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Ammonia volatilization from field-applied animal slurry—the ALFAM model

H.T. Søgaard[a,*], S.G. Sommer[a], N.J. Hutchings[b], J.F.M. Huijsmans[c], D.W. Bussink[d], F. Nicholson[e]

[a] *Department of Agricultural Engineering, Research Centre Bygholm, Danish Institute of Agricultural Sciences (DIAS), P.O. Box 536, DK-8700 Horsens, Denmark*
[b] *Department of Agricultural Systems, Research Centre Foulum, Danish Institute of Agricultural Sciences, P.O. Box 50, DK-8830 Tjele, Denmark*
[c] *Institute of Agricultural and Environmental Engineering (IMAG), P.O. Box 43. NL-6700 AA Wageningen, The Netherlands*
[d] *Nutrient Management Institute, Agrobusiness Park 20, 6708-PW, Wageningen, The Netherlands*
[e] *ADAS Gleadthorpe, Meden Vale, Mansfield, Notts NG20 9PF, UK*

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Abstract

A statistical analysis of European ammonia (NH_3) volatilization data (from Denmark, Italy, the Netherlands, Norway, Sweden, Switzerland and UK) collated in a database produced a model that is supported by theoretical considerations of the effect of explanatory variables (see www.alfam.dk). Volatilization could be described mathematically by a Michaelis–Menten-type equation, with the loss rates as the response variable ($R^2 = 80\%$). Variables significantly affecting NH_3 volatilization throughout Europe are soil water content, air temperature, wind speed, slurry type, dry matter content of slurry, total ammoniacal nitrogen content of slurry ($TAN = NH_3 + NH_4^+$), application method and rate, slurry incorporation and measuring technique. The model was used to estimate the NH_3 volatilization from typical cattle and pig slurries applied in Italy, England, Norway and Denmark. Climate observations from the following three periods in year 2000 were used as input: (1) 1 week before the normal sowing time for spring crops, (2) mid-season, and (3) 1 week after harvesting. There was little difference in the total NH_3 volatilization from slurry applied in the three periods, principally due to interactions between soil water content and air temperature. The time from application to when 10% of the applied TAN was lost was similar for countries in the south and north of Europe, primarily due to the low wind speeds counteracting the effect of higher air temperatures at the southern location. To reduce NH_3 volatilization, the slurry should be incorporated faster in mid- and late-season than in the early spring, due to increasing air temperatures during the growing season.

Keywords: Livestock slurry; Volatilization; Statistical analysis; European database; Agriculture

1. Introduction

Ammonia (NH_3) volatilization from field-applied animal manure represents a major source of atmospheric pollution and reduces the nitrogen fertilizer value of the manure (Jarvis and Pain, 1990). The environmental impact of atmospheric NH_3 forms the background to ongoing international negotiations for reduction of national NH_3 emissions (ECETOC, 1994; IPPC, 1996). In addition, legislation controlling nitrogen use in agriculture, both at the EU and national levels, make it increasingly important for farmers to make optimal use of manure nitrogen.

*Corresponding author. Tel.: +45-76296000; fax: +45-76296100.
E-mail address: henningt.sogaard@agrsci.dk (H.T. Søgaard).

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NH_3 losses from field-applied manure, particularly slurry, have been measured in many European experiments. The full value of the investment in this research can only be realized if the knowledge gained is communicated effectively to farmers, advisors and legislators. NH_3 volatilization from slurries is affected by a wide range of factors, e.g. application techniques, manure composition, crop cover, weather and soil conditions (Sommer and Olesen, 1991, 2000; Bussink et al., 1994; Braschkat et al., 1997; Huijsmans et al., 2002).

NH_3 volatilization experiments are expensive and are typically designed to examine only one or two of the contributory factors. In contrast, the users of the collected information often need to consider NH_3 volatilization under a wide range of weather, soil and agronomic situations, even within a single European region. Alone, the individual experiments conducted by various European research institutes do not provide an adequate basis for this requirement. The ALFAM[1] project (Sommer et al., 2001) addressed this problem by combining the data available from these studies into a single database. The data can be used both for developing mechanistic models of NH_3 losses from slurry and in the construction of decision support systems.

This paper describes the development and validation of the ALFAM model to predict NH_3 loss from field-applied slurry for a range of weather, soil and management conditions. The practical value of the ALFAM model in predicting NH_3 losses is also considered and discussed.

2. Methods

2.1. Database

The ALFAM database contains data provided by seven European countries (Denmark, Italy, the Netherlands, Norway, Sweden, Switzerland and UK; see www.alfam.dk for a detailed description of the database and the institutes providing data). The choice of data requested from these countries was based on the conceptual model described by Hutchings et al. (1996). Existing knowledge was used to identify the range of factors affecting NH_3 volatilization, which included time since manure application, NH_3 volatilization measurement technique, plus a range of climate, soil, manure and agronomic factors. The data derive from about 800 separate experiments: a total of almost 6000 records is currently stored. Each record contains one measurement of volatilization (loss rate), together with associated information on climate, soil conditions, etc., during the measurement period.

[1] Ammonia Loss from Field-applied Animal Manure.

2.2. Statistical modelling and analysis

Fig. 1 illustrates the pattern of NH_3 volatilization from field-applied slurry under constant weather conditions. Loss rates are generally high immediately after slurry application. This is related both to the high initial concentration of total ammoniacal nitrogen ($TAN = NH_3 + NH_4^+$) in the surface of the mixture of soil and slurry, and to the pH rise in the surface of newly applied slurry (Sommer and Sherlock, 1996). Over the following days, NH_3 volatilization rates gradually approach zero, as the concentration of dissolved TAN in the soil surface decreases rapidly, due to volatilization, infiltration and nitrification (van der Molen et al., 1990).

The data in the ALFAM database were analysed by fitting a model with the above-mentioned characteristics to the measured NH_3 volatilization loss rates. The model used was based on the Michaelis–Menten-type equation presented by Sommer and Ersbøll (1994):

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

The model describes the cumulative NH_3 volatilization, $N(t)$, over time, t, since the start of the experiment.

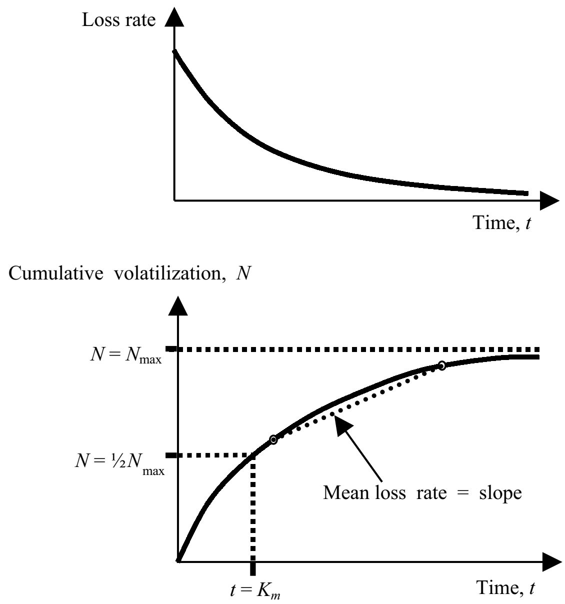

Fig. 1. Schematic representation of (above) NH_3 loss rates and (below) the cumulative volatilization loss from a slurry application as a function of time following the field application of slurry. $N_{\max}$ and K_m are the parameters used in the Michaelis–Menten-type model of the rate of NH_3 loss.

The quantity $N(t)$ is dimensionless, as it expresses the NH_3 lost as fraction of the applied TAN:

$$N(t) = \frac{\text{Cumulative NH}_3\text{ loss over time } t \text{ (kg/N ha)}}{\text{Manure application rate (t manure/ha)} \times \text{TAN content in manure (gN/kg manure)}}. \quad (2)$$

The model parameter N_{max} is the total loss of NH_3 (fraction of applied TAN) as time approaches infinity, and the parameter K_m (h) is the time t satisfying $N(t) = \frac{1}{2} N_{max}$ (see Fig. 1).

Sommer and Ersbøll (1994) fitted this type of model directly to cumulative loss data. However, to minimize the serial correlation between successive measurements, it was more appropriate to model loss rates (loss per time interval) rather than cumulative loss. Another advantage of this approach is that missing loss rate observations during an experiment are permissible, since calculation of cumulative loss values is not needed. However, to develop the NH_3 loss rate model (the ALFAM model), it was necessary to re-formulate Eq. (1): see Appendix A.

Since the loss pattern over time depends on climate, slurry composition, soil conditions, application method, etc., the parameters N_{max} and K_m were modelled as functions of these variables (see Appendix A). Multiplicative rather than additive functions proved to provide a better overall model fit. The variables selected for the model analysis are listed in Table 1. Most of the variables are the so-called indicator variables (values = zero or one), which enable representation of different states of categorical factors (e.g. application method).

The set of explanatory variables that was selected for modelling reflected the need to include variables having a major influence on NH_3 volatilization and the desire to utilize as many records from the ALFAM database as possible. However, in most records, only a subset of variables was recorded, so it was necessary to find a compromise between excluding variables from the model and excluding database records. For example, the initial slurry pH is considered to have an important effect on NH_3 volatilization, but is not included in the ALFAM model (Bussink et al., 1994). The pH was not measured in many of the experiments on the ALFAM database, and consequently inclusion of this factor in the model would have reduced the number of usable records by about 45%. Soil type was not included in the model, as the effect on NH_3 volatilization was small.

To restrict the range of conditions covered by the model, and to avoid extreme and unreliable observations,

Table 1
Explanatory variables used for modelling NH_3 loss rates

Experimental factor	Explanatory variable(s)		Comment
	Symbol	Range	
Soil water content	x_1	[0, 1]	$x_1 = 1$ if wet soil; $x_1 = 0$ if dry soil
Air temperature	x_2	[–5.6, 36.0]	Unit: °C
Wind speed	x_3	[0.0, 9.0]	Unit: m s^{-1}
Slurry type	x_4	[0, 1]	$x_4 = 1$ if pig slurry; $x_4 = 0$ if cattle slurry (only pig and cattle slurry have been included in the analysis)
Dry matter content of slurry	x_5	[0.8, 11.0]	Unit: %
TAN content of slurry	x_6	[0.2, 4.0]	Unit: g N kg^{-1}
Application method	x_7	[0, 1]	$x_7 = 1$ if band spread/trailing hose; $x_7 = 0$ otherwise
	x_8	[0, 1]	$x_8 = 1$ if trailing shoe; $x_8 = 0$ otherwise
	x_9	[0, 1]	$x_9 = 1$ if open slot injection; $x_9 = 0$ otherwise
	x_{10}	[0, 1]	$x_{10} = 1$ if closed slot injection; $x_{10} = 0$ otherwise
	x_{11}	[0, 1]	$x_{11} = 1$ if pressurized injection; $x_{11} = 0$ otherwise (The application method "broadcast spreading" corresponds to $x_7 = x_8 = x_9 = x_{10} = x_{11} = 0$)
Application rate of slurry	x_{12}	[9.6, 99.3]	Unit: t ha^{-1} or m^3 ha^{-1}
Slurry incorporation	x_{13}	[0, 1]	$x_{13} = 1$ if no incorporation; $x_{13} = 0$ if shallow cultivation
Technique for NH_3 loss measurement	x_{14}	[0, 1]	$x_{14} = 1$ if wind tunnel; $x_{14} = 0$ otherwise
	x_{15}	[0, 1]	$x_{15} = 1$ if micromet; $x_{15} = 0$ otherwise (The JTI technique will be represented by the variable constellation $x_{14} = x_{15=}0$)

only database records fulfilling the following criteria were used:

- Only cattle and pig slurry data.
- Only data from experiments on bare soil, stubble or where crop height was <15 cm.
- The observed loss rate of NH_3 was non-negative.
- The first NH_3 loss rate in a measuring series was greater than the second. If not, the first was discarded.
- The application rates were $<100\,t\,ha^{-1}$.
- All the selected explanatory variables were present.

These criteria left 2481 data records for the model analysis, which was completed by the use of the non-linear regression procedure (proc nlin) in the SAS System for Windows, Release 8.00.

3. Results and discussion

3.1. Results from fitting the model

The results of fitting the model to the measured volatilization data are summarized in Table 2. The table

Table 2
Parameter estimates and confidence limits for the ALFAM model of NH_3 loss with multiplicative sub-models (cf. Eqs. (A.7) and (A.8) in Appendix A)

Experimental factor	Interpretation of the corresponding parameter (as a multiplicative factor)	Parameter estimate	Approximate 95% confidence limits	
	Parameters related to N_{max} (see Eq. (A.7), Appendix A)			
None	Common factor	$A_0 = 0.0495$	0.0078	0.3153
Soil water content	Wet soil (vs. dry soil)	$A_1 = 1.102$	1.028	1.181
Air temperature	Increase per °C	$A_2 = 1.0223$	1.0175	1.0273
Wind speed	Increase per $m\,s^{-1}$	$A_3 = 1.0417$	1.0178	1.0662
Slurry type	Pig slurry (vs. cattle slurry)	$A_4 = 0.856$	0.773	0.947
Dry matter content of slurry	Increase per % DM	$A_5 = 1.108$	1.087	1.129
TAN content of slurry	Decrease per g $N\,kg^{-1}$	$A_6 = 0.828$	0.786	0.872
Application method	Band spread/trailing hose	$A_7 = 0.577$	0.496	0.673
	Trailing shoe	$A_8 = 0.664$	0.261	1.685
	Open slot injection	$A_9 = 0.273$	0.198	0.377
	Closed slot injection	$A_{10} = 0.543$	0.327	0.901
	Pressurized injection (vs. broadcast spreading)	$A_{11} = 0.028$	0.012	0.068
Application rate of slurry	Decrease per $t\,ha^{-1}$ or $m^3\,ha^{-1}$	$A_{12} = 0.996$	0.993	0.998
Slurry incorporation	No incorporation. (vs. shallow cult.)	$A_{13} = 11.3$	1.8	72.0
Technique for NH_3 loss measurement	Wind tunnel	$A_{14} = 0.528$	0.436	0.640
	Micromet (vs. the JTI technique)	$A_{15} = 0.578$	0.470	0.710
	Parameters related to K_m (see Eq. (A.8), Appendix A)			
None	Common factor	$B_0 = 1.038$	0.606	1.776
Soil water content	Wet soil (vs. dry soil)	$B_1 = 1.102$	0.967	1.256
Air temperature	Decrease per °C	$B_2 = 0.960$	0.951	0.969
Wind speed	Decrease per $m\,s^{-1}$	$B_3 = 0.950$	0.913	0.988
Slurry type	Pig slurry (vs. cattle slurry)	$B_4 = 3.88$	3.18	4.74
Dry matter content of slurry	Increase per % DM	$B_5 = 1.175$	1.134	1.218
TAN content of slurry	Increase per g $N\,kg^{-1}$	$B_6 = 1.106$	1.004	1.219
Application method	Band spread/trailing hose	$B_7 = 1$[a]	—	—
	Trailing shoe	$B_8 = 1$[a]	—	—
	Open slot injection	$B_9 = 1$[a]	—	—
	Closed slot injection	$B_{10} = 1$[a]	—	—
	Pressurized injection (vs. broadcast spreading)	$B_{11} = 1$[a]	—	—
Application rate of slurry	Increase per $t\,ha^{-1}$ or $m^3\,ha^{-1}$	$B_{12} = 1.0177$	1.0127	1.0227
Slurry incorporation	No incorporation (vs. shallow cult.)	$B_{13} = 1$[a]	—	—
Technique for NH_3 loss measurement	Wind tunnel	$B_{14} = 1.48$	1.04	2.08
	Micromet (vs. the JTI technique)	$B_{15} = 2.02$	1.38	2.94

[a] Parameter fixed to 1 due to very low level of significance ($P > 0.4$).

Table 3
Parameterization of NH_3 volatilization from field-applied animal slurry (significant parameters, $P<0.01$)

Experimental factor	Effect on total NH_3 volatilization
Soil water content	Wet soil 10% higher than dry soil
Air temperature	+2% per °C
Wind speed	+4% per m s^{-1}
Slurry type	Pig slurry 14% less than cattle slurry
Dry matter content	+11% per % DM
TAN content	−17% per g N kg^{-1}
Application method:	
Band spread/trailing hose	42% less than broadcast spread
Open slot injection	73% less than broadcast spread
Pressurized injection	97% less than broadcast spread
Slurry incorporation	"No incorporation" was 11 times higher than "shallow cultivation"
Measurement tech.	No significant difference between wind tunnel and micrometeorological mass balance techniques. Those two were about 45% less than JTI technique

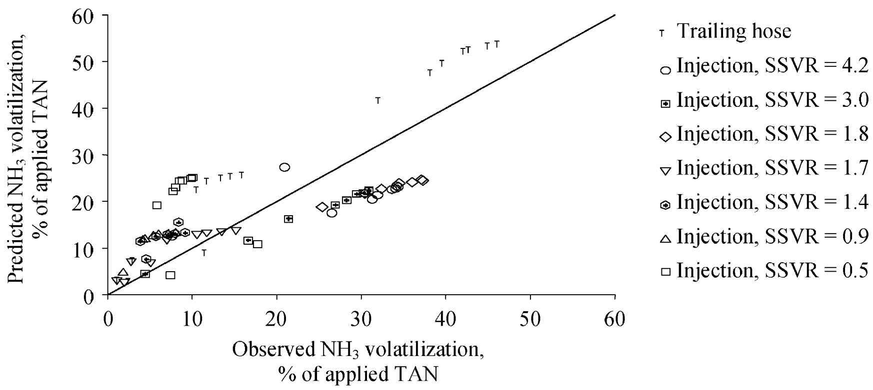

Fig. 2. Relationship between model predictions and measurements of NH_3 volatilization from slurry applied to a grass field (SSVR, at 30 t slurry ha^{-1}).

contains sets of A and B parameters relating the explanatory variables to N_{max} and K_m, respectively (see Appendix A for details). Five parameters with very low statistical significance levels ($P>0.4$) were fixed at 1 to minimize the variance when using the model to predict NH_3 loss for situations (values of the explanatory variables) not covered by the data set used to construct the model.

The parameter values in Table 2 should be interpreted as multiplicative factors. For example, the total NH_3 volatilization (N_{max}) from a wet soil was estimated to be about 10% higher than from a dry soil, as the multiplicative factor is $A_1 = 1.102$. In Table 3 the values of the most significant A parameters have been converted to percentage effect on total NH_3 volatilization.

Care is required when interpreting the A_6 and A_{12} parameters. Both are <1, indicating that the total NH_3 volatilization expressed as a fraction of the TAN applied decreases if the TAN content of the slurry increases or if the slurry application rate is increased. The absolute amount of NH_3 lost (g N ha^{-1}) is obtained by multiplying this result by the amount of TAN applied, so the volatilization will, nevertheless, increase when the TAN content or the slurry application rate is increased.

3.2. Prediction of NH_3 volatilization for an independent data set

The validity of the ALFAM model, NH_3 loss predictions was tested by using an independent data set from an experiment reported by Hansen et al. (2002). In this study, slurry was applied (at 30 t ha^{-1}) by trailing hoses or injected (open slot) to a grass sward (ca. 10 cm sward height). The slurry-to-slot volume ratio (SSVR) was measured to characterize the injection. The relationship between measured and predicted NH_3 volatilizations is shown in Fig. 2. The vertical distances between the symbols and the 1:1 line indicate prediction errors. The model over-estimated the NH_3 volatilization from slurry applied by means of trailing hoses, as it cannot account for the crop height. Compared to the average crop height of about 5 cm in the model data, a 10 cm grass height will reduce the volatilization (Sommer et al., 1997; Huijsmans et al., 2002). This suggests that the model could be improved by including a factor for crop cover (grass, stubble, bare soil or growing crop).

The NH_3 volatilization was under-estimated for injection systems with high SSVR (slurry overflow if SSVR > 1) and vice versa, because the model does not differentiate for SSVR. Studies by Hansen et al. (2002) confirm that high SSVR increases NH_3 losses significantly. SSVR should therefore be included as a factor in volatilization models, and should be measured in future studies of NH_3 volatilization from injected slurry.

3.3. *Effect of slurry composition and environment on* N_{max}

3.3.1. *Effect of air temperature and wind speed*

The ALFAM model predicts that the cumulative NH_3 loss (N_{max}) increases with air temperature and wind speed (A_2 and $A_3 > 1$ in Table 2). This agrees with the results from studies showing that NH_3 volatilization during the initial 4–6 h increases with increasing air temperatures or incident solar radiation (Brunke et al., 1988; Moal et al., 1995; Braschkat et al., 1997; Sommer et al., 1997; Huijsmans et al., 2002). The increase with incident global radiation is due to the energy requirement for endothermic volatilization. In general, the model predicts a lower total NH_3 volatilization from slurry applied early in the morning than from slurry applied in the afternoon, as a consequence of the dependency on air temperature.

Other experiments indicate that total NH_3 volatilization from application of slurry with splash plates to crops is related to wind speed (e.g. Sommer et al., 1997). An increase in wind speed increased the volatilization rate after broadcast spreading, after band application by trailing foot and after open slot shallow injection (Huijsmans et al., 2002). This was not found in all studies (Beauchamp et al., 1978; Bussink et al., 1994), probably because the wind speed is generally high enough for the gas phase resistance to be negligible.

3.3.2. *Effect of dry matter (DM) content and slurry type*

This study has shown that the total NH_3 volatilization increases with increasing slurry DM and TAN concentration. Furthermore, volatilization is lower from pig slurry than from cattle slurry ($A_4 < 1$ in Table 2). In the study by Bussink et al. (1994), it was shown that the NH_3 volatilization during the first 24 h was related to the initial NH_3 concentration in the gas phase, as calculated from slurry TAN, slurry pH and temperature. Also, Huijsmans et al. (2002) showed that TAN affected volatilization rate after broadcast spreading, after narrow band application by trailing foot and after shallow injection. Both TAN and slurry pH after application are important factors when modelling volatilization (Sommer and Olesen, 2000).

The slurry DM content can significantly affect NH_3 volatilization, and field studies have shown that NH_3 volatilization tends to be linearly or sigmoidally related to the DM content (Braschkat et al., 1997; Moal et al., 1995; Sommer and Olesen, 1991). Higher DM contents have also been shown to cause higher NH_3 volatilization from cattle slurry than from pig slurry (Pain et al., 1990).

3.3.3. *Effect of soil water content*

The ALFAM model output confirms the findings of a number of previous studies showing that the NH_3 volatilization is relatively low when slurry is applied on dry soil ($A_1 > 1$, Table 2), even if the air or soil surface temperature is high (Sommer et al., 1991), due to increased soil infiltration. Consequently, NH_3 losses increase if the infiltration is reduced because of a high soil water content (Donovan and Logan, 1983). In a laboratory study, it was shown that the NH_3 volatilization from slurry applied to dry soil (0.01 g H_2O g^{-1} of soil) was 70% of the volatilization from slurry applied to soil with more than 0.8 g $H_2O\,g^{-1}$ of soil (Sommer and Jacobsen, 1999).

3.3.4. *Effect of slurry application method*

The ALFAM model indicates that application of slurry using band spreading or injection reduces NH_3 volatilization compared to broadcast spreading (A_7, A_8, A_9, A_{10} and $A_{11} < 1$). In all cases, except for trailing shoe and closed slot injection methods, the reductions are very significant ($P < 0.01$). The reason why the reductions with two of the application methods are less significant is that the model is based on very few observations representing these methods (25 NH_3 volatilization measurements). The trailing shoe application and closed slot injection methods are well-represented in the original ALFAM database (more than 400 NH_3 volatilization measurements), but the major part of the data records could not be used for modelling, due to missing observations of soil water content, air temperature or wind speed. However, the Dutch data included in the data base show that open slot shallow injection and band spreading by trailing foot on grassland considerably reduce the volatilization compared to broadcast application (Huijsmans et al., 2002).

3.3.5. *Effect of the technique used for* NH_3 *loss measurement*

The analysis indicated that volatilization measured with wind tunnels (Ryden and Lockyer, 1985) and with a micrometeorological mass balance technique (Ryden and McNeill, 1984) was much lower than volatilization measured with the JTI technique (JTI is an acronym for the Swedish institute, which developed the technique, see Svensson and Ferm, 1993) (A_{14} and $A_{15}<1$, Table 2). Similar differences between results from different measuring techniques were found by Nicholson (personal communication, 2001). The JTI technique is a micrometeorological mass balance technique using a chamber to derive the equilibrium concentration. The chamber will provide shelter from rain during measurements but it does not affect the wind and the air temperature. The sheltering effect may have caused higher measured losses compared to measurements made using the conventional micrometeorological mass balance technique, which fully reflect the weather during the measurement period. Wind tunnels will also provide a shelter from rain, but the adjusted wind speed in the tunnel during the experiments may have been lower than the ambient windspeed, leading to lower measurements of NH_3 volatilization than those measured with the JTI technique.

3.4. Effect of slurry composition and environment on K_m and on the initial loss rate

A low value of K_m indicates that a high proportion of the total NH_3 loss will occur soon after application, whereas a high K_m value indicates that losses occur over a longer period. The initial loss rate (at time $t=0$) can be calculated as $N_{\max}/K_m$ (see Appendix A, Eq. (A.1)). This means that if an experimental factor changes $N_{\max}$ by a multiplicative factor A and K_m by a multiplicative factor B, then the initial loss rate will be changed by the multiplicative factor A/B. The ratio between corresponding A and B parameters in Table 2 can therefore be used to assess how a given experimental factor will affect the initial NH_3 loss. It appears that the initial loss rate will increase with increasing air temperature and wind speed ($A_2/B_2=1.06>1$ and $A_3/B_3=1.10>1$, Table 2).

Despite the fact that a high DM content will result in a low initial loss rate ($A_5/B_5=0.94<1$), this loss rate will decline only very slowly, because of the high value of K_m ($B_5>1$). The persistence of high volatilization rates may be due to the TAN being retained in the DM on the soil surface.

Both the initial loss rate and total loss will be lower for pig slurry than for cattle slurry, as $A_4/B_4=0.22<1$ and $A_4<1$. The lower volatilization rate from pig slurry may be attributed to a lower viscosity, so that the TAN infiltrates more easily into the soil.

3.5. Prediction of NH_3 volatilization—selected cases

Climatic conditions, slurry composition, application methods and post-application cultivation vary considerably throughout Europe. It was therefore decided to investigate the variation in volatilization from surface-applied cattle and pig slurry at three different times of the year for four European locations. Furthermore, from the perspective both of a farmer and of a policy maker, it is interesting to examine the variation between locations, how soon incorporation should occur after application of slurry, in order to limit losses to a given percentage of the applied TAN.

The following typical application times were selected:

- 1 week before the normal sowing time for spring crops;
- the time of a mid-season grass cut (if relevant); and
- 1 week after the harvesting of the spring-sown crop.

Seven days of observed weather and soil water content from the year 2000 were used in this exercise, corresponding to the three application times for Italy (Po Valley), Southern England (Devon), Southern Norway (Follo area) and Denmark (Western Jutland). The predictions are representative of some of the most important European climate and soil conditions and used broadcast spreading, the most widely used slurry application technique (broadcast application). The slurry composition for the calculations was chosen according to the values in Table 4. It was decided that 100 kg TAN ha^{-1} should be applied by broadcast spreading in the three periods, resulting in application rates of 95.2 t ha^{-1} for cattle slurry and 39.4 t ha^{-1} for pig slurry. The predictions were calculated assuming that measurements were made using the micrometeorological mass balance technique. It was also assumed that the initial application took place at 07.00 h on day one without any post-application cultivation. The ALFAM model predictions of the cumulative NH_3 loss 7 days after slurry application are shown in Fig. 3.

For each day of the 7-day periods, the time that elapsed from slurry application to when 10% of the applied TAN was lost was calculated and averaged per period. Thus, an average result was obtained for each combination of slurry type (cattle/pig), country and period (1, 2, 3): see Fig. 4. The standard deviations are shown as error bars.

The main determinants of the NH_3 loss in Fig. 3 were the weather and the soil water content in the first 24 h after slurry application. The average air temperature, wind speed and soil water content (wet/dry) for the first 24 h and the corresponding data for the entire 7-day periods are shown in Appendix B. The data in Table 5 are relevant to the results in Fig. 4, since the results are averages corresponding to slurry application each day in these periods.

The ALFAM model predicted that there would be no large differences in NH_3 volatilization between the four

Table 4
Averages of pH, DM percentage, total nitrogen (N) and TAN for the slurry data from the ALFAM database used in the model analysis

Slurry type	pH	DM (%)	N total (g N kg^{-1})	TAN (g N kg^{-1})
Cattle slurry	7.34 (0.38; 162)	4.34 (1.75; 250)	2.30 (1.97; 230)	1.05 (0.50; 250)
Pig slurry	7.55 (0.35; 83)	4.04 (2.41; 115)	3.67 (1.32; 97)	2.54 (0.99; 115)

Standard deviations and numbers of observations are given in parentheses as (standard deviation; number of observations).

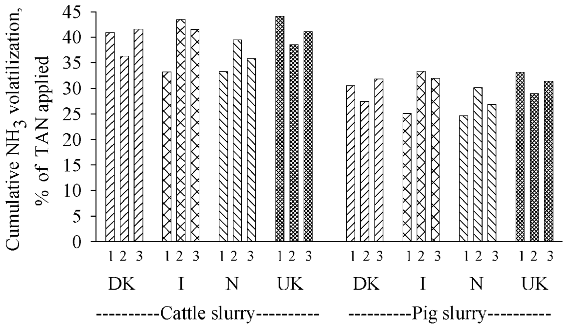

Fig. 3. Predicted cumulative NH_3 volatilization from surface application of cattle and pig slurry applied during three periods (1, before sowing barley; 2, mid-summer; and 3, after harvest) in Western Jutland in Denmark (DK), Po Valley of Italy (I), Southern Norway (N) and Southern England (UK).

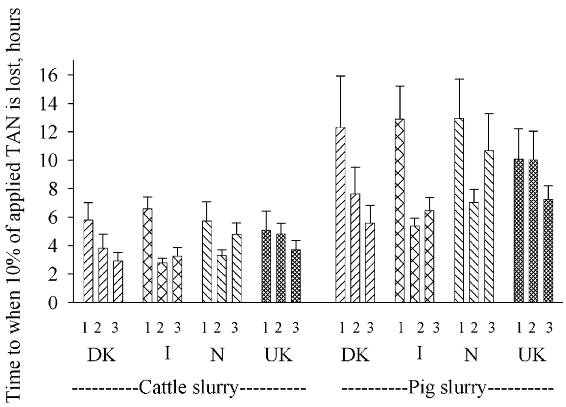

Fig. 4. The time from application time to when 10% of the TAN in applied slurry is lost. The results are based on simulation of slurry application during three periods (as in Fig. 3).

countries (Fig. 3). The NH_3 losses were higher from cattle slurry than from pig slurry, reflecting the higher DM content of the former, although the volatilization patterns across periods were similar for the two slurry types. The expected increase in volatilization between periods 1 and 2 and 3 as a consequence of the increase in air temperature (Appendix B) did not occur, because changes in soil water content and wind speed confounded the expected response in all countries. Wet soil and high wind speeds led to higher losses in period 1 in the UK and Denmark while wind speeds were generally low in Italy and the variations in NH_3 losses here were primarily caused by variations in the air temperature. Higher NH_3 losses as a consequence of higher temperatures in Italy might have been expected but did not occur, due to lower wind speeds than in Northern Europe. In conclusion, wind speed and soil water content were here the major determinants in NH_3 volatilization from field-applied pig and cattle slurry, but effectively counteracted one another.

The results show that soil water content did not influence the time needed for 10% of the applied TAN to be volatilized, so differences in wind speed and temperature can be used to explain the predicted differences between countries (Fig. 4). Mean wind speed does not vary significantly from one period to another within countries (Appendix B), so wind speed is unlikely to explain the within-country differences shown in Fig. 4. Conversely, the mean air temperatures for different periods within countries varied considerably, with lower temperatures for period 1, compared with periods 2 and 3. This difference can explain the longer time interval from spreading for the loss of 10% of the applied TAN in period 1 (Fig. 4).

4. Conclusion

The ALFAM model development and validation has shown that data from European experiments can be collated in one database and analysed statistically to provide a model with meaningful outputs. The outputs from the modelling are supported by theoretical considerations of impacts of the the weather, soil characteristics and slurry composition on NH_3 volatilization from animal slurries applied on fields with short crops (< 15 cm) or on fallow land. A Michaelis–Menten-type model provides a good fit for the measured NH_3 loss rates. The use of multiplicative rather than additive submodels in the ALFAM model improved overall predictive accuracy. The ALFAM model was used to calculate the NH_3 losses from typical slurry applied in four different European countries. The total volatilization rates were similar in Italy (Po Valley) and in North European countries because the effect of high temperatures in Italy was offset by a lower wind speed than in the North European countries. Therefore, the time between surface application with a splash plate and incorporation to achieve a specified emissions target was similar for all the countries. However, to determine whether this is generally the case for Europe, it would require a more comprehensive investigation, involving more locations and more years of weather data.

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Appendix A. Modelling NH_3 loss rates as a function of explanatory variables

The loss rate (loss per time unit, see Fig. 1) is defined as the derivative of the function in Eq. (1):

$$\frac{dN(t)}{dt} = N_{max} \frac{K_m}{(t + K_m)^2}. \tag{A.1}$$

However, loss rates are normally recorded experimentally as mean rates over finite time periods. Assuming that the NH_3 loss has been measured over the time period from t to $t + \Delta t$, then the mean loss rate over this time period can be expressed as

$$\bar{N}_{rate}(t, \Delta t) = \frac{N(t + \Delta t) - N(t)}{\Delta t} = \frac{N_{max} t + \Delta t / t + \Delta t + K_m - N_{max} t / t + K_m}{\Delta t}$$

or

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

The model in Eq. (A.2) was used for the analysis of NH_3 loss rates as a function of time. Sommer and Ersbøll (1994) related N_{max} and K_m to the explanatory variables through linear (additive) functions of the following type:

$$N_{max} = a'_0 + a'_1 x_1 + \cdots + a'_m x_m, \tag{A.3}$$

$$K_m = b'_0 + b'_1 x_1 + \cdots + b'_m x_m, \tag{A.4}$$

where $a'_0, \ldots, a'_m$ and $b'_0, \ldots, b'_m$ are model parameters to be estimated by statistical analysis, and $x_1, \ldots, x_m$ are the explanatory variables.

Since N_{max} and K_m should take only non-negative values and the expressions in Eqs. (A.3) and (A.4) can take any real values, the following relationships may be more appropriate:

$$N_{max} = \exp(a_0 + a_1 x_1 + \cdots + a_m x_m), \tag{A.5}$$

$$K_m = \exp(b_0 + b_1 x_1 + \cdots + b_m x_m), \tag{A.6}$$

where $a_0, \ldots, a_m$ and $b_0, \ldots, b_m$ are model parameters to be estimated. By rewriting these expressions it can be seen that Eqs. (A.5) and (A.6) correspond to multiplicative relationships with the exponentials of the explanatory variables as factors:

$$N_{max} = A_0 \times A_1^{x_1} \times \cdots \times A_m^{x_m}, \quad \text{where } A_i = e^{a_i}, \quad i = 0, \ldots, m, \tag{A.7}$$

$$K_m = B_0 \times B_1^{x_1} \times \cdots \times B_m^{x_m}, \quad \text{where } B_i = e^{b_i}, \quad i = 0, \ldots, m. \tag{A.8}$$

The NH_3 loss model in Eq. (A.2) was analysed with both additive and multiplicative models for N_{max} and K_m (Eqs. (A.3), (A.4)–(A.7) and (A.8), respectively). In both cases a power transformation was introduced in Eq. (A.2) as follows to ensure that the residuals will be approximately Gaussian distributed:

$$[\bar{N}_{rate}(t, \Delta t)]^{\lambda} = \left[N_{max} \frac{K_m}{(t + K_m)(t + \Delta t + K_m)} \right]^{\lambda}. \tag{A.9}$$

The value of the exponent, λ, was chosen to give the best approximation to a Gaussian distribution. The reason why both sides of the equation were raised to the power of λ was that this ensured that the original interpretations of N_{max} and K_m were still valid.

The model with multiplicative submodels for N_{max} and K_m produced a somewhat better fit than the one with additive submodels (R^2 values of 0.80 and 0.77, respectively). These results, together with the non-negativity constraints for N_{max} and K_m, suggest that the multiplicative approach is the more appropriate submodel. Consequently, only results from the former approach are presented in this paper.

Appendix B

Weather and soil water content data used for prediction of NH_3 volatilization for the three 7-day periods (of the year) in each of the four countries. Table 5 refers to the average for the first 24 h of each period, and Table 6 refers to the average for the entire periods.

Table 5
Statistics for first day (24 h) of each period

	Period 1			Period 2			Period 3		
	Average air temp. (°C)	Average wind speed ($m\,s^{-1}$)	Soil water content	Average air temp. (°C)	Average wind speed ($m\,s^{-1}$)	Soil water content	Average air temp. (°C)	Average wind speed ($m\,s^{-1}$)	Soil water content
Denmark	6.0	5.8	Wet	11.1	1.8	Dry	13.4	3.0	Dry
Italy	6.5	0.9	Wet	19.1	0.9	Dry	18.2	1.0	Dry
Norway	4.6	1.1	Wet	12.0	3.1	Dry	8.0	0.6	Wet
England	10.4	5.3	Wet	10.1	3.5	Dry	14.1	3.6	Dry

Table 6
Statistics for entire periods (7 days each)

	Period 1			Period 2			Period 3		
	Average air temp. (°C)	Average wind speed ($m\,s^{-1}$)	Soil water content	Average air temp. (°C)	Average wind speed ($m\,s^{-1}$)	Soil water content	Average air temp. (°C)	Average wind speed ($m\,s^{-1}$)	Soil water content
Denmark	5.0	4.1	Wet	11.1	3.7	Dry	14.1	4.4	Dry
Italy	8.1	1.3	Wet	20.7	0.8	Dry	18.6	1.0	Wet/dry
Norway	4.5	2.1	Wet	13.0	2.5	Wet/dry	8.6	0.7	Wet
England	8.5	3.5	Wet	9.5	2.7	Dry	14.4	2.7	Dry

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