the protein intake at each stage of growth to the pig's protein requirement ('phase feeding') in order to minimise N excretion (S. Gyldenkrne, pers. comm.). The use of these diets may explain the smaller estimates of N excretion compared with those for the UK. Annual N excretion by grazing ruminants is greatly influenced by the N concentration in grazed herbage. This in turn is related to total N inputs to the pasture as fertilizer and manure. In the UK, sheep graze for most of the year and N inputs to sheep pastures are generally $<50\,kg\,N\,ha^{-1}\,yr^{-1}$. Thus N intake and N excretion by the sheep will be limited and are likely to explain differences with estimates from Denmark.

There are two problems with comparing measurements of $NH_3$ losses made in other countries from livestock buildings with those made in the UK. The first applies to all livestock, and is that the plane of nutrition may differ between different countries. However, expressing emissions as a proportion of N or TAN overcomes this difficulty. This is no problem where N excretion is quoted but often, especially for cattle, no

Table 7
Annual $NH_3$ emissions from UK livestock production estimated by NARSES_EM and by the IAEUK

| Livestock sector | Mean ($t \times 10^6$) | NARSES_EM | | | IAEUK |
|---|---|---|---|---|---|
| | | Confidence interval (95%) | | | |
| | | Lower | Upper | As % mean | |
| Cattle | | | | | |
| Buildings | 39.2 | 21.5 | 58.4 | 94 | 39.3 |
| Hard standings | 17.7 | 13.3 | 23.1 | 55 | 17.7 |
| Storage | 10.0 | 5.8 | 14.9 | 92 | 10.0 |
| Spreading | 51.6 | 28.6 | 80.4 | 100 | 54.6 |
| Grazing | 9.4 | 2.8 | 16.3 | 144 | 8.7 |
| Total | 127.9 | 95.9 | 164.7 | 54 | 130.3 |
| Pigs | | | | | |
| Buildings | 14.1 | 1.5 | 27.6 | 185 | 14.1 |
| Hard standings | 0.1 | 0.1 | 0.1 | 69 | 0.1 |
| Storage | 1.2 | 0.1 | 2.4 | 199 | 1.3 |
| Spreading | 9.7 | 3.5 | 19.4 | 165 | 5.7 |
| Outdoor | 0.7 | 0.5 | 1.0 | 65 | 0.8 |
| Total | 25.8 | 14.7 | 36.7 | 86 | 21.9 |
| Sheep, goats and deer | | | | | |
| Buildings | 1.3 | 0.3 | 2.4 | 157 | 1.3 |
| Hard standings | 1.1 | 0.8 | 1.4 | 47 | 0.7 |
| Storage | 0.1 | 0.0 | 0.1 | 164 | 0.1 |
| Spreading | 1.9 | 0.5 | 3.6 | 161 | 1.1 |
| Grazing | 10.0 | 2.6 | 17.2 | 146 | 10.6 |
| Total | 14.4 | 6.8 | 21.9 | 105 | 13.8 |
| Poultry | | | | | |
| Buildings | 15.6 | 7.1 | 24.0 | 108 | 15.8 |
| Storage | 0.4 | −0.1 | 0.8 | 231 | 0.3 |
| Spreading | 22.4 | 5.7 | 40.3 | 154 | 17.8 |
| Outdoor | 0.2 | 0.0 | 0.4 | 165 | 0.2 |
| Total | 38.8 | 20.2 | 58.1 | 98 | 34.1 |
| Horses total | 3.0 | 2.3 | 3.9 | 53 | 3.7 |
| Manure management stage | | | | | |
| Buildings | 70.4 | 45.1 | 95.2 | 71 | 70.2 |
| Hard standings | 18.9 | 14.5 | 24.3 | 52 | 20.3 |
| Storage | 11.6 | 7.2 | 16.7 | 82 | 11.9 |
| Spreading | 85.6 | 52.9 | 122.4 | 81 | 81.4 |
| Grazing and outdoor | 23.3 | 13.0 | 34.5 | 92 | 22.4 |
| Total | 209.8 | 168.7 | 255.5 | 41 | 206.2 |

indication of N excretion is given and emissions are expressed as g $LU^{-1} d^{-1}$ or similar. The other difficulty is that the housing system may not be the same as in the UK. For example, in the Netherlands, where the greatest amount of work has been done on emissions from buildings housing cattle, studies have been made on mechanically ventilated buildings, which are rarely, if ever, used to house cattle in the UK. These difficulties are compounded by the general lack of emissions data from livestock buildings, especially from naturally-ventilated buildings housing cattle. A comprehensive set of EFs for livestock emissions from housing, storage and following spreading, expressed as a proportion of N or TAN, are available only for Denmark (Hutchings et al., 2001). These EFs tend to be smaller than those calculated for the UK, especially for cattle, pigs on FYM and laying hens. For stored slurry, the EFs quoted by Hutchings et al. (2001) are in reasonable agreement for cattle (9% N), but slightly larger for pig slurry (6% N). The much greater EF for UK lagoons is to be expected as a result of the much greater surface area to volume ratio of these stores compared with

Table 8
Estimates of manure-N and TAN derived from NARSES_EM and RB209

| | Nitrogen ($t \times 10^6$) | | | RB209 | TAN ($t \times 10^6$) | | | RB209 |
|---|---|---|---|---|---|---|---|---|
| | 95% CI | | | | 95% CI | | | |
| | Mean | Lower | Upper | | Mean | Lower | Upper | |
| *Cattle slurry* | | | | | | | | |
| Into storage | 83.6 | 64.3 | 103.6 | 83.2 | 40.5 | 29.6 | 54.1 | 41.6 |
| At Spreading | 116.0 | 85.6 | 151.2 | 124.2 | 51.5 | 35.5 | 71.2 | 62.1 |
| *FYM* | | | | | | | | |
| Into storage | 94.1 | 75.5 | 113.4 | 85.1 | 24.4 | 14.3 | 36.7 | 21.3 |
| At Spreading | 197.1 | 161.7 | 236.3 | 189.3 | 38.0 | 22.4 | 56.0 | 34.5 |
| *Pigs slurry* | | | | | | | | |
| Into storage | 9.0 | 6.3 | 12.3 | 10.7 | 5.8 | 3.9 | 8.1 | 6.4 |
| At spreading | 19.7 | 13.7 | 27.4 | 24.9 | 12.3 | 8.4 | 16.1 | 14.9 |
| *FYM* | | | | | | | | |
| Into storage | 17.8 | 10.2 | 27.9 | 21.1 | 7.4 | 1.0 | 15.4 | 5.3 |
| At spreading | 32.5 | 20.4 | 47.5 | 42.1 | 9.3 | 1.5 | 18.9 | 7.4 |
| *Sheep FYM* | | | | | | | | |
| Into storage | 4.2 | 3.3 | 5.3 | 4.1 | 1.6 | 1.0 | 2.3 | 1.0 |
| At spreading | 8.5 | 6.9 | 10.5 | 9.1 | 2.4 | 1.5 | 3.5 | 2.1 |
| *Layers* | | | | | | | | |
| Into storage | 6.8 | 4.8 | 9.1 | 11.3 | 3.6 | 2.1 | 5.3 | 5.6 |
| At spreading | 23.2 | 17.7 | 28.7 | 26.2 | 11.3 | 7.0 | 16.2 | 13.1 |
| *Broilers* | | | | | | | | |
| Into storage | 28.1 | 21.6 | 34.8 | 24.1 | 17.8 | 13.3 | 22.7 | 9.6 |
| At spreading | 86.0 | 73.0 | 99.9 | 52.3 | 51.7 | 42.0 | 62.0 | 20.9 |

above-ground tanks. However, the UK EFs for stored FYM and poultry manure are much less than those quoted by Hutchings et al. (2001) of 15–25% N. The EFs for losses following spreading are similar to those quoted by Hutchings et al. (2001) for slurry.

The smaller estimates of N losses from buildings housing cattle quoted by Hutchings et al. (2001) compared with those used in NARSES_EM, may be a consequence of the animals being housed in buildings with slatted floors so that the excreta will drop into a chamber below. In the UK cattle buildings usually have a solid floor, thus the excreta remain on the floor surface and are more exposed to air movement and the potential emissions will be greater. Braam et al. (1997) measured $NH_3$ emission from a building with a solid floor housing dairy cows, and losses were equivalent to ca. 38% of TAN excreted. The other major discrepancy with housing emissions used by Hutchings et al. (2001) is for pigs on FYM systems, for which the UK EF is greater. In the UK stocking rates for pigs on FYM are less than for pigs on slurry (Chambers, pers. comm.). The greater surface area available per pig will increase the potential for $NH_3$ emissions. Losses of $NH_3$ during the storage of FYM and poultry manure are much smaller (<5% of N) than quoted by Hutchings et al. (2001) (15% N). These differences are not readily explained. Moreover, results quoted by Isermann (1991) indicated that emissions increased with increasing length of storage from 10–14% of N over 2 months to 21–23% of N over 6 months. This is in contrast to UK results, which found emission effectively ceased after 30 days storage.

Only two sets of data are available for $NH_3$ emissions from stored pig FYM, those of Petersen et al. (1998a) who measured losses of 23.5% of N, and Schulze-Lammers (1997) who measured losses of 27% of N. These losses are greater than those used in NARSES_EM (2.3% N) by a factor of 10 and much greater than those reported from cattle FYM. Petersen et al. (1998a) made measurements from both cattle and pig FYM and losses were much smaller from cattle FYM (see above). Thus there appears to be a major inconsistency between UK and other data in respect of $NH_3$ emissions from pig FYM. The UK data suggesting emissions are similar for both pig and cattle FYM, while the (limited) European data suggesting much greater emissions from pig FYM. However, more recent UK work (Webb et al., 2002) also found much greater losses of $NH_3$ from pig FYM during storage.

Losses of $NH_3$-N during the storage of poultry manure range from 8.5% (Rohde and Karlsson, 2000) to 29% of N (Ekinci et al., 2000), with a mean of ca. 18%. These losses are much greater than those used in NARSES_EM and again represent a major discrepancy. However, this may be due to there being little separate storage of poultry manure in the UK, the manure normally being stored within, or below, buildings. Hence, perhaps, the rather greater emissions from buildings reported for the UK.

### 4.2. Estimates of manure-N available at spreading

During storage of cattle and pig FYM, the TAN content of the manure decreases from ca. 25% to ca. 10% of total N (Anon., 2000). This decrease is greater than would be expected from our current estimates of $NH_3$, $N_2O$, and $N_2$ emissions and N leaching. It seems likely therefore that more TAN is immobilized during storage. Quantitative data on this are very scarce. Mahimairajah et al. (1994) found that when mixed with woodchips 26% of the N in layer manure was immobilized; when straw was used immobilization increased to 37% of N. Both litters produced a manure with an initial C:N ratio of 10:1.

### 4.3. Uncertainty analysis and sensitivity of emission estimate to input of 'activity' data

The 95% confidence limits for the NARSES_EM estimate of total emission were estimated at 41% of the mean value (i.e. $\pm 21\%$ or $\pm 43$ kt $NH_3$-N; Table 7). For the individual stages of manure management uncertainties were greatest for grazing/outdoor emissions (92%) and least for emissions from hardstandings (52%) (Table 7). An uncertainty analysis was also conducted on the IAEUK model and the 95% confidence limits for the inventory estimate of total emission were estimated at 38% of the mean value (i.e. $\pm 19\%$ or $\pm 40$ kt $NH_3$-N). As stated earlier, NARSES_EM and the IAEUK are parameterized using the same data, so output from the IAEUK cannot be used to validate NARSES_EM. Nevertheless, the similarity of the output from the uncertainty analysis does not suggest any significant error is being introduced into the calculation of national emissions by adopting the TAN-flow approach.

### 4.4. Sensitivity of emission estimate to input of 'activity' data

The construction of accurate inventories requires the existence of adequate 'activity' data; e.g. housing and manure handling systems, length of grazing period. The sensitivity of the inventory to the accuracy of these activity data was assessed by calculating the impact of changing a number of the input data by 10% (Table 9). The estimate of total emissions was most sensitive to changes in the estimated length of the housing period for cattle. In the UK this is usually around 6 months (mid-October to mid-April) and in consequence ca. 50% of total annual excreta is deposited directly to grassland. However, only ca. 10% of emissions from cattle are from grazed pastures. This is because urine can rapidly infiltrate soil, often before urea hydrolysis is complete, thus reducing emissions. Even quite large errors in estimates of many other activity data often have very small impacts in total emissions.

### 4.5. Areas of uncertainty and priorities for future research on emissions

A major uncertainty lies in the estimation of emissions from livestock buildings when they are occupied for only part of the day. At present NARSES_EM assumes that during the housing period buildings are occupied for 24 h, and they are empty during the grazing period. In practice there may be periods in spring and autumn when cattle graze for part of the day and spend the night inside. Emissions during these transitional periods are treated as being in proportion to the time spent indoors. However, Phillips et al. (1998) found no significant difference ($p<0.05$) between $NH_3$ emissions in summer when the cows were in the buildings for $4\,h\,d^{-1}$, and winter when the cows were housed all day. $NH_3$ emissions per unit of $NH_4$-N voided by housed livestock would be expected to be greater in summer due to the increased mass transfer of $NH_3$ though the liquid/gas boundary at increased temperature (Elzing and Monteny, 1997), and hence there was confounding between season and length of occupancy. However, the data presented show large differences in measured emissions, $400\,g\,NH_3\,d^{-1}$ in summer and $710\,g\,NH_3\,d^{-1}$ in winter, and the estimate of significance was strongly influenced by one low emission rate in winter. Clearly emissions will take place from soiled surfaces in the absence of animals, but emissions cannot continue indefinitely, as the source of TAN deposited in urine will be finite. Preliminary results from a study being carried out to investigate the relationship between the proportion of the day spent inside buildings and emissions from those buildings gave a significant correlation of emissions with length of time spent inside, albeit that the relationship was not linear (Webb et al., 2003).

Current UK estimates of $NH_3$ emissions during storage of FYM, especially from pigs, are much less than other reported data. This may be a consequence of differences in storage. Increasing density of stored FYM has been shown to reduce $NH_3$ emissions (Dewes, 1996), while composting tends to increase $NH_3$ emissions

Table 9
Sensitivity of NARSES_EM output to variation in activity data and in emission factors

| Activity | Livestock class | Variance (%) | $t \times 10^3$ | % Total emission | Source of data[a] |
|---|---|---|---|---|---|
| N Excretion | Dairy cows | +10 | 6.42 | 2.92 | |
| | Beef 1–2 years | +10 | 2.87 | 1.31 | |
| | Fattening pigs | +10 | 2.55 | 1.16 | |
| | Beef cows | +10 | 2.34 | 1.06 | |
| | Beef 6-12 months | +10 | 2.07 | 0.94 | |
| | Broilers | +10 | 1.54 | 0.70 | |
| | Ewes (all) | +10 | 1.33 | 0.60 | |
| | Laying hens | +10 | 1.16 | 0.53 | |
| | All livestock | +10 | 24.21 | 11.00 | |
| Activity data | | | | | |
| Housing period | All dairy | +10 | 3.8 | 1.7 | FPS+MPS |
| | All beef | +10 | 5.9 | 2.7 | FPS+MPS |
| | Total cattle | +10 | 9.7 | 4.4 | FPS+MPS |
| % N deposited on h/s | Dairy cows | +10 | 4.6 | 2.1 | |
| % of cattle on slurry | All cattle | +10 | 3.8 | 1.7 | FPS+MPS |
| % of cattle FYM spread direct | All cattle | +10 | 2.7 | 1.2 | FPS+MPS |
| % of cattle slurry >8% DM | All cattle | +10 | 2.2 | 1.0 | Manure analysis database |
| % Poultry litter incinerated | Broilers, Turkeys etc | +10 | 1.6 | 0.7 | Fibrowatt, EPR |
| % slurry stored in lagoon | All cattle | +10 | 1.1 | 0.5 | FPS |
| % poultry manure spread direct | All poultry | +10 | 0.9 | 0.4 | FPS |
| % cattle slurry spread direct | All cattle | +10 | 0.8 | 0.4 | FPS |
| % Pig FYM spread direct | All pigs | +10 | 0.7 | 0.3 | FPS |
| Estimate of TAN loss | | | | | |
| % Loss in cattle | All cattle–slurry | +10 | 3.1 | 1.4 | — |
| buildings | All cattle–FYM | +10 | 4.2 | 1.9 | |

[a] FPS-2001 Farm Practices Survey, Report to Defra LMID (Scott et al., 2002). MPS-Surveys of manure management practice (Smith et al., 2000a, b, 2001a, b).

(Mahimairajah et al., 1994). In the UK cattle FYM is often only moved to storage after a long period inside buildings during which it will have been compacted by resting animals; there is little active composting of FYM. However, the discrepancy between modelled estimates of the TAN content of pig FYM after storage, and measured values (Table 7) suggest that the model is underestimating either $NH_3$ or other N losses during storage of pig FYM. There is a need for studies to measure all N losses during storage of FYM in order to compile an accurate N balance. The behaviour of N during storage of broiler manure also needs investigation. At present NARSES_EM overestimates the proportion of TAN in broiler manure at spreading. This may be because no immobilization of TAN is estimated to take place by NARSES_EM. This follows the findings of Kirchmann and Witter (1989) who concluded that while the wide C:N ratio of woodshavings might indicate a potential for immobilization of TAN, the majority of C in wood shavings was in the form of lignin or other recalcitrant carbohydrates and thus largely unavailable as a microbial substrate. However, the fate of N in broiler manure during storage needs further investigation.

While NARSES_EM is a mass-flow model in that there is TAN flow from one pool to the next, the EFs used are largely empirical, based on a body of observational data. This can mean that EFs are very specific to certain types of management or climatic regions. It would be valuable to derive models of EFs (expressed as percentage of TAN) in terms of management and environmental conditions. In this way, more generic expressions could be used to derive EFs from input data. Such models may also explain differences in EFs between European countries and allow different countries to use the same functions.

### 4.6. Future of modelling emissions from livestock excreta

This approach to estimating $NH_3$ emissions from livestock together with a model of $NH_3$ emissions from crops and fertilizers, will be integrated with spatially disaggregated data on livestock numbers, soil type, land use, etc., and information on abatement techniques and their costs to enable scenario analysis of abatement policies and production of cost curves (Webb and Anthony, 2002). Also, further development of emission modelling will enable EFs to be developed as functions of management practices and environmental conditions, allowing for better modelling of temporal and regional differences in $NH_3$ emissions from agriculture and testing the effects of climate change scenarios. This mass-flow model of emissions is also being adopted by other countries to enable easy computation of the interaction between abatement techniques at various stages of manure management (Dämmgen et al., 2002).

In the model, preliminary estimates have been made of losses of $N_2O$, $N_2$, and soluble N in order to create a balance sheet of N during manure management. We envisage that the NARSES model will be refined to estimate these losses more accurately, and the model is being built to enable subsequent calculation of the impacts of $NH_3$ abatement as losses of nitrate ($NO_3^-$) and $N_2O$ following manure spreading. The development of a parallel model of carbon transformation in livestock excreta and manure to calculate emissions of $CO_2$, methane ($CH_4$) and non-methane volatile organic compounds (NMVOCs) has been instigated (Dämmgen et al., in preparation).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### Appendix A

An example of the model structure is given in Fig. 1. The example is for dairy cattle and is the most complex, since dairy cattle may have access to outdoor collecting yards before and after milking as well as to outdoor feeding yards. An outline is given here of the working of the model.

The first inputs to the model are the current estimates of annual N excretion by each class of livestock, the % of N in the form of TAN (Table 2) and the number of animals in the class. Thus for dairy cows the total TAN excreted ($\alpha_t$, kg) is given by:

$$\alpha_t = a \times N_{ex} \times 0.6, \qquad (A.1)$$

where $a$ is the number of dairy cows in the UK, $N_{ex}$ the annual N excretion per dairy cow and 0.6 is the estimated proportion of $N_{ex}$ in the form of TAN for dairy cows.

Total N and TAN excretion are then split between the winter housing and summer grazing periods. These amounts of N and TAN are further divided into that deposited in buildings, onto collecting yards, feeding yards and pastures. The amounts of N and TAN deposited within buildings are further divided according to the proportion of animals on liquid (slurry) or litter-based (FYM) manure management systems. The amount of TAN deposited by dairy cows in cubicle buildings producing slurry ($\alpha_{dhs}$, kg) is given by:

$$\alpha_{dhs} = \alpha_t \frac{b}{365} - ((cd) + (ef))g, \qquad (A.2)$$

where $b$ is the housing period (d), $c$ is the proportion of dairy cows that use collecting yards, $d$ is the proportion of daily TAN output that is deposited to collecting yards, $e$ is the proportion of dairy cows that use feeding yards, $f$ is the proportion of daily TAN output that is deposited to feeding yards and $g$ is the proportion of dairy cows housed in cubicle (slurry-producing) systems. The factors used are derived from UK surveys of manures practice (Smith et al., 2001a-c; Webb et al., 2001). The $NH_3$-N emissions from dairy cubicle houses ($B_E$, kg) is given by:

$$B_E = \alpha_{dhs} h, \qquad (A.3)$$

where $h$ is the EF for dairy cow cubicle housing, expressed as a proportion of the TAN deposited within the building.

The amount of TAN deposited by dairy cows onto collecting yards during the housing period is given by:

$$\alpha_{dcy} = \alpha_t \frac{b}{365} cd. \qquad (A.4)$$

However, a proportion of this ($i$) is removed from the yard by scraping, so the emission from dairy cow collecting yards ($C_E$, kg $NH_3$-N) is given by:

$$C_E = \alpha_{dcy}(1 - i), \qquad (A.5)$$

assuming that all TAN remaining on the yard after scraping is lost via $NH_3$ emission. The amount of TAN deposited by dairy cows onto feeding yards in winter ($\alpha_{dfy}$, kg) is given by:

$$\alpha_{dfy} = \alpha_t \frac{b}{365} ef. \qquad (A.6)$$

Assuming all TAN deposited on to feeding yards to be lost by $NH_3$ volatilisation, then $NH_3$-N emission from dairy cow feeding yards ($F_E$) is equal to $\alpha_{dfy}$.

The amount of TAN in slurry collected from the buildings, collecting yards and feeding yards and available to be put into store or spread direct to land ($\alpha_s$, kg) is given by

$$\alpha_s = (\alpha_{dhs} + \alpha_{dcy} + \alpha_{dfy}) - (B_E + C_E + F_E). \qquad (A.7)$$

In practice much slurry is spread direct to land, and only a proportion ($j$) enters slurry stores. The TAN pool in slurry stores ($\alpha_{st}$, kg) is therefore given by:

$$\alpha_{st} = \alpha_s j. \qquad (A.8)$$

Emissions from slurry stores ($S_E$, kg $NH_3$-N) are calculated from

$$S_E = (\alpha_{st}kl) + (\alpha_{st}mn) + (\alpha_{st}pq), \quad (A.9)$$

where $k$, $m$ and $p$ are the proportions of stored slurry held in above-ground tanks, lagoons and weeping-wall stores, respectively, and $l$, $n$ and $q$ are the EFs (as a proportion of the TAN in each pool) for above-ground tanks, lagoons and weeping-wall stores, respectively.

Thus the amount of TAN available to be spread to land ($\alpha_l$, kg) is given by:

$$\alpha_l = \alpha_s - S_E \quad (A.10)$$

and emissions following spreading of slurry to land ($L_E$) are given by:

$$L_E = (\alpha_l rst) + (\alpha_l r(1-s)u) + (\alpha_l vt), \quad (A.11)$$

where $r$ and $v$ are the proportions of slurry spread to grassland and arable land, respectively, $s$ is the proportion of that slurry spread to grassland which is spread in winter and $t$ and $u$ (% TAN applied) are the EFs for winter and summer-applied slurry, respectively (no distinction is made for slurries spread to arable land, the winter EF is used for all application timings).

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## 2.3 Paper 3

Misselbrook, T.H., and M.N. Hansen. (2001). Field evaluation of the equilibrium concentration technique (JTI method) for measuring ammonia emission from land spread manure or fertiliser. Atmospheric Environment 35, 3761-3768.

*Erratum*

Page 50, the symbol $A$ in Equations (8) and (9) should be replaced by $E$, where $E$ represents the area of the emitting surface below the chamber ($m^2$).

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# Field evaluation of the equilibrium concentration technique (JTI method) for measuring ammonia emission from land spread manure or fertiliser

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**Abstract**

Three experiments were conducted in which intercomparisons were made between the equilibrium concentration technique, developed at JTI, Sweden, and the integrated horizontal flux technique for measuring ammonia emissions following applications of urea fertiliser, cattle slurry and solid pig manure to land. Mean square prediction error analysis was used to compare the emission rates measured by the two techniques. There were no significant differences between the measurement techniques, although there was some evidence that emission rates were overestimated by the equilibrium concentration method relative to the integrated horizontal flux technique at higher emission rates ($>400\,g\,N\,ha^{-1}\,h^{-1}$). The equilibrium concentration method provides a practical and relatively inexpensive technique for measuring emissions under ambient conditions from small plots but good sampler preparation, adequate replication of emission measurements and appropriate choice of duration of sampling periods are necessities for obtaining reliable results. © 2001 Elsevier Science Ltd. All rights reserved.

*Keywords:* Ammonia emission; Measurement techniques; Manure

## 1. Introduction

In Europe, land application of livestock manures and, to a lesser extent, fertilisers are two important sources of ammonia ($NH_3$) emission to the atmosphere (Pain et al., 1998). With increasing concern about the potential environmental damage caused by atmospheric transport and subsequent deposition of $NH_3$, it is important to have reliable measurements of emission sources both for development and evaluation of potential abatement strategies and compiling national emission inventories.

Various techniques have been developed for the measurement of $NH_3$ emissions from land amended with livestock manure or fertilisers, with those most commonly used being described by McGinn and Janzen (1998). Measurements may be conducted on a field or large plot scale, using micrometeorological techniques, or on a small plot scale using techniques such as small wind tunnels or chambers (ventilated or closed). For absolute measurements of emission, micrometeorological methods are to be preferred, as the measurement technique does not interfere with the emitting surface. However, the main disadvantage of these methods are that large uniform areas of land are required (minimum fetch lengths of 20 m), with resultant difficulties in achieving replication or studying multiple treatments at the same time.

A method has been developed more recently by Svensson (1994) at JTI, Sweden, which is essentially a micrometeorological approach but suitable for use on small plots. Other advantages of the method are that it relies on inexpensive equipment and does not require

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electric power. The method relies on the measurement of the equilibrium concentration of $NH_3$ in the air at the emitting surface and the mass transfer coefficient for $NH_3$ from the air at the emitting surface to the free atmosphere (Svensson and Ferm, 1993). This method will be referred to as the JTI method throughout this paper.

### 1.1. JTI method

The JTI method uses the micrometeorological law of resistance to determine the flux of $NH_3$ ($\Phi_{NH_3}$, $\mu g\,m^{-2}\,s^{-1}$) from an $NH_3$ emitting surface by estimation of the equilibrium concentration of $NH_3$ in the air at the emitting surface ($C_{eq}$, $\mu g\,m^{-3}$), the $NH_3$ concentration in the air above the emitting surface ($C_a$, $\mu m^{-3}$) and the mass transfer coefficient for $NH_3$ ($K_a$, $m\,s^{-1}$)

$$\Phi_{NH_3} = (C_{eq} - C_a)K_a. \tag{1}$$

The method is described in detail by Svensson and Ferm (1993) and Svensson (1994) but is summarised briefly here for clarity and to aid discussion later in the paper. Passive diffusion samplers (PDS) are used to measure $NH_3$ concentration in the air. Two types of PDS are used which differ in the length of the diffusion path. For the L-type, the $NH_3$ absorbing filter is directly exposed to the ambient air. The C-type has the $NH_3$ absorbing filter placed 10 mm below a Teflon membrane filter. The amount of $NH_3$ collected by the PDS-C type ($X$, $\mu g$) and PDS-L type ($Y$, $\mu g$) is given by

$$X = DCt\frac{A}{(L_R + L_{LBL})} \tag{2}$$

and

$$Y = DCt\frac{A}{L_{LBL}} \tag{3}$$

respectively, where $D$ is the diffusion coefficient for $NH_3$ in air ($m^2\,s^{-1}$), $C$ the concentration of $NH_3$ in the air ($\mu g\,m^{-3}$), $t$ the exposure time for the PDS (s), $A$ the exposed area of the filter ($m^2$), $L_R$ the distance between the Teflon membrane filter and the $NH_3$ absorbing filter for PDS-C type (m) and $L_{LBL}$ the laminar boundary layer above the top of the PDS (m). By combining Eqs. (2) and (3) an expression for $L_{LBL}$ can be derived:

$$L_{LBL} = \frac{XL_R}{(Y - X)}. \tag{4}$$

The mass transfer coefficient can then be derived from the relationship

$$K = \frac{D}{L_{LBL}}. \tag{5}$$

Concentration of $NH_3$ in the air can be determined by combining Eqs. (3) and (4)

$$C = \frac{XYL_R}{DtA(Y - X)}. \tag{6}$$

By using the two types of PDS close to the surface of a treated plot (ca. 2 cm above the soil surface), both the concentration of $NH_3$ in the air just above the emitting surface ($C_a$, $\mu g\,m^{-3}$) and the mass transfer coefficient ($K_a$, $m\,s^{-1}$) can be determined from Eqs. (4)–(6). The other parameter required in Eq. (1), $C_{eq}$, is determined by use of a ventilated chamber. The chamber is ventilated by a fan via small inlet and outlet openings ensuring that condensation does not form on the internal walls. Inlet air is assumed to have an $NH_3$ concentration $C_a$, as measured by the PDS outside the chamber. $NH_3$ flux from the area covered by the chamber can be calculated according to Eq. (1) as

$$\Phi_{NH_{3a}} = (C_{eq} - C_{ch})K_{ch} \tag{7}$$

where $C_{ch}$ is the $NH_3$ concentration of air inside the chamber and $K_{ch}$ the mass transfer coefficient for $NH_3$ inside the chamber (which should be constant for a given flow rate and surface conditions). Flux from the chamber can also be calculated by mass balance

$$\Phi_{NH_{3a}} = (C_{ch} - C_a)F/A \tag{8}$$

where $F$ is the air flow rate through the chamber ($m^3\,s^{-1}$) and $A$ the area of emitting surface covered by the chamber ($m^2$). Combining Eqs. (7) and (8) gives an expression for the equilibrium concentration at the emitting surface:

$$C_{eq} = C_{ch}\left(1 + \frac{F/A}{K_{ch}}\right) - C_a\left(\frac{F/A}{K_{ch}}\right). \tag{9}$$

By exposing both types of PDS within the chamber, values can be derived for $C_{ch}$ and $K_{ch}$, as they were for $C_a$ and $K_a$, using Eqs. (4)–(6), enabling derivation of $C_{eq}$ from Eq. (9). This value can then be used in Eq. (1) together with the determined values for $C_a$ and $K_a$, to derive the flux from the treated area for the measurement period.

### 1.2. Integrated horizontal flux (IHF)—mass balance method

The mass balance method equates the vertical flux of $NH_3$ from a treated area of limited upwind extent with the net integrated horizontal flux at a known downwind distance (Wilson et al., 1983). The horizontal $NH_3$ flux for a given height can be measured using passive flux samplers (Leuning et al., 1985). The mean horizontal flux $\overline{uc}$ ($\mu g\,m^{-2}\,s^{-1}$) is derived from

$$\overline{uc} = M/At \tag{10}$$

where $M$ is the mass of $NH_3$ collected ($\mu g$) in the sampler during sampling period $t$(s) and $A$ is the effective cross-sectional area of the sampler ($m^2$) as determined in wind-tunnel calibrations. Using passive flux samplers mounted at several positions to a height $z$ (m), on masts placed at the upwind edge of an emitting surface and at a known distance $x$ (m), downwind of that edge, the net horizontal flux ($F$, $\mu g\,m^{-2}\,s^{-1}$) is derived from

$$F = \frac{1}{x}\left[\int_0^z (\overline{uc})_{dw}\,dz - \int_0^z (\overline{uc})_{uw}\,dz\right], \tag{11}$$

where $\overline{uc}$ is the mean horizontal flux measured by each sampler at the downwind (dw) or upwind (uw) edge of the treated area.

The aims of the study reported in this paper were to compare the JTI method and the integrated horizontal flux (IHF) mass balance approach and to investigate the constraints of the JTI method when used for measuring $NH_3$ emission from field applied fertiliser and manure.

## 2. Materials and methods

Three experiments were conducted in which $NH_3$ emission measurements were made using the JTI and IHF mass balance methods simultaneously. Experiment 1 was conducted in the UK at IGER, North Wyke, and Experiments 2 and 3 were conducted in Denmark at Research Centre Bygholm.

### 2.1. Experimental

In Experiment 1, granular urea fertiliser was applied uniformly, using a calibrated small-plot applicator, to a $40\,m \times 40\,m$ grassland plot at a rate of $300\,kg\,ha^{-1}$ ($138\,kg\,N\,ha^{-1}$) in October 1999. The grass had been cut the previous day to approximately 6 cm sward height. For the IHF method, a mast supporting five passive flux samplers (Leuning et al., 1985) at heights 0.25, 0.65, 1.20, 2.00 and 3.05 m was positioned at the centre of the treated area and a second mast supporting three samplers at 0.25, 1.25 and 3.05 m was positioned at the upwind edge. For the JTI method, six dynamic chambers and six ambient samplers, each having two replicate C-type and L-type PDS, were positioned randomly across the plot. Sampling periods were identical for both methods, with samplers being changed morning and evening each day for the first 3 days; then measurements were made during the daytime only for days 4–6, giving nine sampling periods. Chambers were moved to new positions between sampling periods.

In Experiment 2, cattle slurry was band spread to a $36\,m \times 36\,m$ recently cut grassland plot at a rate of $38\,m^3\,ha^{-1}$ ($50\,kg\,NH_4^+$-$N\,ha^{-1}$) in June 1999. Measurements using the IHF and JTI method were as for Experiment 1 with the exception that four dynamic chambers and two ambient samplers were used. Measurements continued for 6 days after application. Measurements were only conducted during the daytime using the JTI method whereas measurements of emission both during daytime and overnight were made using the IHF method.

In Experiment 3, solid pig manure was applied to a circular plot of bare soil of 20 m radius at a rate of $9.6\,t\,ha^{-1}$ ($4.3\,kg\,NH_4^+$-$N\,ha^{-1}$). Measurements using the IHF and JTI method were as for Experiment 1 with the exception that five dynamic chambers and two ambient samplers were used. Measurements continued for 6 days after application, with five sampling periods for both methods.

For all three experiments, continuous measurements were made of air temperature ($T$, K) close to the soil surface (at the same height as the PDS were situated), so that the diffusion coefficient required for the JTI method calculations could be determined from

$$D = T^{1.5} \times 4.59 \times 10^{-9}. \tag{12}$$

Differences in $D$ due to variations in atmospheric pressure were not accounted for, as air pressure was not measured, but would have had very small influence on the overall calculation. Wind direction was measured continuously on-site for each experiment, so that the mean fetch length for each sampling period, as required in the IHF method (Eq. (11)) could be determined.

The passive flux samplers of the IHF method were prepared by shaking with a 3% solution of oxalic acid in methanol and discharged after exposure with deionised water as described by Sherlock et al. (1989). Two unexposed samplers were analysed each time to provide a blank value. Ammoniacal-N content of the sample was determined by automated colorimetry (Searle, 1984).

For the PDS of the JTI method, thorough washing of the paper filters was found to be very important to obtain low blank values. Paper filters (Whatman Grade 40) were washed in hot, deionised water for 2 min and then rinsed twice in methanol (pre-shaken with ion exchange resin). (Alternatively, for Experiments 2 and 3, filters were washed in deionised water in an ultrasonc bath for three 15 min periods, followed by three further rinses in deionised water). These were then allowed to dry in a ventilated $NH_3$-free chamber. Filters were then soaked for 2 min in a 3% (w/v) solution of tartaric (Experiment 1) or oxalic (Experiments 2 and 3) acid in methanol and allowed to dry again in the $NH_3$-free chamber. Following exposure, filters were leached with 4 ml deionised water for analysis. Unexposed filters were also analysed to provide a blank value. Ammoniacal-N content of the leachate was determined as for the passive flux samplers.

### 2.2. Ammonia flux calculation

For the IHF method, ammonia flux from the treated area was calculated according to Eqs. (10) and (11). For the JTI method, the mean $C_a$ value for the plot was derived from the ambient samplers. This mean value was used in Eq. (9) together with chamber-specific $C_{ch}$ and $K_{ch}$ values to give a $C_{eq}$ value for each chamber position. These were then used in Eq. (1), together with mean plot values for $C_a$ and $K_a$, to derive a flux value for each chamber position. The flux values for each chamber position were averaged to derive the flux for the plot. A mean blank value was derived for the PDS, and filter concentrations not significantly greater than the mean blank value ($P > 0.05$) were excluded from the calculation.

### 2.3. PDS saturation tests

A knowledge of the absorption capacity of the PDS used in the JTI method is important in determining exposure times, particularly of the L-type samplers situated in the dynamic chamber which may quickly become supersaturated at high emission rates. Two studies were conducted to determine the absorption capacity. In the first, performed at Research Centre Bygholm, 64 L-type filters (impregnated with oxalic acid) were prepared and exposed within a chamber which was ventilated with air containing $12\,mg\,m^{-3}$ $NH_3$. The $NH_3$ concentration in the chamber was monitored continuously (Bryl & Kjaer Multipoint sampler type 1303). Four replicate filters were removed for analysis every 15 min for 3 h, then every 30 min for a further 2 h. In the second study, performed at IGER North Wyke, eight C-type and eight L-type filters (impregnated with tartaric acid) were exposed in a closed chamber to which $NH_3$ gas was introduced. Six exposure experiments were made with $NH_3$ concentrations (as measured using absorption flasks containing orthophosphoric acid) between 0.8 and $6\,mg\,m^{-3}$ $NH_3$-N and exposure times of between 60 and 320 min.

### 2.4. Statistical analyses

Data from the three field experiments were pooled and the two methods for measuring $NH_3$ compared using mean square prediction error (MSPE) analysis (Theil, 1966; Dhanoa et al., 1999) together with the application of concordance correlation coefficient to measure reproducibility (Lin, 1989). This combination of analyses provides a more powerful means of comparing the two methods than simple linear regression analysis, yielding information on departures from equality in addition to correlation. In particular, MSPE quantifies the proportion of the variation accounted for by line bias (i.e. one method consistently giving higher results than the other), systematic bias (i.e. the slope of the regression line being other than unity) and unaccounted for error. Ordinary (Pearson) correlation provides a measure of the precision of a fitted regression line. Concordance correlation provides a measure of reproducibility, or the deviations from a fitted line with slope of one and intercept of zero. A useful discussion on analysis of method comparison studies is given by Altman and Bland (1983).

## 3. Results

In the first of the absorption test studies, increase in concentration measured by the PDS filters was approximately linear to $50\,mg\,N\,l^{-1}$ in 5 ml leachate (Fig. 1), i.e. 250 µg N per filter. In the second study the combination of exposure times and $NH_3$ concentrations resulted in collection of 20–240 µg N on the L-type filters, and the amount collected increased linearly with increase in product of concentration and time over that range.

Ammonia emission rates as measured by the two methods for Experiments 1–3 are given in Tables 1–3, respectively. Emission rates from applied urea reached a maximum rate 46–53 h after application as measured by the IHF technique (Table 1). For sampling periods 4 and 6 in the JTI method, the exposure times for the samplers within the chambers were too long, and this resulted in saturation of the L-type samplers (values in excess of $80\,mg\,N\,l^{-1}$ in the 4 ml leached extract). Although results from the IHF method indicate that emission rate during sampling period 5 was actually greater than for sampling periods 4 and 6, the sampling period was of shorter duration (7 h as compared to 17 h) and there was no saturation of samplers. Cumulative emission for the measurement periods where data were available for both measurement methods (i.e. excluding sampling periods 4 and 6) was 15.13 and $15.42\,kg\,N\,ha^{-1}$ for IHF and JTI methods, respectively. Emission rates from slurry applied to grassland declined rapidly after the first sampling period (Table 2). In this experiment, the blank values for the PDS were rather high and variable, reducing the overall sensitivity of the method. Exposure times were insufficient to obtain a valid measurement for sampling periods 5 and 6. Cumulative emission over the first 4 sampling periods was 5.65 and $4.64\,kg\,N\,ha^{-1}$ for IHF and JTI methods, respectively. Emission rates from the solid manure (Table 3) were much lower, reflecting the much lower application of $NH_4^+$-N to the plot and low temperatures during the experiment, and declined over the measurement period. Cumulative emission over the measurement period was 1.38 and $1.80\,kg\,N\,ha^{-1}$ for IHF and JTI methods, respectively.

MSPE analysis of the pooled data from the three experiments showed that there was good correlation between the two methods, the fitted regression line accounting for 87% of the variation. There was no significant difference between the fitted regression line and a line of equality (i.e. slope of one and intercept of zero) (Fig. 2a), with line bias accounting for $< 1\%$ of the variation and systematic bias for 7%. Plotting the difference (IHF−JTI) in measured emission rate against

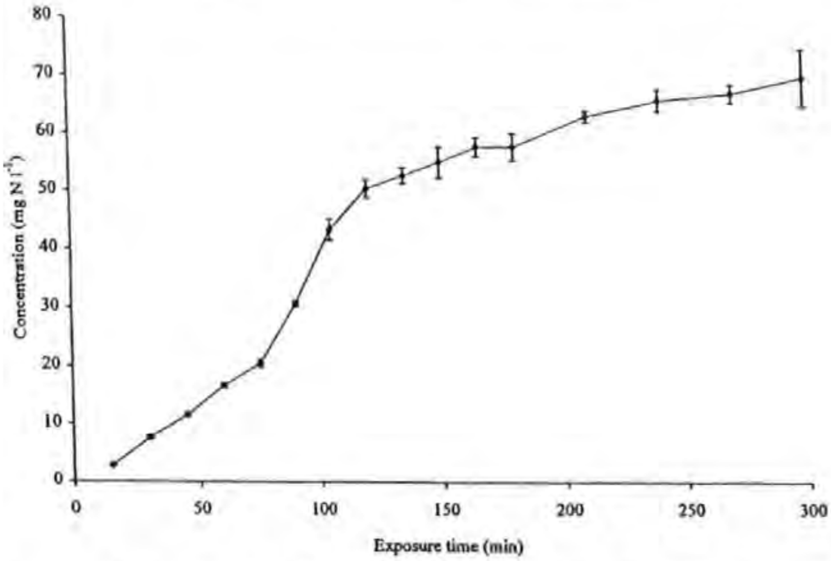


Fig. 1. PDS saturation curve. Concentration of $NH_4^+$-N ($mg\,l^{-1}$) in 5 ml leachate from filters coated in 2% oxalic acid vs. time of exposure to air containing $12\,mg\,m^{-3}$ $NH_3$.

Table 1
Ammonia emission rates ($g\,N\,ha^{-1}\,h^{-1}$) following urea application to grassland (Experiment 1) as measured by IHF and JTI methods

| Sampling period | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|---|---|---|---|---|---|---|---|---|---|
| Hours after application | 0–6.5 | 6.5–22 | 22–30 | 30–46 | 46–53 | 53–70 | 70–77 | 93–101 | 119–125 |
| IHF | 127 | 132 | 429 | 484 | 736 | 458 | 351 | 120 | 81 |
| JTI | 32 | 88 | 537 | [a] | 898 | [a] | 356 | 121 | 44 |
| | (3)[b] | (13) | (189) | | (203) | | (100) | (39) | (49) |

[a] Saturation of PDS.
[b] Standard errors in parenthesis.

Table 2
Ammonia emission rates ($g\,N\,ha^{-1}\,h^{-1}$) following band application of cattle slurry to grassland (Experiment 2) as measured by IHF and JTI methods (results given for matching sampling periods only)

| Sampling period | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|
| Hours after application | 0–2 | 2–6 | 25–30 | 49–53 | 72–77 | 118–126 |
| IHF | 1242 | 487 | 25 | 37 | 24 | 14 |
| JTI | 905 | 679 | 3 | 14 | [a] | [a] |
| | (393)[b] | (336) | (6) | (4) | | |

[a] Below detection limit.
[b] Standard errors in parenthesis.

the mean for each sampling period showed a mean difference of zero (Fig. 2b). It should be noted, however, that the data point to the top right corner of Figs. 2a and b exerts high leverage on the regression line and omitting this point would result in a significant systematic bias (59% variance), with the JTI method giving higher values than IHF at high emission rates. A greater number of mid-to-high emissions data would have been desirable to increase the stability of the systematic bias.

Table 3
Ammonia emission rates (g N $ha^{-1}$ $h^{-1}$) following band application of solid pig manure to arable soil (Experiment 3) as measured by IHF and JTI methods[a]

| Sampling period | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| Hours after application | 0–1.5 | 1.5–5.5 | 5.5–28 | 28–72 | 72–144 |
| IHF | 60 | 29 | 14 | 10 | 6 |
| JTI | 98 | 17 | 15 | 27 | 1 |
| | (76) | (8) | (8) | (8) | (1) |

[a] Standard errors in parenthesis.

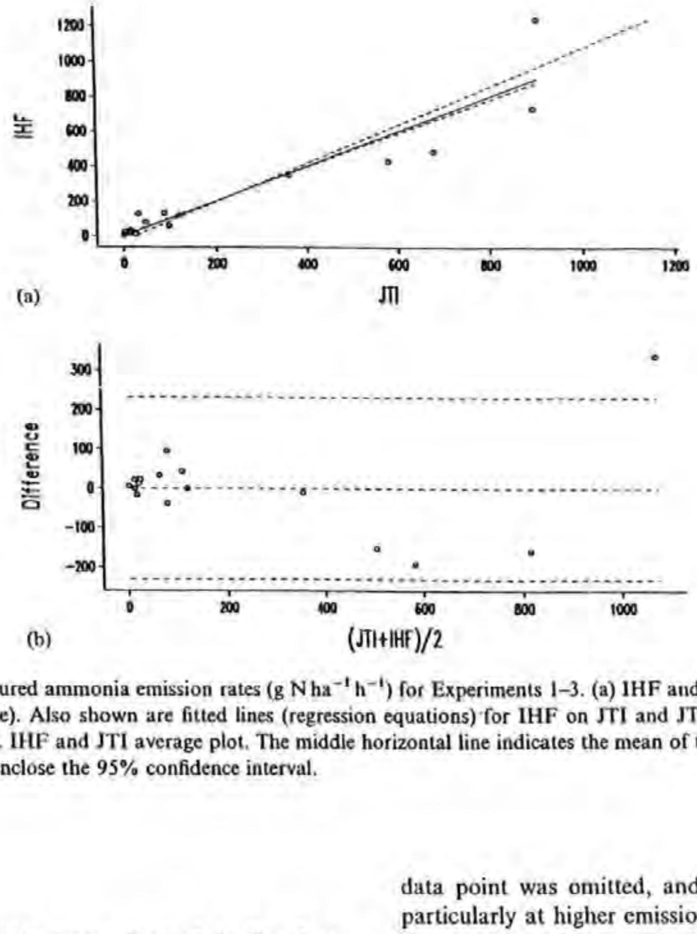


Fig. 2. IHF vs. JTI measured ammonia emission rates (g N $ha^{-1}$ $h^{-1}$) for Experiments 1–3. (a) IHF and JTI values with reference to line of equality (solid line). Also shown are fitted lines (regression equations) for IHF on JTI and JTI on IHF (dashed lines). (b) Difference (IHF−JTI) vs. IHF and JTI average plot. The middle horizontal line indicates the mean of the distribution of differences and the other two lines enclose the 95% confidence interval.

## 4. Discussion

Typical emission rates were observed in the three experiments. Emission rates for applied animal manures are greatest immediately following application (e.g. Pain et al., 1989) but decline rapidly to much lower levels. For urea, a delay in reaching peak emission rate has been noted previously because of the time period necessary for urease activity to develop in response to the addition of urea (Black et al., 1985; Whitehead and Raistrick, 1990).

From the MSPE analysis, the two measurement methods are in agreement. However, there was a suggestion of a systematic bias in the regression if one data point was omitted, and more data are required, particularly at higher emission rates, to be confident in the agreement between the two methods. Ferm et al. (1999) measured $NH_3$ emission by the JTI method and mass balance technique where masts supporting passive flux samplers were mounted around the periphery of the treated area (Schjoerring et al., 1992) following application of pig slurry to cereal crops. Emission measured using the chambers was only ca. 30% of that measured using the mass balance technique. The authors argued that this large difference was due to direct crop uptake of $NH_3$ within the JTI chambers being greater than that outside the chambers. They gave no indication of crop height, but it may be that such an effect is more evident on a taller crop than for short grass swards, such as used in our comparisons. Further intercomparison/validation studies are required to confirm whether the JTI method is appropriate on taller crops. Ferm et al. (1999) also measured emissions following application of pig slurry to bare soil, but no results are given for the mass balance technique.

In the present study, between 4 and 6 chambers and 2–6 ambient samplers were used per plot for the JTI method. As the chambers only cover a small area of the plot, variability in emission rates between chambers can be high (hence high standard errors in Tables 1–3). Variability was less for Experiment 1 because urea fertiliser provided a more uniform $NH_3$ source than slurry or, particularly, solid manure, in Experiments 2 and 3. Generally, variation was less for $C_a$ than $C_{ch}$, therefore a smaller number of ambient samplers than chambers are required. An example of the increased uncertainty introduced by using fewer chambers per plot is given in Fig. 3, using data from Experiment 1 (sampling period 8). Emission rates, together with 95% confidence intervals, were recalculated for each of the possible combinations of 5, 4, 3 and 2 chambers. Mean values for the upper and lower 95% confidence limits were derived, together with the maximum upper limit and minimum lower limit, for each set. The uncertainty in the mean emission rate increases more rapidly as chamber numbers become fewer. The ideal number of chambers per plot would depend on the inherent variation in the emission rate and the desired maximum allowable error level. Obviously there will always be a compromise between the number of replicate chambers used per plot and the number of replicate plots, but this high variability between chambers needs to be considered when designing experiments.

For a given chamber design and surface conditions, $K_{ch}$ will have a constant value, being dependant on wind speed and surface roughness. Establishing the $K_{ch}$ value for different surfaces would negate the requirement to expose L-type PDS in the chambers, thereby reducing the number of filters for preparation and analysis by at least 25%. Mean $K_{ch}$ values for Experiments 1–3 were 0.0119 (short grass), 0.0093 (short grass) and $0.0124\,m\,s^{-1}$ (bare soil), respectively. Svensson (1994) gives a value of $0.0160\,m\,s^{-1}$ for smooth bare soil and Misselbrook (unpublished data) has measured mean values of $0.0104\,m\,s^{-1}$ (range 0.0048–0.0148) and 0.0083 (range 0.0058–0.0093) $m\,s^{-1}$ for manure coated concrete and short grass surfaces, respectively. The range in these reported values means that the use of a common mean $K_{ch}$ for measurements on a particular surface may lead to inaccuracies. For example, using the mean value of $0.0083\,m\,s^{-1}$ from previous measurements on short grass to calculate emission rates in Experiment 1 gave a cumulative total loss for the measured periods of 20.3 kg $N\,ha^{-1}$, compared with 16.5 kg $N\,ha^{-1}$ when the mean value for the experiment ($0.0119\,m\,s^{-1}$) was used and 14.5 kg $N\,ha^{-1}$ when Svensson's value of $0.0160\,m\,s^{-1}$ for bare soil was used. For accurate results, therefore, $K_{ch}$ should always be measured. A compromise might be to measure $K_{ch}$ for the first sampling period only, using the mean value for later sampling periods.

The sensitivity and accuracy of the JTI method are dependant on the preparation of PDS filters with consistently low blank values ($<0.5\,\mu g$ N per filter). The minimum detection level for exposed filters will depend on both the mean and the variability in blank values. An important requirement of the method is the availability of an $NH_3$-free laboratory or chamber for preparation and analysis of the PDS. Minimum emission rates which can be measured will depend on both

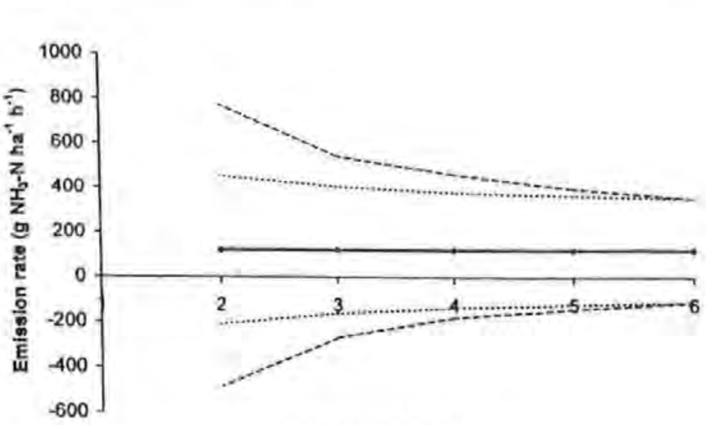


Fig. 3. The effect of reducing the number of chambers per plot on the uncertainty of the estimate of emission rate (data from Experiment 1 sampling period 8). Shown are mean emission rate, $g\,N\,ha^{-1}\,h^{-1}$ (bold line), mean 95% confidence interval (dotted line) and maximum 95% confidence interval for combinations of fewer chambers per plot.

the minimum detection levels of the PDS filters and the duration of exposure. A combination of low blank value and long exposure time enabled an emission rate of 1 g N $ha^{-1}$ $h^{-1}$ to be measured in Experiment 3. Calculation of appropriate exposure times depends on the $NH_3$ concentration, but should be such that C-type ambient PDS reach detectable levels while L-type chamber PDS do not become saturated. Generally, for measurements following manure applications, exposure periods will be short (e.g. 1–2 h) immediately following application and longer (4, 8 or >24 h) on subsequent days. However, prediction of suitable exposure times for measurement of emission following fertiliser application is more difficult. Example curves for exposure time vs. $NH_3$ concentration are given by Svensson and Ferm (1993).

The equilibrium concentration technique for measuring emissions of $NH_3$ following fertiliser or manure applications to land is a practical, relatively inexpensive method which can be used on small plots and which, in this set of comparisons, gave results not significantly different from those measured by a standard mass balance technique. However, to ensure reliable results from the technique, care is required in the preparation of PDS, replication of chambers and ambient samplers is required and consideration needs to be given to the choice of exposure times.

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## 2.4 Paper 4

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# Measuring ammonia emissions from land applied manure: an intercomparison of commonly used samplers and techniques

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*Three commonly used ammonia emission measurement techniques were compared for different manure types and gave CVs between 23 and 74%.*

**Abstract**

A number of techniques have been developed to quantify ammonia ($NH_3$) emissions following land application of manure or fertiliser. In this study, coefficients of variation were determined for three commonly used field techniques (mass balance integrated horizontal flux, wind tunnels and the equilibrium concentration technique) for measuring emissions from a range of manure types. Coefficients of variation (CV) for absorption flasks, passive flux samplers and passive diffusion samplers were 21, 10 and 14%, respectively. In comparative measurements, concentrations measured using passive flux samplers and absorption flasks did not differ significantly, but those measured using passive diffusion samplers were on average 1.8 times greater. The mass balance technique and wind tunnels gave broadly similar results in two out of four field tests. Overexposure of passive diffusion samplers for some sampling periods meant that estimation of cumulative $NH_3$ emission using the equilibrium concentration technique in the field tests could not be made. For cumulative $NH_3$ emissions, CVs were in the range of 23–52, 46–74 and 21–39% for the mass balance, wind tunnel and equilibrium concentration techniques, respectively. Lower CVs were associated with measurements following slurry compared with solid manure applications. Our conclusions from this study are that for the measurement of absolute emissions the mass balance technique is to be preferred, and for small-plot comparative measurements the wind tunnel system is preferred to the equilibrium concentration technique.



*Keywords:* Ammonia emission; Measurement technique; Manure; Variability

## 1. Introduction

The land application of manure represents a major source of ammonia ($NH_3$) emissions to the atmosphere in Europe, often accounting for 30–40% of total national emissions (e.g. Misselbrook et al., 2000). A number of techniques have been developed to quantify $NH_3$ emissions for the construction of national inventories so that impacts on the environment can be assessed and the effectiveness of abatement strategies evaluated. These techniques are equally applicable to the measurement of emissions from fertiliser applications. Generally, the techniques fall into two categories: micrometeorological methods (usually used for large land areas) and enclosure methods (commonly used on small plots for comparative experiments). Most techniques require the measurement of $NH_3$ concentration and

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air flow or wind speed, or alternatively, direct measurement of $NH_3$ flux.

A review of many of the techniques which have been employed by researchers in the measurement of $NH_3$ emissions from land sources is given by McGinn and Janzen (1998). A number of micrometeorological techniques are described, including mass balance (integrated horizontal flux (IHF), single profile measurement, perimeter profile measurements), eddy correlation and relaxed eddy correlation, gradient methods (aerodynamic approach, Bowen ratio/energy balance method), the backward Lagrangian stochastic modelling approach and the equilibrium concentration technique. The backward Lagrangian stochastic modelling approach (Flesch et al., 1995) was highlighted as offering flexibility in plot design and requiring a minimum number of samplers. However, while there is increasing interest in the use of this technique, the mass balance IHF approach has been most commonly employed for measuring emissions from medium-scale (approximately 0.1 ha) manure-treated plots, particularly in north-western Europe (e.g. Pain et al., 1991; Sommer et al., 1997; Huijsmans et al., 2001; Misselbrook et al., 2002). For smaller plots, the equilibrium concentration technique (Svensson, 1994b) has been increasingly used in recent years (e.g. Svensson, 1994a; Misselbrook and Hansen, 2001; Rodhe and Rammer, 2002; Mattila and Joki-Tokola, 2003).

Enclosure techniques, suitable for measurements on smaller plots, may be of a closed (static chambers) or open (dynamic chambers) type. With closed chambers, the flux is calculated from the rate of increase of the gas concentration in the enclosure after the system has been closed. However, the design of the system must be carefully selected to minimise negative feedback on the rate of diffusion of the gases. These restrictions pose practical difficulties for measuring $NH_3$ emissions from manure because the rate of release is often very high immediately after application to land. More commonly used, therefore, are dynamic chamber techniques, with the wind tunnel system described by Lockyer (1984) being used by many researchers (e.g. Pain et al., 1990; Sommer et al., 1991; Misselbrook et al., 1996; Braschkat et al., 1997; van der Weerden and Jarvis, 1997; Smith et al., 2000; Meisinger et al., 2001).

The objectives of this study were to make an intercomparison between three of the most commonly employed measurement techniques (micrometeorological mass balance IHF, equilibrium concentration and wind tunnels) and to determine coefficients of variation for each of the techniques for a range of manure types. In addition, measurements were conducted to determine limits of detection and coefficients of variation for the commonly used $NH_3$ samplers (absorption flasks, passive diffusion samplers and passive flux samplers).

## 2. Materials and methods

### 2.1. Sampler assessments

Sampler tests were conducted using a controlled environment chamber, as described by Hobbs et al. (1997), in which air flow and temperature could be maintained at fixed values. The chamber consisted of an enclosed system of stainless steel ducting ($0.5 \times 0.5$ m internal section, total volume 40 $m^3$) with ends connected to a large Tedlar® bag. The air in the system was kept slightly above atmospheric pressure, to prevent air leaking into the system. Ammonia gas was introduced into the system via an inlet port just downstream of a fan. Three types of sampler were used to measure the $NH_3$ concentration in the chamber: absorption flasks, passive diffusion samplers (PDS) and passive flux samplers (PFS). Because $NH_3$ may have been adsorbed onto the internal surfaces of the chamber, the concentration within the chamber could not be determined with certainty from knowledge of the quantity of $NH_3$ gas introduced. For this reason, concentration measurements using the absorption flasks were taken as the baseline against which the other samplers were compared.

Absorption flasks were used to sample $NH_3$ concentration at six points within the chamber. Two absorption flasks, each containing 30 ml of orthophosphoric acid solution, were connected in series at each sampling point, to determine the trapping efficiency of the first flask. Air was drawn from the chamber to the flasks through 4 mm (internal diameter) PTFE tubing (approximately 0.5 m in length). Comparisons were made between different acid strengths in the flask (0.1, 0.01 or 0.001 mol $l^{-1}$), different sample air flow rates through the acid (2 or 4 l $min^{-1}$) and scintered glass sampling tubes (creating many small bubbles in the acid solution) or open ended sampling tubes (creating fewer, larger bubbles). Following sampling, solution volumes were made up to 100 ml using deionised water and subsampled for analysis of ammoniacal-N content by automated colorimetry (Searle, 1984).

Passive diffusion samplers, as used in the equilibrium concentration technique and described by Svensson (1994b), were of two types. Each had an $NH_3$ absorbing tartaric acid-coated filter, but they differed in the diffusion distance between the free atmosphere and the filter. For the L-type, the filter is exposed directly to the ambient air while for the C-type the filter is located 10 mm below a Teflon diffusion membrane. Four sets of four PDS, each set consisting of two L-type and two C-type samplers were placed within the chamber during each measurement period. Following sampling, the filters were leached with 4 ml of deionised water and the leachate analysed for ammoniacal-N by automated colorimetry (Searle, 1984). Concentrations of $NH_3$ in the air was then calculated according to equations given by Svensson (1994b) and Misselbrook and Hansen (2001).

Passive flux samplers as described by Leuning et al. (1985), coated internally with oxalic acid, were placed in the chamber facing directly into the air flow, with three replicate PFS used on each occasion. For some measurements, PFS were positioned at an angle of 20° or 40° to the air flow, as Leuning et al. (1985) indicated that it was at these angles that maximum deviation of flow rate within the PFS would occur. Following exposure, the PFS were leached with 40 ml deionised water and the leachate analysed for ammoniacal-N by automated colorimetry (Searle, 1984). As PFS give a direct measurement of flux, $NH_3$ concentration in the air was derived by dividing flux by the air flow rate within the chamber.

A total of 34 sampler intercomparison measurements were made with a range of target $NH_3$ concentrations (50–15 000 $\mu g\,N\,m^{-3}$), exposure times (60–360 min) and air flow rates within the chamber (0.5–3.5 $m\,s^{-1}$). For each measurement, a number of 'blank' samplers of each sampler type were included. These samplers were treated in the same way as the measurement samplers, except that they were not exposed in the chamber. Limits of detection (LOD) were determined from the mean amount of $NH_3$-N present in blank samplers ($\overline{\text{blank}}$) and the standard deviation of the mean ($sd_{blank}$):

$$\text{LOD} = \overline{\text{blank}} + (4.65\,sd_{blank}) \quad (1)$$

*2.2. Technique assessments*

Measurements of $NH_3$ emissions were made following the land application of a range of manure types in order to provide an intercomparison between measurement techniques and an indication of the expected variability associated with each technique. The three measurement techniques used were the micrometeorological mass balance IHF technique, the equilibrium concentration technique and a system of small wind tunnels. Measurements were made following four manure applications (dairy cattle slurry, dairy cattle farmyard manure (FYM), poultry layer manure and poultry layer manure wetted with simulated rainfall). Measurements were made over 5 days following application. Each manure type was applied using standard farm machinery to three separate circular plots of 20 m radius, which were separated from each other by at least 40 m in a line perpendicular to the prevailing wind direction. Application dates, rates and manure analyses are given in Table 1.

The mass balance IHF method equates the vertical flux of $NH_3$ from a treated area of limited upwind extent with the net integrated horizontal flux at a known downwind distance (Wilson et al., 1983). In this study, a mast supporting six PFS (at 0.2, 0.4, 0.8, 1.2, 2.2 and 3.3 m above ground) was placed at the centre of each manure-treated circle. Another mast was placed at the upwind edge of each plot, supporting three PFS (at 0.2, 0.8 and 2.2 m). The mean horizontal flux, $\overline{uc}$ ($\mu g\,N\,m^{-2}\,s^{-1}$), at each height was derived from the PFS according to:

$$\overline{uc} = \frac{M}{At} \quad (2)$$

where $M$ is the mass of $NH_3$-N collected ($\mu g$) in the sampler during sampling period, $t$ (s) and $A$ is the effective cross-sectional area of the sampler ($m^2$) as determined in wind tunnel calibrations. The net horizontal flux ($F$, $\mu g\,N\,m^{-2}\,s^{-1}$) was then derived according to:

$$F = \frac{1}{x}\left[\int_0^z (\overline{uc})_{dm}\,dz - \int_0^z (\overline{uc})_{bm}\,dz\right] \quad (3)$$

Table 1
Manure analyses and application rates for the technique comparison experiments

| Manure type | Application date | Plot number | pH | Dry matter ($kg\,t^{-1}$) | Total N ($kg\,t^{-1}$) | Ammonium-N ($kg\,t^{-1}$) | Uric acid-N ($kg\,t^{-1}$) | Application rate ($t\,ha^{-1}$) |
|---|---|---|---|---|---|---|---|---|
| Dairy slurry | 21 March 2000 | 1 | 7.5 | 41 | 2.87 | 1.45 | | 41.1 |
| | | 2 | 7.5 | 39 | 2.86 | 1.48 | | 44.7 |
| | | 3 | 7.5 | 37 | 2.87 | 1.47 | | 44.4 |
| Dairy FYM | 23 May 2000 | 1 | 8.6 | 243 | 5.13 | 0.61 | | 55.7 |
| | | 2 | 8.8 | 214 | 4.71 | 0.47 | | 49.6 |
| | | 3 | 8.9 | 270 | 4.78 | 0.77 | | 54.1 |
| Layer manure | 22 August 2000 | 1 | 6.4 | 612 | 30.2 | 15.5 | 4.7 | 21.4 |
| | | 2 | 6.7 | 574 | 28.3 | 14.5 | 4.4 | 21.5 |
| | | 3 | 6.2 | 545 | 26.9 | 13.8 | 4.1 | 21.8 |
| Wetted layer manure | 5 September 2000 | 1 | 6.5 | 416 | 20.8 | 10.2 | 2.3 | 14.7 |
| | | 2 | 6.5 | 444 | 19.3 | 9.2 | 3.4 | 16.7 |
| | | 3 | 6.3 | 389 | 21.1 | 12.0 | 3.7 | 15.1 |

where $x$ (m) is the mean fetch length (equating to the radius of the treated circle), $z$ (m) the height of the uppermost sampler and $\overline{uc}$ the mean horizontal flux measured by each sampler at the centrally-located downwind (dm) or upwind background (bm) mast. PFS were changed after 1, 3, 6, 24, 48, 72 and 96 h.

For the equilibrium concentration technique, $NH_3$-N emission was derived from:

$$F=\left(C_{eq}-C_a\right)K_{z,a} \tag{4}$$

where $C_{eq}$ ($\mu g\, m^{-3}$) is the equilibrium concentration of $NH_3$-N in the air at the emitting surface, $C_a$ ($\mu g\, m^{-3}$) the concentration in the air just above the emitting surface and $K_a$ ($m\, s^{-1}$) the mass transfer coefficient for $NH_3$-N in air. These three parameters are derived by deploying PDS (both C-type and L-type) close to the emitting surface both within and outside of a small ventilated chamber (see Svensson, 1994b; Misselbrook and Hansen, 2001 for more details). Four ventilated chambers and two ambient air sampling points were placed at random across each of the manure-treated circles. Sampling was not continuous with this technique, with PDS being exposed for 2 h on day 1, 6 h on day 3 (on day 2 for experiments 3 and 4) and 6 h on day 5 (24 h on day 3 for experiments 3 and 4). Chambers were moved to new random positions on the plots for each sampling period.

Three wind tunnels were positioned on each of the manure-treated plots. The tunnels, as described by Lockyer (1984) employ a fan to draw air through a transparent canopy ($2 \times 0.5$ m) covering 1 $m^2$ of treated surface area. Absorption flasks were used to measure the concentration of $NH_3$-N in air at the inlet and outlet of the canopy. Flux from the measurement area was calculated as:

$$F=(C_o-C_i)\frac{v}{t} \tag{5}$$

where $C_o$ and $C_i$ ($\mu g\, m^{-3}$) are the concentrations in the outlet and inlet air, respectively, and $v$ ($m^3$) the volume of air drawn through the tunnel in the sampling period $t$ (s). The tunnels were positioned such that the canopy inlets were located at the upwind edge of the plots. Absorption flasks were changed at the same time intervals as the PFS; i.e. after 1, 3, 6, 24, 48, 72 and 96 h. Wind tunnels remained in the same position on the plots for the duration of each experiment.

## 3. Results

### 3.1. Sampler assessments

Over all measurements, the mean amount of $NH_3$-N collected in the second of each pair of absorption flasks connected in series was 3% (SE 0.004%) of the total collected in both flasks, indicating that the first absorption flask had not become saturated. The acid strength, sample air flow rate or sampling tube end type had no significant effect ($P > 0.05$) on the $NH_3$ concentration measurements. For the PFS, there was no significant influence ($P > 0.05$) of sampler orientation with respect to wind direction. For all sampler types, there was no significant effect of air flow rate within the chamber or sampling duration on the measured $NH_3$ concentrations.

There were strong linear relationships between the $NH_3$ concentration measurements made by the absorption flasks and both the PFS (Fig. 1) and PDS (Fig. 2), although the PDS consistently gave higher $NH_3$ concentrations than the absorption flasks. The slope of the fitted regression line for PFS against absorption flask measurements was not significantly different from unity ($P > 0.05$). Mean coefficients of variation were greater for the absorption flasks than for PFS or PDS (Table 2). Coefficients of variation for the amount of $NH_3$-N collected by the L-type and C-type PDS were not significantly different, with mean values of 14.9 and 13.9%, respectively ($P > 0.05$). The amount of $NH_3$-N collected on the L-type and C-type PDS increased linearly with the $NH_3$ concentration in the chamber as determined by the absorption flasks (Fig. 3). Absorption flasks and PFS had higher limits of detection than PDS (Table 3). However, because they collect more $NH_3$-N for a given exposure time, this does not necessarily mean that they are less sensitive. Upper detection limits were not determined in this study, but no saturation was evident in any of the sampler types within these controlled chamber assessments so it might be assumed that the samplers performed satisfactorily at least up to the maximum amounts collected, as given in Table 3.

### 3.2. Technique assessments

A summary of the $NH_3$ emission rates and total emissions from each manure application are given in Tables 4–6 for the mass balance, wind tunnel and

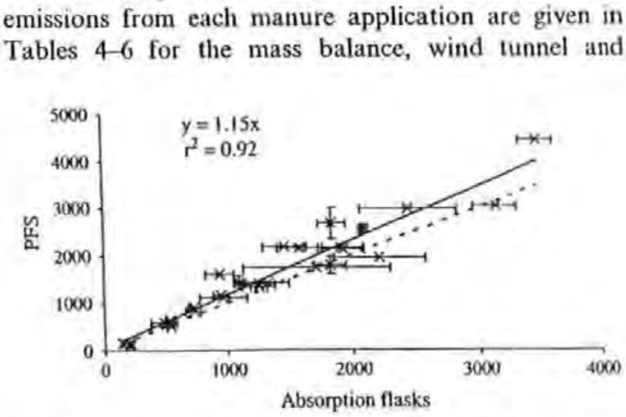


Fig. 1. Ammonia-N concentration ($\mu g\, m^{-3}$) in chamber measured using absorption flasks and PFS. Dashed line is line of equality, solid line is fitted regression line. Error bars show $\pm 1$ standard error.

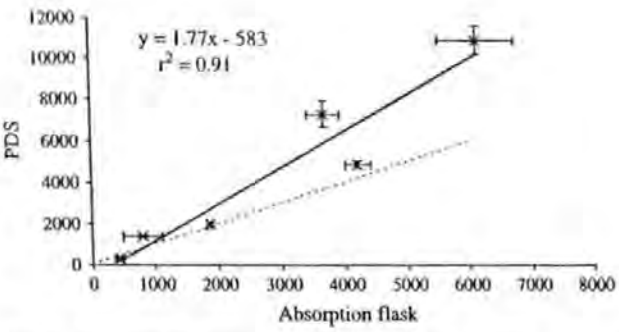


Fig. 2. Ammonia-N concentration (μg $m^{-3}$) in chamber measured using absorption flasks and PDS. Dashed line is line of equality, solid line is fitted regression line. Error bars show ±1 standard error.

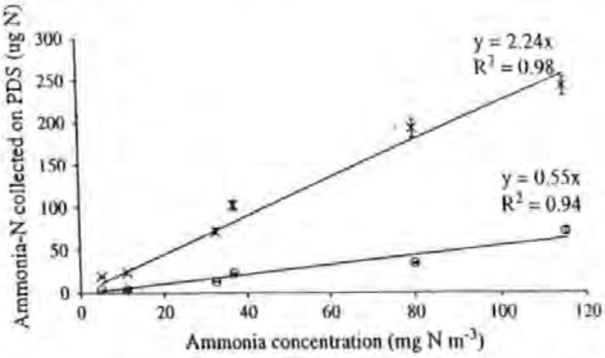


Fig. 3. Amount of ammonia-N (μg) collected on L-type (×) and C-type (o) PDS at different chamber ammonia concentrations (mg N $m^{-3}$, as measured using absorption flasks), together with fitted regression lines. Error bars show ±1 standard error.

equilibrium concentration (emission rates only) techniques, respectively. For the mass balance IHF technique, there was less variation (i.e. a lower CV) in the emission rate data from the three cattle slurry circles (mean CV of 23%) than from the solid manures (mean CV 24 – 52%), particularly in the initial sampling periods when emission rates were highest (Table 4). This was probably because the slurry was easier to spread evenly and more uniform application rates were achieved across the plot. Similarly, for the wind tunnel technique (Table 5), the variability in the emission rate data from the slurry-treated plots was lower (mean CV of 46%) than for the solid manures (mean CV 61–74%). There were some operational problems with the wind tunnels during measurements from the dairy FYM (power failures and wind speed loggers not functioning) so those measurement data have been omitted. The overall variability of the wind tunnel technique was higher than that of the mass balance IHF.

For the equilibrium concentration technique (Table 6), the 6 h PDS exposure period on days 3 and 5 gave results below the detection limit. For this reason, the measurements were brought forward to days 2 and 3 for the layer manure experiments and the PDS exposure period extended to 24 h for day 3. There was some evidence that some filter papers for high available N manures (slurry and layer manure) during the initial exposure period when $NH_3$ emission rates were highest had become saturated (the amounts of $NH_3$-N collected exceeded the maximum given in Table 3 and the limit of linearity given by Misselbrook and Hansen, 2001), making calculations of the $NH_3$ mass transfer coefficients unreliable. Similarly, at low $NH_3$ concentrations where N recovery by the PDS was near the detection limit, calculation of the mass transfer coefficient was also unreliable. For these reasons a modified calculation was employed, using a mean mass transfer rate in chambers for each experiment ($K_{ch}$) and a mean ambient mass transfer coefficient for each sampling period ($K_a$), to recalculate $NH_3$ volatilisation rates. The main effect of the modified calculation was to reduce the calculated volatilisation losses at high emission rates soon after application (Table 6) when loss rates were at their maximum. Although some data were missing, the results again suggested that emission measurements from the cattle slurry were associated with a lower CV (mean 21%) than those from the plots treated with solid manures (mean CV 36–39%).

Total emissions over the 5-day measurement period were calculated using the measured emission rates for the mass balance and wind tunnel techniques and expressed as a percentage of the total uric and ammoniacal-N (UAN) applied (Tables 4 and 5). Coefficients of variation tended to be lower for the 5-day cumulative emission than the mean CV for the emission rates measured during each sampling period, particularly for the wind tunnel measurements. Total emissions estimated by the two techniques were not significantly different ($P > 0.05$) for the slurry and

Table 2
Mean coefficients of variation (CV) for each sampler type

| Sampler type | CV (%) | No. of samplers per test | No. of tests |
|---|---|---|---|
| Absorption flask | 21 | 3 or 6 | 40 |
| PFS | 10 | 2 | 6 |
| PDS | 14 | 4 | 6 |

Table 3
Blank values, detection limits (LOD) and maximum amounts collected for each sampler type (μg N)

| Sampler type | Mean blank (SD) | $n$ | LOD* | Maximum collected |
|---|---|---|---|---|
| Absorption flasks | 7.1 (13.57) | 56 | 70 | 1130 |
| PFS | 12.7 (7.56) | 18 | 48 | 768 |
| PDS | 1.0 (0.33) | 24 | 2.5 | 263 |

*LOD = (4.65 × standard deviation of the blank values) + mean blank value.

Table 4
Summary of $NH_3$ volatilisation rates (kg N $ha^{-1}$ $h^{-1}$) and total losses measured using the mass balance IHF technique

| Time after application | Dairy slurry | | | Dairy FYM | | | Layer manure | | | Wetted layer manure | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Mean | SE | CV (%) | Mean | SE | CV (%) | Mean | SE | CV (%) | Mean | SE | CV (%) |
| 1 h | 8.1 | 0.4 | 9 | 2.9 | 0.9 | 53 | 20.5 | 6.3 | 53 | 11.3 | 4.1 | 62 |
| 3 h | 6.6 | 0.3 | 8 | 2.2 | 0.3 | 24 | 9.3 | 1.4 | 25 | 4.6 | 1.8 | 67 |
| 6 h | 2.5 | 0.2 | 13 | 1.1 | 0.1 | 21 | 2.8 | 1.4 | 85 | 2.1 | 0.6 | 48 |
| 24 h | 0.4 | 0.0 | 16 | 0.3 | 0.0 | 18 | 2.8 | 0.7 | 44 | 0.6 | 0.1 | 25 |
| 2 days | 0.4 | 0.1 | 54 | 0.1 | 0.0 | 12 | 2.4 | 0.1 | 4 | 0.5 | 0.1 | 31 |
| 3 days | 0.1 | 0.0 | 39 | 0.1 | 0.0 | 10 | 1.9 | 0.2 | 17 | 0.1 | 0.0 | 74 |
| 5 days | 0.0 | 0.0 | 21 | 0.1 | 0.0 | 33 | 0.2 | 0.0 | 31 | 0.1 | 0.0 | 54 |
| Mean | 4.5 | 0.1 | 23 | 1.0 | 0.2 | 24 | 5.7 | 1.4 | 37 | 2.8 | 1.0 | 52 |
| Total $NH_3$-N loss (% total UAN[a] applied) | 75 | 1 | 3 | 69 | 8 | 20 | 54 | 4 | 14 | 29 | 9 | 55 |

[a] Uric and ammoniacal-N.

wetted layer manure experiments, but wind tunnels gave a significantly lower loss ($P < 0.05$) for layer manure. For the equilibrium concentration technique, because sampling was intermittent and some data were missing, cumulative emissions over the 5-day period were not calculated. However, a comparison was made between the three techniques of measured emission rates during the first sampling period for each experiment (Fig. 4).

## 4. Discussion

Absorption flasks and PFS proved to be robust samplers for $NH_3$ concentration over the range of concentrations and air flow rates used in this study. It is possible that some adsorption of $NH_3$ took place on the PTFE tubing between the chamber and the absorption flasks, indicating that the flasks would give an underestimate of concentrations compared with the PFS, which were exposed within the chamber. Additionally, derivation of concentrations from the PFS measurements required knowledge of the wind speed within the chamber, for which errors were not quantified. However, this study gives confidence that the two sampler types give the same results.

The results from the PDS and absorption flask comparisons give some cause for concern. The fitted regression line (Fig. 2), based on only six data points, had a slope of 1.77 with two of the data points exerting strong leverage (the two points with the highest PDS measured concentrations) and thereby increasing the slope of the line. Omitting these two points brought the slope of the line to 1.14 (with an $r^2$ of 0.98). Examination of the calculations involved in deriving $NH_3$ concentrations from the C- and L-type PDS showed the result to be very sensitive to the diffusion distance on the L-type filters (the distance between the Teflon membrane and acid-coated paper filter). The L-type filters were prepared with a diffusion distance of 10 mm. However, during preparation and pre-exposure handling of L-type PDS, the membrane filter may become depressed, reducing the mean diffusion distance. To bring the slope of the fitted regression line to unity, the diffusion distance would have to have been reduced

Table 5
Summary of $NH_3$ volatilisation rates (kg N $ha^{-1}$ $h^{-1}$) and total losses measured using the wind tunnel technique

| Time after application | Dairy slurry | | | Layer manure | | | Wetted layer manure | | |
|---|---|---|---|---|---|---|---|---|---|
| | Mean | SE | CV (%) | Mean | SE | CV (%) | Mean | SE | CV (%) |
| 1 h | 14.2 | 4.9 | 59 | 5.8 | 3.0 | 90 | 4.6 | 2.1 | 78 |
| 3 h | 5.4 | 1.5 | 49 | 3.8 | 1.3 | 51 | 2.7 | 1.2 | 76 |
| 6 h | 1.8 | 0.5 | 48 | 1.4 | 0.9 | 90 | 1.3 | 0.8 | 103 |
| 24 h | 0.3 | 0.1 | 45 | 1.1 | 0.4 | 68 | 1.0 | 0.3 | 45 |
| 2 days | 0.2 | 0.1 | 73 | 0.7 | 0.4 | 108 | 0.6 | 0.1 | 21 |
| 3 days | 0.1 | 0.0 | 28 | 0.5 | 0.2 | 68 | 0.4 | 0.2 | 63 |
| 5 days | 0.1 | 0.0 | 17 | 0.1 | 0.0 | 46 | 0.5 | 0.1 | 40 |
| Mean | 3.2 | 1.0 | 46 | 1.9 | 0.9 | 74 | 1.6 | 0.7 | 61 |
| Total $NH_3$-N loss (% total UAN[a] applied) | 71 | 14 | 34 | 21 | 11 | 72 | 39 | 7 | 29 |

Data for dairy FYM have been omitted as there were mechanical problems with the wind tunnels during measurement.
[a] Uric and ammoniacal-N.

Table 6
Mean $NH_3$ volatilisation rates (kg N $ha^{-1}$ $h^{-1}$) measured by the equilibrium concentration technique using standard and modified calculation methods

| Manure type | Sampling day (and period in hours) | Standard calculation (SE) | Modified calculation (SE) | CV (%) |
|---|---|---|---|---|
| Dairy slurry | 1 (2) | 30.7 (6.58) | 9.2 (0.84) | 15.8 |
| | 3 (6) | 0.2 (0.05) | 0.2 (0.02) | 26.5 |
| | 5 (6) | * | * | * |
| | | | Mean | 21 |
| Dairy FYM | 1 (2) | 1.6 (0.63) | 1.5 (0.31) | 37.2 |
| | 3 (6) | * | * | * |
| | 5 (6) | * | 0.03 | * |
| | | | Mean | 37 |
| Poultry (dry) | 1 (2) | 8.7 (4.37) | 7.1 (2.42) | 59.3 |
| | 2 (6) | 2.3 (0.78) | 1.9 (0.51) | 46.5 |
| | 3 (24) | 12.6 (5.51) | 0.9 (0.06) | 10.8 |
| | | | Mean | 39 |
| Poultry (wetted) | 1 (2) | 8.1 (6.73) | 4.8 (1.69) | 61.5 |
| | 2 (6) | 0.8 (0.10) | 0.8 (0.08) | 18.4 |
| | 3 (24) | 0.1 (0.02) | 0.1 (0.01) | 28.8 |
| | | | Mean | 36 |

*Readings below the detection limit.

to 6 mm on the two samplers giving elevated results. In practice, it is unlikely that this occurred on a significant number of samplers, but it is a potential source of error which should be minimised. Alterations to the design, such that the membrane filters could not easily become depressed after preparation, would improve these samplers.

In this study, oxalic acid was used to coat the PFS and tartaric for the PDS but no specific tests were conducted to compare the performance of samplers with different acids. However, Rabaud et al. (2001), assessing a sampler similar to the PDS C-type used in this study,

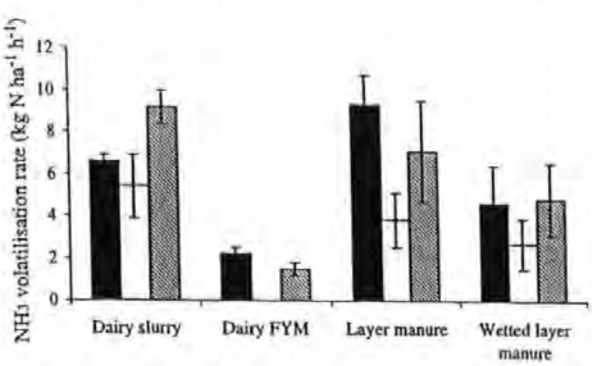


Fig. 4. Comparison of $NH_3$ volatilisation rates (kg N $ha^{-1}$ $h^{-1}$) measured on day 1 of each experiment using the three measurement techniques: mass balance IHF (solid bars), wind tunnels (open bars) and equilibrium concentration technique (hatched bars).

found that the type of acid coating used (oxalic, tartaric, sulfuric or citric) did not influence sampler collection efficiency.

The wind tunnel technique would not necessarily be expected to give the same result as the mass balance IHF technique, as the wind speed through the tunnels was controlled at a fixed rate which may have differed markedly from ambient. Wind speed has previously been shown to be an important factor influencing emission rates (Thompson et al., 1990; Sommer et al., 1991; Misselbrook et al., 2005). Ryden and Lockyer (1985) showed that if the wind speed through the tunnel was matched to the ambient wind speed a good comparison was obtained with the mass balance IHF technique, but not where wind speeds within the tunnels were fixed at a rate of 1 m $s^{-1}$. Rainfall is another important factor which can influence emission rates (Misselbrook et al., 2005), which was incident on plots in some of the experiments, but would not have influenced the areas below the wind tunnel canopies. Wind tunnel canopies may increase the temperature at the emitting surface, relative to ambient conditions, which would also influence emission rates. In addition, Genermont and Cellier (1997) showed that volatilisation rates soon after manure application will be greater from small plots (e.g. wind tunnels) because of local advection effects than for larger plots (e.g. mass balance). For these reasons, it must be emphasised that the wind tunnel technique is best suited to making comparative measurements where treatments have been imposed and should only be used with caution for the estimation of absolute losses following manure applications to land.

The equilibrium concentration technique gave comparable emission rates for the first sampling period to the mass balance technique in this study. The two techniques were in good agreement in a study by Misselbrook and Hansen (2001), although they found, as was the case in this study, that data could easily be lost due to inappropriate exposure times for the PDS. In this study, four dynamic chambers and two ambient samplers were used per plot. A commonly used configuration for small-plot studies is two chambers and one ambient sampler per plot (Svensson, 1994a; Rodhe and Rammer, 2002), under which circumstances the variability associated with the technique might be expected to be greater than shown in this study.

In terms of variability, there were no great differences between the techniques, with the mass balance perhaps being associated with a lower CV (mean CVs for emission rate measurements of 23–52, 46–84 and 21–39% for mass balance, wind tunnel and equilibrium concentration techniques, respectively, across the different manure types) as might be expected for a method which integrates emission rates over a larger land area. The choice of measurement technique will depend on a number of factors, other than just inherent variability,

Table 7
Considerations in choice of measurement technique

| | Mass balance IHF | Wind tunnels | Equilibrium concentrations |
|---|---|---|---|
| Type of study | Absolute measurements | Comparison | Comparison |
| Replication practical | Limited | Yes | Yes |
| Land area requirement | *** | * | * |
| Capital cost | * | *** | * |
| Labour costs (fieldwork) | * | ** | *** |
| Analytical costs | * | ** | *** |
| Practical use problems | * | ** | ** |
| Variability of results | ** | ** | ** |
| Reliability of technique | *** | ** | * |

*Low; **medium; ***high.

and a summary of the considerations to be taken into account is given in Table 7. Our conclusions from this study are that for the measurement of absolute emissions, the mass balance technique is to be preferred, particularly when used with PFS as these require no electricity in the field and give a more accurate measurement of flux than independent concentration and wind speed measurements (Wilson and Shum, 1992). For small-plot comparative measurements, the wind tunnel system is preferred to the equilibrium concentration technique, but is associated with a higher capital cost. Further work is required to improve the reliability of the equilibrium concentration technique, in particular the robustness of sampling devices for field use and estimation of suitable exposure times for the PDS.

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## 2.5 Paper 5

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BIORESOURCE TECHNOLOGY

# Predicting ammonia losses following the application of livestock manure to land

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**Abstract**

A series of experiments was conducted using small wind tunnels to assess the influence of a range of environmental, manure and management variables on ammonia emissions following application of different manure types to grassland and arable land. Wind speed and dry matter content (for cattle slurry in particular) were identified as the parameters with greatest influence on ammonia emissions from *slurries*. For *solid manures*, rainfall was identified as the parameter with most influence on ammonia emissions. A Michaelis–Menten function was used to describe emission rates following manure application. Linear regression was then used to develop statistical models relating the Michaelis–Menten function parameters to the experimental variables for each manure type/land use combination. The fitted models accounted for between 62% and 94% of the variation in the data. Validation of the models for cattle slurry to grassland and pig slurry to arable land against independent data sets obtained from experiments using the micrometeorological mass balance measurement technique showed that the models overestimated losses, which was most probably due to inherent differences between the wind tunnel and the micrometerological mass balance measurement techniques.



*Keywords:* Ammonia emission; Manure; Slurry; Model; Land application

## 1. Introduction

Applications of livestock manure to agricultural land are a significant source of ammonia ($NH_3$) emissions to the atmosphere, with potentially detrimental impacts on the environment. In the UK, $NH_3$ losses following land spreading have been estimated at approximately 70 kt $NH_3$–N per year, accounting for 30% of the total emission from UK agriculture (Misselbrook et al., 2000). In addition to potentially damaging effects on the environment, this emission also represents a loss of available N for crop uptake. A better understanding of the variables affecting both the rate and extent of emissions following land application of manures would improve predictions of $NH_3$ loss in nutrient management models, and give indications of application strategies with mitigation potential.

Predictive models may be mechanistic (process-based) or empirical. Mechanistic models attempt to describe mathematically the processes leading to $NH_3$ loss (e.g. Genermont and Cellier, 1997; van der Molen et al., 1990). However, these models have not been widely validated and can be difficult to use in practice, requiring much input data or calibration for individual cases. Empirical models mathematically fit observed responses to measured variables, often using linear regression procedures, but do not necessarily take account of the underlying physical, chemical or biological processes. Several empirical models have been developed for the prediction of $NH_3$ loss following manure application (e.g. Menzi et al., 1998; Braschkat et al., 1997; Moal et al., 1995). Generally, input parameters required by such models are easily obtained, making them more useable. However, empirical models do not always provide good predictions for situations other than those for the data sets from which they were derived.

Although there have been prior studies on variables controlling $NH_3$ loss from manure applications to land (e.g. Chambers et al., 1997; Moal et al., 1995; Sommer

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and Olesen, 1991; Sommer et al., 1991; Thompson et al., 1990; Brunke et al., 1988), these were often limited in extent. The aim of the present study was to quantify, through field experimentation, the effects of selected environmental and management variables on $NH_3$ emissions from the main types of manure produced by housed livestock, and to develop a simple empirical predictive model for estimating $NH_3$ losses following manure application to both grassland and arable land.

## 2. Methods

### 2.1. Field measurements of ammonia emission

Experimental measurements were conducted at six different sites across England (2 grassland and 4 arable) over a three-year period, representing a range of soil types (Table 1).

A series of 10 trials was conducted using a system of small wind tunnels (Lockyer, 1984) to investigate the influence of a wide range of variables, and some of their interactions, on $NH_3$ loss (Table 2). Measurements were made following the application of cattle and pig slurry and cattle farmyard manure (FYM) to grassland, and pig slurry, pig FYM and poultry manure to arable land (both to stubble and growing cereal crops), in keeping with common practice in the UK (Smith et al., 2000a, 2001a,b). Manure was surface applied to small plots (2×2 m) using either calibrated watering cans (for slurries) or by hand after weighing out specific amounts (for solid manure). After application, wind tunnel canopies were positioned over each plot and air drawn through at a controlled rate. The concentration of $NH_3$–N in both the air entering and leaving each tunnel was determined by drawing a sub-sample of air (at 3–4 $l\,min^{-1}$) through absorption flasks containing orthophosphoric acid. The emission per sampling period was calculated as the product of the volume of air passing through the tunnel and the difference in outlet and inlet air concentrations. The standard application rates used (unless included as an experimental variable) were 40 $m^3\,ha^{-1}$ for cattle and pig slurry, 35 $t\,ha^{-1}$ for cattle and pig FYM, 8 $t\,ha^{-1}$ for broiler litter and 16 $t\,ha^{-1}$ for layer manure, which were typical of the rates that farmers would apply. Wind speeds through the tunnel canopies were controlled at 1 $m\,s^{-1}$, apart from in Trial 1 where wind speeds were in the range 0.5–4 $m\,s^{-1}$. Measurements of $NH_3$ emission continued for 5 d following slurry applications and for 12 d following solid manure applications.

Table 1
Experimental site details

| Site | Location | Topsoil texture | Soil series | Land use |
|---|---|---|---|---|
| 1 | Devon, SW England | Clay loam | Hallsworth | Grassland |
| 2 | Devon, SW England | Sandy clay loam | Crediton | Grassland |
| 3 | Nottinghamshire, E. Midlands | Loamy sand | Wick | Arable |
| 4 | Cambridgeshire, E. Anglia | Clay | Hanslope | Arable |
| 5 | Warwickshire, W. Midlands | Clay loam | Denchworth | Arable |
| 6 | Hampshire, S. England | Silty clay loam | Andover | Arable |

Table 2
Details of wind tunnel experiments to assess the influence of different variables on $NH_3$ loss following field applied manure

| Trial | Variable | Manure type[a] | Sites | No. of experiments | No. of wind tunnels per experiment |
|---|---|---|---|---|---|
| 1 | Temperature × wind speed | CS | 1, 2 | 8 | 10 |
| | | PS | 3, 5 | 8 | 10 |
| 2 | Temperature | CS, PS, CFYM | 1, 2 | 8 | 9 |
| | | PFYM, BL, LM | 3, 5 | 8 | 9 |
| 3 | Slurry dry matter content | CS | 1, 2, 6 | 4 | 10 |
| | | PS | 1, 3, 4 | 4 | 10 |
| 4 | Soil moisture content | PS | 4 | 1 | 8 |
| 5 | Rainfall | CS | 1, 2 | 2 | 9 |
| | | PS | 3, 5 | 2 | 9 |
| 6 | Rainfall | CFYM | 2 | 1 | 8 |
| | | PFYM, BL | 3, 4 | 2 | 8 |
| 7 | Crop cover (× DM for CS) | CS | 1, 2 | 2 | 8 |
| | | PS | 3, 5 | 2 | 9 |
| 8 | Soil pH | CS | 1 | 1 | 8 |
| 9 | Slurry pH | PS | 4 | 1 | 10 |
| 10 | Application rate | CS | 1, 2 | 2 | 10 |
| | | PS | 4 | 1 | 10 |

[a] CS—cattle slurry, PS—pig slurry, CFYM—cattle FYM, PFYM—pig FYM, BL—broiler litter, LM—layer manure.

In addition to $NH_3$ emissions, measurements were also made of manure dry matter (DM) content, pH, total N content, total ammoniacal N (TAN) content and, for poultry manures, uric acid N content, plus soil moisture content and pH (top 10 cm), crop height (and growth stage for cereals), wind speed (at a height of 25 cm), air and soil temperatures (at 5 cm height and 5 cm depth, respectively) for each experiment. For poultry manures, the sum of total ammoniacal N and uric acid N are referred to as uric and ammoniacal N (UAN) hereafter in this paper. Differences in temperature (Trials 1 and 2) were achieved by applying manure at different times of year.

### 2.2. Modelling

#### 2.2.1. Michaelis–Menten curve fitting

For each of the individual wind tunnel measurements, a Michaelis–Menten type curve was fitted to the cumulative $NH_3$ loss with time, as used by Sommer and Ersboll (1994):

$$N(t) = N_{max}\frac{t}{t + K_m} \tag{1}$$

where $N(t)$ (kg N ha$^{-1}$) is the cumulative loss at time $t$ (h) and $N_{max}$ (kg N ha$^{-1}$) and $K_m$ (h) are model parameters representing total loss as time approaches infinity and time at which loss reaches one half of maximum, respectively. As there is a serial correlation between successive measurements, it is considered more robust to model loss rates against time (Sogaard et al., 2002):

$$\overline{N}_{rate}(t, \Delta t) = N_{max}\frac{K_m}{(t + K_m)(t + \Delta t + K_m)} \tag{2}$$

where $N_{rate}$ is the mean emission rate (kg N ha$^{-1}$ h$^{-1}$) between times $t$ and $t + \Delta t$. For each individual manure application, the parameters $N_{max}$ and $K_m$ were derived using the model fitting procedure in GENSTAT (Lawes Agricultural Trust, 1993). Data for which there was a poor curve fit ($r^2 < 0.90$) were excluded from further analyses.

Data from the experiments were divided into six groups for model development, namely: cattle slurry to grassland, pig slurry to grassland, pig slurry to arable, cattle FYM to grassland, pig FYM to arable and poultry manure to arable land. For each of these manure type/land use groups, multiple linear regression was used to relate $N_{max}$ and $K_m$ to measured variables, enabling cumulative $NH_3$ loss to be predicted from Eq. (1). Thus:

$$N_{max} = a + bV_1 + cV_2 + dV_3 + \cdots \tag{3}$$

$$K_m = e + fV_1 + gV_2 + hV_3 + \cdots \tag{4}$$

where letters $a$–$h$ represent fitted regression constants and $V_n$ the measured experimental variables. Measured variables included in the regression analyses were soil pH, soil moisture content (gravimetric), water-filled pore space, crop sward height, wind speed, mean surface temperature for the duration of the experiment, mean surface temperature for the first 6 h following application, rainfall within 1 h of application, relative humidity, manure application rate, manure pH, DM, total N and TAN (and UAN for poultry manure) contents and manure total N, TAN and UAN application rates. The ranges in measured values for each of these variables for each manure type/land use category are given in Tables 3 and 4. Soil type was also included as a variable in

Table 3
Ranges in the measured soil, crop and weather variables for each manure type/land use category over all experiments

| Manure/land use category | Soil | | | | Crop | Weather | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Type[a] | pH | Moisture content (% w/w) | Water-filled pore space (%) | Height (cm) | Wind speed (m s$^{-1}$) | Mean temperature for experiment (°C) | Mean temperature for first 6 h (°C) | Rainfall in first hour (mm) | Relative humidity |
| Cattle slurry to grass | 2, 3 | 4.9–6.8 | 13–41 | 21–56 | 6–21 | 0.3–4.2 | 1–18 | 1–29 | 0–10 | 78–100 |
| Pig slurry to arable | 1, 2 | 7.0–9.2 | 11–44 | 30–100 | ND | 0.5–4.7 | 6–22 | 8–31 | 0–4 | ND |
| Pig slurry to grass | 2, 3 | 5.1–7.9 | 16–39 | 26–76 | 8–15 | 0.8–1.6 | 2–18 | 1–27 | 0 | 80–97 |
| Cattle FYM to grass | 2, 3 | 5.1–5.9 | 16–39 | 26–55 | 8–15 | 0.9–1.4 | 2–17 | 1–27 | 0–3 | 80–97 |
| Pig FYM to arable | 1, 2 | 7.0–8.3 | 11–42 | 30–100 | ND | 0.9–1.3 | 5–24 | 3–25 | 0–3 | ND |
| Poultry manure to arable | 1, 2 | 7.0–8.3 | 10–42 | 26–100 | ND | 0.6–1.9 | 5–24 | 3–31 | 0–3 | ND |

ND, not determined.
[a] 1 = Sandy; 2 = clay; 3 = loam.

Table 4
Ranges in the measured manure characteristics for each manure type/land use category over all experiments

| | Application rate (slurries $m^3 ha^{-1}$; FYM $t ha^{-1}$) | pH | DM (%) | Total N ($g kg^{-1}$) | TAN ($g kg^{-1}$) | Uric acid N ($g kg^{-1}$) |
|---|---|---|---|---|---|---|
| Cattle slurry to grass | 20–80 | 6.7–7.6 | 1.6–9.2 | 1.4–3.5 | 0.4–1.9 | – |
| Pig slurry to arable | 40–65 | 5.0–8.1 | 1.2–12.6 | 3.7–8.2 | 2.4–5.6 | – |
| Pig slurry to grass | 40 | 6.9–7.7 | 1.5–10.4 | 4.0–8.0 | 2.0–5.7 | – |
| Cattle FYM to grass | 35 | 7.8–9.2 | 17–22 | 4.7–30.0 | 0.2–1.0 | – |
| Pig FYM to arable | 35 | 7.9–8.5 | 20–52 | 0.7–20.7 | 0.4–1.2 | – |
| Poultry manure to arable | 8–16 | 8.1–9.2 | 30–79 | 10.3–33.0 | 3.5–13.4 | 0.1–4.5 |

which sandy, clay and loam soils were represented by the values 1, 2 and 3, respectively.

*2.2.2. Model validation*

Experimental results from measurements with the micrometeorological mass balance method were used for model validation, as this is widely accepted as an accurate and robust technique for measurement of $NH_3$ losses under field conditions (Sommer et al., 2001). Data for validation were derived from UK measurements (Misselbrook et al., 2002; Chambers et al., 1997) and also from a database constructed as part of the EU concerted action "Ammonia Losses from Field-applied Animal Manure" (ALFAM–www.alfam.dk). The database contains data from 6 European countries, deriving from about 800 separate experiments, with a total of almost 6000 records. Of the available data, 560 records from 45 experiments satisfied the selection criteria in terms of measurement technique and variables measured. Mean square prediction error (MSPE) analysis (see Dhanoa et al., 1999) was used to compare model predictions with observations where sufficient data existed, yielding information on both the precision and reproducibility of the model.

## 3. Results

*3.1. Variables influencing $NH_3$ emission*

For all applications to grassland, absolute $NH_3$ losses ($kg ha^{-1}$) were greatest from pig slurry and least from cattle FYM, reflecting the respective TAN or UAN contents of the manures. Losses expressed as a percentage of the TAN or UAN applied, however, were greatest from cattle FYM (sometimes exceeding 100%). At the arable sites, absolute $NH_3$ losses ($kg ha^{-1}$) were greatest from poultry manure applications. Expressed as a proportion of TAN or UAN applied, losses were greater from pig FYM (also often exceeding 100% TAN applied) than from poultry manure. The pattern of $NH_3$ loss over time was similar for all manure types; there were no significant differences ($P > 0.05$) in the mean $K_m$ values between manure types.

There were significant relationships ($P < 0.01$) between total $NH_3$ loss (expressed as % TAN or UAN applied) and wind speed for both cattle slurry applied to grassland and pig slurry applied to cereal stubble. As temperature did not have a significant effect ($P > 0.05$) on total $NH_3$ losses for either the grassland or arable experiments, data from the experiments conducted at different times of year were pooled to establish the relationship between total $NH_3$ loss and wind speed. For cattle slurry applied to grassland, parallel regression analysis showed that there was a consistent effect of wind speed at the 2 sites (shown by the two fitted lines in Fig. 1(a) having the same slopes), although losses from site 2 were consistently greater. Similarly, total $NH_3$ losses from site 3 were greater than for site 5 (Fig. 1(b)).

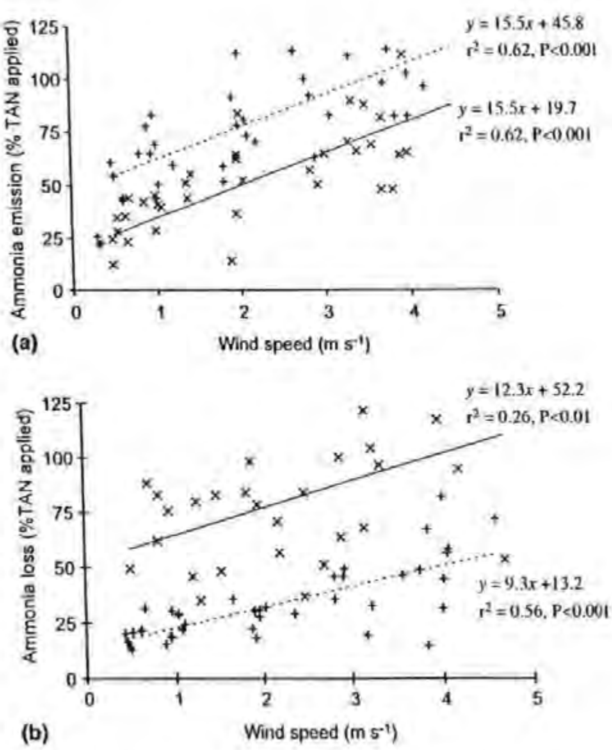


Fig. 1. Influence of wind speed on ammonia emission from (a) cattle slurry applied to grassland ((×) site 1, (+) site 2, (solid line) fitted site 1, (dashed line) fitted site 2); (b) pig slurry applied to cereal stubble ((×) site 3, (+) site 5, (solid line) fitted site 3, (dashed line) fitted site 5).

This was probably through differences in the DM content of the slurries used (mean DM contents were 3.3%, 4.9%, 8.5% and 4.3% for sites 1, 2, 3 and 5, respectively) rather than inherent site characteristics. The slopes of the derived relationships were similar for cattle and pig slurry, with increases in total $NH_3$ loss of 15% TAN applied and 10% TAN applied (mean for the 2 sites in each case) per 1 $m\,s^{-1}$ increase in wind speed for cattle and pig slurry, respectively.

There were no consistent relationships between total $NH_3$ loss (% TAN or UAN applied) and mean ambient air temperature for any of the manure types applied to grassland, or for solid manure applications to arable land at site 3. However, strong linear relationships were established between total $NH_3$ loss and temperature for the measurements at site 5 with increases in loss of 3.6%, 4.0% and 7.9% applied TAN per 1 °C increase in temperature for broiler litter ($P = 0.07$), layer manure ($P = 0.05$) and pig FYM ($P < 0.05$), respectively.

For cattle slurry applied to grassland, a strong relationship ($P = 0.01$) was obtained between total $NH_3$ loss and DM content from the first measurement occasion. However, for the 2 subsequent measurement occasions much poorer relationships were obtained ($P > 0.05$). Pooling all data showed a significant relationship ($P = 0.01$), with total $NH_3$ loss increasing with DM content at the rate of 3.9% TAN applied per 1% DM (Fig. 2(a)). There was no significant effect ($P > 0.05$) of DM content on $NH_3$ loss for pig slurry applications to either of the arable sites. However, pooling data from both sites again showed a relationship ($P = 0.05$) for increasing loss with DM content, at the rate of 4.3% TAN applied per 1% increase in DM content (Fig. 2(b)). This relationship was heavily influenced by results from site 4, without which there would not have been a significant relationship. As initial results suggested that a good relationship existed for cattle slurry applications to grassland, but not for pig slurry to cereal stubble, a 'cross-over' experiment (using similar ranges of DM contents) was conducted, to assess whether this difference was due to the slurry type or land use. A strong relationship was found for cattle slurry application to cereal stubble ($P < 0.01$), with $NH_3$ loss increasing with DM content at the rate of 0.7% TAN applied per unit increase in DM content. However, there was no significant relationship for the pig slurry application to grassland ($P > 0.05$).

There was no difference ($P > 0.05$) between the $NH_3$ losses measured where pig slurry was applied to 'wet' soil compared with 'dry' soil at site 4. Simulated rainfall immediately after application of cattle slurry to grassland reduced ($P < 0.01$) $NH_3$ emissions by 65% and 39% for sites 1 and 2, respectively, although there was no difference between the 5 and 10 mm rainfall rates. However, there was no effect of simulated rainfall on $NH_3$ losses following pig slurry applications to cereal

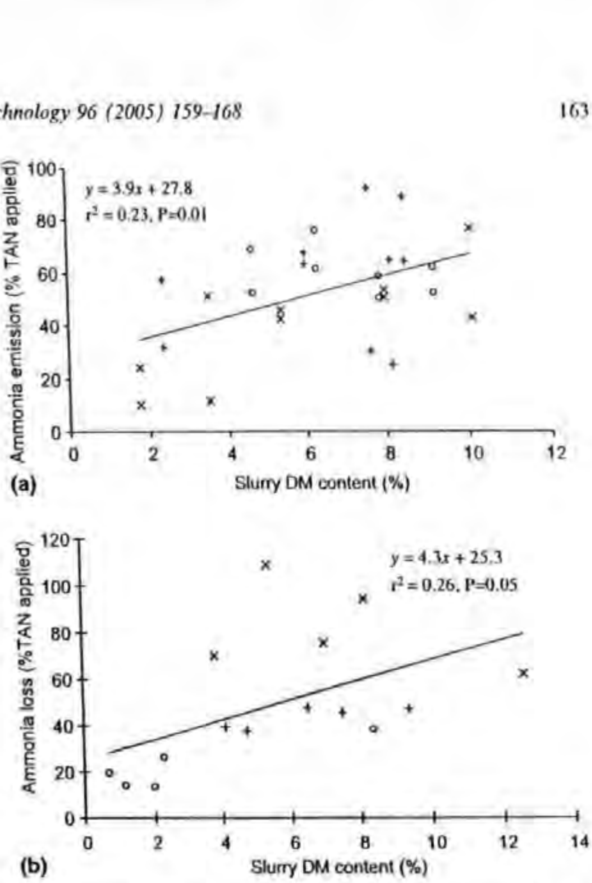


Fig. 2. Influence of slurry DM content on ammonia emission from (a) cattle slurry applied to grassland ((×) site 1, (+) site 2a, (O) site 2b, (solid line) fitted for all sites); (b) pig slurry applied to cereal stubble ((×) site 3a, (+) site 3b, (O) site 4, (solid line) fitted for all sites).

stubble ($P > 0.05$). Following solid manure applications, daily 'rainfall' led to lower losses from cattle FYM applied to grassland (a reduction in emission of approximately 20%), but had no significant effect ($P > 0.05$) on losses from pig FYM or poultry manure applications to arable land.

In Trial 7, grass sward height had no effect ($P > 0.05$) on total $NH_3$ loss from cattle slurry applications to grassland (Fig. 3) although there was a significant effect

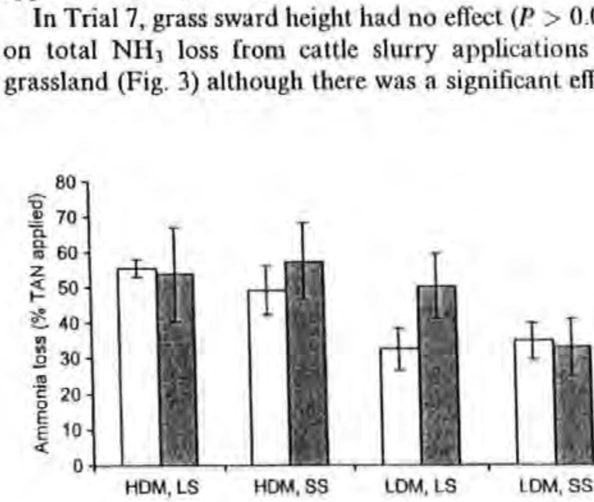


Fig. 3. Influence of sward height and slurry DM content on ammonia emission from applications of cattle slurry to grassland at sites 1 (open columns) and 2 (shaded columns). HDM, high DM slurry (8.5% and 7.3% for sites 1 and 2, respectively); LDM, low DM slurry (2.9% and 1.6%); LS, long sward (15.6 and 21.0 cm for sites 1 and 2, respectively); SS, short sward (6.4 and 6.0 cm). Error bars show ±1 standard error.

of slurry DM content ($P < 0.01$), with increased $NH_3$ loss from higher DM content slurry. For pig slurry applications to cereal cropped land, there were greater losses ($P < 0.05$) from applications to stubble than to either fallow land or the growing crop at site 5, with cumulative losses of 28.5%, 15.0% and 15.8% of the TAN applied, respectively. Similarly, at site 3 there were no differences ($P > 0.05$) in losses following applications to fallow land or the growing crop (a stubble treatment was not included at this site), with mean cumulative losses of 8.7% and 5.9% of the TAN applied, respectively.

Lime additions at the grassland site increased the soil pH from 5.4 to 6.8, although this had no effect ($P > 0.05$) on total $NH_3$ loss following cattle slurry application. Slurry pH (Trial 9) had no significant effect ($P > 0.05$) on total $NH_3$ loss following pig slurry application to cereal stubble. However, losses were very low at all slurry pH values (mean loss of 12% of applied TAN) and other factors may have had a greater influence than slurry pH. There was also an inverse relationship ($P < 0.05$) between slurry pH and DM content, which may have confounded any pH effect (Table 5).

For cattle slurry applications to grassland, absolute $NH_3$ loss ($\mathrm{kg\,N\,ha^{-1}}$) increased with increasing application rate. However, when expressed as a % of the applied TAN, there was a trend ($P < 0.05$) for decreasing loss with increasing application rate at site 1, but not at site 2. There was no significant relationship if data from the two measurement occasions were pooled.

Table 5
Ammonia emission from application of pig slurries (at a rate of 40 $\mathrm{m^3\,ha^{-1}}$) of different pH values to cereal stubble at site 4

| Slurry pH | Slurry DM content | Ammonia loss as % TAN applied |
|---|---|---|
| 7.2 | 2.7 | 10.9 (0.1) |
| 5.9 | 3.9 | 10.1 (0.7) |
| 5.0 | 4.5 | 21.5 (0.2) |
| 4.2 | 5.6 | 6.0 (1.0) |
| 3.3 | 6.1 | 9.8 (0.9) |

Values in parentheses are standard errors of the mean.

### 3.2. Modelling

The models derived for $N_{max}$ (the total $NH_3$ loss) and $K_m$ (the time at which $NH_3$ loss is one half of $N_{max}$) for each manure type/land use category are given in Table 6. Generally, better relationships were derived for $N_{max}$ than for $K_m$, with a particularly poor model for $K_m$ for pig slurry application to arable land ($r^2 = 0.09$). Manure DM content, TAN or UAN content (or TAN or UAN applied) and wind speed were important predictive variables for $N_{max}$ for most categories. Slurry DM content and ambient air temperature were also important in predicting $K_m$ for slurries.

Values for $N_{max}$ and $K_m$ were calculated for each experimental measurement using the relationships given in Table 6. Emission rates were then calculated for each of the experimental measurement times using Eq. (2). Regression of the modelled against the measured emission rates showed that overall the models for each manure type/land use group accounted for between 62% and 94% of the observed variation (Table 7). The constants for the fitted regression lines were not significant ($P > 0.05$), therefore the relationships were forced through the origin. The slopes varied between 0.90 and 0.96 (Table 7).

Validation data sets of sufficient size were available for cattle slurry to grassland and pig slurry to arable land. There was only a limited amount of data for pig slurry to grassland and poultry manure applications to arable land which was insufficient for model validation

Table 6
Models derived for $N_{max}$ ($\mathrm{kg\,N\,ha^{-1}}$) and $K_m$ (h) using Michaelis–Menten type curve fitting

| Manure type/land use | Model[a] | No. of observations | $r^2$ |
|---|---|---|---|
| Cattle slurry to grassland | $N_{max} = -11.8 + 13.24(ST) - 6.80(SpH) + 7.13(WS) + 2.98(DM) + 0.86(SH) + 0.37(TANA)$ | 110 | 0.66 |
| | $K_m = 62.5 - 3.38(ST) - 1.81(SpH) - 0.39(T) - 0.42(WS) + 1.72(DM) - 5.78(MpH) + 0.25(SH)$ | | 0.46 |
| Pig slurry to arable | $N_{max} = 62.2 - 35.71(ST) - 2.44(T) + 14.28(WS) + 6.86(DM) + 7.07(TAN)$ | 103 | 0.61 |
| | $K_m = 17.4 - 0.31(T) - 0.90(WS) - 1.01(TAN)$ | | 0.09 |
| Pig slurry to grassland | $N_{max} = -31.7 + 1.20(T) + 39.3(WS) + 10.16(DM) - 1.50(SH)$ | 25 | 0.85 |
| | $K_m = -13.4 + 17.22(WS) + 1.05(DM) - 0.32(SH)$ | | 0.61 |
| Cattle FYM to grassland | $N_{max} = 14.51(ST) + 8.79(T) - 2.09(DM) + 1.07(TANA) - 5.49(T6)$ | 27 | 0.74 |
| | $K_m = -46.2 + 3.48(SpH) - 0.99(T) + 17.95(WS) + 1.45(DM)$ | | 0.60 |
| Pig FYM to arable | $N_{max} = 48.5 - 67.9(WS) + 7.45(R) + 1.73(TANA) - 0.10(TNA) + 3.27(T6)$ | 15 | 0.84 |
| | $K_m = 52.8 + 5.63(R) - 0.03(TNA) - 2.32(T6)$ | | 0.65 |
| Poultry manure to arable | $N_{max} = -46.12(ST) + 106.30(WS) + 68.90(R) + 5.30(TANA) - 4.08(AUNA)$ | 34 | 0.88 |
| | $K_m = 422.9 - 7.86(ST) - 2.13(T) + 0.35(DM) - 43.31(MpH) + 0.87(TANA) - 0.56(AUNA) - 0.16(TNA)$ | | 0.81 |

[a] ST, soil type; SpH, soil pH; MpH, manure pH; WS, wind speed ($\mathrm{m\,s^{-1}}$); DM, manure DM content (%); TAN, manure TAN content ($\mathrm{g\,kg^{-1}}$); TANA, TAN applied ($\mathrm{kg\,N\,ha^{-1}}$); AUNA, total ammoniacal and uric acid N applied ($\mathrm{kg\,ha^{-1}}$); TNA, total N applied ($\mathrm{kg\,N\,ha^{-1}}$); $T$, mean temperature (°C); $T6$, mean temperature for first 6 h following application (°C); $R$, rainfall (mm); SH, sward height (cm).

Table 7
Regression equations for modelled vs. observed $NH_3$ emission rates ($kg\,N\,ha^{-1}$) for the experimental data sets used to derive the models

| Manure type/land use | Regression equation | No. of observations | $r^2$ |
|---|---|---|---|
| Cattle slurry to grassland | modelled = 0.90 (observed) | 763 | 0.88 |
| Pig slurry to arable | modelled = 0.95 (observed) | 712 | 0.71 |
| Pig slurry to grassland | modelled = 0.93 (observed) | 194 | 0.90 |
| Cattle FYM to grassland | modelled = 0.90 (observed) | 277 | 0.93 |
| Pig FYM to arable | modelled = 0.96 (observed) | 206 | 0.94 |
| Poultry manure to arable | modelled = 0.92 (observed) | 457 | 0.62 |

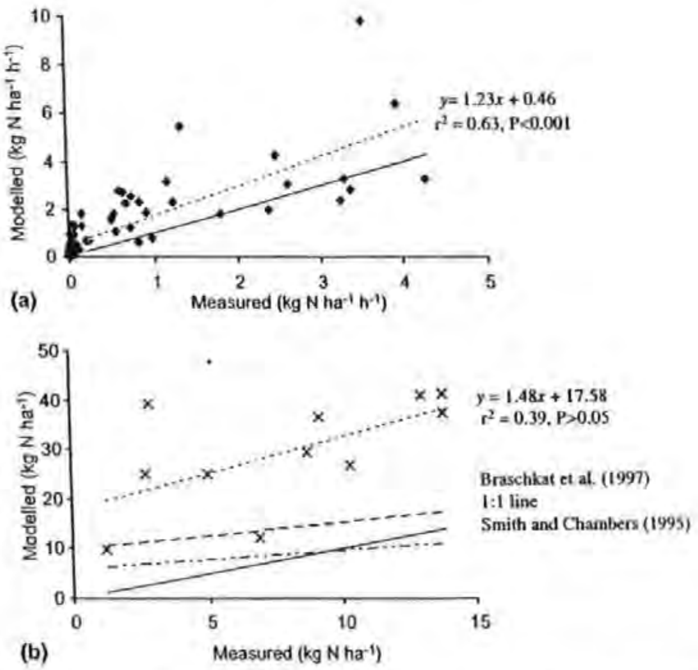


Fig. 4. Model validation for Michaelis–Menten approach, cattle slurry applications to grassland: (a) emission rates, showing fitted (dashed) and 1:1 (solid) lines; (b) cumulative emission over 5d, showing fitted and 1:1 lines together with fitted lines for models of Smith and Chambers (1995) and Braschkat et al. (1997).

purposes. For the other manure type/land use categories no validation data sets were available, largely because the experiments that had been conducted did not include measurements of all the variables required by the models. Wind speed measurements in the micrometeorological mass balance experiments were typically made at a height of 2 m. These had to be adjusted to give values at 0.25 m, the height at which measurements were made in the wind tunnels and used in the models. The correction was made using a standard wind speed vs. height profile generated from a number of existing data sets.

For cattle slurry applications to grassland, the model predictions overestimated both the emission rates and the 5 d cumulative emission (Fig. 4). MSPE analysis showed there to be significant systematic bias (regression line shifted from the line of equality) and line bias (slope of regression line different from 1), so overestimation was greater at higher emission rates. The fitted model for 5 d cumulative emissions substantially overestimated the emissions, due to the cumulative effect of overestimating individual emission rates. The model derived for pig slurry applications to arable land gave emission rate predictions much closer to the measured values (slope of 1.09, intercept of 0.13, $r^2 = 0.59$), although all the measured emission rates were low (all $<3\ kg\,N\,ha^{-1}\,h^{-1}$). Again, MSPE analysis showed there to be some systematic and line bias. Cumulative emission over 5 d was also overestimated.

## 4. Discussion

### 4.1. Variables influencing $NH_3$ emission

The experimental measurements showed that wind speed for cattle and pig slurry, and DM content for cattle (but less so for pig) slurry were the most important variables influencing $NH_3$ loss, with some influence also of rainfall and crop cover. For *solid manure*, of the variables studied, persistent rainfall following application was the most important in controlling $NH_3$ loss.

Wind speed has previously been identified as an important controlling variable for $NH_3$ loss from surface applied slurry (Sommer et al., 1991; Thompson et al., 1990). Sommer et al. (1991) reported increasing $NH_3$ loss with wind speed up to 2.5 m $s^{-1}$ during the first 12 h after application, but no further increase in emission was observed up to wind speeds of 4 m $s^{-1}$. They proposed that at low wind speeds the volatilisation rate would be small and gas phase resistance to transport within the laminar boundary layer above the soil surface would dominate. At higher wind speeds, resistance to transport within the liquid phase would become the dominant controlling factor. In this study, the relationship was linear (although subject to high variability) for wind speeds in the range 0.5–4.5 m $s^{-1}$, in agreement with that found by Thompson et al. (1990).

Dry matter content had an important influence on $NH_3$ loss from cattle slurry, but less so from pig slurry. This may be due to the different nature of the solid material in cattle and pig slurry. Cattle slurry typically contains more fibrous material, which increases the viscosity and gives a greater water holding capacity and may impede soil infiltration to a greater extent than the more 'gravelly' natured solid material in pig slurry. Slurry DM content is commonly, although not universally, reported as one of the most important factors affecting $NH_3$ volatilisation. Pain et al. (1989) suggested that the more rapid infiltration of dilute slurries into soil may account for the lower $NH_3$ losses compared with thicker slurries. Reducing the dry matter content of cattle slurry, either by separation or dilution, has been shown to be an effective means of reducing $NH_3$ volatilisation following land application (Vandre et al., 1997; Frost, 1994; Stevens et al., 1992; Frost et al., 1990). Smith and Chambers (1995) derived a relationship between $NH_3$ emission (% TAN applied) and slurry DM content, using data from 27 experiments in the UK which were predominantly for cattle slurry applications to grassland (2 derived from measurements of pig slurry to arable land, 3 from pig slurry to grassland and 2 from cattle slurry to arable land). Smith et al. (2000b) derived a similar relationship between $NH_3$ losses and DM following cattle slurry applications to grassland under moist soil conditions, with $NH_3$ loss increasing by 6% of the TAN applied for each 1% increase in DM content. The findings from experiments in this project, particularly the differences between pig and cattle slurry, may have implications for the algorithms used in these models.

Surprisingly, no relationship was found between total $NH_3$ losses and temperature for both the slurry and solid manure applications. Theory would indicate that, for an ammonium solution, losses increase with temperature as both the dissociation constant (determining the $NH_4^+/NH_3$ ratio in solution) and the Henrys law constant (determining the $NH_3$ in solution/$NH_3$ gas ratio) are temperature dependent. However, achieving temperature differences by applying manure at different times of year may have resulted in interactions with other variables, such as soil moisture content (and infiltration rate for slurries), relative humidity, solar radiation input and possibly sward density for grassland sites, which were not necessarily the same on all measurement occasions. In addition, crusting of the surface layer of manure at higher temperatures may have reduced emission. Sommer et al. (1991) reported an increase in emission with increasing temperature from cattle slurry, with the effect being most pronounced in the first 6 h after application. They also noted that high temperatures resulted in high initial rates of loss, but limited loss thereafter, whereas at low temperatures loss rates were lower but continued for longer. Braschkat et al. (1997) measured volatilisation from cattle slurry applied to grassland and found no relationship between emission and air temperature, but reported that mean solar radiation was an important factor.

Rainfall was of some importance in determining $NH_3$ loss from manure applications, with lower total $NH_3$ losses from cattle slurry and FYM, where simulated rainfall was applied immediately after spreading. The intensity and duration of rainfall were not included as experimental variables, but are also likely to be of importance. The fibrous nature of cattle slurry results in grass leaves becoming coated in slurry following broadcast application to grassland, increasing the surface area for emission. Rainfall immediately following application will clean the leaf surfaces, thereby reducing the surface area for emission, and will wash slurry TAN into the soil. The effect of rainfall on $NH_3$ emissions from solid manure was less apparent. Daily wetting will prevent the manure from drying, and so prolong the length of time that $NH_3$ is emitted, but it may also leach $NH_4^+$ from the manure to the soil, where it will be less susceptible to loss via volatilisation. The capacity of the manure to absorb and retain water may be important in this respect.

Other variables were less important in controlling $NH_3$ loss. It is unfortunate that there was an inverse relationship between slurry pH and DM content in the pig slurry pH experiment, which has confounded data interpretation, as pH is generally regarded to be an important factor controlling $NH_3$ loss. It has been demonstrated that reducing slurry pH to a value of 5.5 by the addition of inorganic acids will decrease $NH_3$ volatilisation following slurry spreading by up to 85% (Pain et al., 1994; Stevens et al., 1992; Frost et al., 1990; Stevens et al., 1989). Relatively small differences in pH, within the natural pH range of slurries, have also been shown to reduce volatilisation significantly. Martinez et al. (1996) reported a 37% decrease in total emission over a 4 h period from pig slurry by lowering pH from 7.8 to 7.0. Further work is required to assess the influence on $NH_3$ loss of relatively small changes in slurry pH (between the values of 7 and 8) as pH adjustment by the addition of relatively small volumes of an inorganic acid may represent a practical abatement option.

Increasing slurry application rate has previously been shown to decrease the proportion of TAN emitted as $NH_3$ (Frost, 1994; Thompson et al., 1990), presumably because of a decreased surface area to volume ratio for higher application rates. Soil moisture content, although not shown to have a significant effect in this study, has previously been shown to influence $NH_3$ loss. Sommer and Jacobsen (1999) showed that $NH_3$ loss was 30% less from a dry soil (1% moisture w/w) than for wetter soils (8%, 12% and 19% moisture), and that this was because of increased infiltration of $NH_4^+$–N into the dry soil. In contrast, Smith et al. (2000b) reported emissions from cattle slurry applied to hard dry grassland to be greater than for applications to moist grassland or arable soils. This was probably due to the hydrophobic nature of the dry grassland soil, meaning that the slurry infiltration rate into the soil was slower than for the moist grassland and arable soils.

The loss of $NH_3$ in excess of 100% of TAN applied was measured from some of the solid manures in this study. This raises the question as to whether rapid mineralization occurred during the measurement period (12 d for solid manures), increasing the potential for $NH_3$ loss, or whether the TAN content of solid manures was systematically under-estimated. The TAN contents of cattle and pig FYM were very low in comparison to their total N contents (Table 4), much less than the standard UK book value of 10% for stored manure (Anon, 2000). Further work on improving sampling techniques for and measuring mineralization rates of applied solid manures will give further insight into these apparently anomalous results.

### 4.2. Predictive models

The regression fits for $N_{max}$ and $K_m$ for poultry manure were particularly good, considering the more complex nature of poultry manure with the breakdown of uric acid and hydrolysis of urea required as precursors to $NH_3$ emission. The models for cattle slurry applications to grassland and pig slurry applications to arable land resulted in the over prediction of emissions compared with the model validation data set. However, both provided a better fit to the data (based on the $r^2$ values) than either the model of Smith and Chambers (1995) based solely on slurry DM content, or that of Braschkat et al. (1997) based on slurry DM content and ambient temperature, which had $r^2$ values of 0.14 and 0.18, for the cattle slurry data set (Fig. 4) and both $r^2$ values <0.15 for the pig slurry data set, respectively.

There were a number of possible reasons for the over-estimation of emissions by these two models. Firstly, there were differences in the height at which wind speeds were measured. Whilst this was corrected during the validation procedure, the correction was subject to some uncertainty. Secondly, the turbulence of the air drawn through a wind tunnel may be quite different from that in an ambient situation, leading to differences in resistance to $NH_3$ emission at the manure surface. Thirdly, wind tunnels measure emission from a 2 m long plot of land, which in effect, might be considered to be the edge of a manure-applied field. Emissions towards the upwind edge of a field will be greater than at points further downwind over the treated area, because of clean air entering the upwind edge offering less resistance to emission. It has been shown that small plots can over-estimate emissions by as much as 50–75% compared with micrometeorological measurements on larger plots (Genermont and Cellier, 1997). Finally, there may be other variables important in determining emission rates that were not measured in these experiments (such as slurry infiltration rate and crop density).

The models presented above, even if further developed and calibrated against validation data, require input data which would not be readily available to farmers or consultants (such as detailed meteorological data). For use in decision support systems, it is important that the models are simple, and in addition have the capacity to account for abatement techniques such as slurry application method and the rapid soil incorporation of manure following application.

## 5. Conclusions

From the wind tunnel experiments conducted, wind speed and DM content (for cattle slurry in particular) were identified as the most important variables influencing % $NH_3$ loss from slurry applications. For solid manures, of the variables studied, rainfall was the most important. There were important differences in the strength of the relationships between emission and DM content for the cattle and pig slurries, with the relationship for pig slurry being more tenuous. These differences warrant further investigation. Of the statistical models derived, those for cattle slurry applications to grassland and pig slurry to arable land were most robust as they were based on the largest data sets. Inherent differences between the modelling and validation data sets meant that while the derived models accounted for a large proportion of the variation within the experimental data (62–94% of the variation), they were generally not quantitative in their predictions for the validation data set. Therefore further work is required in the development of simple models to ensure that decision support systems aimed at farmers and consultants give reliable predictions of $NH_3$ loss following manure applications to land.

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### 2.6 Paper 6

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# Using time domain reflectometry to characterize cattle and pig slurry infiltration into soil

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**Abstract.** The rate and extent to which cattle or pig slurry infiltrates into soil after application is one of the important factors determining the rate and extent of subsequent ammonia ($NH_3$) volatilization. Better characterization of the infiltration process is required to improve predictive models of $NH_3$ losses after land spreading. This paper describes a laboratory system using time domain reflectometry to measure slurry infiltration into soil columns. This system enabled semi-continuous, non-destructive infiltration measurements to be made, assessing the influence of slurry type, dry matter (DM) content, soil type and soil water tension. Differences were noted in the infiltration behaviour of cattle and pig slurries. For cattle slurry, DM content (range 1.7–7.1%) was the main influencing factor. Infiltration rate rapidly decreased with increasing DM content and there was no influence of soil type or water tension. For pig slurry, all of the slurry infiltrated into a sandy clay loam soil within the first hour, regardless of DM content (range 1.5–4.7%), whereas only 60% infiltrated into a clay loam soil over the same time period (slurry DM content 2.1%).

**Keywords:** Slurry infiltration, time domain reflectometry, ammonia emission, land spreading

## INTRODUCTION

Approximately 37 million tonnes of liquid manure (slurry) arise from dairy, beef and pig production systems in England and Wales each year (Chambers *et al.* 2000), which pose a significant risk of pollution to air and water if not managed properly. When applied to agricultural land at agronomically appropriate times and rates, the nutrient content of these manures can be offset against mineral fertilizer use (e.g. Chambers *et al.* 1999). However, crop response to manures, and nitrogen (N) content in particular, is often unpredictable because of the different N transformations and loss pathways which may occur before crop uptake. Much of this unpredictability is due to the great variation which can occur in the volatilization of ammonia ($NH_3$) in the few days following slurry application, depending on a range of weather, slurry, soil and management factors (Sommer & Hutchings 2001). A number of mechanistic (van der Molen *et al.* 1990; Hutchings *et al.* 1996; Genermont & Cellier 1997) and empirical (Smith & Chambers 1995; Braschkat *et al.* 1997; Menzi *et al.* 1998; Sogaard *et al.* 2002; Misselbrook *et al.* 2005b) models have been developed to improve the predictability of $NH_3$ loss after spreading. Some of these models have been incorporated into decision support systems (e.g. Mannheim *et al.* 1997; Chambers *et al.* 1999; Brown *et al.* 2004); however, as yet none adequately describes the infiltration process of slurry into the soil.

Rapid infiltration of slurry into the soil reduces the rate of $NH_3$ volatilization (Pain *et al.* 1989; Sommer & Ersboll 1994; Sommer & Jacobsen 1999; Sommer *et al.* 2004), as the slurry is no longer subject to the direct effects of wind speed and temperature at the soil surface, and ammonium ($NH_4^+$) ions will become adsorbed on to soil particles. It is hypothesized here that the infiltration process will be influenced by both slurry and soil factors. The importance of slurry dry matter (DM) content as a factor influencing infiltration can be inferred from the relationship between cumulative $NH_3$ emission and slurry DM, emission increasing with DM content (e.g. Thompson *et al.* 1990; Sommer & Olesen 1991; Smith & Chambers 1995). Slurry DM accumulating at the soil surface as infiltration occurs will progressively decrease the hydraulic conductivity of the soil surface layer. Additionally, the sorptivity of the soil surface layer, which will depend on soil structure, water content and soil water tension, will influence slurry infiltration. Sommer & Jacobsen (1999) found that low soil water content enhanced mass movement of slurry ammonium-N into soil, thereby decreasing $NH_3$ volatilization.

Slurry infiltration begins immediately after application to the soil, and the changes in infiltration rate as influenced by the factors described above will also occur rapidly. In order to improve the mechanistic models for $NH_3$ volatilization a description of the infiltration process with a sufficiently small time-step (i.e. $<1$ min) is required, particularly for the period immediately following slurry application. Previous slurry infiltration studies have relied on destructive soil sampling at fixed intervals, together

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with chemical tracers to follow movement into the soil profile (Sommer & Jacobsen 1999; Sommer *et al.* 2004). Time domain reflectometry (TDR) is a non-destructive technique for making continuous, or semi-continuous, measurements of soil water content (Topp *et al.* 1980). The present paper describes laboratory experiments using TDR to measure slurry infiltration into soil columns, with preliminary experiments assessing the influence of slurry type, DM content, soil type and soil water tension.

## MATERIALS AND METHODS

*Experimental configuration*

Soil water measurements were made using TDR at five depths in each of six soil columns using 30 probes connected via a multiplexer to a Tetronix 1502B cable tester (Tetronix Inc., Beaverton, Oregon, USA). The columns were of Perspex construction, 0.3 cm wall thickness with an internal diameter of 14.4 cm and 13 cm soil depth. Each column was mounted on the scintered-glass plate of a large Buchner funnel, connected to a moveable column of water so that the soil water tension in the soil column could be controlled. The probes were of the three-rod type, with the outer rods connected to the outer sheath of the coaxial cable and the central rod connected to the core of the coaxial cable linking the probe to the cable tester. The rods were 0.08 cm diameter stainless steel, 14 cm in length with 0.5 cm separation distance between rods. Probes were mounted horizontally through the soil column walls at depths of 0.5, 1.5, 3.0, 5.0 and 7.0 cm below the soil surface.

Soil-specific calibrations were made to relate the measured dielectric constant using TDR to the volumetric soil water content. Two soil types were used in this study: a sandy clay loam composed of 59% sand (0.063–2.000 mm), 20% silt (0.002–0.063 mm), 21% clay (<0.002 mm) and a clay loam (20% sand, 50% silt, 30% clay) of the Crediton (Brown Earth; USDA Dystric Eutochrept) and Hallsworth (Stagnogley; USDA Haplaquept) series, respectively (Findlay *et al.* 1984). Soils were sieved through a 5 mm screen and air-dried prior to packing into narrow plastic vessels (7 cm diameter, 15 cm height) at bulk densities of 1.1 and 0.6 $Mg\,m^{-3}$ for the sandy clay loam and clay loam, respectively, which approximated the bulk densities of these soil types in the field. Water was added to the vessels to achieve a range of 15 different volumetric water contents for each soil type. Two probes were inserted into each vessel and continuous readings of the dielectric constant made over a 2 h period. A best-fit relationship was then derived between volumetric soil water content and dielectric constant for each soil type, based on plotting the square root of the measured dielectric constant against the volumetric water content. This relationship has a physical basis, unlike the empirical polynomial functions often used, and is a linear calibration function and therefore simpler than polynomials previously used (Whalley 1993). The validity of using the soil-specific calibration with the probes mounted horizontally in the larger soil columns, as described above, was checked by comparing TDR-derived soil water content for each soil layer with that derived from gravimetric soil water content and bulk density after destructive sampling of the soil column.

Table 1. Slurry infiltration experiments.

| Experiment | Slurry type | Slurry DM content (%) | Soil type | Soil water tension (cm) |
|---|---|---|---|---|
| 1 | Cattle | 1.7 | Sandy clay loam | 40 |
| 2 | Cattle | 2.4 | Sandy clay loam | 40 |
| 3 | Cattle | 3.8 | Sandy clay loam | 40 |
| 4 | Cattle | 3.8 | Clay loam | 40 |
| 5 | Cattle | 4.8 | Sandy clay loam | 40 |
| 6 | Cattle | 7.1 | Sandy clay loam | 40 |
| 7 | Pig | 1.5 | Sandy clay loam | 40 |
| 8 | Pig | 2.1 | Sandy clay loam | 40 |
| 9 | Pig | 2.1 | Clay loam | 40 |
| 10 | Pig | 4.7 | Sandy clay loam | 40 |
| 11 | Cattle | 4.8 | Sandy clay loam | 10 |
| 12 | Cattle | 4.8 | Sandy clay loam | 80 |
| 13 | Pig | 2.1 | Sandy clay loam | 10 |
| 14 | Pig | 2.1 | Sandy clay loam | 80 |

*Infiltration experiments*

A series of experiments was conducted in which the infiltration of slurry into the soil columns was followed using TDR to assess the influence of slurry type (pig or cattle), soil type, slurry DM content and soil water tension (Table 1). Soils were sieved (5 mm screen) and air-dried prior to packing at the appropriate bulk density (1.1 and 0.6 for the sandy clay loam and clay loam, respectively) in the Perspex soil columns. The TDR probes were installed during the packing process. The soil columns were placed on the Buchner funnels and the desired water tension set. The columns were then leached with 1 $dm^3$ deionized water and left overnight to equilibrate at the desired water tension. Following equilibration, 0.1 $dm^3$ of slurry was applied to the surface of each soil column, equivalent to a 6 mm depth of slurry, or 60 $m^3\,ha^{-1}$. TDR measurement commenced several hours before slurry application and continued until 24 hours after application. The TDR system measured dielectric constant from each probe in turn, via the multiplexer, with an interval of approximately seven minutes between measurements from the same probe. Three replicate columns were used for each treatment, allowing two treatments to be run simultaneously using the six columns.

*Data analysis*

Measured dielectric constant from each probe at each time interval was converted to volumetric water content using the soil-specific calibrations. The change in water content relative to mean water content for the hour prior to slurry application was then derived for each soil layer at each measurement time. For calculation purposes, the soil column was divided into five theoretical layers, each with a TDR probe at the vertical mid-point of each layer. Using the volume of each soil layer and the measured change in volumetric water content, the volume flow of water across the top boundary of each layer and the cumulative infiltration from the surface against time were derived.

Mean cumulative infiltration over the first hour following slurry application for the three replicates of each treatment were compared using the analysis of variance procedure of GENSTAT (Lawes Agricultural Trust 1993) to assess the influence of slurry DM content, soil type and soil water tension on cumulative slurry infiltration.

## RESULTS

*Soil-specific TDR probe calibrations*

Measured volumetric soil water content was best related to the square root of the TDR-derived dielectric constant, with good fitted relationships for both soil types (Figure 1). Fitted calibration functions were derived as:

$$\theta = 0.0596\sqrt{\varepsilon} + 0.0903 \quad (1)$$

for the sandy clay loam and

$$\theta = 0.0574\sqrt{\varepsilon} + 0.1946 \quad (2)$$

for the clay loam soil, where $\theta$ is the volumetric soil water content and $\varepsilon$ the soil dielectric constant. Separate measurements showed the calibration functions to be valid for the laboratory system as used for the infiltration experiments, although measurements were more variable for the sandy clay loam soil (Figure 1).

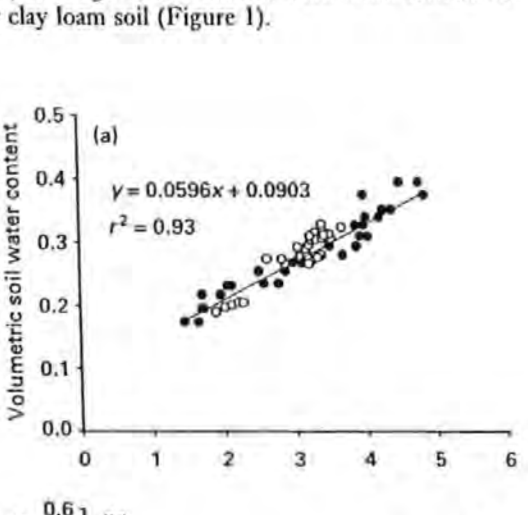


Figure 1. Time domain reflectometry soil water calibration curves for (a) sandy clay loam and (b) clay loam showing data points used for calibration (•), fitted calibration lines and validation data points from independent measurements (o).

*Infiltration measurements*

The typical changes in soil water content through the soil profile following slurry application to the soil surface are shown in Figure 2. Water content increased rapidly in the first soil layer (0–1 cm) followed by sequentially lesser increases in the lower soil layers. The magnitude of the increase in soil water content and the sharpness of the peaks for each soil layer in Figure 1 varied between the different treatments, but the overall pattern was the same.

Infiltration rate of slurry rapidly decreased after application, and for cattle slurry was influenced by slurry DM content (Figure 3). The volume infiltrated in the first hour following application to the sandy clay loam decreased with increasing DM content for cattle slurry, but not for pig slurry (Figure 4). For the smallest cattle slurry DM content (1.7%) and the two smallest pig slurry DM contents (1.5 and 2.1%), the soil water content of the lowest soil layer (6–8 cm depth) had increased between slurry application and the first TDR measurement at that depth, indicating a rapid movement from the surface through the soil profile. As the outflow from the bottom of the soil column was not measured, volume infiltration calculations based on the increase in soil water content will have been underestimated for these three treatments (marked A, B and C on Figure 4). Visual observations suggested that infiltration of the pig slurries was approximately 100% within the first hour and approaching that value for the cattle slurry at 1.7% DM. For pig slurry, therefore, a 6 mm application to a sandy clay loam completely infiltrated within one hour for slurry DM content of up to at least 4.7%. For a 6 mm application of cattle slurry to a sandy clay loam, a declining exponential relationship between proportion infiltrated within the first hour ($V$) and DM content was fitted to the data ($r^2 = 0.81$), without accounting for the underestimate in point A, Figure 4:

$$V = 110e^{-0.357(DM)} \quad (3)$$

Two experiments were conducted where the influence of soil type on slurry infiltration following 6 mm slurry application was assessed. For the cattle slurry (3.8% DM), there was no significant difference ($P > 0.05$) in infiltration over the first hour, with a mean of 26% of the volume applied (Figure 5). For the pig slurry (2.1% DM), infiltration was significantly less ($P = 0.031$) over the first hour into the clay loam than the sandy clay loam. There was no increase in soil water content at the lowest soil layer between the time of application and the first TDR measurement at that depth, so the volume infiltration in this case was not considered to be significantly underestimated.

Increasing the soil water tension from 10 to 80 cm had no significant effect ($P > 0.05$) on the infiltration of cattle slurry (4.8% DM) applied to the sandy clay loam soil, with a mean infiltration over the first hour of 27% of the applied volume. For applications of pig slurry (2.1% DM) to sandy clay loam soil at different soil water tensions, there was infiltration through the lowest soil layer between the time of application and the first TDR measurement at that depth. Infiltration rates were therefore underestimated to

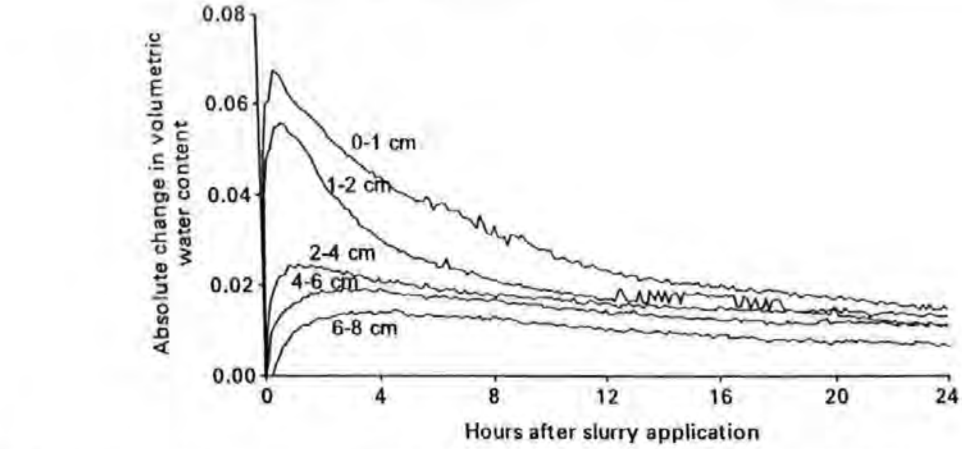


Figure 2. Changes in volumetric soil water content at different depths following application of cattle slurry (4.8% DM) to sandy clay loam at 40 cm soil water tension (mean result for three soil columns). From the top to the bottom, the lines represent moisture content changes within soil layers of increasing depth to 8 cm.

a certain (unknown) extent at all three soil water tensions and valid comparisons could not be made.

## DISCUSSION

Results from this study have revealed an interesting interaction between slurry and soil factors influencing slurry infiltration. Of particular interest is the difference between cattle and pig slurries. For cattle slurries the slurry DM content was the predominant factor influencing infiltration rate and cumulative infiltration over the first hour. For pig slurries, although based on a limited number of measurements, the soil properties appeared to be more important than slurry DM content. This confirms previous research where a much stronger relationship between $NH_3$ emission and slurry DM content was established for cattle than for pig slurries (Misselbrook *et al.* 2005b), with the suggestion that the physical nature of the DM content was the important influencing factor. Typically in the UK, the DM

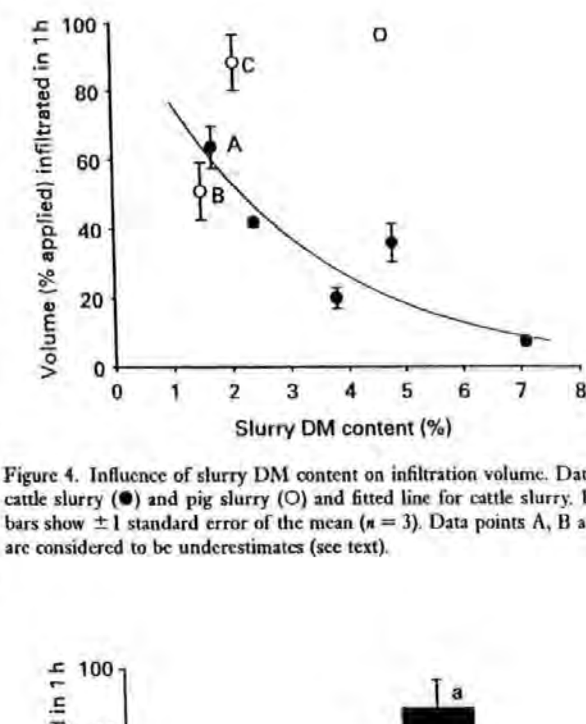


Figure 4. Influence of slurry DM content on infiltration volume. Data for cattle slurry (●) and pig slurry (○) and fitted line for cattle slurry. Error bars show ±1 standard error of the mean ($n = 3$). Data points A, B and C are considered to be underestimates (see text).

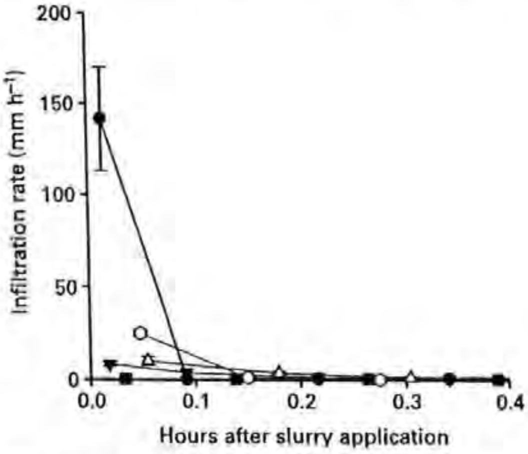


Figure 3. Infiltration rates for cattle slurries of varying DM content applied to sandy clay loam at 40 cm soil water tension. Slurry DM contents: 1.7% (●), 2.4% (○), 3.8% (▼), 4.8% (△) and 7.1% (■). Error bars show ±1 standard error of the mean ($n = 3$).

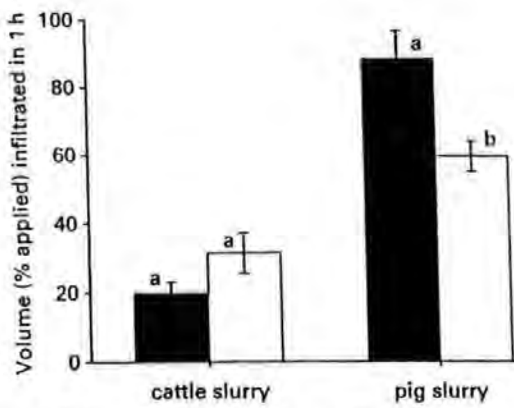


Figure 5. Influence of soil type on slurry infiltration volume. Cattle slurry (3.8% DM) and pig slurry (2.1% DM) applied to sandy clay loam (solid bars) and clay loam (open bars). Error bars show ±1 standard error of the mean ($n = 3$). Within each slurry type, bars with different letters were significantly different ($P < 0.05$).

content of pig slurries is colloidal in nature and tends to settle out of suspension rapidly following agitation whereas that of cattle slurries is more fibrous (and linear) and less dense, remaining in suspension following agitation. These differences account for the observation that in the UK cattle slurry stores tend to form surface crusts, which rarely develop on pig slurry stores, and that the diet of the cattle can influence crust formation, presumably influencing the nature of the slurry DM content (Misselbrook *et al.* 2005a).

Only a limited range of interactions were included in this study, but the slurry DM ranges and the specific DM contents used for the soil type and soil water tension studies were considered typical of those found in the UK. It might be surmised that for dilute cattle slurries (<2% DM) the soil factors would become more important, as was the case for the pig slurries. Equally, above a certain slurry DM content threshold, pig slurries may behave more like cattle slurries, with the slurry DM content being the overriding influence. Soil water tension would be expected to be important in determining the initial, instantaneous infiltration rate immediately after application and continue to be so for the slurries where DM content was not an important factor, but the time resolution of the TDR measurements in this study was too insensitive for that to be established for the 2.1% DM pig slurry. Further measurements are required for a range of slurry DM contents and application rates (not included in this study) over several differing soil types and soil water tensions to fully explore the interactions.

The broader aim of the research described here is the development of a mechanistic model describing the slurry infiltration process. Infiltration into the topsoil layer will be determined by the pressure head difference and the hydraulic conductivity of the top soil layer. Accumulation of slurry DM at the soil surface will progressively decrease the hydraulic conductivity of the surface layer, thereby reducing the infiltration rate. Indeed, Haraldsen & Sveistrup (1994) showed that infiltration rates into soils in Norway were smaller for up to three months following slurry applications. Model development should therefore focus on relating the hydraulic conductivity to the cumulative slurry infiltration, but also including a function related to the nature of the slurry DM content (e.g. particle size distribution, water release characteristics).

This study has demonstrated the potential of using TDR measurements both to parameterize and validate such a model. However, the system used in this study was subject to two limitations that need to be addressed. First, the time resolution of successive measurements for one probe (7 min) was too coarse: a much finer resolution is required to measure the rapidly changing infiltration rate immediately following slurry application. Second, the outflow from the bottom of the soil column was not measured, meaning that absolute volume infiltration could not be calculated for those treatments where this occurred. Automated measurement of outflow with the same time resolution as that of the TDR probe measurements would enable such calculations to be made.

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# Reduction of Ammonia Emission by Slurry Application Techniques

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Livestock manures and slurries are, currently, almost entirely surface applied to land in the UK but research has shown that, under experimental conditions, injection of slurry or restricted surface placement, can considerably reduce ammonia ($NH_3$) emissions following land spreading. In experiments reported in this paper, treatments were based around a slurry plot applicator, incorporating surface broadcast, band-spread, trailing shoe and shallow injection (open slot) application techniques. In a total of 16 experiments over the period July 1995–June 1997, $NH_3$ losses following application were significantly reduced (probability $P < 0{\cdot}05$) on five occasions by at least one of the modified application techniques and averaged, 40, 25, 23 and 17% of the ammonium-N ($NH_4$-N) applied, respectively, for splash-plate, band spread, trailing shoe and shallow injection techniques. The overall reduction in $NH_3$ emissions provided by the band-spread, trailing shoe and shallow injection techniques, was 39, 43 and 57% relative to conventional surface broadcast application. Whilst application technique consistently affected $NH_3$ emissions, there was generally little observable effect on crop yield or nitrogen offtake in assessments undertaken within this project. It is apparent that soil moisture content, soil temperature, slurry dry matter content and crop growth are all factors with potential to affect the results obtained. Greater understanding of the interaction of application technique with these factors is required.



## 1. Introduction

Recent estimates of ammonia ($NH_3$) emissions for UK agriculture indicate that around 33% of the total is attributable to land spreading of manures (Pain *et al.*, 1998). The United Nations Economic Commission for Europe (UNECE) is preparing a new protocol to reduce emissions of nitrogen (N) compounds, in which the importance of agriculture, especially livestock production, is well recognized as the major source of gaseous $NH_3$. This, together with the EU Integrated Pollution Prevention and Control Directive (IPPC) (EC, 1996), may result in the need to abate emissions of $NH_3$ to decrease the risk of long-range transport, deposition and damage to fragile ecosystems.

Livestock manures and slurries are, currently, almost entirely surface applied to land in the UK (Smith *et al.*, 2000). Frost (1994) demonstrated large reductions in $NH_3$ emission from careful placement of slurry in narrow bands (60% reduction) or injection slots (> 90% reduction), compared with surface application, in small-scale plot experiments. Research in the Netherlands and Germany using field-scale machinery, has shown that the injection of slurry or restricted surface placement, compared with surface broadcast application, can reduce $NH_3$ emissions by as much as 90% (Mulder & Huijsmans, 1994; Lorenz & Steffens, 1997; Huijsmans *et al.*, 1997). Whilst land spreading of manures is therefore a serious concern, it also offers great potential for cost-effective abatement, through slurry application technique.

However, the few data available from experiments carried out under UK conditions suggest that shallow injection abatement methods may not be so effective (Misselbrook *et al.*, 1996; Pain & Misselbrook, 1997). Moreover, because of the variability in soils in the UK, including a large proportion of stony soils, and different climatic conditions, it is necessary to further investigate the effectiveness of newly developed slurry application technology. This paper describes the results of experiments undertaken on grassland at the Institute of Grassland and Environmental Research (IGER) N Wyke, Devon, and on grassland and arable sites at ADAS centres, from July 1995 to spring 1997. Results of grass dry matter (DM) yield, grain yield, and N offtake are presented, as well as $NH_3$ emission measurements.

## 2. Materials and methods

### 2.1. *Sites*

Experiments were established on three grassland and two arable sites in lowland England. The grassland sites were situated at IGER, Devon, 1995, on well-drained sandy loam; ADAS Rosemaund, Herefordshire, 1995, on moderately well-drained silty clay loam; and IGER, Devon, 1995/1996–1996/1997, on poorly drained clay. The arable sites were at: ADAS Bridgets, Hampshire, 1995/1996, on well-drained silty clay loam over chalk; and ADAS Gleadthorpe, Nottinghamshire, 1996/1997, on freely drained loamy sand.

### 2.2. *Slurry application*

All slurry treatments were applied using a slurry plot applicator, specifically designed and developed for plot work by ADAS and Briggs Irrigation, UK (*Fig. 1*). The machine comprises a 2 $m^3$ slurry supply tank, positive displacement pump with re-circulation/mixing facility and distribution to a mini tractor-drawn toolbar unit via a rotating head manifold with multiple outlets. Design and performance details have been reported by Basford *et al.* (1996). The required application rate is achieved by adjustment of the PTO drive-speed of the positive displacement pump (according to pump calibration charts) and verified by an electronic flow meter (ABB Kent Taylor, London), monitoring (to an accuracy of $\pm 2\%$) the delivery to the applicator toolbar. Four application techniques were studied:

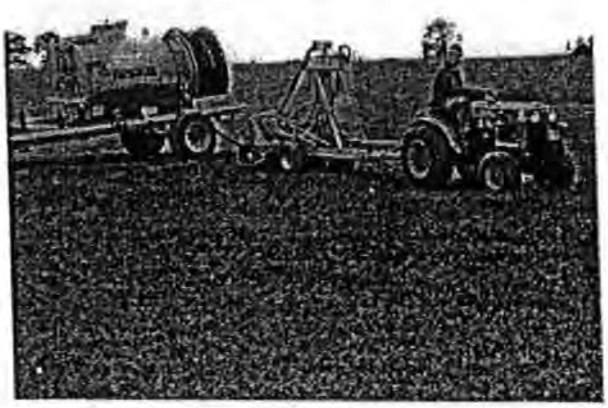

*Fig. 1. Plot applicator showing supply tank and applicator toolbar*

(1) *Surface broadcast* — slurry applied by tanker with a single outlet and splash-plate (conventional practice on the great majority of UK farms).
(2) *Surface band-spreading (via trailing hoses)* — involving multiple hoses that hang 5–10 cm above, or drag over the ground, depositing slurry in bands 5–10 cm wide, with approximately 30 cm between bands.
(3) *Surface placement (via trailing shoes)* — delivery pipes supply trailing feet elements that slide over the ground, placing the slurry in bands approximately 3 cm wide and 20 cm apart, between and below the crop canopy.
(4) *Shallow slot injection (ca. 50 mm depth)* — slurry placed in open slots (*ca.* 2–3 cm wide) created by two disc coulters to about 5 cm depth and approximately 20 cm apart.

These techniques have been described in detail elsewhere (Mulder & Huijsmans, 1994). Application techniques were readily interchangeable on the plot applicator and using this approach allowed for a critical comparison of application method, whilst minimizing the risk of variability in slurry consistency or delivery between treatments.

To enable slurry nutrient application rate to be accurately determined, a sample of slurry was collected for each application treatment (*i.e.* a total of four samples per application date). Each sample was then analysed for dry matter (DM), total nitrogen (N), ammonium N ($NH_4$-N), phosphorus (P), potassium (K), pH and conductivity (MAFF, 1986). A slurry application rate of 30 $m^3 ha^{-1}$ was selected as standard for the treatment comparisons, this being a sensible target rate for shallow injection, albeit slightly higher than considered normal practice for the band-spreading and trailing shoe techniques. This compromise was necessary to enable a sensible target rate of $NH_4$-N supply (30–40 $kg ha^{-1}$ N) from the relatively dilute slurries used in these experiments; a lower rate would have reduced the potential for measurable differences in $NH_3$ emission or crop N recovery, between treatments.

### 2.3. *Experimental design*

The slurry application treatments were made at three different timings, providing a range of soil and crop conditions. Applications were made to the grassland sites in winter (Nov–Dec), early spring (Feb–March) and post-first-cut silage (May–June); also on the arable sites, in autumn/winter (Oct–Nov) and top dressing in early spring (Feb–Mar) or spring (April). In year 1 (1995), treatments were applied to the grassland sites after second-cut silage only, but included comparisons of high and low topsoil moisture content (IGER) and two contrasting slurry DM contents (ADAS Rosemaund).

Crop response was assessed at six levels of fertilizer N, including nil (control), with the chosen levels of N dependent upon crop and site factors. For the slurry application experiments, a split-plot design was generally used, with slurry timing on main plots and application method on sub-plots. All treatments were replicated within each of three blocks, with main plots and fertilizer N plots fully randomized within blocks and sub-plots fully randomized within main plots. At Gleadthorpe in 1997, a two-way factorial design (four application methods by three timings) was used.

### 2.4. *Ammonia volatilization*

A system of small wind tunnels (Lockyer, 1984) was used to measure $NH_3$ emissions following slurry application. Each tunnel comprised a transparent polycarbonate canopy measuring 2 m by 0·5 m, coupled to a steel duct which housed an electrically driven fan and an anemometer, enabling airflow through the tunnel to be controlled, in these experiments at 1 m $s^{-1}$, which is thought to be typical of air speed at 25 cm above the soil, under lowland, UK conditions. It is recognized that wind speed has a significant effect on emissions and that estimates of absolute emissions, using wind tunnels, would need to be made while matching tunnel wind speed with ambient wind speed; however, Ryden and Lockyer (1985) recognized the application of wind tunnels (without wind speed control), in the study of factors affecting $NH_3$ loss following slurry application to replicated experimental plots. The $NH_3$ flux within the tunnel was measured by drawing air at 4 $l$ $min^{-1}$ through absorption flasks containing 0.02 M orthophosphoric acid, at the tunnel entry and exit and the level of absorbed $NH_3$ determined by analysis. Ammonia emission from the area beneath the canopy was then calculated as the product of the difference in outlet and inlet air concentrations and the volume of air passing through the tunnel. It was necessary to rotate the long axis of the plots used for $NH_3$ emission measurements slightly. This allowed the wind tunnels to be positioned perpendicular to the direction of slurry application without drawing air directly from the immediately adjacent slurry plot (*Fig. 2*). This plot layout also avoided either the need for travel over previously spread slurry plots or for excessive spatial separation of plots and greatly increased amounts of ducting and cables.

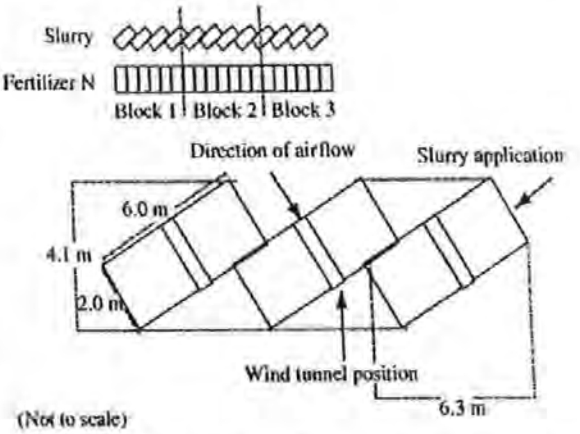


*Fig. 2. Diagram of plot layout for ammonia loss measurements*

During the first year, where treatments were applied at contrasting topsoil moisture status (IGER) and with contrasting DM content slurries (ADAS, Rosemaund), measurements were required on a total of 24 plots during the period after slurry application (Table 1, experiments 1a, 1b, 2a and 2b). The 12 tunnels available were used to monitor emissions for the first 24 h following application on the first set of plots and then switched to the second set of plots (after application on those plots the following day — contrasting soil moisture or slurry DM), for the next 24 h. Thereafter, the tunnels were alternated between the two sets of plots, *i.e.* monitoring days 1, 3 and 5, in each case.

### 2.5. *Crop response*

For the grass experiments, yield assessments were undertaken on the same plots as those used for $NH_3$ emission measurements. In the cereal experiments, however, yields were measured on separate plots to those used for $NH_3$ emission assessments. This enabled the fertilizer N response plots to be fully randomized within the slurry timing and application method treatments. Moreover, larger plots (3 m by 12 m) were required to allow sufficient area for cutting by a plot combine harvester. Grass fresh weights were recorded and from samples of herbage taken for analysis, grass DM yield and N offtake were estimated; in the arable experiments grain yield, corrected to 85% DM, grain %N and grain N offtake, were recorded.

In addition to the inorganic fertilizer N response plots (N applied at six rates), P, K and S fertilizers were applied across the site, according to soil analysis and crop recommendations (MAFF, 1994), to ensure that these nutrients were not limiting to crop response.

**Table 1**
**Details of slurry applications and nutrient content***

| *Experiment* | *Site* | *Date* | *Slurry type*† | *DM, %* | *N* | *$NH_4$-N* | *P* | *K* | *pH* | *$NH_4$-N / $N_{total}$* | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | kg $m^{-3}$ | | | | | | *N* | *$NH_4$-N* |
| 1a‡ | IGER | 11.7.95 | DS | 3·4 | 1·8 | 1·0 | 0·40 | 1·97 | 7·3 | 0·56 | 54 | 30 |
| 1b‡ | IGER | 12.7.95 | DS | 3·6 | 1·7 | 1·0 | 0·37 | 1·93 | 7·4 | 0·59 | 51 | 30 |
| 2a§ | Rosemaund | 18.7.95 | BS | 8·8 | 5·0 | 2·0 | 1·28 | 4·04 | 7·5 | 0·40 | 150 | 60 |
| 2b§ | Rosemaund | 19.7.95 | BS | 4·0 | 2·1 | 1·1 | 0·55 | 1·90 | 7·5 | 0·52 | 63 | 33 |
| 3 | Bridgets | 8.11.95 | DS | 2·5 | 1·6 | 1·0 | 0·25 | 1·33 | 7·4 | 0·62 | 48 | 30 |
| | | | | (0·2) | (0·1) | (0·07) | (0·05) | (0·09) | (0·0) | | | |
| 4 | IGER | 15.11.95 | DS | 3·6 | 1·6 | 0·8 | 0·43 | 1·56 | 7·3 | 0·50 | 48 | 24 |
| | | | | (0·4) | (0·1) | (0·02) | (0·03) | (0·12) | (0·0) | | | |
| 5 | Bridgets | 4–5.3.96 | DS | 2·0 | 1·5 | 1·1 | 0·22 | 1·45 | 7·5 | 0·73 | 45 | 33 |
| | | | | (0·03) | (0·1) | (0·03) | (0·00) | (0·04) | (0·0) | | | |
| 6 | IGER | 19.3.96 | DS | 4·6 | 2·3 | 1·4 | 0·53 | 3·29 | 7·3 | 0·61 | 69 | 42 |
| | | | | (0·05) | (0·1) | (0·05) | (0.01) | (0·07) | (0·0) | | | |
| 7 | Bridgets | 1.5.96 | DS | 2·0 | 1·4 | 0·9 | 0·20 | 1·35 | 7·2 | 0·64 | 42 | 27 |
| | | | | (0·08) | (0·1) | (0·03) | (0·04) | (0·03) | (0·1) | | | |
| 8 | IGER | 4.6.96 | DS | 4·6 | 2·3 | 1·1 | 0·52 | 3·01 | 7·3 | 0·48 | 69 | 33 |
| | | | | (0·01) | (0·1) | (0·05) | (0·02) | (0·02) | (0·2) | | | |
| 9 | Gleadthorpe | 1.10.96 | DS | 1·9 | 1·1 | 0·6 | 0·26 | 2·44 | 6·7 | 0·55 | 33 | 18 |
| | | | | (0·03) | (0·1) | (0·02) | (0·02) | (0·02) | (0·0) | | | |
| 10 | IGER | 12.11.96 | DS | 4·6 | 1·9 | 1·5 | 0·44 | 2·90 | | 0·79 | 57 | 45 |
| | | | | (0·04) | (0·2) | (0·06) | (0·02) | (0·01) | | | | |
| 11 | Gleadthorpe | 25.2.97 | DS | 2·1 | 1·1 | 0·8 | 0·23 | 2·08 | 7·2 | 0·73 | 33 | 24 |
| | | | | (0·07) | (0·2) | (0·02) | (0·07) | (0·04) | (0·2) | | | |
| 12 | IGER | 24.3.97 | DS | 4·8 | 2·4 | 1·0 | 0·48 | 3·00 | 6·9 | 0·42 | 72 | 30 |
| | | | | (0·01) | (0·1) | (0·01) | (0·03) | (0·02) | (0·0) | | | |
| 13 | Gleadthorpe | 15.4.97 | DS | 2·4 | 1 | 0·4 | 0·11 | 0·84 | 7·6 | 0·40 | 30 | 12 |
| | | | | (0·02) | (0·0) | (0·03) | (0·06) | (0·06) | (0·1) | | | |
| 14 | IGER | 2.6.97 | DS | 4·4 | 2·3 | 1·1 | 0·50 | 3·24 | 7·4 | 0·48 | 69 | 33 |
| | | | | (0·06) | (0·1) | (0·01) | (0·02) | (0·01) | (0·0) | | | |

*Note.* ( ) SD of the mean values given in parentheses (four samples); *Single samples experiments 1–3, mean of four samples other experiments; ‡Experiments on dry and moist soils; §Experiments testing high and low dry matter (DM) content slurries; †DS dairy slurry; BS beef slurry.

## 3. Results

### 3.1. *Slurry application*

The plot applicator performed well and, on visual inspection, the spreading pattern obtained by the four application techniques matched closely the results expected from field-scale equipment. Slurry analyses, for each of the experiments, are summarized in Table 1. Apart from initial experiments carried out in summer 1995, when only a single, composite, sample of slurry was taken from treatments as applied, the analyses represent a mean of four samples collected during slurry application by each of the four separate techniques. The slurries used, notably at ADAS Bridgets and ADAS Gleadthorpe, were dilute by comparison with what, at 6·0% DM content, is generally regarded as typical (MAFF, 1994). Hence, nitrogen content was also low but, otherwise, analyses were within the range expected for nutrient content. However, the range and variability of slurry analysis was low, giving confidence in the consistency of mixing and hence, in the uniformity of the slurry used in the experiments.

As a consequence of the dilute slurries and the modest application rate, the rate of $NH_4$-N applied was also relatively low. Also, because of the impact of slurry DM content on $NH_3$ emissions (Smith & Chambers, 1995) and, with such low additions of slurry N, it would be anticipated that treatment effects (arising from $NH_3$ volatilization losses of only a few kg ha$^{-1}$ N), would be difficult to identify or measure quantitatively.

### 3.2. *Ammonia volatilization*

Ammonia losses were rapid during the first few hours after spreading, particularly following application via the splash-plate method. Cumulative losses at the IGER site, for spring 1996, are shown in *Fig. 3*. These data were typical of the $NH_3$ emissions at each of the sites.

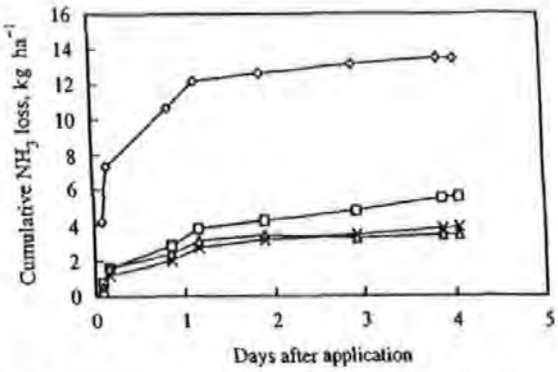


*Fig. 3. Cumulative loss of ammonia following cattle slurry application (IGER, March 1996): ◇, splash-plate; □, band-spread; △, trailing shoe; ×, shallow inject*

#### 3.2.1. *Application technique*

Cumulative losses from each of the experiments are summarized in Table 2; it is clear that losses were consistently reduced with slurry applied by surface placement technique compared to the conventional splash-plate method, though reductions in emissions reached statistical significance ($P < 0·05$) on a few occasions only. Results for $NH_3$ emissions are summarized in Table 3 and, overall, average $NH_3$ losses (% of $NH_4$-N applied), were: 40% for splash-plate; 25% for band-spread; 23% for trailing shoe and 17% for shallow injection. Thus, compared to the conventional practice of slurry application by the surface broadcast method, overall reductions in $NH_3$ emissions following application were 39, 43 and 57%, respectively, for the band-spread, trailing shoe and shallow injection techniques. These averages excluded the results of experiment 13, which because of the low slurry $NH_4$-N content, low rate of $NH_4$-N applied and variable $NH_3$ emissions, were considered to make the estimates (in relative terms) unreliable.

#### 3.2.2. *Soil condition and moisture status*

The experiments were initiated in summer 1995 when the dry, hard soil conditions and short grass at ADAS Rosemaund and IGER, following second-cut silage increased $NH_3$ emissions across all treatments (see experiments 1 and 2, Table 2). Careful scrutiny of the results in Table 2 suggests that soil conditions and, in particular, moisture status have an important impact on $NH_3$ emissions from applied slurries. The application of 20 mm of water to the soil, prior to slurry application at the IGER 1995 site, reduced $NH_3$ losses overall and, also, the differential between surface broadcast and other application techniques (Table 2, experiments 1a and 1b). Ammonia losses following application via splash-plate were significantly higher than from the other techniques, on the dry soil (experiment 1a).

The results have therefore been grouped on the basis of grass or arable soil and, also, whether dry or moist at the time of application, the latter affected largely by application time or, in specific cases (experiments 1a and 1b), treatment (Table 3). From these data, it is clear that $NH_3$ losses from slurry applied to hard, dry grassland soils are higher than from moist grassland or arable soils. The effectiveness of application technique in reducing $NH_3$ emissions under different conditions, is shown in *Fig. 4*; overall, injection was most effective on moist arable soils and least effective on dry, hard grassland.

#### 3.2.3. *Slurry solids content*

Slurry DM content also has an important effect on $NH_3$ losses following application; experiments 2a and 2b

**Table 2**
**Cumulative ammonia loss, following slurry application**

| *Experiment* | *Soil condition* | *Cumulative ammonia loss, $NH_3$-N, kg ha$^{-1}$* | | | | *SEM* (res. df 6)* | *P†* | *Ammonia loss, % of applied $NH_4$-N* | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | *Splash-plate* | *Band spread* | *Trailing shoe* | *Shallow injection* | | | *Splash-plate* | *Band spread* | *Trailing shoe* | *Shallow injection* |
| 1a | Dry, hard | 28·8 | 10 | 10·2 | 11·5 | 2·74 | *0·007* | 96 | 33·3 | 34 | 38·3 |
| 1b | Moist | 12·4 | 7·1 | 9·5 | 5·8 | 3·44 | *ns* | 41·3 | 23·7 | 31·7 | 19·3 |
| 2a | Dry, hard | 37·6 | 37·5 | 24·3 | 25·4 | 5·36 | *ns* | 62·7 | 62·5 | 40·5 | 42·3 |
| 2b | Dry, hard | 16·3 | 12·2 | 15·8 | 14·9 | 3·36 | *ns* | 49·4 | 37 | 47·9 | 45·2 |
| 3 | Moist | 6·9 | 6·7 | 5·4 | 2·2 | 1·28 | *ns* | 23 | 22·3 | 18 | 7·3 |
| 4 | Moist | 5·3 | 3·8 | 3·5 | 1 | 1·62 | *ns* | 22·1 | 15·8 | 14·6 | 4·2 |
| 5 | Moist | 3 | 3·4 | 4·6 | 0·7 | 0·5 | *0·007* | 9·1 | 10·3 | 13·9 | 2·1 |
| 6 | Moist | 13·4 | 5·5 | 3·3 | 3·8 | 2·36 | *0·073* | 31·9 | 13·1 | 7·9 | 9 |
| 7 | Moist | 5·9 | 4·5 | 4·3 | 3 | 1·41 | *ns* | 21·1 | 16·1 | 15·4 | 10·7 |
| 8 | Dry | 20·2 | 13 | 8·7 | 6·1 | 2·62 | *0·035* | 59·4 | 38·2 | 25·6 | 17·9 |
| 9 | Moist | 9·4 | 4·3 | ‡ | −2·6 | 4·19 | *ns* | 49·5 | 22·6 | ‡ | −13·7 |
| 10 | Moist | 11·2 | 6 | 4·3 | 2·8 | 2·82 | *ns* | 24·9 | 13·3 | 9·6 | 6·2 |
| 11 | Moist | 3·8 | 2·4 | 3·1 | 4·6 | 1·09 | *ns* | 16·5 | 10·4 | 13·5 | 20 |
| 12 | Moist | 13·2 | 6 | 4·8 | 6·1 | 2·14 | *ns* | 44 | 20 | 16 | 20·4 |
| *13§* | *Moist* | *3·8* | *2·1* | *5·4* | *3·9* | *1·07* | *ns* | *31·7* | *17·5* | *45* | *32·5* |
| 14 | Dry | 16 | 9·5 | 9·7 | 9 | 1·33 | *0·028* | 50 | 29·7 | 30·3 | 28 |

*SEM, standard error of mean; res. df, residual degrees of freedom; †*P*, probability; ns, not significant at the 5% level of significance; ‡Treatment not applied due to adverse soil conditions; §Only a very low rate $NH_4$-N applied; these results excluded from overall mean losses (Table 3), to avoid bias as a result of errors associated with this run.

Table 3

Average ammonia losses, following slurry applications on grassland (moist and dry soils) and arable (moist soils) sites

| Site class (Experiment nos.) | Application period | Soil condition | Slurry DM% | Slurry $NH_4$-N kg $ha^{-1}$ | Cumulative ammonia loss, $NH_3$-N kg $ha^{-1}$ | | | | Ammonia loss, % of applied $NH_4$-N | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | Splash-plate | Band spread | Trailing shoe | Shallow injection | Splash-plate | Band spread | Trailing shoe | Shallow injection |
| Grass (1b, 4, 6, 10, 12) | November–March | Moist | 4·2 | 34·2 | 11·1 | 5·7 | 5·1 | 3·9 | 32·8 | 17·2 | 16·0 | 11·8 |
| Grass (1a, 2a, 2b, 8, 14) | June–July | Dry (hard) | 5·0 | 37·6 | 23·8 | 16·4 | 13·7 | 13·4 | 63·5 | 40·1 | 35·7 | 34·3 |
| *Mean, grass sites* | | | *4·6* | *35·9* | *17·4* | *11·1* | *9·4* | *8·6* | *48·2* | *28·7* | *25·8* | *23·1* |
| Arable (3, 5, 7, 9, 11) | October–April | Moist | 2·1 | 26·2 | 5·8 | 4·3 | 4·4 | 1·6 | 23·8 | 16·3 | 15·2 | 5·3 |
| *Overall mean, all sites* | | | | *32·7* | *13·6* | *8·8* | *8·0* | *6·3* | *40·1* | *24·6* | *22·8* | *17·1* |
| **Reduction in $NH_3$ loss, % relative to splash-plate** | | | | | | | | | **0·0** | **38·7** | **43·1** | **57·2** |

DM, dry matter content.

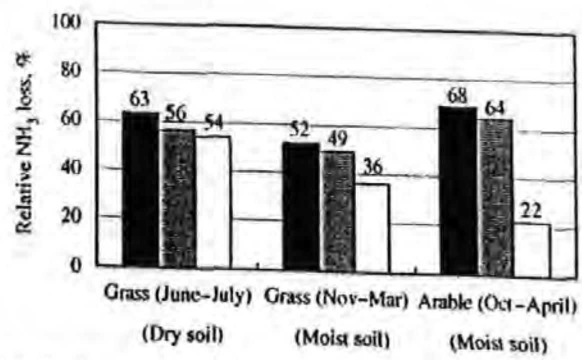


*Fig. 4. Ammonia emissions following slurry application by surface placement techniques relative to splash-plate application:* ■, *bandspread;* ▦, *trailing shoe;* □, *shallow injection*

allowed a contrast between high (8·8%) and lower (4·0%) DM content, with $NH_3$ losses reduced overall, for the lower DM slurry, although there were no significant differences (probability $P < 0{\cdot}05$) between application techniques, in either case. Taking all results obtained for broadcast slurry on moist soil (Table 2), a linear relationship was found with $NH_3$ loss increasing with slurry dry matter (*Fig. 5*).

### 3.3. *Crop response*

Grass silage yield and N offtake data were recorded for the 3 years at IGER, and for 1995, third cut only, at ADAS Rosemaund but, in the absence of significant differences as a result of treatment, these data are not presented here. Grass DM yield and N offtakes were generally low and experimental error, due also to the

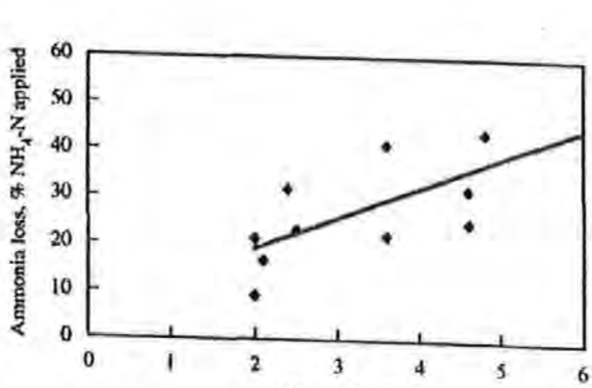


*Fig. 5. Effect of slurry dry matter content (DM) on ammonia loss, splash-plate treatments;* % $loss_{(NH4-N)} = 6{\cdot}17\ (DM) + 6{\cdot}70$, $r^2 = 0{\cdot}44$, $P < 0{\cdot}01$; *$r^2$, coefficient of determination; P, probability; DM, slurry dry matter*

Table 4
Crop response to manures — ADAS Gleadthorpe 1997

| *Application time (Experiment no.)** | *Treatment* | | | | *P* | *SEM* | *Res. df* |
|---|---|---|---|---|---|---|---|
| | *Splash-plate* | *Band spread* | *Trailing shoe* | *Shallow injection* | | | |
| *Autumn (Nov, 1996) (9)* | | | | | | | |
| Grain yield, t $ha^{-1}$ at 85% DM | 2·21 | 2·52 | 2·37† | 1·78 | 0·025 | 0·215 | 20 |
| N offtake in grain, kg $ha^{-1}$ | 27·2 | 31·0 | 30·0† | 20·9 | 0·063 | 3·236 | 20 |
| *Early spring (March 1997) (11)* | | | | | | | |
| Grain yield, t $ha^{-1}$ at 85% DM | 2·40 | 3·19 | 3·32 | 3·47 | 0·025 | 0·215 | 20 |
| N offtake in grain, kg $ha^{-1}$ | 28·8 | 39·7 | 42·8 | 41·5 | 0·063 | 3·236 | 20 |
| *Late spring (May 1997) (13)* | | | | | | | |
| Grain yield, t $ha^{-1}$ at 85% DM | 2·63 | 2·49 | 2·72 | 2·73 | 0·025 | 0·215 | 20 |
| N offtake in grain, kg $ha^{-1}$ | 31·3 | 30·2 | 32·6 | 33·7 | 0·063 | 3·236 | 20 |

*Note. P*, probability; SEM, standard error of mean; Res. df, residual degrees of freedom. *Experiment number listed in Table 1; †Missing values estimated by GENSTAT.

small harvest area enforced by the requirements of the $NH_3$ emission measurements, masked any treatment differences present.

Despite a marked response to fertilizer N in winter wheat at ADAS Bridgets ($P < 0·001$), there were no statistically significant ($P > 0·05$) slurry treatment effects on grain yield or N offtake. Grain yields from the slurry treatments were low as a result of low N supply; a trend towards increasing yield and N offtake, from the surface placement slurry applications, was not observed with the autumn applied slurry treatments. Such differences in crop response would not be anticipated, as a result of overwinter leaching losses of any extra slurry N conserved by application treatment. At ADAS Gleadthorpe, despite low rates of slurry $NH_4$-N applied (12–23 kg $ha^{-1}$), at the first spring application in March 1997, the splash-plate treatment gave the lowest yield ($P < 0·05$), which was reflected also in grain N offtake (Table 4). Slurry injection in November gave lower yield and grain N offtake than the other application methods. There were no significant treatment differences at the May slurry application timing.

The average grain yield from the slurry plots at ADAS Bridgets was calculated as being equivalent to an application of 16 kg $ha^{-1}$ N as ammonium nitrate, representing manure N efficiencies of 33, 36 and 38% at the three timings. Equivalent efficiencies of 21, 21 and 23% were obtained at ADAS Gleadthorpe. Whilst low trajectory application of slurry in the spring, tended to increase grass DM and cereal grain yield and N offtake, these trends disappeared when considered across the three application timings studied.

## 4. Discussion

The observed rates of $NH_3$ emission following conventional, surface application of slurry (*Fig. 3*) were in close agreement with those reported by Jarvis and Pain (1990), who suggested that, from broadcast slurries, 40–50% of the total losses occurred within 6 h, 70% within 24 h and more than 90% over 5 days. The three surface placement slurry application techniques consistently reduced $NH_3$ emissions when compared with surface broadcast application, though these reductions often failed to reach statistical significance ($P < 0·05$) in the current studies. Ammonia losses were generally high during the early observations, in summer 1995, when the results were likely to have been affected by the dry, hard soil conditions prevailing following an extended period of low rainfall. When the experiments were carried out under moister soil conditions $NH_3$ emissions were reduced and the variability of the results appeared less. For surface broadcast slurries, a linear relationship was found between $NH_3$ loss and slurry dry matter (*Fig. 5*); over the limited range (slurry DM of 2–5%) represented by these data, $NH_3$ loss increased by about 6% for every 1% increase in slurry solids content — similar to results reported elsewhere (Sommer & Olesen, 1991; Smith & Chambers, 1995). In addition to the reduced potential for $NH_3$ emission as a result of the generally low DM content slurries used in these experiments, it has already been pointed out that as a consequence of the dilute slurries and the modest application rate, the rate of $NH_4$-N applied was also relatively low. It would therefore be anticipated that treatment effects (arising from $NH_3$ volatilization losses of only a few kg $ha^{-1}$ N), would be difficult to identify or measure quantitatively.

### 4.1. *Application technique*

Ammonia losses were consistently reduced with slurry applied by surface placement technique compared to the conventional splash-plate method, at 39, 43 and 57% of the emission from surface broadcast application, respectively, for the band-spread, trailing shoe and shallow injection techniques. However, abatement was considerably less than the potential benefits reported by some other researchers (Mulder & Huijsmans, 1994; Lorenz & Steffens, 1997) where, under experimental conditions, reductions in $NH_3$ emissions by injection or rapid incorporation, of up to 90%, have been achieved. The slightly disappointing results from the current experiments may have been, at least in part, due to the low DM content slurries used.

However, variable control was also the conclusion from a number of other, related studies. Misselbrook *et al.* (1996) found that shallow injection gave a 40 and 79% reduction in emission compared to surface broadcast for March and June applications, respectively, representing 35 and 21% of the total ammoniacal nitrogen (TAN) applied. Mannheim *et al.* (1995) reported the following losses (N as % TAN) in experiments on cattle slurry applied to grassland/arable land: broadcast (grassland) 38–74%, shallow injection (grassland) 7–23%, shallow injection (arable) 0–6%. In these studies, band-spreading was much less effective, with increased emissions recorded on some occasions; similarly, Matilla (1998) found that band spreading gave no effective reduction in emissions compared to broadcast cattle slurry on grassland, whereas no emissions were detected from injected slurry. In contrast, Sommer *et al.* (1997) recorded up to 80% reduction in emissions using trailing hoses to apply pig slurry to winter wheat. Morken and Sakshaug (1998) found that the direct ground injection system, a slightly different approach using a high-pressure jetting technique but with no soil penetrating coulters, gave a reduction of *ca.* 50% in emissions.

Within these experiments, crop responses (yield and/or N offtake) were few and of limited extent, which is hardly surprising when differences in plant available N (arising from differences in $NH_3$ volatilization) may only have amounted to a few $kg\,ha^{-1}$. Moreover, sites were not selected on the basis of their likely responsiveness to N supply (a normal pre-requisite of N response experiments). Similarly, there have been few reported agronomic benefits in the literature. Lorenz and Steffens (1997) showed grass yield responses at similar $NH_4$-N application rates for trailing shoe and shallow injection, compared to surface broadcast, but no benefit from band spreading. Significant yield increase was obtained when conditions at the time of spreading were conducive to large $NH_3$ losses from surface broadcast application (*i.e.* hot and dry conditions rather than cool and wet). Some negative effects have also been recorded with injection, for example, Misselbrook *et al.* (1996) found that shallow injection led to reduced yield and N recoveries following grassland application in June (thought to be due to sward damage). Rees *et al.* (1993) recorded reduced first-cut yield following injection, but second- and third-cut yields were improved, with no significant differences when assessed over the full season, compared to surface broadcast.

### 4.2. *Other factors*

There seems to be a wide range in the effectiveness of application techniques for reducing $NH_3$ emissions, both in these experiments and in the literature. The results, overall, suggest that the net effects of the different application techniques are likely to vary according to soil conditions (both in terms of moisture and soil/ambient temperatures—low temperatures reducing losses) and cultivation; loose tilth (associated with arable seedbeds) facilitating rapid infiltration of slurry and reducing $NH_3$ losses. It appears likely that very dry soils, especially grassland soils high in organic matter may become, to an extent, hydrophobic unless subjected to a gradual re-wetting process. Under dry conditions, it is possible that slurry may remain on the soil surface for an extended period, rather than infiltrating into the soil matrix, during which time, warm ambient conditions may increase $NH_3$ emissions. In contrast to these results, Sommer *et al.* (1997) found that $NH_3$ losses increased with increasing volumetric soil moisture content but this was due to impeded infiltration of $NH_4^+$ at high soil water content (Petersen & Andersen, 1996), which did not apply in these experiments.

Sommer *et al.* (1997) indicated the importance of crop canopy (leaf area index and crop height) for more effective reduction of $NH_3$ emissions by surface placement application technique and this will be particularly so in the case of the trailing shoe. Crop cover was not tested in these experiments, as slurry was applied to short grass swards or to arable crops at early growth stages or low plant density. Experimental conditions were standardized to include slurry applications at $30\,m^3\,ha^{-1}$ and applications from the different techniques all made at the same timing; these limitations may have introduced a bias in favour of one treatment or other, depending upon the conditions.

## 5. Conclusions

From the results on grassland in dry conditions, there appears to be little to choose between the three low trajectory application methods, with all three providing some benefit compared to surface broadcasting. On moist grassland and on arable soils (also moist within these studies), where more rapid infiltration of slurry into the soil is likely, shallow injection appeared to hold a marginal advantage over the other surface placement techniques. It is clear that soil moisture content, soil temperature, slurry DM content and crop conditions, *e.g.* sward height, are all factors with potential to affect emissions following slurry application and the interaction of these factors with application technique will require further investigation. The lack of convincing evidence of any agronomic benefit, as a result of reducing $NH_3$ emissions following slurry application, either in this study or in the literature, also indicates the need for further investigation. For wider application and relevance, however, it is important that such studies focus on slurries of higher DM content.

Overall reductions in $NH_3$ emissions of *ca.* 40–60% were obtained, comparing surface placement application with surface broadcasting, considerably less control than has been reported elsewhere in Europe. Nevertheless, such practices still offer potential for cost-effective abatement and, as land spreading of livestock manures is estimated to be responsible for over 30% of total $NH_3$ emissions from UK agriculture, their widespread use would make a significant contribution to reducing pollution from this source.

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## 2.8 Paper 8

Misselbrook, T.H., K.A. Smith, R.A. Johnson, and B.F. Pain. (2002). Slurry application techniques to reduce ammonia emissions: Results of some UK field-scale experiments. Biosystems Engineering 81, 313-321.

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# Slurry Application Techniques to reduce Ammonia Emissions: Results of some UK Field-scale Experiments

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Shallow injection, trailing shoe and band spreading machines were evaluated, in terms of their potential for reducing ammonia ($NH_3$) emission, by making measurements after application and in direct comparison with surface broadcast applied cattle slurry (pig slurry on one occasion). Several sets of comparative measurements were made with each type of machine on both grassland and arable land (mostly cereal stubbles), covering a range of soil, crop and weather conditions. Measurements of $NH_3$ emissions were made for 5–7 days following application using a micrometeorological mass balance technique. Mean reductions in $NH_3$ emission achieved from grassland, in comparison with surface broadcast application, were 73, 57 and 26% for shallow injection, trailing shoe and band spreading, respectively, the latter not being significant (probability $P > 0{\cdot}05$). Mean cumulative emissions, expressed as % total ammoniacal N applied in the slurry, were 13, 12 and 35% for shallow injection, trailing shoe and band spreading, respectively. There was a trend (probability $P = 0{\cdot}029$) for decreasing emissions with increasing sward height (between 10 and 20 cm) following trailing shoe applications. Abatement was generally less effective when these techniques were used on arable land, with mean reductions of 23, 38 and 27% achieved for shallow injection, trailing shoe and band spreading, respectively, with none achieving statistical significance (probability $P > 0{\cdot}05$). There was considerable variation in the efficiency of shallow injection, with reductions achieved in individual experiments ranging from 0 to 90%. The considerable variability in efficiency of the techniques for $NH_3$ emission abatement warrants further investigation. 

## 1. Introduction

Increasingly, there are pressures on agriculture to reduce emissions of ammonia ($NH_3$) to the atmosphere, because of concerns about environmental impact. The land spreading of animal manures accounts for approximately one-third of the total $NH_3$ emissions from agriculture (Misselbrook *et al.*, 2000) so there has been much interest in the development of abatement measures in this area. There are four main types of slurry application system in use on farms in NW Europe and which are represented in the present study (*Fig. 1*). Each of the following four techniques can be fitted onto a vacuum or pumped tanker or used with an umbilical supply system: (1) broadcast spreading—slurry forced under pressure through a nozzle, usually onto an inclined plate designed to increase lateral spread; (2) band spreading—a boom with a number of hoses distributing slurry close to the ground in narrow bands, slurry being fed to the hoses in advanced systems via a rotary distribution manifold which controls the flow of slurry evenly to each hose outlet; (3) trailing shoe applicator—similar in configuration to the band spreader, with the hoses discharging via a 'shoe' device which parts the crop canopy allowing the slurry to be deposited onto the soil surface; (4) injection—slurry injected beneath the soil surface either via open slot, shallow injection (to 50 mm) or via deep tines (to

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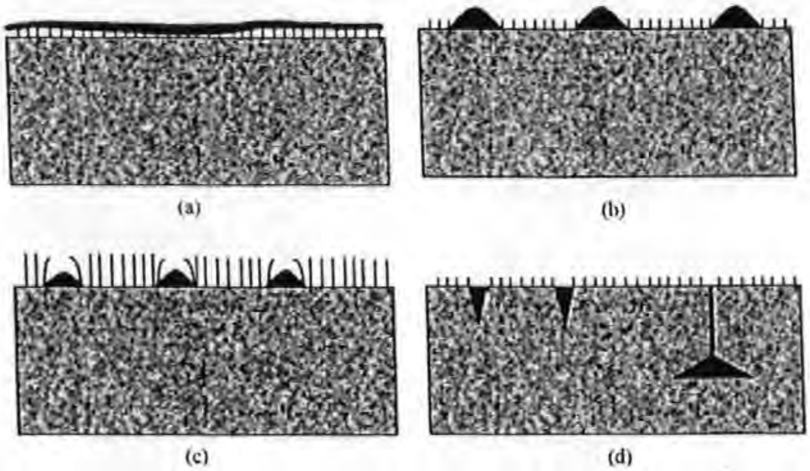

*Fig. 1. Schematic representation of slurry applied to soil using different application techniques: (a) surface broadcast—uniform covering of slurry across the crop; (b) band spreading—slurry placed in discrete bands on the crop by trailing hoses; (c) trailing shoe—slurry placed in discrete bands on the soil surface below the crop canopy; (d) injection—slurry placed in shallow, open slots or deep, closed slots within the soil*

>150 mm). An additional technique is direct ground injection, where jets of slurry are forced into the soil under pressure, mixing with the soil in discrete pockets (Morken & Sakshaug, 1998). This technique has not yet been widely taken up and, due to problems in importing the appropriate machinery, was not used in this study.

Research elsewhere in Europe (particularly in the Netherlands and Germany) has indicated that the recently developed surface placement application techniques for slurry (shallow injection, band spreading and trailing shoe), have resulted in reductions in $NH_3$ emission of between 70 and 95% compared with surface broadcast application (Huijsmans *et al.*, 1997; Lorenz & Steffens, 1997). However, early experiences with shallow injection using field-scale equipment (Misselbrook *et al.*, 1996; Pain & Misselbrook, 1997) and more recent trials with a small-plot applicator (Smith *et al.*, 2000) suggested that abatement efficiencies under UK conditions may not be so high. The aim of this study was to evaluate the efficiency of these slurry application techniques (excluding the direct ground injection technique) at the field-scale for reducing $NH_3$ loss on representative grassland and arable soils in the UK.

## 2. Materials and methods

### 2.1. *Site details*

Experiments were conducted on seven sites across England in order to achieve a range of soil types (Table 1) between 1997 and 2000.

### 2.2. *Application techniques*

Three application techniques (viz. shallow injection, trailing shoe application and band spreading) were assessed for reductions in $NH_3$ emission in comparison with conventional surface spreading via a vacuum tanker fitted with a splashplate. For grassland, shallow injection applications were made using either a Greentrac (Greentrac Ltd, Antrim, Northern Ireland) or Duport (Duport BV, Dedemsvaart, Netherlands) machine. The Greentrac had a solid tine to cut the injection slot, a 2·5 m working width and 0·20 m tine spacing. The Duport was of newer design, with angled double discs to cut the injection slot, a working width of 4·4 and 0·20 m disc spacing. For the arable experiments, a Greentrac arable injector was used, with tines preceded by a curved slot cutter, a working width of 4·5 m and tine spacing of 0·25 m. A trailing shoe machine was provided by Buts Meulepas BV, Oss, Netherlands. This machine had a 6 m boom width with slurry applied in narrow bands at 0·20 m intervals. As a dedicated band spreader could not be secured for use in this project, band spreading to grassland was simulated by adapting the use of the trailing shoe machine and, similarly, to arable land using the Greentrac arable injector. A single measurement using an SAK band spreader (S.A.K. Pumpen A/S, Løgstør, Denmark), with a 21 m boom width and hose spacing of 0·33 m, was made towards the end of the project. Slurry application rates were targeted by previous calibration runs using the equipment and confirmed by weighing the slurry applicator before and after application and measuring the treated area.

**Table 1**
**Site details**

| *Site* | *Location* | *Soil type* | *Soil series* | *Soil pH* |
|---|---|---|---|---|
| 1 | Devon | Coarse sandy loam | Crediton | 5·7–5·8 |
| 2 | Devon | Heavy clay | Hallsworth | 5·1–6·0 |
| 3 | Hampshire | Calcareous silty clay loam | Andover | 8·0–8·2 |
| 4 | Worcestershire | Clay/clay loam | Denchworth | 6·8 |
| 5 | Cheshire | Loamy sand | Newport | 7·2 |
| 6 | Herefordshire | Silty clay loam | Bromyard | 6·1–6·6 |
| 7 | Yorkshire | Silty clay loam over weathered chalk | Panholes | 8·0–8·2 |

### 2.3. *Ammonia volatilization*

Comparisons were usually made between conventional surface broadcast application and one of the new application techniques, although on some occasions three-way comparisons were also made. Measurements of $NH_3$ emission were made using a micrometeorological mass balance technique (Denmead, 1983), employing passive flux samplers (Leuning *et al.*, 1985). A mast supporting five passive flux samplers at approximate heights of 0·25, 0·65, 1·20, 2·00 and 3·30 m was placed either at the centre of a slurry-treated square plot (approximately 40 m by 40 m) or downwind of a slurry-treated strip of 20 m by 50 m, such that fetch length (*i.e.* the distance between the upwind edge of the plot and the downwind sampling position in a windward direction) was always at least 20 m. A background mast, supporting three samplers at approximately 0·25, 1·25 and 3·00 m was positioned at the upwind edge of the treated area. The $NH_3$ flux, $F$ in g $[NH_3\text{-}N]\,m^{-2}\,s^{-1}$, from the treated area was calculated for each sampling period as the difference between the vertically integrated horizontal flux at the downwind mast (subscript *dw*) and that at the upwind mast (subscript *uw*), divided by the fetch length, $x$ in m. Thus:

$$F = \frac{1}{x}\left[\int_0^z (\overline{uc})_{dw}\,dz - \int_0^z (\overline{uc})_{uw}\,dz\right] \qquad (1)$$

where: $u$ is the wind speed in m s$^{-1}$; $c$ is the $NH_3$ concentration in g m$^{-3}$; and $z$ the vertical height in m. The passive flux samplers measure directly the mean horizontal flux, $\overline{uc}$, calculated from:

$$\overline{uc} = \frac{M}{At} \qquad (2)$$

where: $M$ is the mass of $NH_3$ collected in g in the sampler during sampling period $t$ in s; and $A$ in m$^2$ is the effective cross-sectional area of the sampler (determined in wind-tunnel calibrations).

All experiments [excepting one, which used pig slurry at the site in Yorkshire (Table 1)] were conducted using cattle slurry. Measurements of $NH_3$ emission were conducted for 5–7 days after slurry application. Additionally, measurements were made of slurry composition [dry matter, pH, total N, total ammoniacal-N (TAN)], soil type and moisture content at application, crop height or growth stage and meteorological conditions (temperature, relative humidity, rainfall, incident solar radiation). Target application rates were 25–35 m$^3$ ha$^{-1}$, according to manufacturer's recommendations. Details of experiments conducted on grassland are given in Table 2 and those on arable land in Table 3.

## 3. Results

The main effect of the new slurry application techniques was to reduce the peak emission rate observed in the first few hours after application [*e.g.* *Fig. 2(a)*—data from Experiment 1], with differences in emission rates on subsequent days being of less significance. As upward of 50% of total emission can occur within the first few hours following application, the difference in emission rates during this period can lead to appreciable differences in total cumulative emission [*Fig. 2(b)*]. Cumulative emissions reported here are those measured over the measurement period, with no extrapolation for periods beyond 5–7 days.

Target application rates were not always achieved (Tables 2 and 3) and were considerably exceeded in some of the experiments. However, visual observations at the time of application confirmed that the machines performed satisfactorily even at high application rates; slurry did not overspill the injection slots for shallow injection application and remained in narrow bands beneath the herbage with the trailing shoe application. Composition of slurry between treatments, within each experiment, was generally consistent.

As the reduction achieved by an alternative application technique may be biased within individual comparisons, *e.g.* in some instances when there were exceptionally low losses from surface broadcast application, the data from each set of comparisons were pooled to derive a mean emission for each of the alternative application techniques which could be compared with that for surface broadcast application

**Table 2**
**Experimental details for grassland applications**

| *Expt.* | *Site* | *Appn. type** | *Month of appn.* | *Slurry* | | | | *Soil moisture status* | *Crop height, cm* | *Mean value for first 6 h after appn.* | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | *DM*†, % | *TAN*‡, % | *pH* | *Rate* $m^3\,ha^{-1}$ | | | *Temp.,* °*C* | *Rainfall, mm* |
| 1 | 1 | SB | Feb | 4·8 | 0·77 | 7·3 | 34 | Moist | 7·3 | 8·8 | 0 |
| | | SI | | 4·5 | 0·79 | 7·2 | 31 | | | | |
| 2 | 1 | SB | Mar | 6·4 | 1·2 | 6·9 | 23 | Moist | 9·8 | 9·6 | 0 |
| | | SI | | 9·2 | 1·3 | 7·1 | 30 | | | | |
| 3 | 1 | SB | Jun | 4·9 | 1·1 | 6·9 | 21 | Moist | 13·6 | 18·2 | 1·6 |
| | | SI | | 5·0 | 1·2 | 6·9 | 29 | | | | |
| 4 | 2 | SB | Jun | 4·1 | 1·2 | 6·8 | 31 | Moist | 11·5 | 16·0 | 0 |
| | | SI | | 4·4 | 0·8 | 6·8 | 28 | | | | |
| | | BS | | 4·9 | 1·1 | 6·9 | 45 | | | | |
| 5 | 2 | SB | Jul | 4·0 | 1·0 | 7·3 | 30 | Moist | 9·8 | 15·6 | 0 |
| | | SI | | 4·0 | 1·0 | 7·3 | 30 | | | | |
| 6 | 1 | SB | Jul | 4·2 | 1·0 | 7·2 | 23 | Dry | 10·9 | 14·2 | 0 |
| | | SI | | 3·7 | 1·0 | 7·2 | 27 | | | | |
| | | BS | | 3·2 | 1·1 | 7·2 | 24 | | | | |
| 7 | 1 | SB | Aug | 2·4 | 1·1 | 7·5 | 32 | Dry | 15·1 | 18·7 | 0 |
| | | SI | | 2·4 | 1·0 | 7·5 | 34 | | | | |
| 8 | 4 | SB | Feb | 4·8 | 1·5 | ND | 40 | Moist | ND | 7·5 | ND |
| | | TS | | 4·9 | 1·3 | ND | 40 | | | | |
| 9 | 3 | SB | Mar | 2·0 | 0·9 | ND | 27 | Moist | 11·3 | ND | 1·8 |
| | | TS | | 2·7 | 1·1 | ND | 27 | | | | |
| 10 | 5 | SB | Mar | 5·6 | 1·3 | ND | 32 | Moist | 12·2 | 17·2 | ND |
| | | TS | | ND | 1·6 | ND | 36 | | | | |
| 11 | 4 | SB | May | 1·2 | 0·62 | 7·6 | 25 | Dry | 10·0 | 14·5 | 0·2 |
| | | TS | | 1·1 | 0·62 | 7·5 | 36 | | | | |
| 12 | 2 | SB | Jun | 4·7 | 1·0 | 7·0 | 34 | Moist | 17·4 | 21·6 | 0 |
| | | TS | | 4·3 | 1·3 | 7·1 | 38 | | | | |
| 13 | 1 | SB | Jun | 4·6 | 1·2 | 7·1 | 31 | Dry | 18·9 | 18·1 | 0 |
| | | TS | | 5·1 | 1·2 | 7·0 | 50 | | | | |
| 14 | 3 | SB | Jun | 2·5 | 1·1 | 7·0 | 24 | Dry | 17·0 | ND | 1·2 |
| | | TS | | 2·4 | 1·1 | 7·0 | 36 | | | | |
| | | BS | | 2·5 | 1·1 | 7·1 | 33 | | | | |
| 15 | 4 | SB | Jul | 1·3 | 0·6 | 8·0 | 42 | Dry | 10·0 | 20·1 | ND |
| | | TS | | 5·1 | 1·5 | 7·5 | 32 | | | | |
| 16 | 1 | SB | Aug | 1·7 | 0·7 | 7·5 | 28 | Dry | 21·0 | 15·7 | 0 |
| | | TS | | 1·7 | 0·7 | 7·5 | 31 | | | | |
| 17 | 2 | SB | Sep | 1·3 | 0·8 | 7·9 | 42 | Dry | 17·6 | 16·1 | 0 |
| | | TS | | 1·8 | 0·8 | 7·9 | 42 | | | | |
| 18 | 2 | SB | Sep | 2·6 | 0·8 | 7·2 | 28 | Moist | 20·4 | 19·5 | 0 |
| | | TS | | 2·6 | 0·8 | 7·2 | 51 | | | | |
| 19 | 2 | SB | Oct | 1·4 | 0·7 | 7·4 | 34 | Moist | 20·0 | 10·6 | 0 |
| | | TS | | 1·2 | 0·8 | 7·5 | 42 | | | | |
| 20 | 1 | SB | Nov | 4·2 | 1·0 | 7·7 | 33 | Moist | 15·5 | 9·3 | 2·0 |
| | | TS | | 4·2 | 1·0 | 7·7 | 44 | | | | |
| 21 | 2 | SB | Oct | 3·5 | 1·1 | 7·2 | 45 | Moist | 19·4 | 16·0 | 2·4 |
| | | BS | | 3·9 | 1·2 | 7·4 | 40 | | | | |

*SB, surface broadcast; SI, shallow injection; TS, trailing shoe; BS, band spread.
†DM, dry matter content.
‡TAN, total ammoniacal-N content; ND, no data.

under the same conditions. Paired *t*-test analysis was used to compare the mean emission (% TAN applied) for each application technique with that for surface broadcast application for grassland and arable applications.

### 3.1. *Applications to grassland*

Significant reductions in $NH_3$ emission were achieved with shallow injection or trailing shoe application compared with surface broadcast application

**Table 3**
**Experimental details for arable land applications**

| *Expt.* | *Site* | *Appn. type** | *Month of appn.* | *Slurry* | | | | *Soil moisture status* | *Crop type and height, cm* | *Mean value for first 6 h after appn.* | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | *DM*†, *%* | *TAN*‡, *%* | *pH* | *Rate, $m^3\ ha^{-1}$* | | | *Temp., °C* | *Rainfall, mm* |
| 22 | 1 | SB | May | 4·8 | 1·3 | 7·4 | 32 | Moist | Spring barley (11·7) | 13·1 | 0·2 |
| | | TS | | 5·3 | 1·3 | 7·2 | 36 | | | | |
| 23 | 3 | SB | Sep | 3·2 | 1·1 | ND | 25 | Moist | Cereal stubble (8·4) | 15·5 | 8·8 |
| | | $SI_4$ | | 5·5 | 1·1 | ND | 25 | | | | |
| | | $SI_6$ | | 5·2 | 1·1 | ND | 32 | | | | |
| 24 | 3 | SB | Sep | 7·5 | 1·2 | 7·1 | 28 | Dry | Cereal stubble (15·4) | 9·0 | 0·8 |
| | | SI | | 7·3 | 1·0 | 7·0 | 43 | | | | |
| | | BS | | 7·4 | 1·0 | 7·0 | 51 | | | | |
| 25 | 6 | SB | Oct | ND | 0·9 | ND | 33 | Moist | Cereal stubble | ND | ND |
| | | SI | | ND | 0·9 | ND | 20 | | | | |
| 26 | 3 | SB | Dec | 1·8 | 0·9 | 7·3 | 41 | Moist | Cereal stubble (9·9) | 13·6 | 7·8 |
| | | $SI_4$ | | 1·7 | 0·8 | 7·1 | 44 | | | | |
| | | $SI_8$ | | 1·7 | 0·9 | 7·1 | 44 | | | | |
| 27 | 3 | SB | Dec | 2·9 | 0·7 | 7·1 | 45 | Moist | Cereal stubble (15·4) | 8·2 | 0·8 |
| | | SI | | 1·7 | 0·6 | 7·2 | 42 | | | | |
| | | BS | | 1·6 | 0·6 | 7·2 | 54 | | | | |

*SB, surface broadcast; SI, shallow injection (subscripts refer to depth of injection in cm); TS, trailing shoe; BS, band spread.
†DM, dry matter content.
‡TAN, total ammoniacal-N content; ND, no data.

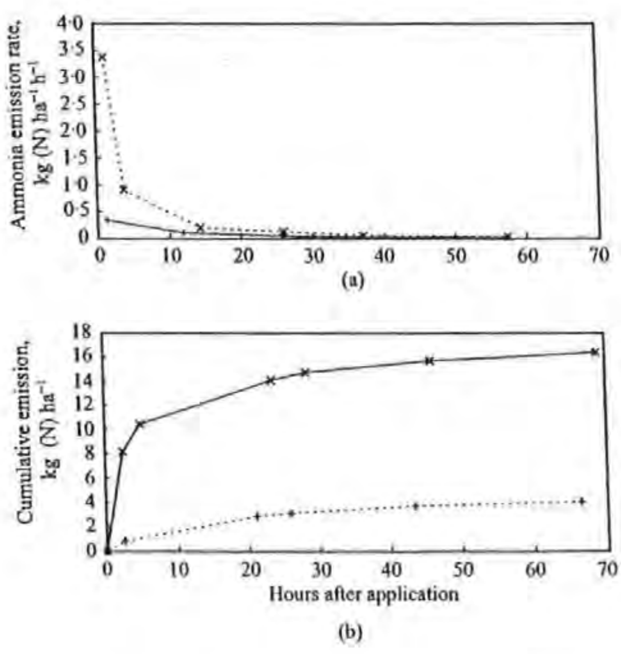


*Fig. 2. Typical curves for ammonia emission rate (a) and cumulative emission (b) following slurry application by surface broadcast (×) and shallow injection (+) (data from Experiment 1)*

(Table 4). There were only a few observations for band spreading and the mean reduction of 26% achieved was not significant (probability $P > 0{\cdot}05$), although this was based on only a few observations. Coefficients of variation for emission were large, reflecting the influence of a wide range of factors (which varied with application date) on both emission and efficiency of abatement by each technique. Mean emissions from surface broadcast

Table 4
**Mean $NH_3$ emission (% TAN applied) and reduction in emission, compared with surface broadcast, achieved by alternative application techniques on grassland**

| *Technique* | *No. of observations* | *Mean $NH_3$ emission, % [TAN]* | | *Reduction,%* | *Significance (P)* |
|---|---|---|---|---|---|
| | | *Surface broadcast* | *Reduced emission technique* | | |
| Shallow injection | 7 | 48 (41) | 13 (96) | 73 | 0·002 |
| Trailing shoe | 13 | 28 (68) | 12 (121) | 57 | <0·001 |
| Band spreading | 4 | 47 (64) | 35 (85) | 26 | 0·091 |

*Note*: (·) coefficient of variation %.

application were lower for the trailing shoe comparison experiments, possibly due to the length of the sward used in these experiments (10–31 cm); surface broadcast slurry may have infiltrated through the longer canopy where restricted air movements and lower temperatures are likely to have reduced volatilization.

Seven experiments were conducted in which comparisons were made between surface broadcast application and shallow injection on grassland. In all but two of the comparisons, reduction in emission with shallow injection was >70%. In Experiment 4, emission from surface broadcast application was low (19% applied TAN) so the relative reduction in emission achieved using shallow injection was less. Experiment 6 was conducted under dry soil conditions, which may have impeded soil penetration by the shallow injector, leading to a lower abatement efficiency. However, Experiment 7 was also conducted under dry soil conditions and on that occasion shallow injection was a very effective abatement technique, although the greater sward height may have further reduced emission following injection. Only two of the experiments were on clay soil but there was no suggestion that injection performance was affected by soil type.

Thirteen experiments were conducted in which comparisons were made between surface broadcast and trailing shoe application to grassland. Results were more variable than for shallow injection, with reductions in emission achieved within the comparisons ranging from 0 to 100%. In Experiment 8, where there was no apparent reduction in $NH_3$ emission with the trailing shoe, slurry was applied to grass which had previously been grazed very short by sheep and the slurry placed in bands by the trailing shoe flowed across the soil surface, with bands merging and providing a much larger surface area from which volatilization could occur. The application rate, in this case at $40\,m^3/ha^{-1}$, was significantly above the normally recommended operational range for this machine. Losses with trailing shoe application were very low in Experiments 16–20, the placement of slurry beneath a longer sward restricted flux to the atmosphere. In Experiments 17 and 19, emissions after trailing shoe application were below the limit of detection of the measurement technique being employed. In Experiment 18, emissions following both surface broadcast and trailing shoe application were low (7 and 6% of applied TAN, respectively), therefore giving an apparently poor abatement efficiency. An emission of 57% applied TAN after trailing shoe application in Experiment 14 was much greater than for the other experiments. This experiment was conducted on the regrowth following silage harvest of a newly sown ley and, although mean sward height was 17 cm, sward density (which was not measured) was low, therefore offering less protection from volatilization than a denser sward of the same height. Excluding this result from the dataset, there was a trend for decreasing emission with increasing sward height (probability $P = 0\cdot029$) with trailing shoe applications (*Fig. 3*).

Four experiments were conducted in which comparisons were made between surface broadcast application and band spreading, using the trailing shoe applicator to simulate band spreading by applying slurry with the tines lifted just above the top of the sward. Although the effect of slurry being delivered to the sward via trailing hoses may not have been exactly replicated, this method gave a comparison between the delivery of slurry beneath the canopy and that when there was coating of the herbage with narrow bands of slurry. Reductions in emission achieved in the individual comparisons were generally much lower than for shallow injection or trailing shoe application, ranging between 7 and 52%.

### 3.2. *Applications to arable land*

Fewer experiments were conducted on arable land. Mean reduction in emission achieved on arable land using shallow injection was much smaller and not significant ($P > 0\cdot05$); the mean reduction with band spreading was of a similar order to that for grassland applications, but not significantly different from the

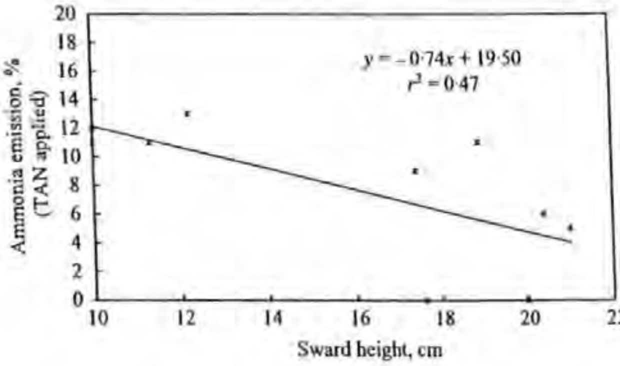


*Fig. 3. Relationship between sward height and ammonia loss following trailing shoe application of cattle slurry to grassland; $r^2$, coefficient of determination*

**Table 5**
**Mean $NH_3$ emission (% TAN applied) and reduction in emission, compared with surface broadcast, achieved by alternative application techniques on arable land**

| *Technique* | *No. of observations* | *Mean $NH_3$ emission, % [TAN]* | | *Reduction, %* | *Significance (P)* |
|---|---|---|---|---|---|
| | | *Surface broadcast* | *Reduced emission technique* | | |
| Shallow injection | 5 | 47 (66) | 36 (94) | 23 | 0·128 |
| Trailing shoe | 1 | 32 (–) | 20 (–) | 38 | — |
| Band spreading | 3 | 83 (9) | 61 (21) | 27 | 0·361 |

*Note*: (-) coefficient of variation %.

broadcast slurry ($P > 0.05$), again, there were few observations (Table 5).

Shallow injection to cereal stubble was evaluated in five comparisons, two of these involving injection to different depths. In three of the experiments, no effective reduction in emission was achieved with shallow injection. In Experiment 25, there was very heavy rainfall following application and $NH_3$ emissions were low from both surface broadcast and shallow injected slurry (to either 4 or 8 cm). However, in Experiments 24 and 26 there was appreciable emission from both surface broadcast and shallow injection but the reason for this was not clear. In only one experiment (Experiment 22) was the reduction in emission comparable to that achieved on grassland. The trailing shoe was used on one occasion to apply slurry to a growing spring cereal crop and a reasonable reduction in emission (38%) was achieved despite the relatively low ground cover provided by the crop. However, the 6 m application width of the trailing shoe machine meant that passes had to be made between the established tramlines, resulting in crop damage. This machine was therefore deemed unsuitable for application to growing cereals and no further comparisons were made. Band spreaders (trailing hose machines) have been specifically developed for applications to growing cereal crops, with boom widths compatable with tramline spacings, but no such machine was available to allow comparisons within this project. Two experiments were conducted with the trailing shoe to simulate band spreading applications to cereal stubble and these gave reductions in emission similar to those achieved on grassland.

## 4. Discussion

Results from this study have shown reductions in $NH_3$ emission following slurry applications to land using surface placement and injection techniques in comparison with surface broadcasting of 73, 57 and 26% for shallow injection, trailing shoe and band spreading, respectively, to grassland and 23, 38 and 27%, respectively, to arable land. Cumulative emissions were reported for a 5–7-days period. In practice, additional emission beyond this period would be minimal for slurries, although for solid manures (broiler litter in particular) emissions may continue for a significantly longer period (Chambers *et al.*, 1997). Results from recent, related research (Smith *et al.*, 2000), involving the same application techniques on a small-plot scale, suggested that there was little difference in the abatement efficiency of the three techniques, with reductions in emission of 39, 43 and 57% for band spreading, trailing shoe and shallow injection, respectively, as compared with surface broadcast application. The improved abatement efficiencies reported in the present paper for shallow injection and trailing shoe applications to grassland are probably due to the application techniques being used under more appropriate conditions than in the earlier studies (*i.e.* shallow injection used on moist soils and trailing shoe used when sward height > 10 cm) and using application rates which were closer to the design specifications of the machines.

The abatement efficiencies reported here are comparable with those reported in the Netherlands by Huijsmans *et al.* (1997) (*i.e.* reductions of 80% for open slot shallow injection and 69% for trailing shoe) and those reported in Germany by Lorenz and Steffens (1997) (*i.e.* reductions of 90, 70 and 30% for shallow injection, trailing shoe and band spreading, respectively). Lorenz and Steffens (1997) also reported a negative relationship between sward height and $NH_3$ emission for trailing shoe applications to grassland. Application rates used in both the Dutch and German studies were generally lower than those used in the present study, ranging between 7–50 $m^3$/ha. Previous work by Misselbrook *et al.* (1996) recorded reductions in emission of 40 and 79% following applications to grassland in March and June, respectively, by shallow injection compared with surface broadcast application. The range of abatement efficiencies quoted by various researchers suggests that performance of the reduced emission application techniques may be influenced by a number of factors, including machine configuration (there are various types of shallow injector or trailing shoe machine commercially available), slurry analysis, soil, weather and crop conditions, as well as by operational conditions such as application rate, machine set-up (*e.g.* angle of tines for trailing shoe machine) and operator skill. These areas warrant further investigation to enable optimal performance of reduced emission slurry application machinery.

Band spreading to growing cereal crops has been evaluated elsewhere in Europe as a means of reducing $NH_3$ emission with mixed results. Ferm *et al.* (1999) reported little difference in emission from pig slurry applied by band spreading or surface broadcast, whereas Dosch and Gutser (1996) reported a 40% reduction. Sommer *et al.* (1997) reported reductions of up to 80%, with greatest reductions achieved when applications were to a tall, dense crop. They measured no reduction when slurry was applied to 10 cm high crop with a leaf area index of only 0·3. Direct uptake of $NH_3$ by the plant leaves was estimated to account for up to 25% of the observed reduction in emission.

It is unclear why shallow injection appeared to be so ineffective as an abatement measure for applications to cereal stubbles, although the build-up, under some soil conditions, of stubble trash in front of the injection tines may have been a contributory factor. Little information exists on the use of shallow injection on arable land; Weslien *et al.* (1998) reported large reductions in emission with shallow injection to soil prior to cereal planting, with a mean emission of just 1·2% applied TAN. In the earlier, small-plot studies of Smith *et al.* (2000), a reduction in emission of almost 80% was achieved by shallow injection compared with surface broadcast on arable soils (assessments were generally on moist soils), which makes the disappointing results for the shallow injection on the arable soils in this project of greater concern.

Reducing $NH_3$ emission from slurry application to land may have the adverse effect of increasing subsequent denitrification and nitrous oxide ($N_2O$) emissions (Thompson *et al.*, 1987; Ellis *et al.*, 1998), although $N_2O$ emissions have not always been increased (Sommer & Sherlock, 1996; Dendooven *et al.*, 1998; Weslien *et al.*, 1998). Measurements of $N_2O$ emission and denitrification were made in some of the present experiments, and the interactions between these and $NH_3$ emissions will form the subject of a separate paper.

In addition to the efficiency of $NH_3$ emission abatement, the cost of the machines and the agronomic benefits need consideration, particularly as the evidence of the latter is both limited and unconvincing (Smith *et al.*, 2000).

## 5. Conclusions

1. Mean reductions in $NH_3$ emission achieved by applying cattle slurry by shallow injection, trailing shoe or band spreading on grassland, as compared with surface broadcast, were 73, 57 and 26%, respectively, of which the first two were statistically significant (probability $P > 0 \cdot 05$). Abatement efficiencies were less on arable land at 23, 38 and 27%, respectively, none of which were statistically significant (probability $P > 0 \cdot 05$).
2. Efficiencies of the application techniques for reducing emissions were variable, particularly for shallow injection on cereal stubble. Taken together with the results of other research, it is apparent that a range of ambient, soil and crop conditions, as well as operational factors, will influence the effectiveness of the emission abatement achieved using these techniques and would justify further research.
3. An economic evaluation of using the new application techniques, together with a detailed assessment of factors influencing any agronomic benefits, are areas which would benefit from further study.

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# Dietary manipulation as a means of decreasing N losses and methane emissions and improving herbage N uptake following application of pig slurry to grassland

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## SUMMARY

Slurry was collected from two groups of finishing pigs fed either a standard commercial diet (containing 205 g/kg crude protein (CP)) or a specially formulated lower CP content diet (140 g/kg CP). The slurries were surface applied to grass/clover plots on a freely draining soil in SW England in mid-March 1995 at three application rates: 25, 50 and 70 $m^3$/ha. Measurements were made from the 50 $m^3$/ha plots of ammonia volatilization, denitrification, nitrous oxide and methane emissions and nitrate leaching. Measurements of herbage yield and apparent N recovery (ANR) were made from all plots. Decreasing the CP content of the pigs' diet reduced N excretion by the pigs and also changed other characteristics of the slurry. Slurry from pigs fed the lower CP diet (the slurry referred to hereafter as LS) had a higher dry matter (DM) content, lower pH, lower total ammoniacal N (TAN), total N and VFA content with a similar total C content compared with slurry from pigs fed the standard commercial diet (the slurry hereafter referred to as CS). From the 50 $m^3$/ha treated plots, losses by ammonia volatilization represented 38 and 58% of the applied TAN and net losses through denitrification represented 5·3 and 12% of the applied TAN for LS and CS respectively. Nitrous oxide emission was similar from the two slurries, with net emissions of *c.* 0·5% of the applied TAN. Methane emission was significantly less from LS. No nitrate leaching was detected either in spring or in the following autumn. Yield and ANR increased with increasing slurry application rate up to 50 $m^3$/ha. The best % N recovery was from the 50 $m^3$/ha application rate with 58 and 47% of the applied TAN being recovered from LS- and CS-treated plots respectively. Changes in the slurry characteristics due to the lower CP diet resulted in lower losses to the environment and an improved utilization of the slurry N by the herbage.

## INTRODUCTION

Intensive pig production leads to the accumulation of large volumes of slurry, most of which is spread on land. Applying slurry to the soil can result in pollution through nitrate leaching, ammonia ($NH_3$) volatilization and emission of greenhouse gases such as nitrous oxide ($N_2O$) and methane ($CH_4$). The problem of nitrate pollution, in particular, from animal effluents has led to constraints on the amount of slurry nitrogen (N) that can be applied per hectare of land, thereby increasing the area required for slurry disposal. There are potential benefits, therefore, in decreasing the N content of slurry by decreasing N excretion by pigs.

Lenis (1989) suggested the better balancing of dietary protein as the best means of decreasing N excretion by pigs, but recognised the difficulty of formulating a diet in an economic way without the oversupply of certain amino acids. Some decrease is achievable by the use of different feedstuffs, as shown by Jondreville *et al.* (1993) substituting peas for wheat and soyabean meals. With improved knowledge of the amino acid requirements of pigs (Wang & Fuller 1989; Lenis *et al.* 1990), a greater decrease in N excretion can be achieved by decreasing the crude protein (CP) content of the diet and including synthetic amino acids to maintain a balance (Gatel & Grosjean 1992; Lee *et al.* 1993; Roth & Kirchgessner 1993).

Having established that N excretion by pigs can be decreased by decreasing dietary CP content, it is generally assumed that this will decrease subsequent N pollution (i.e. after slurry application to land), although little work has been done to confirm this. Decreasing the CP content of the diet may lead to

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other changes in slurry characteristics. Fremaut & Deschrijver (1991) reported an increase in excretal dry matter (DM) content and Hobbs *et al.* (1996) reported a decrease in the concentration of major odorants in the slurry. Changes in slurry characteristics other than N content may have an effect on the fate of N and may also have implications for methane emissions following slurry application to land.

The aims of this experiment were to investigate the effect of decreasing dietary CP content on the characteristics of pig slurry and to assess the effect of these changes on emissions, losses and utilization following application to grassland.

## MATERIALS AND METHODS

### *Site*

The experiment was conducted in 1995 on a freely draining, sandy loam (Crediton series) in SW England with an established grass/white clover sward. The field had been in grass since 1991, with a combination of silage harvests and sheep grazing, and cereal production prior to that. Clover was to have been sprayed out of the sward, but weather conditions precluded this. However, clover content of the sward was judged to be low (< 5% of the dry matter content of the sward) and uniform across all plots (although no objective assessments were made). Annual rainfall on the site was 1040 mm for 1995 (compared to an annual 30-year average of 1054 mm).

### *Experimental design*

Slurry was collected from two groups of finishing pigs (12 pigs per group) which were fed either a standard commercially available diet (the slurry hereafter referred to as CS) or a specially formulated lower crude protein diet (the slurry hereafter referred to as LS) in which synthetic amino acids were included to maintain the ideal ratios of essential amino acids. The CP content of the diets was 205 and 140 g/kg for the commercially available and lower CP diets, respectively. The pigs had been housed in slatted pens with individual slurry stores beneath each pen.

Slurries were stored at ambient temperature for 2 months and then surface-applied in mid-March to grass/white clover plots, using watering cans fitted with splash-plates. Slurry was applied at three rates: 25, 50 and 70 $m^3$/ha and a control treatment receiving no slurry or fertilizer N was included. Equal amounts of mineral P and K fertilizer were added to all plots to maintain recommended soil contents. Slurry samples were taken at the time of spreading and analysed for total solids, pH, total ammoniacal-N (TAN), total N, carbon (C) and volatile fatty acid ($C_2$–$C_5$) content. Measurements were made from the control and the 50 $m^3$/ha slurry treated plots of ammonia volatilization, denitrification, nitrous oxide and methane emissions and nitrate leaching. Measurements of herbage yield and N recovery were made from all treatments, on a separate area of the plot from that used for N loss and methane emission measurements.

Three replicate plots of each treatment were arranged in a randomized block design, with plots of 3 × 4 m for treatments with N loss, methane and herbage yield measurements and 3 × 2 m for treatments with herbage yield measurements only. Results were analysed using the analysis of variance procedure of GENSTAT (Lawes Agricultural Trust 1993).

### *Ammonia volatilization*

Ammonia volatilization was measured for 4 days following slurry application using a system of small wind tunnels (Lockyer 1984), each covering an area of 1 $m^2$, with windspeed through the tunnels set to 1 m/s. The concentration of ammonia in the air entering and leaving each wind tunnel was measured using absorption flasks containing orthophosphoric acid. The loss of ammonia from the area beneath the tunnel was calculated as the product of the volume of air which flowed through the tunnel and the difference between the concentrations of ammonia in the air entering and leaving the tunnel.

### *Denitrification*

Nitrogen losses due to denitrification were measured for 50 days following slurry application using a slight modification of the soil core incubation system with acetylene inhibition as described and evaluated by Ryden *et al.* (1987). Eight soil cores, each 3·3 cm diameter × 10 cm deep, were taken from each plot and placed in a 1 litre gas-tight jar; then 50 ml air was withdrawn from the jar prior to injecting 50 ml acetylene to give a 10% (v/v) concentration at atmospheric pressure. The jars were incubated in the field for 24 h, after which the concentration of $N_2O$ was measured using gas chromatography with an electron capture detector. The rate of denitrification was calculated from the concentration of $N_2O$ and the cross-sectional area of the soil cores. Losses between measurements were estimated by averaging rates of loss either side of a time period.

Following incubation and measurement of $N_2O$, the soil cores from each jar were analysed for mineral N content ($NH_4^+$-N and $NO_3^-$-N) by extraction with 2 M KCl followed by automated colorimetry.

### *Nitrous oxide and methane emissions*

$CH_4$ and $N_2O$ were measured for a period of 60 days following slurry application, using the static chamber technique (Mosier 1989). Steel boxes (20 × 15 × 50 cm) were pushed or lightly hammered into the soil to a depth of 2 cm. At each sampling period clear perspex lids were clamped to the boxes and left for 40 min, after which 20 $cm^3$ samples of gas were taken via the 'suba-seal' port in each lid and stored in evacuated glass storage vials. Ambient air samples were taken as the lids were clamped to the box and appropriate $N_2O$ and $CH_4$ standards were stored in a similar manner. After each sampling the lids were removed but the boxes remained *in situ*.

$N_2O$ and $CH_4$ were measured using gas chromatography. Rates of emission were expressed as µg $N_2O$-N/$m^2$ per h and cumulative losses were estimated by averaging rates of loss either side of a sampling point.

### *Nitrate leaching*

Measurements of nitrate leaching were made using methods similar to those described by Lord & Shepherd (1993), validated for freely draining soils by Webster *et al.* (1993), with porous ceramic cups placed at 50 cm depth in the soil at an angle of 30° to the vertical. Fine silica sand was introduced around the ceramic cup to ensure good contact between soil and cup, and a bentonite plug inserted around the top of the tube (just below the topsoil layer) to prevent the preferential flow of water down the tube. Samples were taken by applying a suction of 0·7 bar to the cups and removing any sample collected after 1–2 h. Drainage between sampling periods was estimated by subtracting potential evapotranspiration figures from rainfall. Cups were sampled at about every 30 mm drainage both in the spring period immediately following slurry application and in the autumn when drainage recommenced. The amount of nitrate-N leached over the period was then calculated as the product of the nitrate-N concentration and drainage volume (Lord & Shepherd 1993).

### *Herbage yields*

Three herbage cuts were taken during the season (10 May, 20 July and 31 October) using a Haldrup small-plot harvester. The harvester cut a 1·5 m strip from the centre of each plot for yield assessment. Subsamples were taken for dry matter (DM) determination by drying to constant weight at 85 °C and analysed for N content. Apparent N recovery (ANR) was calculated by subtracting the N removed in cut herbage on control plots from that on slurry-treated plots. %ANR was also calculated, as (ANR/TAN) × 100.

## RESULTS

### *Slurry characteristics*

Decreasing the CP content of the pig's diet resulted in a slurry with a higher DM content, lower pH, TAN, total N and VFA content and a similar total C content (Table 1). TAN content was 40% lower, although total N and VFA contents were only 20% lower.

### *Ammonia volatilization*

Ammonia volatilization was significantly less ($P <$ 0·05) from LS both in absolute terms and when expressed as a proportion of the TAN applied. During the 4 days following slurry application, 109 and 43 kgN/ha were lost from CS and LS respectively, representing 58 and 38% of the applied TAN.

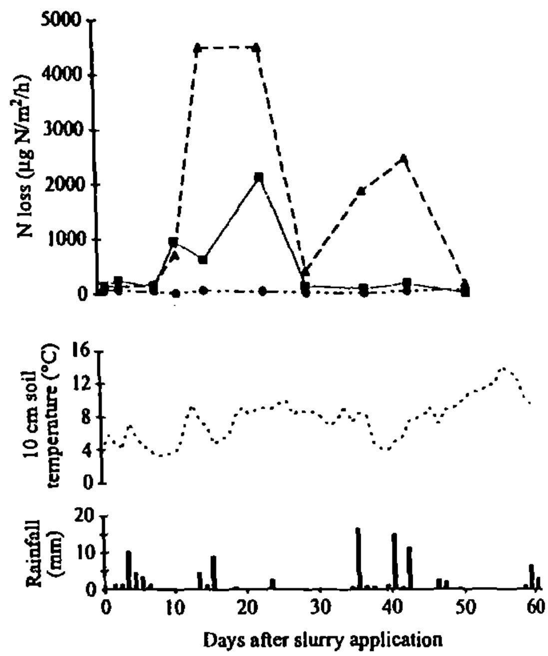


Fig. 1. Denitrification losses following application to grass/clover plots of slurries from pigs fed a standard commercial diet (--▲--), a lower crude protein diet (—■—) and from plots receiving no slurry or mineral N fertilizer (-···-●-···-).

Table 1. *Analyses of slurries from pigs fed standard commercial (CS) or lower crude protein (LS) diets*

| Slurry | % Dry matter | pH | Total ammoniacal N (mg/g) | Total N (mg/g) | Total C (mg/g) | Volatile fatty acids (mg/g) |
|---|---|---|---|---|---|---|
| CS | 3·9 | 7·8 | 3·78 | 5·56 | 27·3 | 8·86 |
| LS | 5·7 | 7·2 | 2·28 | 4·46 | 29·6 | 7·08 |

*Denitrification and nitrous oxide*

There were two peak events in denitrification activity over the first 50 days following slurry application, although the second peak was only evident for CS plots; both peaks were associated with increased rainfall (Fig. 1). There were significant differences ($P < 0.05$) in the net cumulative N loss via denitrification with losses of 22·6 and 6·0 kgN/ha from CS and LS plots respectively, representing 12·0 and 5·3% of the applied TAN.

$N_2O$ emissions followed a similar pattern to denitrification, with a large peak between days 10 and 25 and a smaller peak between days 30 and 50 (Fig. 2). Cumulative emission over the 60 days following slurry application was lower for LS plots, although there was no significant difference ($P > 0.05$) between treatments when expressed as% TAN applied, with losses of 0·5 and 0·6% from CS and LS respectively.

Nitrification of the TAN content of the slurries resulted in the soil concentrations declining over 40 days following slurry application (Fig. 3). $NO_3^-$-N concentrations in the soil increased after 15 days with higher concentrations on CS plots than LS plots, reflected in the higher rates of denitrification from CS.

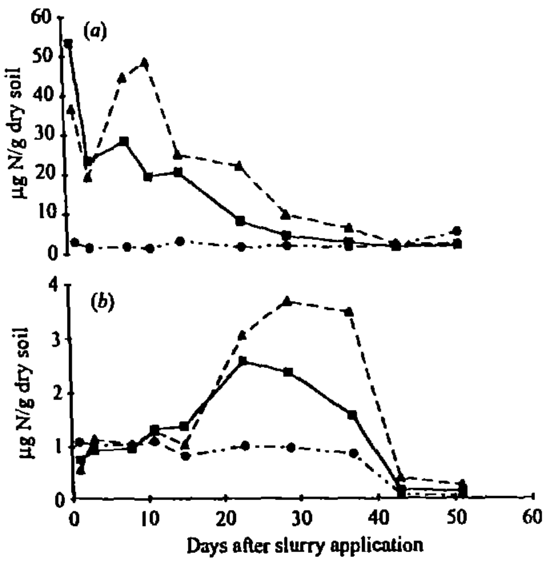


Fig. 3. (*a*) Soil ammonium-N and (*b*) nitrate-N contents following application to grass/clover plots of slurries from pigs fed a standard commercial diet (– –▲– –), a lower crude protein diet (—■—) and for plots receiving no slurry or mineral N fertilizer (– · · –●– · · –).

*Methane*

Methane emissions were short-lived following the slurry applications with $> 95\%$ of the emission occurring in the first 24 h. Emissions over the 60-day measurement period were significantly lower ($P < 0.05$) from LS than from CS. The net cumulative losses of $CH_4$-C from the LS and CS were 0·12 and 0·23 kg/ha respectively, representing 0·008 and 0·017% of the added C. The control plots acted as minor sinks for $CH_4$ over the experimental period.

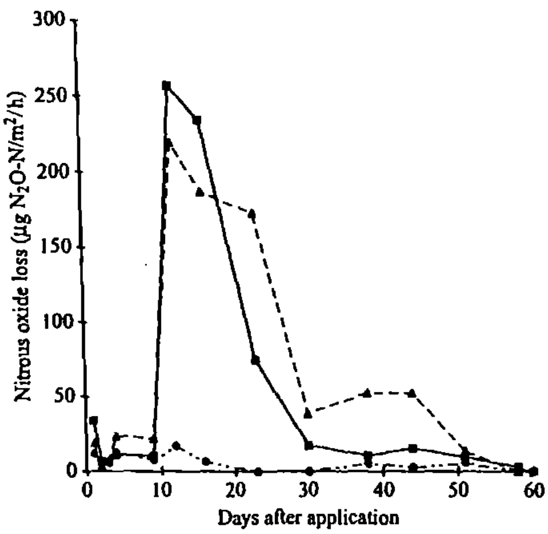


Fig. 2. Nitrous oxide emission following application to grass/clover plots of slurries from pigs fed a standard commercial diet (– –▲– –), a lower crude protein diet (—■—) and from plots receiving no slurry or mineral N fertilizer (– · · –●– · · –).

*Nitrate leaching*

There was minimal drainage in the weeks following slurry application and consequently little nitrate leaching. 140 mm drainage was recorded over the period from the return of field capacity in the autumn to the last sampling date (22 December 1995). There was no significant difference ($P > 0.05$) in N loss through nitrate leaching between slurry treatments and control, with a mean of 1·7 kg N/ha leached.

*Herbage yields and N recoveries*

The main herbage response was evident in the first cut following slurry applications (Table 2). The low DM yield of 2·11 t/ha from the control treatment implies that N fixation was low, due to the low clover content of the sward. There was no effect of slurry type on DM yield ($P > 0.05$), although yield increased with increasing slurry application rate ($P < 0.05$). Similarly, N offtake was unaffected by slurry type and increased with increasing slurry application rate from 25 to 50 $m^3$/ha. ANR was also unaffected by slurry type but, by taking account of the different TAN contents of the slurries and expressing ANR as%

Table 2. *Herbage yields and N offtakes for first herbage cut and total of three herbage cuts following application of slurries from pigs fed standard commercial (CS) or lower crude protein (LS) diets to grass/clover swards*

| Treatment | Slurry application (m³/ha) | Slurry ammonium N applied (kg/ha) | Dry matter yield (t/ha) 1st cut | Dry matter yield (t/ha) Total of 3 cuts | N offtake (kg/ha) 1st cut | N offtake (kg/ha) Total of 3 cuts |
|---|---|---|---|---|---|---|
| Control | 0 | 0 | 2·11 | 3·60 | 38·4 | 73·6 |
| CS | 25 | 95 | 3·36 | 5·03 | 65·4 | 106·4 |
| LS | 25 | 57 | 3·34 | 4·78 | 63·6 | 100·6 |
| CS | 50 | 189 | 3·79 | 6·54 | 105·0 | 163·0 |
| LS | 50 | 114 | 3·85 | 5·98 | 92·0 | 139·5 |
| CS | 70 | 265 | 3·94 | 6·13 | 94·3 | 143·7 |
| LS | 70 | 160 | 3·95 | 5·76 | 98·4 | 143·5 |
| S.E.* Slurry type (D.F.) | | | 0·150 (10) | 0·198 (10) | 4·83 (10) | 6·16 (9) |
| S.E.* Application rate (D.F.) | | | 0·183 (10) | 0·243 (10) | 5·92 (10) | 7·54 (9) |

* For slurry treatments only.

Table 3. *Apparent N recoveries (ANR) from first herbage cut and total of three herbage cuts following application of slurries from pigs fed standard commercial (CS) or lower crude protein (LS) diets to grass/clover swards*

| Slurry | Application rate (m³/ha) | ANR (kgN/ha) 1st cut | ANR (kgN/ha) Total of 3 cuts | ANR as % applied ammonium-N 1st cut | ANR as % applied ammonium-N Total of 3 cuts |
|---|---|---|---|---|---|
| CS | 25 | 27·0 | 32·8 | 28·5 | 34·8 |
| LS | 25 | 25·2 | 27·0 | 44·1 | 42·8 |
| CS | 50 | 66·6 | 89·4 | 35·2 | 47·3 |
| LS | 50 | 53·5 | 65·9 | 47·0 | 57·8 |
| CS | 70 | 55·9 | 70·1 | 21·1 | 26·5 |
| LS | 70 | 60·0 | 69·9 | 37·6 | 43·8 |
| S.E. Slurry type (D.F.) | | 4·83 (10) | 6·16 (9) | 3·60 (10) | 4·50 (9) |
| S.E. Application rate (D.F.) | | 5·92 (10) | 7·54 (9) | 4·41 (10) | 5·51 (9) |

TAN applied (%ANR), slurry type does have a significant effect ($P < 0·01$), with LS plots recovering 15% more of the applied TAN than CS plots when averaged across all application rates (Table 3).

Yields from second and third cuts were much smaller. Residual effects of the slurry applications were apparent in the second cut, with significant effects ($P < 0·05$) of both treatment and slurry application rate, CS plots having greater DM yields and ANR. There were no significant effects of treatment or slurry application rate in third cut DM yields or ANR ($P > 0·05$). The effects of the slurry treatments on the total DM yield and ANR over the season were therefore similar to those in the first cut, with no effect of slurry treatment on DM yield or ANR but a significantly greater %ANR (ANR expressed as % TAN applied) from LS-treated plots. The best %ANR was at the 50 m³/ha application rate, where ANR was 47 and 58% of the applied TAN, or 32 and 30% of the applied total N for CS- and LS-treated plots respectively.

## DISCUSSION

Decreasing N excretion from pigs by reducing the CP content of the diet has been established previously. Hobbs *et al.* (1996) showed reductions of 37 and 40% in N excretion and 44 and 13% in VFA content of the slurry from diets in which the CP content had been decreased by 26 and 31%, respectively. Simmins *et al.* (1996) demonstrated a 32% decrease in N excretion by feeding a diet containing 130 g/kg CP decreased from 160 g/kg, with no significant effect on pig performance and Fremaut & Deschrijver (1991) achieved a 39% decrease in N excretion by decreasing dietary CP content from 185 to 129 g/kg. There was no significant effect of diet on the performance of the pigs used in our experiment, with similar growth rates being achieved, although pigs on the lower CP diet did have a greater backfat depth (Kay & Lee 1996). The 20% decrease in total N content of the slurry in our experiment was lower than these quoted values (although decrease in TAN content was 40%). The slurry N concentrations may not be directly comparable, however, as different volumes of slurry were produced by the two groups of pigs. Total slurry volumes were less from the pigs fed the reduced CP diet, largely due to a lower water intake and urination (R. M. Kay, personal communication), as reflected in the higher DM content. Fremaut & Deschrijver (1991) reported a 21% lower water intake and an increase in DM content of excreta (faeces and urine collected in metabolism crates) from 11·7 to 17·1% for pigs fed a lower CP diet. Thus, in terms of N excretion by the pigs, the differences between the groups would have been greater than the observed differences between the slurries, and more comparable with quoted values. As most of the TAN content is derived from urine, it would appear that decreasing the CP content of the diet was more effective at decreasing urine N than faecal N.

Slurry pH is largely determined by the relative concentrations of VFA and TAN and increases as the VFA:TAN ratio decreases (Paul & Beauchamp 1989*a*). Both VFA and TAN content were lower in LS than CS (Table 1), but TAN had decreased by a greater amount, thus the VFA:TAN ratio had increased with a resultant decrease in pH from 7·8 to 7·2. As VFAs in slurry are largely degradation products of lipids and carbohydrates, a diet with lower CP content, while decreasing TAN content, would not necessarily decrease slurry VFA content.

Substantial losses of N can occur via $NH_3$ volatilization following slurry application to grassland, typically between 15 and 75% of the applied TAN being lost (Pain *et al.* 1989; Klarenbeek & Bruins 1991; Moal *et al.* 1995), depending on factors such as environmental conditions and soil and slurry characteristics. As the slurries were applied at the same time on the same site, differences in $NH_3$ volatilization must have been due to differences in the slurry characteristics. Correlations have been found previously between slurry DM content and $NH_3$ volatilization (Sommer & Olesen 1991; Moal *et al.* 1995), so we might have expected a greater loss from LS with the higher DM content. It would appear that the difference in slurry DM content was not such an important factor in this case as other factors, such as slurry pH. It has been previously demonstrated that lowering slurry pH to a value of 5·5 will decrease $NH_3$ volatilization by up to 85% (Stevens *et al.* 1989; Frost *et al.* 1990; Pain *et al.* 1994). Martinez *et al.* (1996) achieved a 37% decrease in volatilization from pig slurry by lowering pH from 7·8 to 7·0, evidence that even a small decrease in pH, such as in our experiment, can give a substantial decrease in volatilization.

Rate of denitrification increased after periods of rainfall, presumably as the number of water-filled pore spaces, and the anaerobicity, of the soil increased (Aulakh *et al.* 1992). As plant uptake of nitrate increased with increasing soil temperature, and soil became drier, denitrification became minimal. The C:N ratios of the slurries were different, with ratios of 4·9 and 6·6 for CS and LS respectively. This was not reflected in a proportionally greater denitrification loss from LS-treated plots as may have been expected with the increased addition of C (Thompson 1989), although it has been suggested that under grassland soils, with high root density and therefore a good supply of exudate and decomposing root material, denitrification is unlikely to be limited by organic matter (Clark & Paul 1970; McGill *et al.* 1981). Other workers (Beauchamp *et al.* 1989; Paul & Beauchamp 1989*b*) found that denitrification was influenced by readily available C in the form of VFAs. This may account for the lower denitrification losses from LS, as, although LS had a higher total C content, the VFA content was lower than CS.

While there were significant differences in denitrification rates, $N_2O$ emissions were similar from both treatments. Although two different methods were used to determine these fluxes, it would appear that the differences were due to $N_2$ emissions. Weier *et al.* (1993) showed that the addition of available C increased denitrification and also increased the ratio of $N_2$:$N_2O$ produced. The higher VFA content of CS therefore appears to have favoured the production of $N_2$ rather than $N_2O$ as the product of denitrification. This is possibly due to the increased microbial respiration from the additional available C, reducing the oxygen content of the soil atmosphere, thus favouring production of $N_2$ rather than $N_2O$, as proposed by Comfort *et al.* (1990).

It would appear that $CH_4$ emission was better related to VFA content than to total C content. The 50% reduction in $CH_4$ emission from the LS plots was probably a result of the reduced VFA content of the LS. As with $NH_3$ volatilization losses, we may have expected lower $CH_4$ emission from CS due to the lower slurry DM content, enabling the slurry to infiltrate into the soil more rapidly and be more susceptible to the action of methanotrophs (Chadwick & Pain 1997). Again, however, the differences in DM content did not appear to be as important as other factors – VFA content in this case.

The lack of any nitrate leaching in either the spring or autumn drainage periods implies that March applications of pig slurry to grassland may not pose a significant leaching risk, although measurements were

Table 4. *N sinks (kgN/ha) following application of slurries from pigs fed standard commercial (CS) or lower crude protein (LS) diets to grass/clover swards at 50 m³/ha*

| Slurry | Slurry ammonium-N applied | Ammonia volatilization | Denitrification | Leaching | (Remaining TAN)* | Herbage N | Total† |
|---|---|---|---|---|---|---|---|
| CS | 189 | 109 | 23 | 0 | (57) | 89 | 221 |
| LS | 114 | 43 | 6 | 0 | (65) | 66 | 115 |

* Total ammoniacal-N (TAN) remaining for herbage growth after subtracting ammonia volatilization, denitrification and leaching losses from TAN applied.
† Total of applied ammonium-N accounted for by ammonia volatilization, denitrification, leaching and herbage N.

not continued through the entire winter period to confirm this. Other studies have also shown that nitrate leaching is much lower from late winter applications than autumn applications (Froment *et al.* 1992; Misselbrook *et al.* 1996). Leaching losses are influenced by the mineral N content of the soil at the end of the summer (Steenvoorden 1989) and the low DM yields and N offtakes from the second and third herbage cuts in this experiment indicate that relatively little mineral N remained in the soil. It is unlikely that any significant mineralization of residual organic N would have occurred after the third herbage cut in October until the following spring.

Utilization of slurry N on grassland can vary greatly, but ANR in herbage in the year of application is usually < 35% total N applied (Pain *et al.* 1986; Unwin *et al.* 1986), as found in this experiment. Generally only a small proportion of slurry organic N becomes available for crop growth during the first season, so comparisons are better made on the available N (TAN) content. N recoveries of 47 and 50% applied TAN in the herbage from CS- and LS-treated plots respectively are comparable with recoveries of 79 and 49% applied TAN given by Laws (1996) following surface application of cattle slurry in March to grass/clover plots on a similar site for 1993 and 1994 respectively. The lack of any further yield response from the 50–70 m³/ha slurry applications for both slurry treatments was probably due to the negative effects of high slurry application rates, such as smothering and scorching (Smith *et al.* 1995), offsetting any benefits of the additional N available for herbage growth.

The greater losses from CS-treated plots (via $NH_3$ volatilization and denitrification) resulted in yields and N recoveries not significantly different from those from the LS-treated plots, despite the 40% reduction in TAN applied to the LS plots. TAN remaining for herbage growth after subtracting $NH_3$ volatilization and denitrification losses from the applied TAN were, in fact, very similar for the two slurries (Table 4), although this takes no account of N immobilization or mineralization. Clover content of the sward was not assessed (although estimated to be low, borne out by the low DM yield from the zero N treatment) and an assumption was made in the calculation of ANR that N fixation was equal on all plots. However, it has been shown that mineral N and slurry N applications decrease the clover content of grass/clover swards (although slurry N apparently to a lesser extent) (Nesheim *et al.* 1990) giving poorer yield responses to applied N on grass/clover than grass only swards.

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## 2.10 Paper 10

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# Dietary Manipulation in Dairy Cattle: Laboratory Experiments to Assess the Influence on Ammonia Emissions

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## ABSTRACT

Improvements to the efficiency of dietary nitrogen use by lactating dairy cattle can be made by altering the concentration and form of protein in the diet. This study collected urine and feces from dairy cows from selected crude protein (CP) treatments of 2 lactation studies. In the first trial, collections were made from cattle fed a diet with high (19.4%) or low (13.6%) CP content (HCP and LCP, respectively). In the second trial, collections were made from cattle fed diets in which the forage legume component was alfalfa (ALF) or birdsfoot trefoil with a low (BFTL) or high (BFTH) concentration of condensed tannins (CT). A system of small laboratory chambers was used to measure $NH_3$ emissions over 48 h from applications of equal quantities of urine and feces to cement (simulating a barn floor) and from applications of slurries, made by combining feces and urine in the proportions in which they were excreted for each treatment, to soil. Reducing dietary CP content resulted in less total N excretion and a smaller proportion of the excreted N being present in urine; urine N concentration was 90% greater for HCP than LCP. Surprisingly, $NH_3$ emissions from the barn floor were similar in absolute terms despite the great differences in urine urea-N concentrations, presumably because urease activity was limiting. Cumulative emissions from fresh slurries applied to soil represented 18% of applied N for both HCP and LCP. Following storage at 20°C for 2 wk, cumulative emissions from LCP were much lower than for HCP, representing 9 and 25% of applied N, respectively. Emissions were also lower when expressed as a proportion of slurry total ammoniacal N (TAN) content (24 and 31%, respectively) because of treatment differences in slurry pH. Increasing CT content of the dietary forage legume component resulted in a shift in N excretion from urine to feces. Cumulative $NH_3$ emissions from the barn floor were greater for ALF than for BFTL or BFTH. Emissions from fresh and stored slurries were in proportion to slurry TAN contents, with approximately 35% of applied TAN being lost for all treatments. Emissions expressed as a proportion of total N applied were consistently lower for BFTH than for ALF.

(**Key words:** dietary manipulation, crude protein, tannin, ammonia emission)

**Abbreviation key:** **ALF** = alfalfa, **BFTH** = birdsfoot trefoil with high tannin concentration, **BFTL** = birdsfoot trefoil with low tannin concentration, **CT** = condensed tannins, **HCP** = high CP diet, **LCP** = low CP diet, **TAN** = total ammoniacal N.

## INTRODUCTION

Dairy cows use feed N much more efficiently than many other livestock, but they excrete 3 times more N in manure than in milk. An average cow producing 8200 kg of milk annually excretes 21,000 kg of manure containing about 110 kg of N (van Horn et al., 1996), with approximately equal proportions excreted in feces and urine. The majority of urinary N (depending on diet and animal condition) is in the form of urea, which is hydrolyzed by fecal urease to $NH_3$. About 25% of dairy manure N is lost as $NH_3$ under current US practices (Pinder et al., 2004), contributing to the total annual $NH_3$ redeposition rates in the Upper Midwest of 23 to 40 kg of N/ha (Burkart and James, 1999). Environmental and potential human health impacts occur both from the relatively local redeposition of $NH_3$ and from aerosols that travel greater distances (Dockery et al., 1993; Davidson and Mosier, 2004).

Ammonia losses begin directly after urine deposition in the dairy barn and continue throughout manure handling, storage, and land application. Most efforts to reduce nutrient loss from dairy operations have focused on improved methods for land application of manure, where a large impact can be made at relatively low cost (Misselbrook et al., 1996; Smith et al., 2000; Huijsmans et al., 2001; Misselbrook et al., 2002; Thompson and Meisinger, 2002). However, reducing N excretion through dietary manipulation represents another opportunity where large impacts could be made, as subse-

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quent losses would be reduced throughout the manure management continuum, particularly if combined with other abatement strategies (e.g., at manure application).

A number of dietary studies have shown that reducing the CP content of the diet, above that needed to meet requirements, leads to better efficiency of N use i.e., a higher proportion of N intake is secreted in milk N and a lesser proportion excreted in urine and feces (Krober et al., 2000; Kulling et al., 2001; Broderick, 2003). Reducing urinary N excretion should lead to reductions in subsequent $NH_3$ emissions. Kebreab et al. (2002) presented a model of N metabolism for a lactating dairy cow that predicted significant reductions in $NH_3$ emissions (based on modeled urea-N outputs) from cattle associated with reducing CP content or increasing energy content of the diet. A number of studies using laboratory chamber systems measuring $NH_3$ emissions from slurries (mixtures of urine and feces) have shown reductions in $NH_3$ emission associated with lower CP content of the diet (Paul et al., 1998; James et al., 1999; Kulling et al., 2001; Frank and Swensson, 2002), as might be expected. However, Paul et al. (1998), working with dairy cattle, and Misselbrook et al. (1998), working with pigs, showed that diet might influence other manure characteristics, such as pH, thereby influencing the proportion of N that is lost as $NH_3$.

Brito and Broderick (2003) found that an equal mix of forage from alfalfa silage with corn silage in lactating dairy cows' diet gave the greatest improvement in N efficiency, without loss of yield of milk, fat, and protein, compared with diets dominated by either one of these forages. Beyond the improvements seen with proper mixes of alfalfa and corn silage, the feeding value of perennial forages is enhanced by condensed tannins (CT) and polyphenols, which are lacking in most feeds used in the United States. Modest amounts of CT (2 to 4% of DM), as is found in birdsfoot trefoil (*Lotus corniculatus*), reduce protein breakdown during ensiling and rumen fermentation by up to 50% (Albrecht and Muck, 1991; Broderick and Albrecht, 1997). Studies with sheep indicate that modest concentrations of tannin permit extensive protein digestion in the abomasum and small intestine, and greater subsequent absorption of amino acids, without adversely affecting feed consumption or digestion (Min et al., 2003). In a New Zealand study, tannins in birdsfoot trefoil increased milk production of nonsupplemented Holstein cows by 2.7 kg/d (Woodward et al., 1999). In addition to enhancing protein use by ruminants, experiments with forage and browse in Africa suggest that tannins and polyphenols shift N excretion from urine to feces and from soluble to insoluble N forms in feces (Powell et al., 1994).

Two recent trials were conducted to assess the influence of dietary protein concentration (manipulating the CP content of the diet) or protein form (different concentrations of CT in the forage legume component of the diet) on the performance of lactating dairy cows. Details of these studies are reported elsewhere (Olmos Colmenero and Broderick, 2003, 2004; Hymes-Fecht et al., 2004). Briefly, Olmos Colmenero and Broderick (2003) showed that poorer N use was associated with diets higher in CP, with no significant increase in milk yield for an increase in dietary CP content from 15 to 19%. Hymes-Fecht et al. (2004) suggested that improved use of CP in the forage legume component of the diet was associated with an increased concentration of CT in the silage. The objectives of the present study were to assess (using urine and feces from the above trials and a system of laboratory chambers) the influence of manipulating dairy cattle dietary protein concentration and form on $NH_3$ emissions from urine and fecal deposits to a concrete floor and from fresh and stored slurries applied to soil.

## MATERIALS AND METHODS

### Dietary Treatments

Urine and feces were collected from lactating Holstein cows housed in a tie-stall system, from 2 dietary trials varying either in dietary protein concentration or protein form. Urine and feces collections were made from a randomly selected subgroup of the cows on each diet after completion of the lactation trials, with each subgroup continuing to be fed the treatment diet until the completion of urine and feces collection.

In the first trial, cattle were fed diets with high (19%) or low (14%) CP content (treatments **HCP** and **LCP**, respectively) with 2 cows per dietary treatment. In the second trial, cows were fed diets of similar composition, with the exception of the forage legume component, which was alfalfa (**ALF**; *Medicago sativa*), or birdsfoot trefoil with low tannin (~2% of the forage, 1% of the total diet on a DM basis, **BFTL**), or high tannin (~7% of the forage, 3.5% of the total diet on a DM basis, **BFTH**) content, with 3 cows per diet. Details of the diets for both trials are given in Table 1. Total feces and urine were collected separately from the cows while in the tie stalls (i.e., excluding periods when the cows were being milked) over a period of 60 to 100 h. Feces were scraped by hand from metal catchment containers fitted into the tie-stall gutters; urine was collected via indwelling catheter tubes draining into plastic containers embedded in ice. Volume of urine and mass of feces were recorded on an individual cow basis and subsamples of material were retained for total N analyses. Composite fecal and urine samples for each dietary

**Table 1.** Composition of the diets used in the dietary protein concentration and protein form manipulation trials for lactating dairy cattle from which urine and feces samples were collected.

| | Dietary protein concentration trial | | Dietary protein form trial | | |
|---|---|---|---|---|---|
| Ingredient[1] | Low CP | High CP | Alfalfa | BFT,[2] low tannin | BFT, high tannin |
| Alfalfa silage | 25 | 25 | 50 | | |
| BFT, low tannin | | | | 50 | |
| BFT, high tannin | | | | | 50 |
| Corn silage | 25 | 25 | 10 | 10 | 10 |
| Rolled high-moisture shelled corn | 44.0 | 30.4 | 34.6 | 33.5 | 33.5 |
| Roasted soybeans | 2.5 | 2.5 | | | |
| Solvent-extracted soybean meal | 2.4 | 16.0 | 4.7 | 5.8 | 5.8 |
| Sodium bicarbonate | 0.6 | 0.6 | 0.3 | 0.3 | 0.3 |
| Salt | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 |
| Dicalcium phosphate | 0.2 | 0.2 | 0.1 | 0.1 | 0.1 |
| Vitamin and minerals | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 |
| Chemical composition of TMR | | | | | |
| DM, % | 53.8 | 55.0 | 45.0 | 45.1 | 43.2 |
| N, % | 2.2 | 3.1 | 2.7 | 2.5 | 2.6 |
| CP, % | 13.6 | 19.4 | 17.1 | 15.8 | 16.4 |
| NDF, % | 26.2 | 26.2 | 26.1 | 26.0 | 26.3 |

[1]Percentage on a DM basis.
[2]BFT = Birdsfoot trefoil.

treatment were frozen after collection until required for the laboratory trials.

## Laboratory Chambers for Ammonia Emission Measurement

The laboratory set-up consisted of 6 chambers in which the manure was exposed to a constant airflow (Figure 1), similar to the system described by Chadwick et al. (2001). Air was drawn through the system by means of a vacuum pump, with the airflow rate through each chamber being controlled at 4 L/min. An acid trap (containing 0.075 L of 0.02 *M* orthophosphoric acid) before each chamber removed $NH_3$ from inlet air and a second acid trap on the outlet side of each chamber collected any $NH_3$ emitted during the measurement period. Glass or fluorinated ethylene propylene (FEP) tubing was used between the chamber and outlet acid trap to minimize adsorption of $NH_3$ to tubing walls. The set-up was housed in a large incubator such that all experiments were conducted at a constant temperature (15°C).

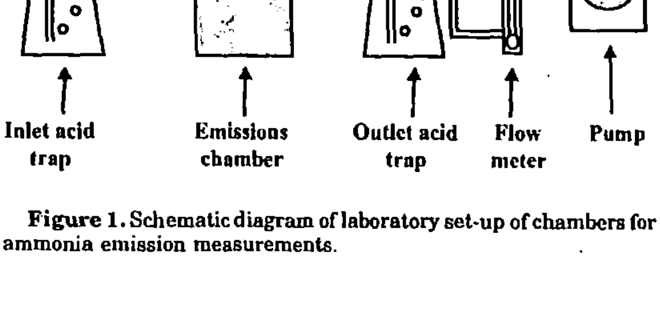


**Figure 1.** Schematic diagram of laboratory set-up of chambers for ammonia emission measurements.

The chambers were constructed from plastic drainage pipe of 10 cm diameter and 19 cm height. An end-cap was glued to the base of the chamber and a lid fitted to the top, with silicone grease used to ensure an air-tight seal. The internal surfaces of the lid were sprayed with Teflon coating to minimize adsorption of $NH_3$. Each chamber lid had 4 horizontally positioned inlet and outlet ports to ensure good mixing of air within the chamber. The main body of the chamber was filled with cement (to simulate a barn floor) or soil, leaving a head-space of approximately 0.35 L. The flow rate through the chamber (4 L/min) ensured that the number of head-space changes per minute was such that the emission rate would not be greatly influenced by small differences in flow rates between chambers (Kissel et al., 1977).

Tests were conducted to assess the quantitative recovery of $NH_3$ emitted from a solution within the chamber by the acid traps. Two acid traps were connected in series on the chamber outlets to determine whether a single acid trap was sufficient to trap all $NH_3$ in outflow air. Recovery tests were performed by placing a shallow Petri dish containing 0.02 L of ammonium sulfate solution (2 g/L of N) in each chamber. The solution pH was raised by adding 1 mL of sodium carbonate/sodium bicarbonate mixture (1 *M*) through a port in the chamber lid, to promote $NH_3$ volatilization. The system was run with airflow of 4 L/min for a 4-h period. To stop volatilization, 1 mL of 2 *M* sulfuric acid was added to the solution in the chamber via the port in the chamber lid. Samples of the initial and final solutions in the Petri dishes within each chamber and the solutions in the outlet acid traps were analyzed for ammonium-N by automated colorimetry (Searle, 1984).

### Emissions from Simulated Deposits to Barn Floor

Deposits of urine and feces to a barn floor would normally be scraped, leaving a thin layer from which emission occurs. In the simulation experiments, therefore, a constant mass of feces (8 g) and volume of urine (8 mL) were applied to the chambers to achieve a thin emitting layer of approximately 1 mm above the cement surface [similar to the methodology used by Elzing and Monteny (1997)]. Immediately after adding the urine, the chamber lid was closed and sealed with silicon grease, and the airflow through the system started. Acid traps were changed after 1, 3, 6, 12, 24, and 36 h, and measurement was stopped at 48 h. At the end of each sampling period, acid from the outlet acid traps was made up to 0.1 L with deionized water and then analyzed for ammonium-N using automated colorimetry (Searle, 1984). Three replicate chambers were used for each of the selected dietary treatments. Samples of feces and urine were retained for chemical analyses.

Ammonia emission rates (*F*, mg of N/m$^2$ per h) for each sampling period were calculated as:

$$F = \frac{XV}{At} \qquad [1]$$

where *X* is ammoniacal-N concentration of the acid trap solution (mg/L), *V* is the volume of acid trap solution (L), *A* is the exposed surface area of the chamber (m$^2$), and *t* is the duration of the sampling period (h). The total emission for the period (mg of N) is calculated as *XV*, and total emission for the duration of the experiment (48 h) is derived by summing emissions for each sampling period. Total emission was expressed as a proportion of the total N, urine N, or urea N applied to each chamber.

### Emissions from Slurry Applied to Soil

For simulated emissions from land applications, the urine and feces from each selected treatment were mixed in the proportions in which they were excreted to produce slurries, which were then standardized at 7% DM content by the addition of water. Two experiments were conducted in which $NH_3$ emission measurements were made from fresh (stored for 24 h at 4°C) or stored (2 wk at ambient temperature, mean 20°C) slurries applied to soil in the laboratory chambers. The chambers were packed with a sieved (to 2 mm) silt loam soil of the Plano series (Munoz et al., 2003) at a bulk density of 1.2 g/cm$^3$, leaving 0.35 L of headspace. Water was added to the soil to achieve 60% water-filled pore space. Following addition of water, the chambers were left for 24 h at 15°C to equilibrate before slurry application.

Slurry was applied to the soil at a standard rate of 40 mL to each chamber, equivalent to a field application rate of 50 m$^3$/ha. Lids were replaced and measurements commenced immediately after slurry application to each chamber. Measurement continued for 48 h, with acid traps being replaced after 1, 3, 6, 12, 24, and 36 h. Emission rates for each period and cumulative emissions were calculated as described above. Three replicate chambers were used for each of the slurry treatments. Samples of slurry were retained for chemical analyses.

### Chemical Analyses

Samples of feces used in the barn-floor simulation studies were analyzed in triplicate for DM content, pH, total N, total ammoniacal N (TAN), and undigested feed N content. Dry matter content was determined by drying in an oven to constant weight at 100°C. The pH of a water/feces mixture (2:1 ratio) was measured using a calibrated portable pH meter (Accumet AP61, Fisher Scientific, Pittsburgh, PA). Acidified samples of feces were freeze-dried and ground for total N determination by combustion assay (Leco FP-2000 nitrogen analyzer, Leco, St. Joseph, MI). Total ammoniacal N content was determined by automated colorimetry (Searle, 1984) following KCl extraction (5 g of feces in 50 mL of 2 *M* KCl, shaken for 2 h and filtered through Whatman no. 42 filter; Fisher Scientific). Cell wall components of feces were determined using the detergent system (Goering and van Soest, 1970) as NDF, and the N content of the NDF was determined by combustion assay (Leco FP-2000 nitrogen analyzer).

Samples of urine used in the barn-floor simulation studies were analyzed in triplicate for pH, total N, TAN, and urea N content. Following pH determination, samples were acidified (60 mL of 0.07 *N* $H_2SO_4$ and 15 mL of urine) before subsequent analyses. Total N was measured by combustion assay (Elementar Vario MAX CN analyzer, Elementar, Hanan, Germany), with 200 mg of sucrose being added to the 2.5-mL urine sample

Table 2. Proportion of N excretion in urine and feces as influenced by dietary protein concentration or form in lactating dairy cattle. Values are the mean for the 2 (protein concentration trial) or 3 (protein form trial) cows on each diet.

| | Dietary protein concentration trial | | Dietary protein form trial | | |
|---|---|---|---|---|---|
| | Low CP | High CP | Alfalfa | BFT,[1] low tannin | BFT, high tannin |
| Urine [total N], g/L | 4.5[b] | 8.5[a] | 7.5[b] | 8.8[a] | 6.7[b] |
| Feces [total N], g/kg of DM | 20.6 | 24.4 | 26.7 | 29.5 | 33.1 |
| Urine volume,[2] L/h | 1.09 | 1.05 | 0.93 | 1.09 | 1.07 |
| Feces volume,[2] kg of DM/h | 0.21 | 0.17 | 0.20 | 0.21 | 0.30 |
| Relative proportion of total N in | | | | | |
| Urine, % | 52[b] | 68[a] | 55[a] | 60[a] | 40[b] |
| Feces, % | 48[a] | 32[b] | 45[b] | 40[b] | 60[a] |

[a,b]Within each trial, values with different superscripts are significantly different ($P < 0.05$).

[1]BFT = Birdsfoot trefoil.

[2]Based on total amount collected per cow over the 60- to 100-h collection period, which excluded times when cows were being milked.

to aid combustion. Total ammoniacal N was measured following KCl extraction, as for the fecal samples. Urea N was determined using an automated colorimetric assay (Broderick and Clayton, 1997) adapted to a flow-injection analyzer.

Slurry samples were analyzed in triplicate for DM content, pH, total N, and TAN content, using the same procedures as for the fecal samples.

### Statistical Analyses

For each of the individual chamber measurements, a Michaelis-Menten type curve was fitted to the cumulative $NH_3$ loss with time, as used by Sommer and Ersboll (1994):

$$N(t) = N_{max} \frac{t}{t + K_m} \qquad [2]$$

where $N(t)$ (kg of N per ha) is the cumulative loss at time $t$ (h), and $N_{max}$ (kg of N per ha) and $K_m$ (h) are model parameters representing total loss as time approaches infinity and time at which loss reaches one-half of maximum, respectively. For each manure application, the parameters $N_{max}$ and $K_m$ were derived using the model-fitting procedure in GENSTAT (Lawes Agricultural Trust, 1993). Mean cumulative losses after 6, 12, 24, and 48 h and $N_{max}$ for the simulated barn floor trials and 6, 24, and 48 h and $N_{max}$ for the slurry to soil trials were compared between treatments (within the protein concentration or protein form trial) using the 1-way ANOVA procedure in GENSTAT (Lawes Agricultural Trust, 1993)

## RESULTS

### Laboratory Chamber Recovery Tests

Mean recovery of $NH_4^+$–N over 7 recovery tests was 97% (standard error = 1.0%), with a range from 92.1 to 100.2%. Mean capture of $NH_4^+$–N in the first of 2 acid traps on the outlet side of each chamber was 99.5% of the total captured in both acid traps, indicating that a single acid trap on each outlet was sufficient for measurements.

### Nitrogen Excretion

During the dietary protein concentration trial, urine N concentration in HCP was almost twice that in LCP (Table 2). There were no significant differences between the protein concentration treatments in fecal N concentrations or in the volumes of urine and mass of feces collected over the collection period ($P > 0.05$). The greater N concentrations in urine for HCP resulted in a shift in the relative proportion of N excreted in urine or feces from approximately equal amounts in LCP to a much greater proportion in the urine for HCP. Based on the concentration and volume outputs, mean hourly total N excretion per cow over the collection period was 30% lower for LCP than HCP ($P < 0.05$), with respective values of 9.2 and 13.1 g/cow per h. Urine N excretion was 45% higher ($P < 0.05$) for HCP than for LCP (8.9 vs. 4.9 g/cow per h, respectively).

From the protein form trial, urine N concentration was highest in BFTL, with no significant differences between that of ALF and BFTH (Table 2). There were no significant dietary effects ($P > 0.05$) on total N concentration in the feces or in the volumes of urine and mass of feces collected. Thus a greater proportion of the

Table 3. Analyses of composite urine and feces samples used in the ammonia emission studies.[1]

| | Dietary protein concentration trial | | Dietary protein form trial | | |
|---|---|---|---|---|---|
| | Low CP | High CP | Alfalfa | BFT,[2] low tannin | BFT, high tannin |
| Urine | | | | | |
| pH | 9.0 (0.01) | 8.8 (0.03) | 7.8 (0.02) | 7.8 (0.02) | 7.9 (0.02) |
| Total N, g/L | 4.50 (0.007) | 9.35 (0.041) | 6.38 (0.260) | 5.41 (0.016) | 5.57 (0.022) |
| Urea N, g/L | 1.91 (0.019) | 5.83 (0.563) | 4.23 (0.357) | 3.70 (0.075) | 3.54 (0.009) |
| TAN,[3] g/L | 0.43 (0.161) | 0.23 (0.090) | 0.43 (0.016) | 0.33 (0.006) | 0.26 (0.005) |
| Feces | | | | | |
| pH | 6.5 (0.03) | 6.8 (0.04) | 6.6 (0.02) | 6.6 (0.04) | 6.6 (0.08) |
| DM, % | 17.9 (0.35) | 18.0 (0.08) | 14.6 (0.10) | 14.8 (0.14) | 14.6 (0.41) |
| Total N, g/kg of DM | 26.9 (0.47) | 28.4 (0.53) | 23.8 (0.09) | 22.8 (0.36) | 24.7 (0.10) |
| TAN, g/kg of DM | 1.80 (0.730) | 0.90 (0.860) | 3.42 (0.090) | 2.95 (0.050) | 3.52 (0.070) |
| NDF N, g/kg of DM | 2.35 (0.244) | 2.16 (0.100) | 2.37 (0.090) | 2.95 (0.069) | 3.60 (0.088) |

[1]Values in parentheses are standard errors of the mean (n = 3).
[2]BFT = Birdsfoot trefoil.
[3]TAN = Total ammoniacal N.

N was excreted in the urine for ALF and BFTL and in the feces for BFTH (Table 2). Total N excretion per cow over the collection period did not differ significantly between treatments ($P > 0.05$), averaging 12.3, 15.8, and 17.1 g/cow per h for ALF, BFTL, and BFTH, respectively. Urine N excretion was significantly greater ($P < 0.05$) from BFTL than from ALF or BFTH (9.6 vs. 7.0 and 7.2 g/cow per h, respectively).

## Ammonia Emissions from Simulated Deposits to Barn Floor

***Protein concentration.*** Analyses of the urine used in the simulated barn floor emissions trials showed that HCP had a significantly higher total N and urea N concentration (Table 3). It should be noted that the urine and fecal N concentrations given in Table 3 are for composite samples of material and differ from the averages of individual animal values as given in Table 2. The proportion of urine N as urea N was also higher in HCP (62% compared with 42% for LCP). There were no significant differences between LCP and HCP in terms of fecal analyses, with the exception of pH. For both urine and feces, differences in pH were statistically significant, but small in absolute terms and likely to have been of little consequence in influencing $NH_3$ emissions.

Cumulative $NH_3$ emissions from the urine and feces in the chambers over the 48-h measurement period were not significantly different ($P > 0.05$) between LCP and HCP (Figure 2a). Thus when expressed as a proportion of either the total N applied (Figure 2b) or urea N applied (Figure 2c), losses were significantly greater from LCP as the urine from the LCP treatment had a lower total N and urea N concentration. Projected $N_{max}$ values could not be derived using equation [2] because there was insufficient curvature within the cumulative emission against time relationship to 48 h.

***Protein form.*** For the manure spread in the chambers, urine total N concentration was greater for ALF than for BFTL or BFTH, which were not significantly different (Table 3). There were no differences in urea N concentrations, but urine TAN concentration decreased with the increasing concentration of CT in the forage legume. There were small differences in fecal total N concentration, with that from BFTL being lower, and an increase in NDF-N content with increasing CT content of the forage legume, suggesting a greater amount of undigested feed N in those diets. Urine and fecal pH values were similar, as were fecal DM and TAN contents.

Cumulative $NH_3$ emission over the 48-h measurement period was significantly greater ($P < 0.05$) from ALF than from BFTL and BFTH, which were not significantly different in absolute terms or when expressed as a proportion of the total N or urea N applied (Figure 3). As the cumulative emission curves were of similar shapes, the predicted $N_{max}$ values were also higher for ALF than the other 2 treatments (Table 4).

## Ammonia Emissions from Slurry Applications to Soil

***Protein concentration.*** The DM content of the prepared fresh slurries was greater than the target value of 7% (Table 5). Differences in DM content and pH between the treatments were small in absolute terms. Total N and TAN concentrations were greater for HCP, although TAN represented a greater proportion of total N for LCP than HCP, with respective values of 33 and

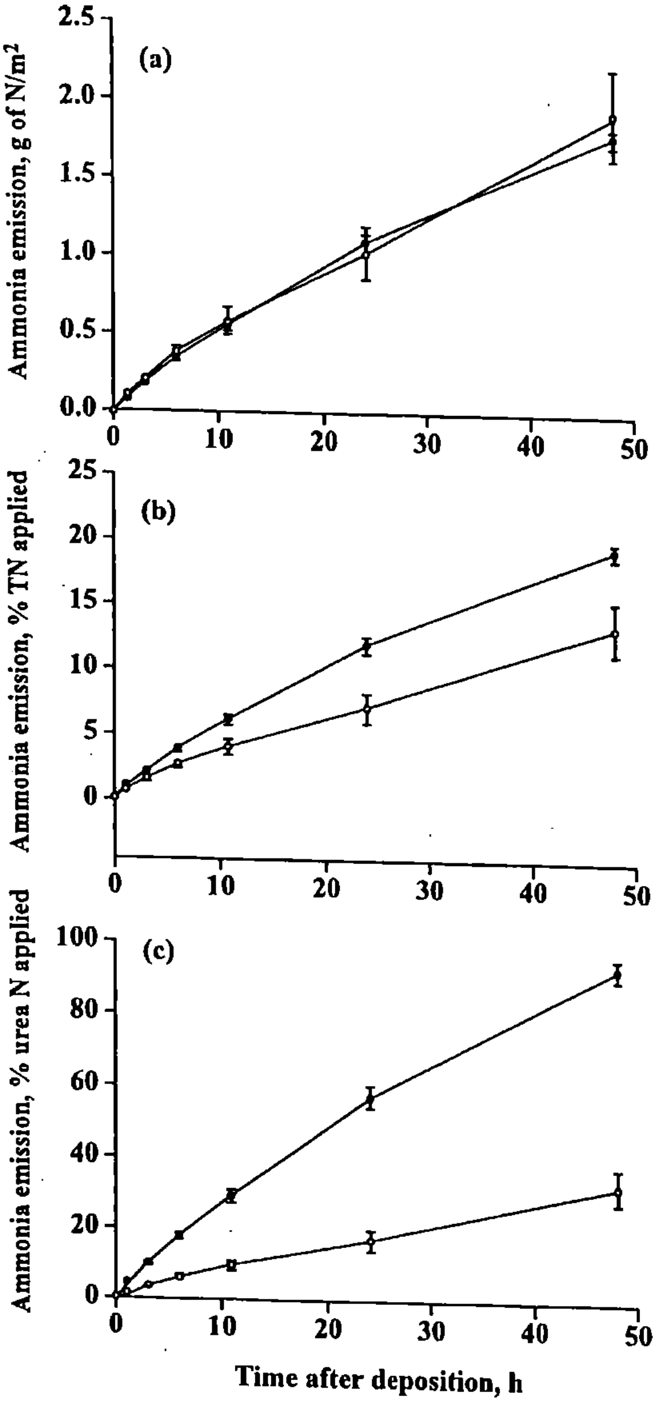


**Figure 2.** Influence of dietary CP content on ammonia emissions from dairy cattle urine (8 mL) and feces (8 g) deposited on a simulated barn floor: a) expressed as g of N/m$^2$; b) as percentage of total N applied; c) as percentage of the urea N applied. Dietary CP contents: 13.6% (●) and 19.4% (○). Error bars show ± 1 SE (n = 3).

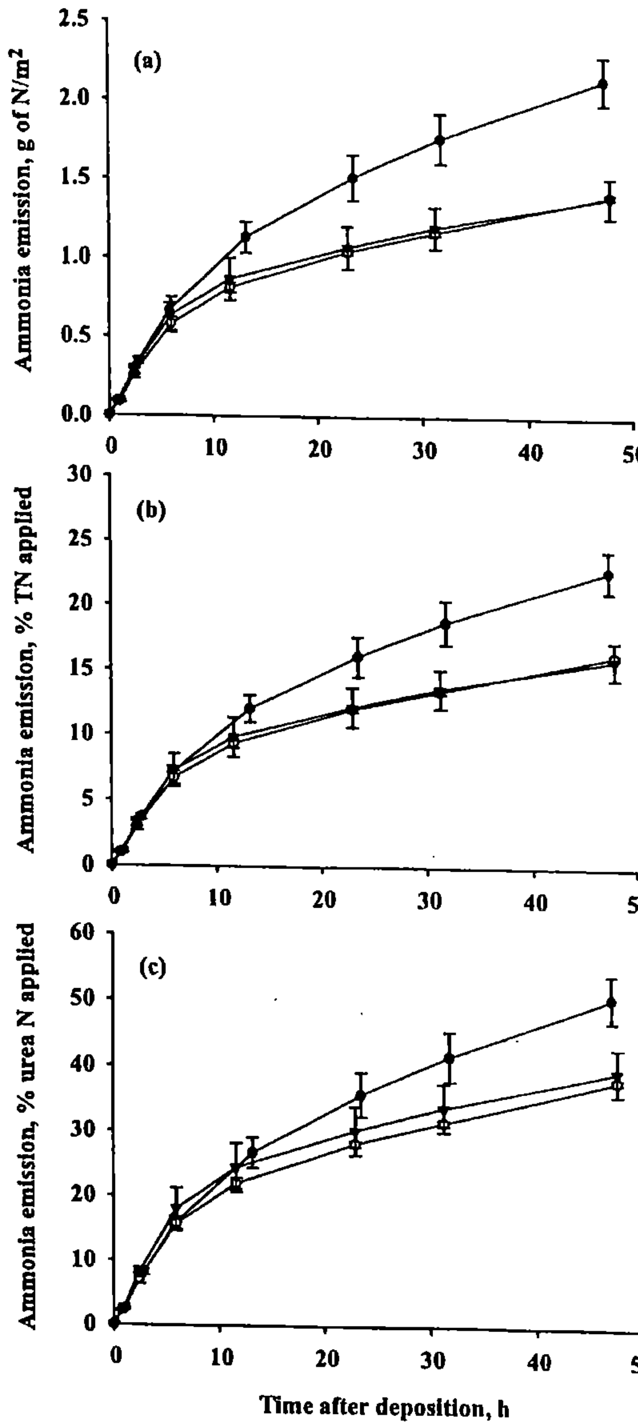


**Figure 3.** Influence of dietary protein form on ammonia emissions from dairy cattle urine (8 mL) and feces (8 g) deposited on a simulated barn floor: a) expressed as g of N/m$^2$; b) as percentage of total N applied; c) as percentage of the urea N applied. Dietary forage legume component: alfalfa (●); birdsfoot trefoil with low tannin content (○); birdsfoot trefoil with high tannin content (▼). Error bars show ± 1 SE (n = 3).

**Table 4.** Predicted maximum cumulative ammonia emissions ($N_{max}$), estimated from a fitted Michaelis-Menten function to the cumulative emissions curve, for urine and feces applied to a simulated barn floor and for fresh and stored slurries applied to soil.

| | Dietary protein concentration trial | | Dietary protein form trial | | |
|---|---|---|---|---|---|
| | Low CP | High CP | Alfalfa | BFT, low tannin | BFT, high tannin |
| Barn floor simulation | | | | | |
| g/m$^2$ | ND[3] | ND | 3.15[a] | 1.74[b] | 1.66[b] |
| % of total N applied | ND | ND | 34[a] | 20[b] | 19[b] |
| % of urea N applied | ND | ND | 75[a] | 47[b] | 47[b] |
| Fresh slurry to soil | | | | | |
| g/m$^2$ | ND | ND | 3.69[a] | 3.58[a] | 2.72[b] |
| % of total N applied | ND | ND | 31[a] | 33[a] | 25[b] |
| % of TAN[2] applied | ND | ND | 45 | 44 | 48 |
| Stored slurry to soil | | | | | |
| g/m$^2$ | 1.42[b] | 4.80[a] | 3.94[a] | 3.09[b] | 2.55[b] |
| % of total N applied | 12[b] | 29[a] | 30[a] | 23[b] | 19[b] |
| % of TAN applied | 32 | 36 | 45 | 41 | 47 |

[a,b]Within each trial, values with different superscripts are significantly different ($P < 0.05$).
[1]BFT = Birdsfoot trefoil.
[2]TAN = Total ammoniacal N.
[3]ND = Not determined.

24%. After 2 wk of storage, pH had increased in HCP (Table 5). Dry matter contents had decreased for both treatments. Total N and TAN concentrations were greater for HCP and there was a substantial change in the proportion of the total N represented by TAN, with values of 38 and 82% for LCP and HCP, respectively. Pre- and poststorage volume measurements were not made, so it was not possible to determine N loss during storage.

Cumulative $NH_3$ emissions over 48 h from the application of fresh slurries to soil were significantly greater ($P < 0.05$) for HCP than LCP, both in absolute terms and when expressed as a percentage of the initial TAN concentration, but not when expressed as a proportion of the total slurry N content (Figure 4). There were differences in the shapes of the cumulative emission curves, with that for HCP still rising steeply after 48 h. Projected $N_{max}$ values could not be derived using equation [2] because there was insufficient curvature within the cumulative emission against time relationship to 48 h. Cumulative emissions over 48 h from the application of stored slurries to soil were also significantly greater ($P < 0.05$) for HCP, in absolute terms and as a proportion of the initial total N or TAN (Figure 5). Predicted maximum emission from HCP as a proportion of the total N applied was more than twice that

**Table 5.** Analyses of slurries derived from urine and feces samples collected from lactating dairy cows fed diets varying in protein concentration and protein form.[1]

| | Dietary protein concentration trial | | Dietary protein form trial | | |
|---|---|---|---|---|---|
| | Low CP | High CP | Alfalfa | BFT,[2] low tannin | BFT, high tannin |
| Fresh slurry | | | | | |
| pH | 7.7 (0.02) | 8.1 (0.01) | 8.5 (0.02) | 8.3 (0.02) | 8.0 (0.02) |
| DM (%) | 7.7 (0.21) | 8.4 (0.20) | 7.9 (0.25) | 7.6 (0.01) | 7.4 (0.16) |
| Total N, g/L | 3.02 (0.031) | 4.97 (0.044) | 2.42 (0.051) | 2.18 (0.014) | 2.19 (0.018) |
| TAN,[3] g/L | 1.01 (0.028) | 1.20 (0.036) | 1.63 (0.020) | 1.61 (0.012) | 1.15 (0.034) |
| Stored slurry | | | | | |
| pH | 7.6 | 8.7 | 8.0 | 7.6 | 7.5 |
| DM (%) | 4.7 (0.73) | 6.3 (0.44) | 6.5 (1.11) | 5.6 (1.47) | 6.5 (0.35) |
| Total N, g/L | 2.37 (0.064) | 3.27 (0.071) | 2.61 (0.008) | 2.70 (0.044) | 2.68 (0.013) |
| TAN, g/L | 0.90 (0.021) | 2.69 (0.154) | 1.74 (0.030) | 1.50 (0.049) | 1.10 (0.001) |

[1]Values in parentheses are standard errors of the mean (n = 3).
[2]BFT = Birdsfoot trefoil.
[3]TAN = total ammoniacal N.

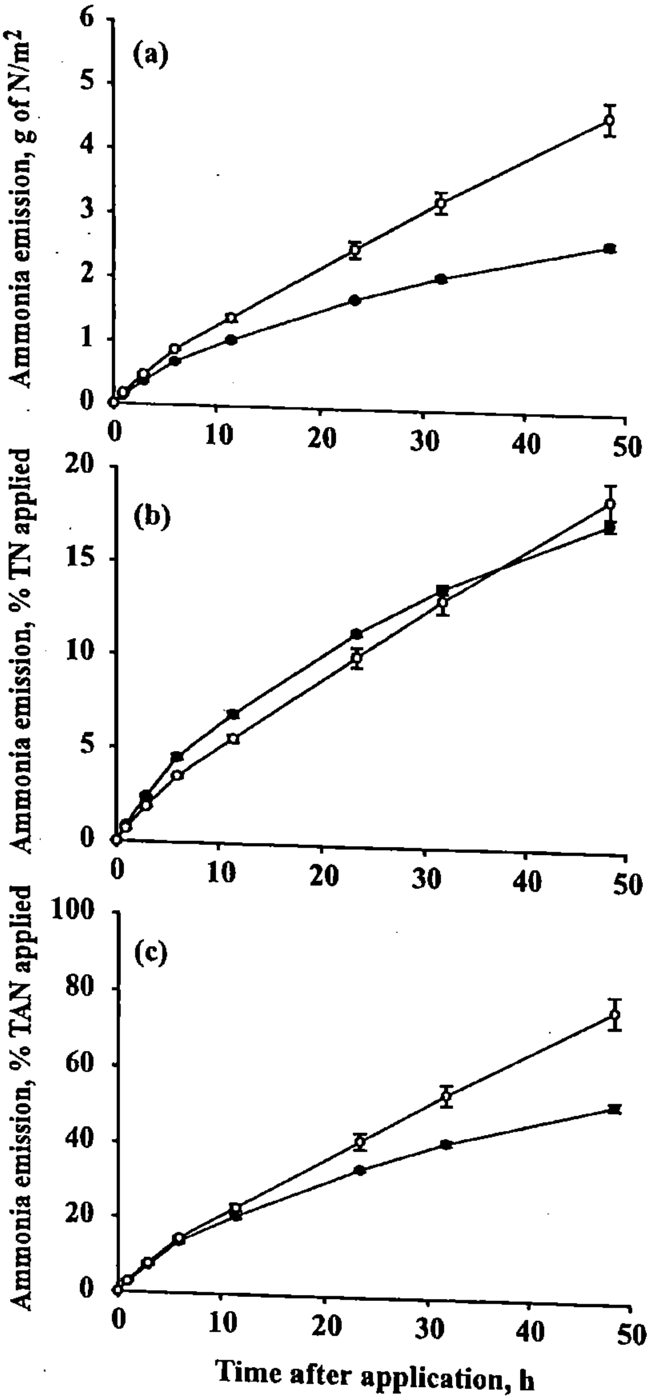


**Figure 4.** Influence of dietary CP content on ammonia emissions from fresh slurry applied to soil: a) expressed as g of N/m$^2$; b) as percentage of total N applied; c) as percentage of the total ammoniacal N (TAN) applied. Dietary CP contents: 13.6% (●) and 19.4% (O). Error bars show ± 1 SE (n = 3).

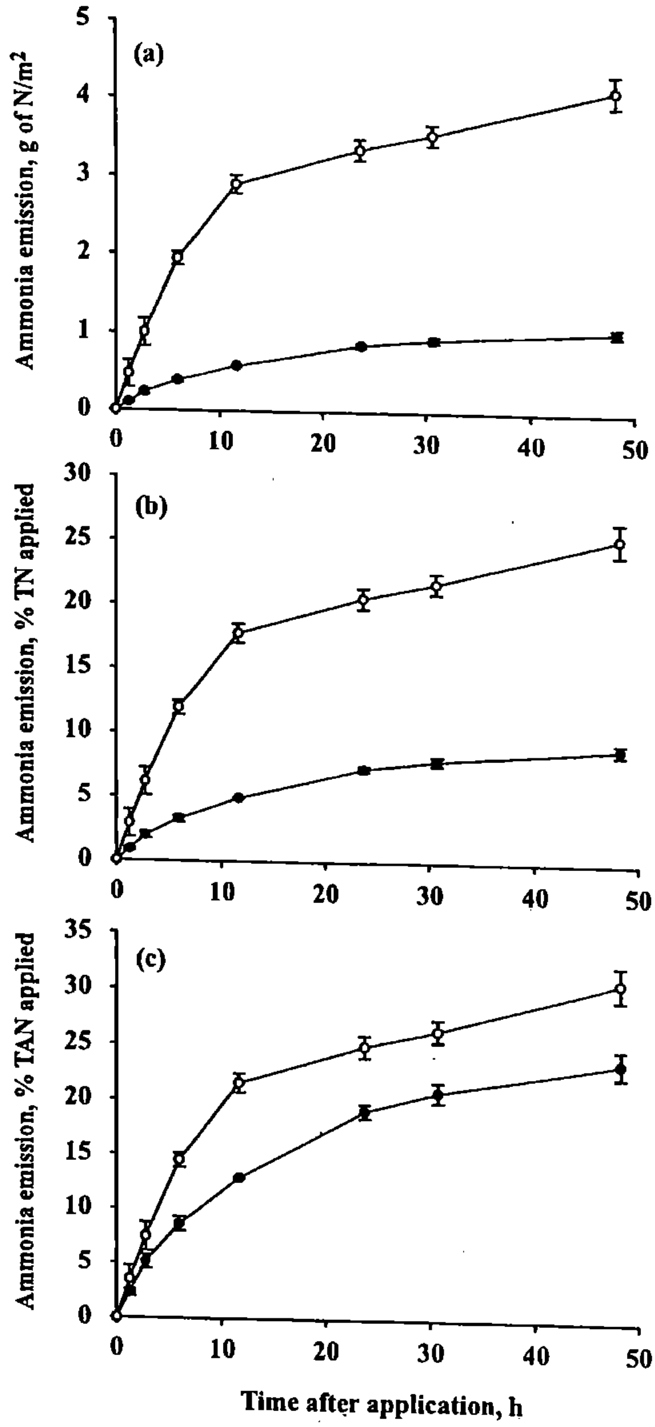


**Figure 5.** Influence of dietary CP content on ammonia emissions from stored slurry applied to soil: a) expressed as g of N/m$^2$; b) as percentage of total N applied; c) as percentage of the total ammoniacal N (TAN) applied. Dietary CP contents: 13.6% (●) and 19.4% (O). Error bars show ± 1 SE (n = 3).

for LCP but as a proportion of the TAN applied, there was no significant difference ($P > 0.05$) between treatments, with a mean loss across both treatments of approximately 34% of applied TAN.

***Protein form.*** There were no differences in the DM content of the fresh slurries prepared from the urine and feces from the protein form trial (Table 5) although target DM content of 7% was marginally exceeded. There were small differences in fresh slurry pH, with the pH declining with increasing CT content of the dietary forage legume. Total N content was greater for ALF than for either BFTL or BFTH, whereas TAN content was similar in ALF and BFTL, both being greater than for BFTH. Total ammoniacal N expressed as a proportion of total N content was therefore greatest in BFTL (74%) and least in BFTH (52%). After 2 wk of storage, slurry DM contents were lower than for the fresh slurries with no differences between treatments, with a mean value of 6.2%. Slurry pH was lower for the BFTL and BFTH treatments than for ALF. Total N concentrations were similar, but TAN content declined with increasing CT content, so TAN expressed as a proportion of total N also declined with increasing condensed tannin content with values of 67, 56, and 41% for ALF, BFTL, and BFTH, respectively.

Cumulative $NH_3$ emissions over 48 h following application of the fresh slurries to soil were significantly greater ($P < 0.05$) for ALF and BFTL than for BFTH in absolute terms and as a proportion of the total N applied, but there were no treatment differences as a proportion of TAN applied (Figure 6). The cumulative emission curve shapes were similar between treatments and the predicted $N_{max}$ values followed the same pattern (Table 4). Following application of the stored slurries, cumulative emissions over 48 h were significantly greater ($P < 0.05$) from ALF than either BFTL or BFTH in absolute terms and as a proportion of total N applied, but again, there were no significant differences ($P > 0.05$) when expressed as a proportion of the TAN applied (Figure 7). Again, similarities in the emission curve shapes meant that treatment effects on predicted $N_{max}$ values (Table 4) were the same as those on cumulative emissions at 48 h.

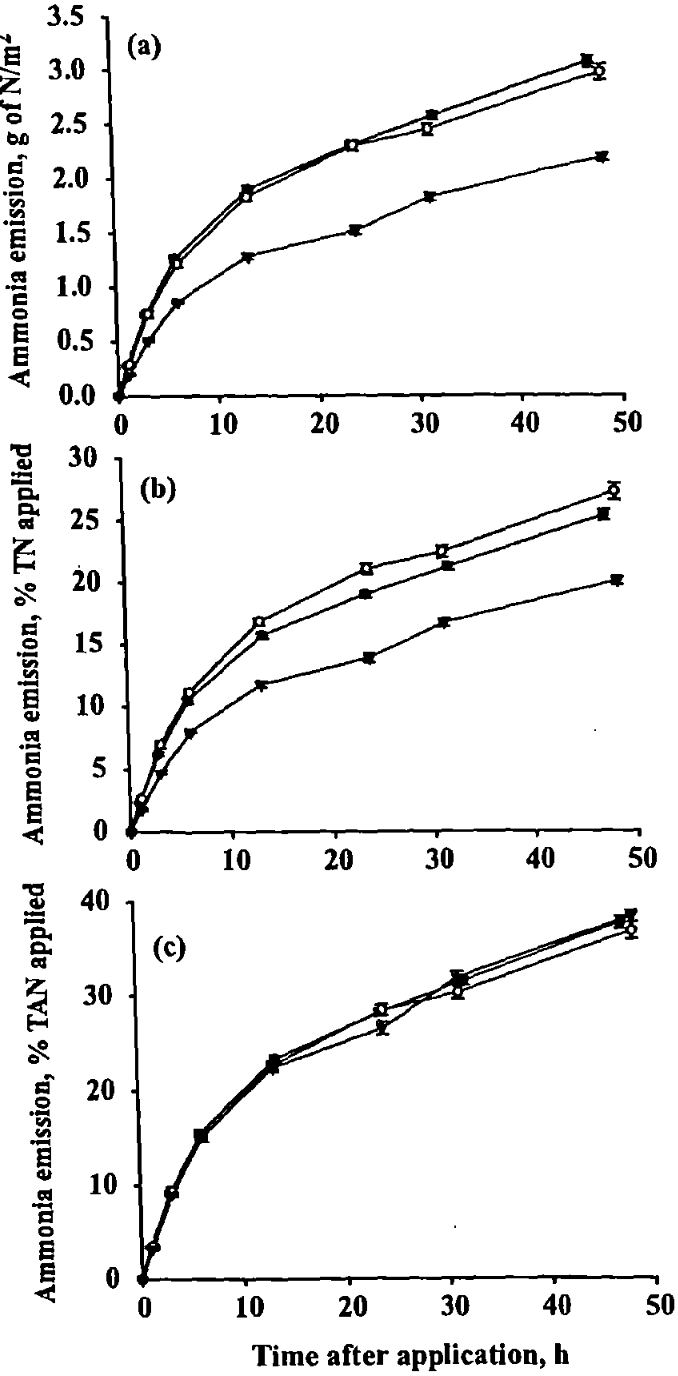


**Figure 6.** Influence of dietary protein form on ammonia emissions from fresh slurry applied to soil: a) expressed as g of N/m$^2$; b) as percentage of total N applied; c) as percentage of the total ammoniacal N (TAN) applied. Dietary forage legume component: alfalfa (●); birdsfoot trefoil with low tannin content (O); birdsfoot trefoil with high tannin content (▼). Error bars show ± 1 SE (n = 3).

## DISCUSSION

Nitrogen excretion was reduced by 30% and urinary N excretion by 45% when dietary CP content was lowered from 19.4 to 13.6%. These values are not based on a full daily collection of urine and feces and the possibility that there were differences in excretal volumes while the cows were away from the stalls cannot be excluded. In addition, the mean hourly rate of excretal output may have been different while the cows were being moved and milked, so mean daily output values were not predicted from our data. However, these results confirm the work of others that N excretion can be reduced by lowering dietary CP content and that the reduction is predominantly in the urea N content of the urine (Krober et al., 2000; Kulling et al., 2001; Broderick, 2003). The magnitude of the reduction in urinary N excretion was not as large as that reported by Castillo et al. (2000), who concluded from a number of published studies that reducing CP content from 20 to 15% would

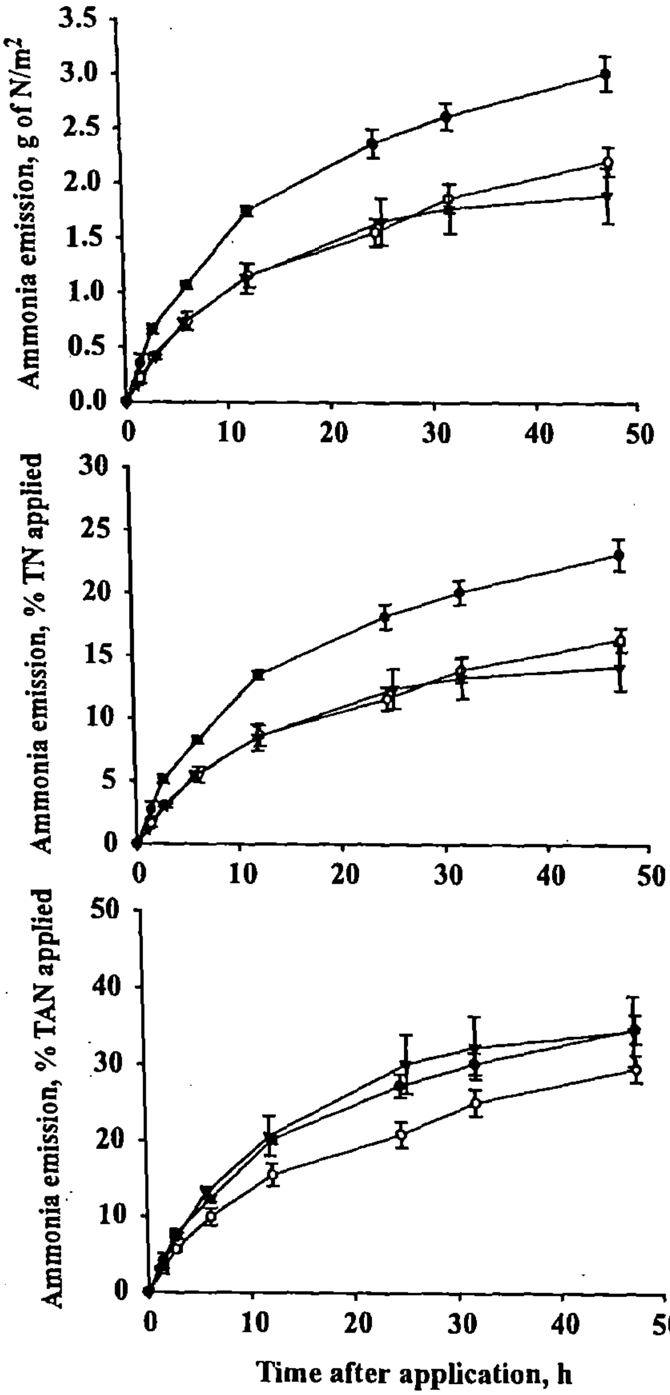


**Figure 7.** Influence of dietary protein form on ammonia emissions from stored slurry applied to soil: a) expressed as g of N/m$^2$; b) as percentage of total N applied; c) as percentage of the total ammoniacal N (TAN) applied. Dietary forage legume component: alfalfa (●); birdsfoot trefoil with low tannin content (O); birdsfoot trefoil with high tannin content (▼). Error bars show ± 1 SE (n = 3).

result in a 66% reduction in urinary excretion. Castillo et al. (2000) also reported reductions in fecal N excretion of up to 21%, but no significant reductions were found in the present study. Although not assessed in this study, increasing the energy content of the diet may improve efficiency of N use (e.g., Broderick, 2003), and replacing grass forage with maize or concentrates has been shown to improve N use (Valk, 1994; Kulling et al., 2003).

Increasing the CT content of the dietary forage legume component did not reduce total N excretion; indeed, it appeared to have the opposite effect, but the shift from urinary to fecal excretion between the BFTL and BFTH treatments was obvious. There were some differences in the CP content of the diets, with that for ALF being greater than that for the birdsfoot trefoil treatments, which may have led us to expect lower N excretion from the BFTL and BFTH treatments. Results from the lactation trial suggested no differences in N intake between diets but an improved milk N output for the birdsfoot trefoil diets (Hymes-Fecht et al., 2004), so, again, we might have expected less N excretion from the birdsfoot trefoil diets compared with ALF. Fewer cows were used for the manure collection for this study and intake measurements were not made, so differences in intakes cannot be excluded as a possible reason for differences in excretal N output. In addition, as discussed above, fecal and urine outputs as collected may not be representative of daily outputs. The amount of undigested feed N in feces increased with increasing concentration of CT in the diet (Table 3) and a balance is required between protecting sufficient protein from rumen degradation to improve postrumen absorption of essential amino acids and protecting too much protein such that it passes through the animal undigested. Previous research has shown that in sheep, feeding birdsfoot trefoil with medium concentrations of CT (3 to 5%) improved N use efficiency without reducing intake, whereas high concentrations (7.5 to 10%) depressed voluntary feed intake and rumen carbohydrate digestion (Barry and McNabb, 1999).

Measurements from the simulated barn floor trials indicated that cumulative $NH_3$ emissions would continue to increase beyond the 48-h measurement period (Figures 2 and 3). This is consistent with the time required for complete hydrolysis of the urea content of the urine, which has to occur before $NH_3$ volatilization can take place. Rate of hydrolysis is temperature-dependent but from the data given by Whitehead and Raistrick (1993), complete hydrolysis at 15°C (as used in the present study) would occur within 10 to 15 d. Muck (1981) reported much faster hydrolysis of urea on dairy barn floors, with >95% urea decomposition in urine within 6 h at 30°C and within 24 h at 10°C. Elzing and Monteny (1997) showed that peak emission rate (occurring within 1 to 5 h of urine application to a concrete floor) increased with increasing urea N concentration of the urine. The results from the protein form trial are consistent with this, where cumulative emission after 48 h was greater from ALF, which had a higher urea N concentration than either BFTL or BFTH. However, in the protein concentration trial, the emission rates were similar over the first 48 h despite large differences in urea N concentration of urine for HCP and LCP. It is possible that urease activity was limiting in this case and that emissions would have continued for longer from HCP. The higher pH of the urine from the protein concentration trial (Table 3) may have influenced urease activity; Muck (1981) showed that maximum urease activity occurred between pH 6.8 and 7.6 and that activity decreased linearly with pH outside this range. Cumulative emission from LCP after 48 h accounted for almost 100% of the applied urea N and some of this emission probably derived from other urine and fecal N components, as was noted by Whitehead and Raistrick (1993) and Muck and Richards (1983). Actual losses from a dairy barn floor will depend on a number of variables including temperature, airflow, cleaning frequency, urease activity, and urine puddle replenishment rate (Monteny et al., 1998), but the results of the present study suggest that dietary manipulation may not always result in a reduction in emissions proportional to the reduction in excreted urea N.

Urea hydrolysis appeared to be a limiting factor controlling emission rates from the fresh slurries applied to soil in the protein concentration trial. Slurry TAN content was only 20% higher for HCP compared with LCP, whereas a much greater difference would be expected based on differences in urine urea N concentrations. Continued hydrolysis over the 48-h measurement period, replenishing the slurry TAN content, resulted in the cumulative emissions curve for HCP rising more steeply than that for LCP (Figure 4). Two weeks of storage at 20°C was sufficient for complete hydrolysis to have occurred and consequently there was a much greater difference in TAN contents between the 2 treatments in the stored slurries. The stored HCP slurry had a higher pH, resulting in a greater proportional loss of $NH_3$ (Figure 5c). A higher slurry pH associated with higher dietary CP content was noted in cattle by Paul et al. (1998) and in pigs by Misselbrook et al. (1998). Slurry pH is largely determined by the relative concentrations of VFA and TAN and increases as the VFA:TAN ratio decreases (Paul and Beauchamp, 1989). Reducing the CP content of the diet, resulting in a lower slurry TAN content, would not necessarily reduce slurry VFA content. For the protein form trial, there were no additional effects of other slurry compositional changes on $NH_3$ emission and differences in losses were related to the differences in slurry TAN contents.

## CONCLUSIONS

Manipulating the concentration and form of protein in the diet of lactating cows influenced the amount and form of N excretion and subsequent $NH_3$ emissions from the barn floor and manure management. Reducing dietary CP content from 19 to 14% reduced total N excretion and resulted in a greater proportion of the N excretion in urine, with an increase in urine N concentration of 90%. Surprisingly, losses from a simulated barn floor were similar from both treatments in the short term (48 h), presumably because urease activity was limiting, but losses from slurries applied to soil were lower for the LCP treatment both in absolute terms and as a proportion of the TAN applied. Increasing the concentration of CT in the forage legume component of the diet shifted N excretion from urine to feces and led to reduced losses from the barn floor (in absolute terms and as a proportion of urine urea N applied) and slurries applied to soil (in proportion to the reduction in the TAN content of the slurries).

## ACKNOWLEDGMENTS

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