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Analysis of ammonia losses after field application of biogas slurries by an empirical model

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Abstract

Due to energy crises and stricter environmental regulations, renewable energy sources like biomethane produced by anaerobic digestion (biogas) become increasingly important. However, the application of slurries produced by biogas fermentation to agricultural land and subsequent ammonia emission may also create environmental risks to the atmosphere and to N-limited ecosystems. Evaluating ammonia loss from agricultural land by model simulation is an important tool of agricultural-systems analysis. The objective of this study was the systematical comparison of ammonia volatilization after application of two types of biogas slurries containing high amounts of energy crops in comparison with conventional animal slurries and to investigate the relative importance of factors affecting the emission process through an empirical model. A high number of ammonia-loss field measurements were carried out in the years 2007/08 in biogas cropping systems in N Germany. The study consisted of simultaneous measurement of NH_3 losses from animal and biogas slurries in multiple-plot field experiments with different N-fertilization levels. The derived empirical model for the calculation of NH_3 losses based on explanatory variables gave good predictions of ammonia emission for both biogas and pig slurries. The root mean square error (*RMSE*) and mean bias error (*MBE*) of the empirical model for validation data were 2.19 kg N ha^{-1} (*rRMSE* 29%) and –1.19 kg N ha^{-1}, respectively. Biogas slurries produced highest NH_3 emissions compared to the two animal slurries. In view of the explanatory variables included in the model, total NH_4^+ application rate, slurry type, temperature, precipitation, crop type, and leaf-area index were important for ammonia-volatilization losses.

Key words: ammonia volatilization / N loss / crop type / animal slurry / trail hoses

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1 Introduction

Ammonia (NH_3) volatilization from field application of organic slurries not only results in fertilizer-N loss and thus financial loss, but also adverse effects on the environment. Ammonia volatilization from agriculture is considered as the main source of atmospheric pollution by NH_3 (*Bouwman* and *VanderHoek*, 1997; *Sommer* and *Hutchings*, 2001; *Vitousek* et al., 2009). Subsequent excess NH_3 deposition from the atmosphere causes soil acidification and eutrophication of N-limited natural and seminatural ecosystems as well as surface water bodies (*Dragosits* et al., 2002; *Sanderson* et al., 2006). With increasing concern about climate change and other environmental issues, there are international obligations in the EU to limit environmentally critical trace-gas emissions such NH_3 (NEC directive; directive 2001/81/EC of the European Parliament and of the Council).

In order to assess NH_3 emissions or evaluate control measures to reduce NH_3 loss, many models have been developed. However, NH_3 loss is affected by a variety of factors and it is still difficult to quantify the comprehensive effects on NH_3-emission processes (*Sommer* et al., 2003). Mechanistic or process-based models describe mathematically transport processes in the NH_3 source, the soil, and the atmosphere (*Teye* and *Hautala*, 2008; *Sommer* et al., 2006). To obtain the mass-transfer coefficient, these models need detailed climate, soil, and slurry variables and parameters in high temporal resolution as input. That data is not easy to obtain under conditions of agricultural practice. Alternatively, statistical regression models like ALFAM (*Sogaard* et al., 2002) were developed based on experimental data under a wide range of experimental conditions (*Menzi* et al., 1998; *Nyord* et al., 2008). Empirical regression models can help to predict the NH_3 loss after slurry application to farmland and can explain a significant amount of the variance in the data (*Sommer* et al., 2003). Empirical models can be used as analytical tools for identifying of the effect of environmental and treatment factors on NH_3 losses, while the mere statistical comparison of treatment factors gives only reduced insight into the relative importance of different factors in the ammonia-loss process.

In European countries like Germany, bio-energy has become more and more attractive for farmers and energy-producing companies. The increasing number of biogas plants has led

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to more and more biogas slurries of a new type, containing a high share of energy crops, applied to the farmland as a fertilizer (*Loria* et al., 2007). Biogas slurry is a cheap source of plant nutrients and can offer extra benefits to soil fertility and crop yield (*Terhoeven-Urselmans* et al., 2009). However, the NH_4^+ content and pH of the biogas slurry increase during fermentation of biogas crops (*Wulf* et al., 2002). This could result in high potential NH_3 emissions after application to arable land. Nevertheless, the effect of the application of the new type of biogas slurries on NH_3 losses has not yet been quantified extensively and there exists no particular model development for the calculation of NH_3 emission after application of biogas slurries. In our work, a simple empirical regression model was tested and used to analyze NH_3 emissions based on the same approach as used in the ALFAM model (*Sogaard* et al., 2002). Our aim was to analyze the results of NH_3-emission measurements from different slurries under identical conditions and to discriminate significantly between the effects of new types of biogas slurries and conventional slurries on NH_3 losses after field application under a large variety of experimental conditions. In contrast to many other studies, the influence of a wide range of environmental variables on NH_3 loss is thereby included in the analysis which allows an unbiased comparison between slurry treatments. This analysis also included variables such as application time, slurry viscosity, precipitation, crop type, and leaf-area index (LAI), which are tested firstly together with commonly used variables as slurry pH or temperature in such a model framework. Moreover, possible reduction measures through analysis of the effects of relevant factors on the NH_3 emissions are discussed.

2 Materials and methods

2.1 Field-experiments description

2.1.1 Site description

Experiments for the determination of NH_3 losses after biogas-slurry application were carried out in fields of the farms Karkendamm (KD) and Hohenschulen (HS) attached to Kiel University (Schleswig-Holstein, N Germany). The soil type in Karkendamm is a typical Podsol (FAO). The plow layer was characterized by a pH ($CaCl_2$) of 6.1, a high organic-C content of 6.3% (moor outskirts) as well as a high NH_4^+-adsorption capacity.

The soil types (FAO) in Hohenschulen vary between Cambisol, Stagnosol, and Colluvisol due to the hilly landscape. The most common soil texture in the plow layer is sandy loam. The organic-C content of the top soil is 3%, and the top layer shows a similar NH_4^+-adsorption capacity to the Karkendamm soil. Both locations are characterized by a maritime climate with an annual average temperature of 8.4°C and an annual mean precipitation of 760 mm.

2.1.2 Experimental design

Ammonia losses were determined in different crop rotations for biogas production and under weather, soil, and canopy conditions typical of practical farming. In addition to the usual continuous maize cropping, alternative biogas-crop rotations with maize, wheat, and rye grass were established and NH_3 losses were determined under different canopy conditions (bare, cut rye grass, wheat with different growth stages, and maize). For comparison, pig and cattle slurry were also applied as organic N fertilizers in addition to biogas slurries. All treatment combinations were tested with 4 replicates. Experimental plots (12 m × 12 m) were arranged without interspaces in rows consisting of 16 plots. Rows were separated by pathways of 8 m breadth. Total number of plots was 240 in HS and 96 in KD. Altogether, 8 different N-levels (0, 40, 60, 80, 100, 120, 140, 180 kg N ha^{-1}) were tested. Slurries were applied with trail hoses with a range of 6 m. Altogether, 15 measurement campaigns for the determination of NH_3 losses after simultaneous application of organic fertilizers were carried out in the years 2007/08.

2.1.3 Organic-fertilizers application

Two types of monofermented and one cofermented biogas slurries were used, both containing high amounts of energy crops exclusively grown for biogas production. Monofermentation implies that only renewable primary products (crops) were used in the fermentation process. Cofermented residues contain crops as well as animal slurries. Both biogas slurries were obtained from farmer-operated regional biogas plants. The monofermented biogas slurry used in 2007 consisted of maize (90%) and cereals (10%). The second monofermented biogas slurry used in 2008 was derived from 100% maize biogas substrate. The cofermented biogas slurry contained pig slurry (50%) and maize (50%), temporarily cattle slurry from neighboring farmers. As all biogas slurries applied had very similar properties (Fig. 1), they were tested in the empirical model as one slurry type. For logistical reasons, the different organic fertilizers could not be applied at the same time, *i.e.,* applied one slurry type after the other. The effect of slurry application time on NH_3 emissions is considered in the model analysis.

2.1.4 Ammonia-loss measurement method

Ammonia-loss measurements are based on the combination of passive samplers as employed in the Standard Comparison Method (*Vandre* and *Kaupenjohann*, 1998) and an open-dynamic-chamber method, the Dräger Tube Method (*Pacholski* et al., 2006). Passive sampling results give semi-quantitative differences between treatments, *i.e.,* the ratio of differences between treatments is properly reflected. Ammonia losses from passive sampling can be scaled into actual absolute cumulative NH_3 losses *via* transfer coefficients, as demonstrated in *Vandre* and *Kaupenjohann* (1998). In the original publication, a NH_3-emission system was used to obtain known absolute NH_3 fluxes. In our study, transfer coefficients were determined from absolute NH_3 fluxes obtained by the Dräger Tube Method (*Roelcke* et al., 2002; *Pacholski* et al., 2006). This method allows quantitative NH_3-loss measurements on small plots in a relative short time (≈ 5 min) and showed a good agreement with micrometeorological techniques (*Pacholski* et al., 2008). The Dräger Tube Method consists of 4 stainless-steel chambers (height 15 cm, 100 cm^2 area covered by each chamber) placed onto the soil which are connected *via* Teflon tubing to a hand pump. The pump induces a flux of ambient air through the system which is enriched with NH_3 emitted from the soil surface while passing through the chambers. The concentration of NH_3 in the air leaving the chambers is instantaneously determined by Dräger Tubes before it is sucked into the pump. The method gives NH_3 fluxes at a specific point in time, and cumulative losses are calculated by linear interpolation between two subsequent measurements in the sequence. The results of this method are in close agreement with true absolute losses due to its calibration on a high number of simultaneous measurements with a micrometeorological method (*Pacholski* et al., 2008) which is the most precise methodology for quantifying ammonia losses in the field (*Harper* and *Sharpe,* 1998).

The passive samplers were made of polyethylene widemouth bottles (Lamaplast 250 mL, SciLabware Ltd, Staffordshire, UK) with circular holes on each side (10 cm^2) covered by mosquito mesh to allow flux of ambient air through the samplers. Samplers were filled with 20 mL H_2SO_4 (0.05 M) to absorb NH_3. Passive samplers were fixed on a steel stand covered on top by a plastic protection shield and placed 0.15 m above soil surface or canopy. Putting the samplers in the center of the quadratic plots minimized the influence of wind-direction variation on NH_3 absorption by the samplers. Sampling was conducted simultaneously by placing passive samplers in each of the experimental plots. Solutions in the passive samplers were replaced every 3 to 6 h in the daytime and 10 to 12 h at night. Ammonia concentrations in the collected solutions were determined by an NH_3 electrode (Orion 4 Stars, Thermo Scientific, Hialeah, FL, USA).

Ammonia losses from two plots equipped with passive samplers were also determined quantitatively by the Dräger Tube Method. Transfer coefficients were calculated as the ratio of cumulated NH_3 collected by passive samplers and cumulated absolute NH_3 losses determined by the DTM at the end of each experimental campaign. Ammonia losses were determined for $\approx$ 3 d after slurry application until NH_3 fluxes became undetectable. In earlier studies (*Gericke* et al., 2011a; *Quakernack* et al., 2011), the combination of passive samplers with the Dräger Tube Method showed the same dynamics and cumulated losses of NH_3 emissions from field-applied biogas residues applied by trail hoses in comparisons to micrometeorological measurements under a large variety of environmental conditions.

2.1.5 Meteorological-data measurement

Meteorological data were obtained from two weather stations installed at both locations. The stations included two cup anemometers. One was mounted at a height of 0.2 m, which was a Thies First Class anemometer, and another one at a height of 2 m (Thies economy, Thies GmbH, Göttingen, Germany). Air temperature and atmospheric pressure were measured at 1.5 m height with a Thermo Hygro Sensor STANDARD, soil temperature at a depth of 5 cm with a soil-temperature sensor (PT1000). Global radiation was determined with a CM3 (Kipp & Zonen).

2.1.6 Lab analysis of slurry characteristics

Samples of all slurries (biogas slurry as well as animal residuals) were taken at every application date from the trail hoses during application. In addition to the standard parameters, dry-matter (DM) content, total N content, pH value (pH electrode HI1291 D, Hanna Instruments, Ukraine), and the buffer capacity (*Sommer* et al., 1995) were determined. Slurry viscosity was measured with a HAAKE Viscotester 71 (Thermo Scientific, USA). For the analysis of slurry mineral N, slurry was sampled and extracted with a 2M KCl (pH 1) solution (1:4 w/v) for 1 h. The extracts were then filtered with a Whatman 602 filter paper and immediately analyzed. The concentrations of NH_4^+ in slurry extracts were measured using a TRAACS 800 auto-analyzer (Bran and Luebbe, Hamburg, Germany).

2.2 Methods of statistical modeling

2.2.1 Response variables and explanatory variables

During the field experiments, NH_3 loss and influencing factors were measured. Cumulative NH_3 loss, as characterized by parameters of an empirical model fitted to the time courses of NH_3 loss (Eq.1), was treated as a response variable. Other variables were considered as explanatory variables. Mean values of explanatory variables during the duration of NH_3-loss measurements were used for model fitting. As correlation between variables hampers the interpretation of a regression analysis, a correlation matrix was created (not presented) to test for correlation between variables. If the significance level of a correlation test between two variables was smaller than 0.05 ($p < 0.05$), one of the two variables was excluded. As an exclusion criterion, variables which were considered as drivers were kept in the data set whereas derived or dependent variables were excluded (*e.g.,* air temperature [included] *vs.* soil temperature [excluded]). Finally, 15 variables were used for the development of the model, while 10 variables were excluded. Included and excluded variables are shown in Tab. 1. The explanatory variables could be divided into four categories: slurry parameters, crop parameters, application parameters, and environment parameters.

The data sets include some indicator variables (values equal to zero or one), which enable representation of different states of classified factors (*e.g.,* slurry type). Slurry type was defined as cattle slurry, pig slurry, cobiogas slurry, and monobiogas slurry. Both biogas-slurry types tested in our study were merged into one factor due to very similar slurry characteristics (Fig. 1). Crop type included maize, wheat, and grass. Precipitation was set as precipitation (one) or nonprecipitation (zero). If cumulative precipitation was < 5 mm during the measurement campaign, the value of precipitation was zero, otherwise one. This threshold value was chosen because NH_3-volatilization rates in measurements after slurry application strongly decreased when rainfall was > 5 mm in earlier studies (*Sommer* and *Olesen*, 2000).

Table 1: Explanatory variables selected for modeling parameterization of the initial model. Excluded variables are listed at the bottom.

Variables	Code	Range	Comments
Slurry factors			
Slurry type	X_1	[0, 1]	X_1 = 1 if S2 (cattle slurry)
	X_2	[0, 1]	X_2 = 1 if S3 (pig slurry)
			slurry type is biogas when $X_1 = X_2 = 0$
pH	X_3	[6.72, 8.04]	
Viscosity	X_4	[14, 313]	unit: mPa s
DM content	X_5	[2.99,10.40]	unit: %
TANA[a]	X_6	[15.65, 148.54]	unit: kg ha^{-1}
Precipitation	X_7	[0, 1]	X_7 = 1 if precipitation amounts more than 10 mm
Crop factors			
Crop type	X_8	[0, 1]	X_8 = 1 if crop is wheat
	X_9	[0, 1]	X_9 = 1 if crop is maize
			crop is grass when $X_8 = X_9 = 0$
LAI	X_{10}	[0,4.65]	
Environment factors			
Air temperature	X_{11}	[1.4, 29.9]	unit: °C
Wind speed	X_{12}	[0.7, 7.5]	unit: m s^{-1}
Global radiation	X_{13}	[10.32, 79.17]	unit: W m^{-2}
Application factors			
Application time	X_{14}	[0,1]	X_{14} = 1 if slurry applied before 11:00 a.m.
	X_{15}	[0,1]	X_{15} = 1 if slurry applied between 11:00 a.m. and 03:00 p.m. represents noon
			slurry applied after 03:00 p.m. represents afternoon if $X_{14} = X_{15} = 0$

[a]TANA represents total ammonium nitrogen-application rate; LAI = leaf-area index; DM = dry matter: **excluded variables**: NH_4^+ concentration (kg m^{-3}), total N concentration (kg m^{-3}), relative NH_4^+ content (%), slurry application rate (t ha^{-1}), measurement duration (h), crop height (cm), soil temperature (°C), temperature sum (°C), air pressure (hPa), air humidity (%), saturation deficit of the air (mbar)

2.2.2 Model algorithms

(1) A Michaelis-Menten-type equation, which fits the general shape of NH_3-loss time curves well, was used to obtain the final cumulative NH_3 loss at infinite time (Eq. 1). It was used for the first time for NH_3-loss studies by *Sommer* and *Ersboll* (1996) and was applied in several more NH_3-emission studies (*Misselbrook* et al., 2005; *Nyord* et al., 2008):

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

$N(t)$ (kg N ha^{-1}) represents cumulative ammonia loss during a specific time span (t) after slurry application. N_{max} represents the total ammonia loss when time approaches infinity and K_m (h) represents the time interval when $N(t)$ reaches 0.5 of N_{max}. N_{max} and K_m estimates were derived by fitting Eq. 1 to the observed time courses of NH_3 loss by nonlinear regression using least squares (coefficient of determination) as optimization criterion, and are referred to as *fitted* N_{max} and *fitted* K_m. *Fitted* N_{max} and *fitted* K_m were considered as observation values of measured ammonia losses.

(2) The *fitted* N_{max} and *fitted* K_m and explanatory variables were used to derive N_{max} and K_m as functions of explanatory variables, further referred to as *predicted* N_{max} and *predicted* K_m. As in the ALFAM model approach (*Sogaard* et al., 2002), a multiplicative equation (Eq. 2) was chosen for the calculation of *predicted* N_{max} and *predicted* K_m by explanatory variables to avoid negative values. The letters x_i indicate explanatory variables in the exponent, and A_i and B_i are connected parameters which are estimated during model fitting for *predicted* N_{max} and *predicted* K_m, respectively.

$$\begin{aligned} &\textit{predicted } N_{\max} = A_0 \times A_1^{x_1} \times A_2^{x_2} \ldots \times A_m^{x_m} \text{ and} \\ &\textit{predicted } K_m \quad = B_0 \times B_1^{x_1} \times B_2^{x_2} \ldots \times B_m^{x_m} \end{aligned} \qquad (2)$$

Coefficient estimates $A_i > 1$ indicate that the corresponding factors have a positive relationship with N_{max} and *vice versa*. With respect to K_m, coefficient estimates $B_i > 1$ indicate that the duration of NH_3 volatilization would be prolonged. Otherwise, NH_3 losses are faster and more intensive.

Introducing measured explanatory variables into Eq. 2, *predicted* N_{max} and *predicted* K_m can be calculated for all experimental conditions.

2.2.3 Parameterization and validation data sets

To avoid the effect from the differences between replicates, mean values for each treatment and application date were used for model development. Measurement campaigns lasted for ≈ 3 d and in general, *fitted* N_{max} values were very close to measured final cumulated losses. On average, measured final losses corresponded to 85% of *fitted* N_{max}. However, in some cases *fitted* N_{max} values were much higher than measured final losses. This means that average values of explanatory variables observed during the NH_3 measurements could only explain a relatively small proportion of the *fitted* N_{max} value. To avoid this source of uncertainty, records were excluded from the data set if the *fitted* K_m exceeded 24, which indicates a very slow emission process. Many published studies showed that cumulative NH_3 emission during the first day would amount to more than half the final NH_3 loss (*Sommer* and *Olesen*, 2000; *Sogaard* et al., 2002; *Wulf* et al., 2002). As a result, 46 records from measurements on individual plots were considered in the model development. The selected records were divided into two data sets. We chose 9 records from 3 application campaigns in different seasons including different slurries, weather conditions, and crops for model validation, and the others were used for parameterization (37 records from 12 measurement campaigns). A larger data set was used for model development in order to include most of the field trials for data analysis and to obtain robust model parameters. The smaller validation data set was set-up to include all slurry types tested as well as different N-fertilization levels and weather conditions.

2.2.4 Parameter estimation for the predictive model

In the parameter-estimation process for Eq. 2, *fitted* N_{max} and *fitted* K_m were logarithm-transformed in order to derive model parameters by model fitting based on multiple-linear-regression procedures using least square deviations as the optimization criterion. Only parameters which significantly contributed to the model prediction ($p < 0.05$) were considered in the model equations. In a second step, Akaike's information criterion (AIC) was applied for model simplification by stepwise regression (*Akaike*, 1974). The performance of parameterization was evaluated by the value of adjusted R^2 in the regression results. At the same time, 95% confidence intervals were also calculated as estimates of parameter uncertainty. The model after AIC simplification was adopted as the final model.

2.2.5 Evaluation of model performance

The performances of the model were assessed by root mean square error (*RMSE*) and mean bias error (*MBE*) which were calculated by using the *fitted* N_{max} and *predicted* N_{max}.

$$RMSE = \sqrt{\frac{\sum_{i=1}^{N}(O_i - P_i)^2}{N}}, \quad (3)$$

$$rRMSE(\%) = \sqrt{\frac{\sum_{i=1}^{N}\left(\frac{O_i - P_i}{O_i}\right)^2}{N}} \times 100, \quad (4)$$

$$MBE = \frac{\sum_{i=1}^{N} P_i - O_i}{N}, \quad (5)$$

where O_i is the observed value (*fitted* N_{max}), P_i is predicted value (*predicted* N_{max}), and N is the number of observations.

2.2.5 Nonparametric test

For the comparison with the results obtained from the analysis by the empirical model, fitted final cumulated relative NH_3 losses [% NH_4^+-N applied] were also analyzed by statistical testing. As NH_3-loss data were nonnormally distributed, even after log-transformation (Shapiro-Wilk Normal distribution test, $p < 0.05$), a nonparametric test was employed for investigating the effect of slurry type and application time on ammonia-loss ratio. The data set used was identical with the model parameterization data set including 138 records of final cumulated NH_3-loss values (individual plot measurements).

All fitting and testing of the empirical model as well as statistical testing were performed using the statistical software package R (version 2.9.2; *R Development Core Team*, 2009). The package "pairwiseCI" and the method of Student were used for nonparametric testing of the effect of application time and slurry type.

2.2.6 Exemplary model output

Owing to the model complexity, it is essential to demonstrate the comprehensive effect of identical environmental conditions on NH_3 emissions from different slurries. Depending on the final model, typical slurry characteristics, identical application rates and weather conditions were specified for investigating the behavior of ammonia emissions after simultaneous application of different slurries.

The median values of slurry characteristics for three different slurries (DM, viscosity, NH_4^+-N content, pH) were used as input. The weather data were extracted from May 25, 2007 in Hohenschulen (HS), and mean values of air temperature, wind speed, and global radiation for 72 h after application were calculated for model input.

3 Results

3.1 Slurry characteristics

The parameters of slurries including pH, DM content, viscosity, and total NH_4^+-N content (TAN) are shown in Fig. 1. Generally, the pH of biogas slurry (S3 and S4), ranging between

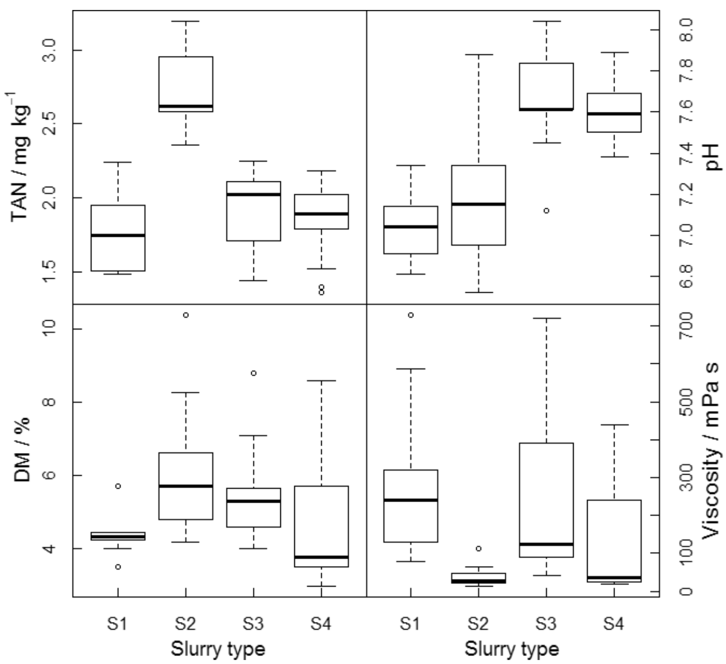

Figure 1: Chemical characteristics of tested slurries: total NH_3 content (TAN), pH, dry-matter content (DM), and viscosity. S1 = cattle slurry, S2 = pig slurry, S3 = cofermented biogas slurry, S4 = monofermented biogas slurry (only energy crops as fermentation substrate).

7.4 and 8.0, was higher than of cattle slurry (S1) and pig slurry (S2) which varied between 6.4 and 7.83, with pig slurry (S2) showing considerable variation. Moreover, the total NH_4^+-N content in the pig slurry (S2) was > 2.2 mg kg^{-1}, significantly higher than in other slurries. The DM content varied considerably except in cattle slurry (S1) with ≈ 4.2%. Viscosity of pig slurry (S2) was lower than the other slurries.

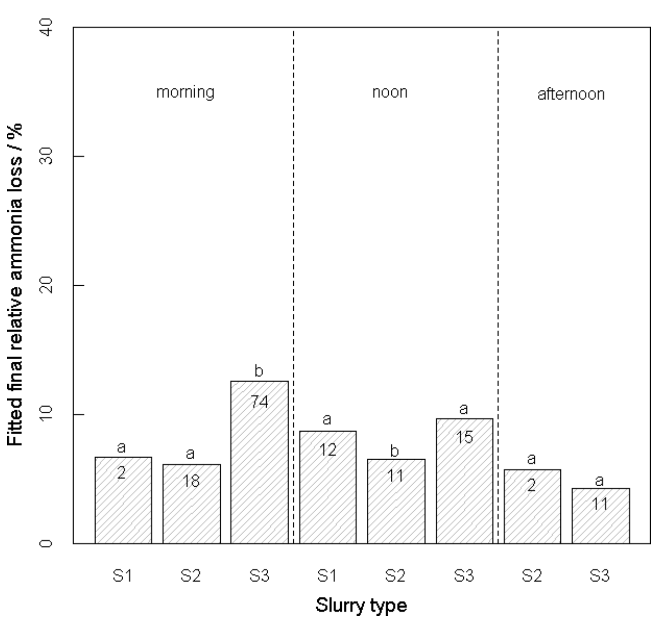

Figure 2: Fitted final relative ammonia losses of different slurries when applied at different times. S1, S2, and S3 represent cattle slurry, pig slurry, and biogas slurry, respectively. The letters on the top of the bar indicate the multiple comparison results by a nonparamatric test (Wilcox method), and the number of observations is given in the bar.

3.2 Relative ammonia losses of different slurries

The results of the multiple comparisons of fitted final relative NH_3-N ammonia losses are presented in Fig. 2. The mean values of biogas slurry were 13%, 10%, and 4% when applied in the morning, noon, and afternoon (Fig. 2), respectively. However, with respect to cattle slurry, relative losses increased from the morning (6.63%) to noon (8.68%). The nonparametric multiple two-way comparison (Wilcox method) indicated that there were significant differences between the pig slurry and the other two slurries when applied at noon ($p < 0.05$), while there was no significant difference between pig slurry and cattle slurry when applied in the morning (p = 0.1). In most situations, NH_3 losses from biogas slurries were significantly higher as those from pig and cattle slurry.

3.2 Regression analysis of N_{max} and K_m

3.2.1 Parameters estimation

Fitting the Michaelis-Menten Equation (Eq. 1) to the time courses of NH_3 loss of the individual plot measurements yielded high coefficients of determination (average R^2 = 0.93, median R^2 = 0.95). Therefore, *fitted* N_{max} and *fitted* K_m closely reflected the actual time courses of NH_3-N loss.

With respect to the parameterization data set for the predictive model (Eq. 2), after AIC stepwise regression, the adjusted R^2 values for the final empirical model regression for *predicted* N_{max} and *predicted* K_m were 77.8% and 79.7%, respectively. The parameter estimates from the stepwise regression are summarized in Tab. 2. It includes the parameters connected with the explanatory variables for the calculation of *predicted* N_{max} and *predicted* K_m and the corresponding 95% confidence intervals, respectively.

Table 2: Parameter estimation and confidence limits for the regression model with multiplicative submodels (Eq. 3). Blank in the table means the variable was excluded by the AIC criteria.

Factors	N_{max}			K_m		
	estimates	95% confidence interval		estimates	95% confidence interval	
Common factor	1.7367	0.8929	3.3780	9.64E+04	2.63E+03	3.53E+06
Cattle slurry	0.5858	0.3300	1.0402			
Pig slurry	0.6290	0.4568	0.8662	0.5452	0.3710	0.8011
pH				0.4239	0.2695	0.6667
Viscosity				0.9988	0.9978	0.9998
DM				1.1669	1.0640	1.2796
TANA[a]	1.0122	1.0074	1.0169			
Precipitation	0.2123	0.1253	0.3596	0.1609	0.1055	0.2453
Wheat				0.1208	0.0444	0.3292
Maize	0.2913	0.1480	0.5734			
LAI	0.7982	0.6492	0.9814	1.9390	1.4560	2.5823
Air temperature	1.1278	1.0782	1.1796	0.8663	0.8163	0.9195
Wind speed	1.2508	1.0749	1.4554			
Global radiation	0.9967	0.9946	0.9988	0.9971	0.9947	0.9995

[a]TANA represents total NH_4^+-N rate (kg ha^{-1}).

For model simplification, pH, viscosity, and DM content were excluded from the N_{max} model by the AIC criterion. Only total NH_4^+-N-application rate remained and showed significant positive relations with *predicted* N_{max} since their estimates were > 1. Moreover, the estimates for slurry-type factors indicated that biogas slurry induced higher NH_3 loss than the other two slurries. Among the three crop types, the parameter for maize was 0.2913, indicating that a maize-crop cover induced lower NH_3 losses than wheat or grass. Leaf-area index also showed a significant negative relationship with *predicted* N_{max}. Regarding weather factors, air temperature, and wind speed had stimulating effects on ammonia loss, and precipitation was negatively related to absolute *predicted* N_{max} implying that precipitation could reduce NH_3 loss.

With respect to K_m, the estimate for air temperature was < 1, which indicated that high temperature entails a short-term ammonia-emission period. The small K_m value indicated intensive emission after slurry application. Similarly, pH, slurry viscosity, and precipitation were negatively related to K_m, but some variables showed positive relationship with K_m. Higher NH_4^+-N-application rates and large LAI would prolong the duration of NH_3 loss.

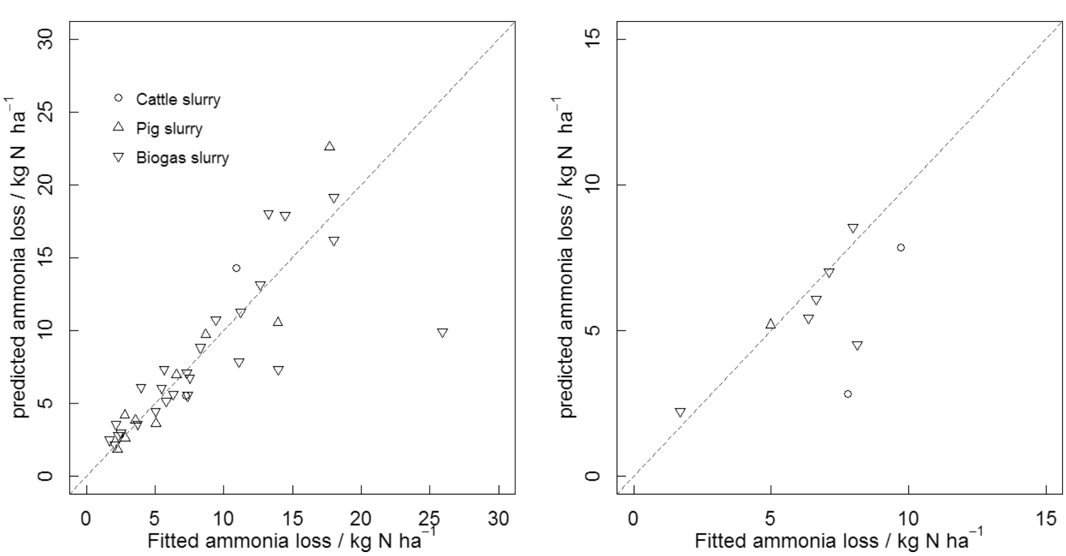

Figure 3: Relationship between predicted N_{max} and fitted N_{max} with the 1:1 line for the parameterization dataset (left) and the validation dataset (right). N_{max} represents final absolute NH_3 loss.

Table 3: Evaluation of the statistical empirical model for final absolute NH_3 loss (*predicted* N_{max}) by two datasets (*fitted* N_{max}, parameterization and validation) and the measured final loss.

Slurry type	Parameterization N_{max}		Validation N_{max}		Validation measured final loss	
	RMSE / kg N ha^{-1}	*MBE* / kg N ha^{-1}	*RMSE* / kg N ha^{-1}	*MBE* / kg N ha^{-1}	*RMSE* / kg N ha^{-1}	*MBE* / kg N ha^{-1}
Cattle slurry*	2.70 (2)	0.84	3.76 (2)	–3.42	5.20 (2)	–4.68
Pig slurry*	2.14 (9)	0.28	0.22 (1)	0.22	2.04 (1)	–2.04
Biogas slurry*	3.77 (26)	–0.51	1.58 (6)	–0.68	2.64 (6)	–1.82
All slurries (*rRMSE*%)	3.39 (25)	–0.24	2.19 (29)	–1.19	3.42 (30)	–2.59

*Numbers in the brackets represent case number.

3.2.2 Evaluation of the empirical model

The evaluation of *predicted* N_{max} calculated by the empirical model for parameterization and validation data sets is shown in Fig. 3. The agreement between calculated and measured values was close for all slurries for the parameterization data set. In the validation, predicted values were well distributed on both sides of the 1:1 line, only when NH_3 emission was low, the N_{max} prediction error increased.

The evaluation of model performance is summarized in Tab. 3. The *RMSE* for final ammonia losses (N_{max}) over all slurry types for parameterization data (N = 37) and validation data (N = 9) were 3.39 (*rRMSE* = 25%) and 2.19 kg N ha^{-1} (*rRMSE* = 29%), respectively. The values of the mean bias error (*MBE*) for parameterization and validation were –0.24 and –1.19 kg N ha^{-1}, respectively. With respect to different slurries, *RMSE* in validations for cattle slurry, pig slurry, and biogas slurry were 3.76, 0.22, and 1.58 kg N ha^{-1}, respectively. Only for cattle slurry, a strong bias from the 1:1 line was observed. In parameterization, most predicted NH_3-loss values were well distributed on both sides of the 1:1 line (Fig. 3), with only one predicted record deviating strongly from the measured value. Based on the *predicted* N_{max}, the measured final NH_3 losses were also calculated. The root mean square error (*RMSE*) and the mean bias error (*MBE*) for calculated cumulative losses at the end of measurement including application of cattle slurry were 3.42 kg N ha^{-1} and –2.59 kg N ha^{-1}, respectively.

3.3 Exemplary model calculations for identical conditions

Under the specified identical weather conditions and NH_4^+-N-application rates and average characteristics for each slurry type, time courses for the three slurry types are shown in Fig. 4. Ammonia losses increased with NH_4^+-N-application rate, and biogas-slurry application showed higher NH_3 losses than the other slurries. Ammonia losses are decreased by precipitation. In the model example, NH_3 loss decreased by > 50% when precipitation was > 5 mm.

4 Discussion

Ammonia emissions after field application of a new type of biogas slurries containing a large proportion of energy crops

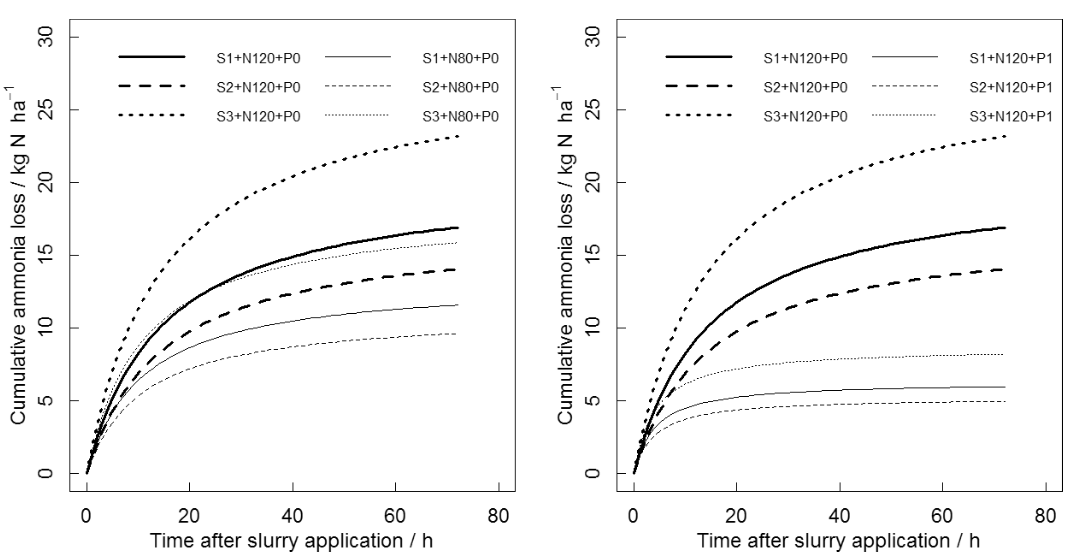

Figure 4: Model example results for different slurries applied under identical conditions: application time 9 a.m., mean temperature 14°C, wind speed (height of 2 m) 3.3 m s^{-1}, and global radiation 120 W m^{-2}. S1, S2, and S3 represent cattle slurry, pig slurry, and biogas slurry, respectively. N120 and N80 indicate total NH_4^+-N-application rate (kg ha^{-1}). P0 and P1 indicate no precipitation < 5 mm (P0) and precipitation > 5 mm (P1).

were analyzed with an empirical model approach as compared to NH_3 losses from conventional animal slurries. Higher NH_3 losses occurred from biogas slurry than from conventional animal slurries under the same environmental conditions. This is also in agreement with the statistical analysis of the measured cumulated losses with a nonparametric test and other studies carried out with biogas slurries with a high share of energy crops (*Moeller* and *Stinner,* 2009). Although typical weather and slurry variables for the prediction of NH_3 losses were included in the final model, novel variables such as slurry characteristics, crop and environmental factors, and application time also played a significant role in describing the ammonia-emission processes.

4.1 Performances of the model prediction

In general, the model prediction was in good agreement with experimental measurements indicating that the model was a valid basis for process analysis (Tab. 3). However, the *RMSE* of cattle slurry was 3.76 kg N ha^{-1}, much higher than for the other two slurries in the validation. If records related to cattle slurry were excluded from the dataset, the *RMSE* and *MBE* of validation decreased to 1.44 (*rRMSE* = 22%) and –0.53 kg N ha^{-1} (not presented). Similarly, after exclusion of the strongly deviating records (only one), the *RMSE* of parameterization sharply decreases to 2.13 kg N ha^{-1} (*rRMSE* = 22%).

4.2 Effect of meteorological factors and soil types on NH_3 losses

Our model parameterization with respect to environmental conditions is in good agreement with general findings on the effect of environmental conditions on the NH_3-loss process. This underpins the overall validity of the measurement approach and the developed model. Ammonia loss had a positive relationship with temperature and wind speed. High wind speed could significantly increase the turbulence in the atmosphere, and this could increase the transport of ammonia away from the slurry surface (*Sommer* and *Hutchings*, 2001). High temperature increases the NH_3 diffusion constant and the transfer of NH_3 from the aqueous to the gaseous phase (Henry constant) while high wind speed can enlarge the NH_3 concentration gradient between soil solid and gaseous phase. Thus, temperature and wind speed alter the equilibrium of NH_4^+ in the liquid to gaseous NH_3 (*Sommer* et al., 2003).

Precipitation suppressed NH_3 emissions in our study, which was also demonstrated in many current studies (*e.g., Sharpe* et al., 2004; *Smith* et al., 2009). Precipitation simultaneously decreased the ammonia concentration in the slurry–soil mixture to restrain NH_3 emissions (*Bouwmeester* et al., 1985).

Two soil types were included in this study: a sandy soil and a loamy soil. With respect to the observed difference of NH_3 emissions between slurry types, no differences due to slurry infiltration or effect of soil type were observed (*Gericke* et al., 2011b). This was tested for dry and wet soil conditions. This experimental finding is supported by the good fit of the model to the data from both study sites without inclusion of explanatory soil variables. As biogas slurries had a high viscosity compared to pig slurry and high pH values compared to both animal slurries, relative differences between slurries are expected to be the same as observed in this study even under drastically different infiltration conditions. High-pH soils (> 7.5) may change these relationships but these are rarely used as arable soils in Central Europe.

4.3 Influence of slurry types on NH_3 emissions

After model simplification by the AIC criterion, slurry-type factor combined with crop and weather factors constituted the final model to describe the final NH_3 loss (*predicted* N_{max}). Biogas slurry showed higher a NH_3-loss potential than pig slurry and cattle slurry. The confidence interval of the estimate for cattle slurry included 1, indicating the insignificance of the estimate for cattle slurry for N_{max}. It could be attributed to the smaller number of observations for cattle slurry, which led to a decreased accuracy of statistical inference. The estimate of NH_4^+-N-application rate showed a significant positive relationship with final NH_3 loss (*predicted* N_{max}), which implies the higher the NH_4^+-application rate, the higher the absolute NH_3 loss. However, with respect to relative NH_3 losses (% NH_4^+-N applied) the opposite effect was observed, relative losses decreased under high NH_4^+-N-application rates (data not shown). Both results are in line with earlier studies and model calculations (*Sogaard* et al., 2002).

The influence of pH on NH_3 emission, in particular high pH values > 7, is a well-known physico-chemical process (*Sommer* et al., 1991; *He* et al., 1999). However, in our empirical model, pH and other slurry characteristics were excluded from the model for *predicted* N_{max} by the AIC criterion. This can be attributed to the inclusion of slurry-type factor, since the pH was significantly different between slurries (Fig. 1). If slurry type was excluded from the model, pH would have a significant positive effect on ammonia loss in the parameterization procedure, accounting for the high losses observed after application of biogas slurries. The slurry-type factor is an indicating variable which includes the whole pattern of different slurry characteristics. In this way, a test could be made of whether the slurry type as such could explain variability in the data which could not be accounted for by the slurry characteristics explicitly included as explanatory variables. The overall effect of slurry type on NH_3 emissions was stronger than the explanatory power of pH and DM values included in model parameterization. The effect of other slurry chemical characteristics like slurry dilution rate and NH_4^+ concentration related to NH_3 loss which were not included due to correlation with other explanatory variables may account for this result. With respect to K_m, pH had a significant effect on K_m, indicating an accelerated NH_3 emission after application.

The positive relationship between DM content and K_m implies a slower NH_3-loss process in the case of high DM contents. High DM can reduce the infiltration of slurry into soil and increase the proportion of NH_4^+-N remaining on the soil surface and prolong the subsequent NH_3 volatilization (*Hutchings* et al., 1996; *Sommer* et al., 2006).

The inclusion of slurry-type factor, which was based on a limited number of slurries tested in this study, restricts the general applicability of the model and model results. However, slurry properties were fairly representative for biogas-slurry properties as reported from 6 intensively studied biogas-crop field trials in Germany (pH 7.5–8.2; 1.3%–4.1% N; 29%–81% NH_4-N of total N; 3.2%–8.3% DM; Formowitz, 2010, Bavarian State Research Center for Agriculture, Institute for Crop Science and Plant Breeding, personal communication). The inclusion of the slurry-type factor as such complicates the transfer of this model to other slurries; however, the same approach was followed in the original ALFAM model (*Soegaard* et al., 2002). As discussed above, model development was also possible on the basis of slurry properties only, which would make the model approach more easily adaptable to new slurries. But a crucial amount of variation was covered by the slurry-type factor for the best model fit. With respect to both, inclusion and omitting of slurry-type factor, model parameterization has to be based on a far more extensive data base than used in this study for general applicability of the model parameterization.

4.4 Effect of novel explanatory variables on NH_3 loss

Slurry application in maize showed a lower ammonia-loss potential than in grass and wheat. This effect could be attributed to the properties of the soil surface under a maize canopy. As slurry is applied shortly after seeding of maize, the soil surface has a higher roughness enhancing slurry infiltration.

A negative relationship between LAI and *predicted* N_{max} (estimates < 1) was also found, which indicates that high LAI suppresses ammonia loss from soil. Large leaf area reduces turbulence above the soil surface, thereby inhibits NH_3 volatilization, and directly absorbs released NH_3 simultaneously (*Sommer* et al., 1997). *Sommer* and *Olesen* (2000) found that spreading slurry with trail hoses to a 60 cm high crop reduced losses by 75% compared to a spreading onto bare soil. *Thorman* et al. (2008), combining a new algorithm with the ALFAM model, predicted a decrease in the emission factor for cattle-slurry application by trail hoses to winter wheat from 25% to 15% of applied NH_4^+-N for applications in January and May, respectively. A positive relationship between LAI and K_m was found in our study, which may be attributed to the suppression of evaporation and slower drying of the slurry surface.

In a previous study, it was reported that application carried out in the afternoon (after 02:00 p.m.) could reduce NH_3 loss by 30% *versus* in the morning (*Gordon* et al., 2001). *Rana* and *Mastrorilli* (1998) found that 70% of the daily NH_3 was emitted around noon after field application of green manure. A negative linear relationship was observed in a model study between NH_3 emissions and the time of day for slurry application (*Smith* et al., 2009). In the present study, this linear relationship was also observed (Fig. 2). This is probably due to the effect of air temperature which strongly affects NH_3 volatilization (*Sommer* et al., 1991; *He* et al., 1999). The NH_3-loss rate is usually high immediately after slurry application partly due to the high initial concentration of total NH_4^+-N and partly due to a rise in pH (*Sommer* and *Hutchings*, 2001). Comparatively, slurry application in the evening is preferable to the morning, because temperature is lower during the whole night, while the temperature would increase gradually when applied in the morning. However, application in the evening could also result in high concentrations of undesirable odors due to reduced mixing of the atmosphere at that time of the day. This may restrict slurry application in the evening close to residential areas or calls for the immediate incorporation of slurries by slurry injection

In our model, the application-time factor was excluded by the AIC criterion, which could be due to the flattening of results from using mean values. When the model was constructed on the basis of original records (nonaverage), application time showed a significant effect. The discrepancy between empirical model and statistical testing with respect to the effect of application time may also be due to the effect of other factors like application rate, which could not be included in the two-way statistical analysis but were considered in the empirical model.

5 Conclusions

The main objective of this study was to systematically analyze and predict NH_3 losses after field application of a new type of biogas slurry as compared to conventional animal slurries by a statistical empirical model. Based on the description of a Michealis-Menten-type kinetics NH_3-volatilization losses after slurry application with trail hoses were predicted. New explanatory variables biogas slurry, application time, slurry viscosity, precipitation, crop type, and LAI interacting with typical explanatory factors for prediction of NH_3 losses were tested for the first time in such a model framework. In general, these new factors had significant effects on ammonia emission and the prediction was consistent with the measured values.

The model estimation showed that application of biogas slurries was characterized by significantly higher NH_3 losses as compared to conventional animal slurries when applied at identical rates and in identical weather conditions. Ammonia emissions of slurries applied to maize were lower when compared to wheat or grass, and slurry applied in the evening resulted in reduced losses in the morning or at noon. To reduce NH_3 emissions, slurry should be applied in the evening to avoid high temperatures and strong winds after application, or close to rainfall events. Furthermore, in order to prevent NH_3 volatilization, irrigation or incorporation during (injection) and after slurry application (plow) are recommended to accelerate infiltration and reduce exposure time on the ground.

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