

Modelling Ammonia Losses After Field Application of Biogas Slurry in Energy Crop Rotations

Dirk Gericke · Lüder Bornemann ·
Henning Kage · Andreas Pacholski

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Abstract Over the past few years the number of biogas slurries, which are generally used as nitrogen fertilisers, have seen a steady increase in Germany. A mechanistic ammonia volatilisation model was developed to predict the ammonia losses of these slurries when applied to bare soil, maize, wheat and rye grass canopies. Data for model development were collected from several field measurements carried out at two locations in Northern Germany between the years of 2007 and 2008. Additionally, the behaviour of the slurries on and in the soil was investigated through the use of infiltration pot experiments. The model includes three main compartments: slurry, atmosphere and soil. The soil compartment model is relatively simple, as the slurry infiltration, nitrification and ploughing dislocation into the soil determined in the experiments showed quantitatively no significant differences between the tested slurries (mono-fermented, co-fermented and pig slurry) and soils (sand soil and loamy sand). Hence, instead of a complex soil model, stable reduction factors, as derived from the experiments, were implemented in the model. Simulated ammonia emissions were statistically compared (root mean square error (RMSE), modelling efficiency (ME), linear regression) to the observed emissions. All evaluations showed an acceptable model performance (RMSE=1.80 kg N ha⁻¹), although there

were a few number of anomalies which could not be modelled in an adequate way. A model sensitivity analysis showed that temperature and slurry pH value are the main drivers of NH₃ volatilization in the model. Following a change of +1°C or of +0.1 pH unit ammonia volatilization will increase by about 1% and 1.6% of the applied total ammoniacal nitrogen, respectively. We were able to show that a simple model approach could explain most factors of ammonia volatilization in biogas crop rotations.

Keywords Biogas slurry · Ammonia volatilization · Mechanistic model

Nomenclature

Weather Data

Humidity	Air humidity (percent)
Wind	Wind speed in a height of 2 m (metre per second)
T_{soil}	Soil temperature (Kelvin)
T_{air}	Air temperature (Kelvin)
T_{air_K}	Air temperature (Kelvin)
Radiation	Global radiation (watts per square metre)
Precipitation	Precipitation (millimetre)

PenMonteith

Rn	Net solar radiation (watts per square metre)
e_a	Actual vapour pressure (millibar)
e_s	Saturation vapour pressure (millibar)

D. Gericke (✉) · L. Bornemann · H. Kage · A. Pacholski
Christian-Albrechts-Universität zu Kiel,
Kiel, Germany
e-mail: kridgericke@web.de

δ	Slope of vapour pressure deficiency curve (millibar per Kelvin)
ρ	Air density (kilogramme per cubic metre)
C_p	Heat capacity of the air (joules per kilogramme per Kelvin)
ζ	Psychrometric constant (millibar per Kelvin)
λ	Latent heat of evaporation (joules per kilogramme)
$r_{c\ pen}$	Vegetation resistance for H ₂ O (seconds per metre)
ETp	Actual evapotranspiration (millimetre per second)
kumETp	Cumulative evapotranspiration (millimetre)
LAI	Leaf area index (square metre per square metre)
exkg	Extinction coefficient (–)

Atmosphere

h	Vegetation height (metre)
k_a	Von Karman's constant (–)
l	Height of internal boundary layer (metre)
Ri	Richardson number (–)
z	Height above ground (metre)
z_0	Roughness length (metre)
u^*	Friction wind velocity (metre per second)
r_a	Resistance in turbulent layer for NH ₃ (seconds per metre)
r_b	Resistance in the laminar boundary layer for NH ₃ (seconds per metre)
r_c	Resistance within the slurry surface layer for NH ₃ (seconds per metre)
d	Zero plane displacement height (metre)
k_{loss}	Transfer coefficient for NH ₃ volatilisation (metre per second)
$\beta_0, \beta_1, \beta_2$	constants for the calculation of r_c (for NH ₃) (–)
β	Constant for the calculation of r_c (for NH ₃) (–)
$\theta_{surface}$	Relative volumetric water content of slurry layer (–)
ξ	Atmospheric stability correction (–)

Ploughing

plough	Trigger (0=no ploughing; 1=ploughing) (–)
incorptime	Time step of ploughing event (–)
pH _{inc}	pH reduction factor for ploughing event (–)
water _{inc}	Water reduction factor for ploughing event (–)

NH _{4,inc}	NH ₄ reduction factor for ploughing event (–)
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Ammonium

concNH ₃	NH ₃ concentration in slurry surface layer (grammes per square metre)
TAN _{akt}	Total ammoniacal nitrogen in slurry surface layer (grammes per square metre)
AmnN	Ammonium content of slurry (grammes per square metre)
loss _{cum}	Cumulative NH ₃ losses (kilogrammes per hectare)
nitrate	Nitrate in surface layer (kilogrammes per hectare)
pH _{slurry}	pH of the slurry liquid (–)
NH _{4,applied}	Ammonium applied (grammes per square metre)
amount	Biogas slurry liquid (litres per square metre)
DM	Dry matter of slurry (–)
infiltration	Infiltration loss constant (–)
θ_{soil}	Relative volumetric water content of soil surface layer (–)
α	Constant for the calculation of nitrate (–)
ε	Constant for the calculation of nitrate (–)

1 Introduction

Currently, with over 6,000 biogas plants (Fachverband Biogas 2011), Germany is the largest biogas producer in Europe (Weiland 2006). These plants with an electric power of ~2,300 MW produce approximately 29 million cubic metres of biogas slurries per year (or ~115 million kilogramme nitrogen). Biogas slurries are by-products of the methane production and consist of anaerobically digested animal slurries and plant material. Nearly 100% of these residues are transferred back to agricultural ecosystems as nitrogen fertiliser due to the high ammonium concentrations and the high amount of other plant nutrients. In general, most biogas plants run under mesophilic conditions (~38°C) with a pH environment just below 8.0. The pH value of biogas slurries is slightly below (Gericke et al. 2011). It is well-known that high ammonium concentrations, in combination with high pH values (using conventional application techniques), cause an intensive ammonia (NH₃) volatilisation process (Stevens et al.

1992; Sommer and Husted 1995; Vandr  and Clemens 1996).

The German subsidies for biogas plants and their by-products are fixed for 20 years. As biogas production increases, also in many other European countries, it is becoming increasingly important to investigate the effects of the field application of biogas slurries originated from energy crops. The available data pool, however, is limited because the fermentation of energy crops only becomes quantitatively important just after 2000, when Germany enacted the Renewable Energy Sources Act. For that reason, a model-based scenario analysis can be considered as the only scientific tool available for the evaluation of environmental effects of field application of biogas slurries on NH_3 emissions and for exploring options to reduce these emissions. Such a model could be also seen as an important component for a broader analysis of the effects of different slurry properties, plant growth and weather dynamics on N turnover including the long-term effects of biogas slurry application. A dynamic NH_3 loss model for biogas slurries, next to other model modules for, e.g. plant growth or nitrogen leaching, would be a central component for such a comprehensive model.

Put simply, biogas slurries are comparable to animal slurries, so that related process factors for NH_3 volatilisation like temperature, pH value of the slurry or wind speed (Bouwmeester et al. 1985; Sommer et al. 1991) are the same for animal and biogas slurries. For predicting NH_3 losses of slurries, an empirical NH_3 loss model is available, which was developed on a very broad database, the ALFAM model (S gaard et al. 2002). It has been successfully used for pig and cattle slurry, and it was already successfully re-parameterised to estimate NH_3 losses from biogas slurries (Ni et al., under review). This has been done using the same field measurements which are used for the development of the mechanistic model approach described in this study. The Alfam model is robust and showed acceptable prediction accuracy, but because the influences of weather, crop and management conditions are incorporated via a regression type approach, this model type cannot guarantee an unbiased insight into the interaction of the different processes underlying NH_3 emissions under variable environmental conditions. This model's approach is

therefore of limited value for detailed scenario analysis.

During recent years, some dynamic model appendages were developed for animal slurries (Genermont and Cellier 1997; Hutchings et al. 1996; Sommer and Olesen 2000; Wu et al. 2003; Beuning et al. 2008). Several of those are based on a very detailed description of matter fluxes through soil, which require a long simulation time and are hard to integrate in comprehensive soil–crop models. Such models are preferable for detailed analysis of all the soil processes connected with NH_3 emissions.

The approach by Sommer and Olesen 2000 already reflects a great proportion of NH_3 loss processes without a particularly detailed simulation of soil slurry interactions, which allows for the inclusion of this approach in more complex model structures. However, it did not include the interaction of the NH_3 loss process with slurry infiltration into soil, evaporation (slurry crust formation, especially important for biogas slurries), nitrification and precipitation and was only calculated for pig slurry. The dynamic NH_3 models cited above were tested on a comparatively small amount of experimental data (one to six experimental campaigns, mostly one slurry type and one study site). Therefore, no dynamic NH_3 loss model is yet available, which allows the simulation of animal and biogas slurries alike and no existing model was parameterised on a comprehensive data set and gives reliable scenario analysis data.

The aim of this study therefore was to construct a new model based on existing knowledge and model approaches that included features enabling the model to consider the specific characteristics of biogas and conventional animal slurries, canopy conditions and weather dynamics for the calculation of NH_3 emissions in a mechanistic way. A large data set containing a huge variation of environmental and management conditions in combination with different slurry parameters for its parameterisation and validation was available containing 13 NH_3 measurement trials with simultaneous measurement of NH_3 emissions from several types of field applied organic slurries (Gericke et al. 2011). Additionally, a small scale laboratory and field studies focussing on single processes involved in the overall NH_3 emission process were carried out to test and confirm model assumptions.

2 Materials and Methods

2.1 Model Theory

2.1.1 Modelling Assumptions

The NH_3 emission model was constructed according to the principle to be able to predict NH_3 volatilisation in energy crop rotations and thus, for a large variety of situations on the one hand but to be as simple as possible on the other hand. One of the main model assumptions was that after the application only the liquid remaining on the surface has to be considered in the calculation of NH_3 volatilisation and therefore no complex soil water model as described in Genermont and Cellier (1997) or Wu et al. (2003) was included. Instead, the infiltration was empirically implemented based on field and laboratory infiltration experiments. Therefore, only the soil water content at application has to be considered. NH_3 volatilisation of biogas slurry is structured in the model as a process which evolves in the three main compartments: slurry,

atmosphere and soil (Fig. 1), where some model components of the atmosphere and pH level of the slurry are based on algorithms published by Sommer and Olesen (2000).

2.1.2 Slurry/Biogas Slurry

In the field experiments, biogas slurries were applied with trail hoses (see Section 2.2.1). We made the simplification that all biogas slurry reached the soil and that no slurry stayed on the plant surface. The concentration of total ammoniacal nitrogen (TAN, [grammes per litre]) in the slurry was calculated by using Eq. 1.

$$\text{TAN}_{\text{akt}} = \frac{\text{NH}_4\text{applied}}{\text{amount}} \quad (1)$$

Where the *amount* is the quantity of slurry applied per square metre and NH_4 applied is the applied TAN content [grammes per square metre].

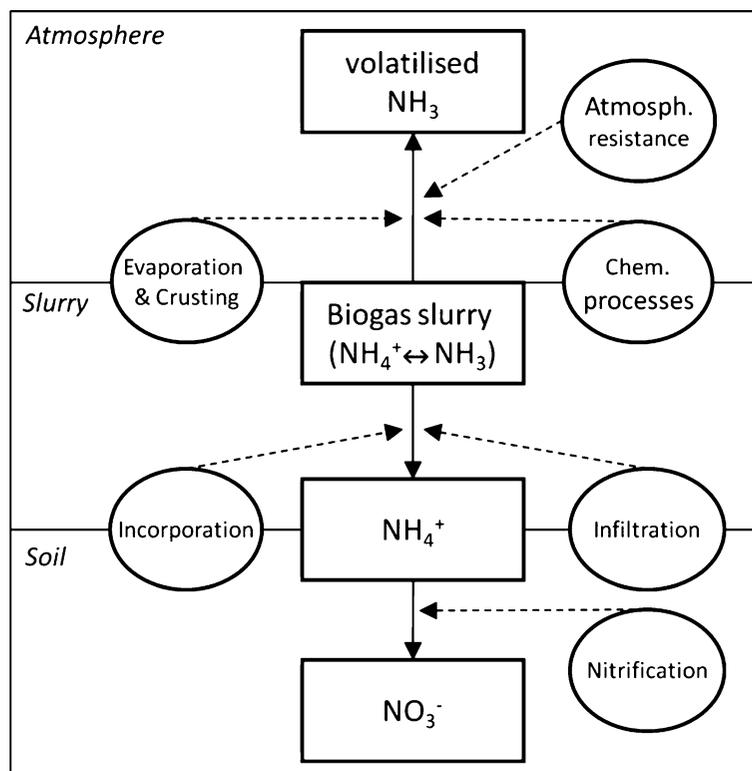


Fig. 1 Schematic modelling concept including the three main compartments slurry, atmosphere and soil

In the slurry, ammonium is in equilibrium with NH_3 (Freney et al. 1983). Concentrations of NH_3 in the liquid was calculated according to Denmead et al. (1982; Eq. 2).

$$\text{NH}_{3,l} = \text{TAN}_{\text{akt}} / \left[1 + 10^{0.09018 + 2729.92 / T_{\text{air}} - \text{pH}_{\text{actual}}} \right] \quad (2)$$

where T_{air} is the air temperature [Kelvin] measured in 2 m and $\text{pH}_{\text{actual}}$ is the pH in the slurry liquid.

Here, the calculated NH_3 concentration in the liquid phase depends on air temperature and the actual pH of the solution. The transfer from the liquid phase to the gaseous phase is consequently provided by Eq. 3.

$$\text{NH}_{3,g} = \text{NH}_{3,l} * \frac{14 * K_h}{R * T} \quad (3)$$

where K_h is the Henry law constant, R is the gas constant and T the absolute temperature [Kelvin].

The dynamics of slurry pH after the field application, necessary for the calculation of the ammonium concentration, was implemented as an empirical function (Sommer and Olesen 2000, Eq. 4), in which the actual pH value depends on the water content of the first 5 mm of the soil slurry mixture.

$$\text{pH}_{\text{actual}} = \text{pH}_{\text{slurry}} - 0.52 * \ln(\theta_{\text{soil}})^2 \quad (4)$$

where $\text{pH}_{\text{slurry}}$ is the pH at application and θ_{surface} is the water content in the soil slurry surface (0–5 mm) [litres per kilogramme].

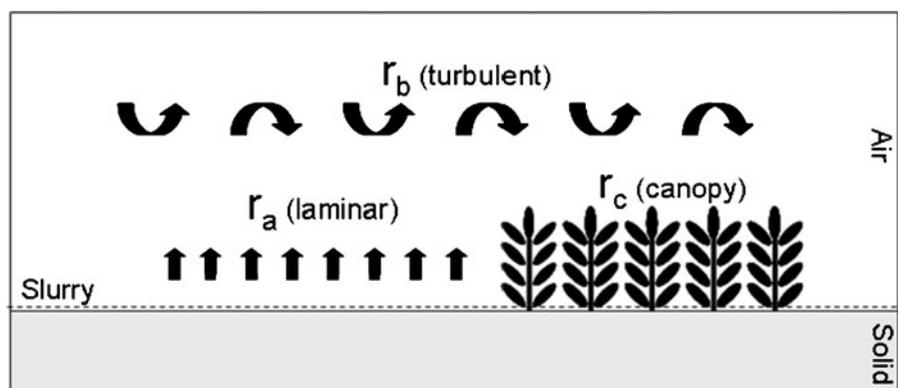
It was assumed that after adding additional moisture to the soil at rain events, the pH value of the slurry would stay at the same level and will not increase. This assumption is supported by our own in situ pH measurements of the soil slurry surface in spring 2007 and 2008, which showed no significant pH fluctuations under wet conditions, while laboratory measurements with severe drying of the surface soil showed a fast decline. Nevertheless, the database was not large enough to derive an empirical pH function from our own findings.

2.1.3 Atmosphere

There are two TAN loss pathways from the slurry liquid, to the atmosphere as NH_3 and to the soil as NH_4^+ . The atmosphere flux is influenced by crop characteristics, the slurry liquid remaining on the soil surface as well as the laminar boundary layer and the turbulent layer above the crop canopy (Fig. 2).

Hence, Sommer and Olesen (2000) implemented three resistance variables to calculate one transfer coefficient to the air (Eq. 5). The resistance in the turbulent layer was calculated according to Padro et al. (1994; Eq. 6). The resistance of the laminar boundary layer was calculated by an empirical function (Thom 1972; Eq. 7) based on the friction velocity. For the calculation of the resistance of the crop canopy and the soil slurry surface, a function of Sommer and Olesen (2000; Eq. 8), which depends on the vegetation height as well as the water content, was used. It originally includes three empirical parameters β_0 , β_1 and β_2 . In our model, the relative water content θ_{air} only relates to the slurry liquid that stays on the soil surface instead of the water content of a 5-mm soil layer. As a result, the

Fig. 2 Atmospheric resistances r_a , r_b and r_c influencing the NH_3 volatilisation



transfer coefficient for NH_3 in the slurry liquid to the atmosphere including the three resistances was calculated following Eqs. 5, 6, 7, 8.

$$k_{\text{loss}} = \text{NH}_{3,g}^* \left(\frac{1}{r_a + r_b + r_c} \right) \quad (5)$$

$$r_a = \frac{\ln\{(1-d)/z_0\}}{k^*u_*} \zeta \quad (6)$$

$$r_b = 6.2^*u_*^{-0.67} \quad (7)$$

$$r_c = \beta_0 + h \cdot \beta_1 + \beta_2^*(1 - \theta_{\text{surface}}) \quad (8)$$

where r_a [seconds per metre] is the resistance in the turbulent layer above the vegetation cover, r_b [seconds per metre] is the resistance in the laminar layer, r_c [seconds per metre] is the resistance within the crop canopy and the soil slurry surface (Fig. 2), l is the height of the internal boundary layer [metre], d is the zero plane displacement height [metre], z_0 is the roughness length [metre], k is the Karman's constant, u_* is the friction wind velocity [metres per second], β_i are empirical constants and θ_{surface} is the relative water content in the slurry liquid remaining on the soil surface.

Only the parameters β_0 , β_1 and β_2 included in the atmospheric resistance variable r_c were used for model parameterization of NH_3 losses for all three slurry types by fitting the model to the experimental data. For each of the two experimental years and each slurry type, one early, one mid and one late, a season application trial ($n=18$) was used (Table 1). Every trial was parameterised separately because a simultaneous parameterisation could not be done in our modelling environment.

Biogas slurries contain, due to the fermentation process, large amounts of small plant particles. Slurries, remaining on the soil surface, generally dry out during the relevant time for NH_3 volatilisation (<3 days), so that these particles can cause a thin crust comparable to the natural layer of slurry tanks. Misselbrook et al. (2005) showed that such layers can reduce the NH_3 emissions by up to 50%. As the relative proportion of dry slurry after evaporation is comparatively large as compared to slurry tanks, the maximum reduction factor of 0.5 was chosen in the model when the biogas slurry liquid is completely evaporated.

The decrease in the relative water content of the slurry remaining on the soil surface (θ_{surface}) due to evaporation of the biogas slurry liquid was calculated based on a variant of the Penman and Monteith equation

Table 1 Overview of the measurement campaign in the years 2007 and 2008, N levels as total N (mineral N and organic N)

Date	Soil	Crop	Vegetation cover	LAI [$\text{m}^2 \text{m}^{-2}$]	Average temperature [$^{\circ}\text{C}$]	Average wind speed [m s^{-1}]	Highest N level [kg ha^{-1}] ^a	Use
03/27/2007	Loamy sand	Winter wheat	BBCH 25	1.32	9.6	1.8	120	P
04/11/2007	Sand	Maize	Pre-emergence	0.00	10.9	1.1	180	V
05/22/2007	Sand	Maize	BBCH 13	0.05	16.0	0.7	180	P
05/22/2007	Sand	Rye grass	Cut 5 cm	1.00 ^b	16.0	0.7	140	V
06/06/2007	Loamy sand	Maize	BBCH 13	0.06	19.7	1.5	180	V
07/12/2007	Sand	Rye grass	Cut 5 cm	1.00 ^b	16.7	0.9	120	P
03/17/2008	Loamy sand	Winter wheat	BBCH 22	0.14	2.7	3.2	120	V
04/08/2008	Loamy sand	Winter wheat	BBCH 29	0.68	5.3	1.9	120	P
05/19/2008	Sand	Rye grass	Cut 5 cm	1.00 ^b	19.7	3.4	140	P
05/28/2008	Sand	Maize	BBCH 14	0.15	10.6	0.5	180	V
06/03/2008	Loamy sand	Maize	BBCH 14	0.19	17.1	3.8	180	V
06/04/2008	Loamy sand	Winter wheat	BBCH 62	4.37	17.2	3.8	120	P
07/03/2008	Sand	Rye grass	Cut 5 cm	1.00 ^b	18.5	1.1	120	V

P parameterisation, V validation

^aRelated ammonium N applied is given in Table 2

^b Assumption, not measured

for evapotranspiration (Monteith and Unsworth 1973, Eq. 9).

$$ETP = \frac{\delta * Rn + \rho * Cp * (e_s - e_a) / r_a}{(\delta + \zeta * (1 + r_{c,pen}) / r_a) / \lambda} \quad (9)$$

where δ is the slope of vapour pressure deficiency curve [millibar per Kelvin], Rn is the net solar radiation [watt per square metre], ρ is the air density [kilogramme per cubic metre], Cp is the heat capacity of the air [joules per kilogramme per Kelvin], e_s is the saturation vapour pressure [millibar], e_a is the actual vapour pressure [millibar], r_a is the resistance of the turbulent layer [seconds per metre], ζ is a psychrometric constant [millibar per Kelvin], $r_{c,pen}$ the resistance parameter within the crop cover [seconds per metre] and λ is the latent heat for evaporation [joules per kilogramme].

Equation 9 determines evapotranspiration which is the sum of evaporation and transpiration, but in the model the water content in the topsoil and the liquid on the soil surface are affected by the evaporation process only. Hence, transpiration of the plants has no influence on the water content in the slurry liquid staying on the topsoil. Evaporation was calculated as the difference between evapotranspiration and transpiration. The transpiration fraction was calculated by using Eq. 10 (Stockle et al. 1994). The atmospheric resistance of the crop canopy and the surface layer ($r_{c,pen}$) is considered in the evaporation equation (Eq. 9), as well as the atmospheric compartment for calculating the NH_3 flux (Eq. 8). However, the resistance for water (evapotranspiration) and NH_3 (atmosphere) are different. Thus, for evaporation, the atmospheric resistance was calculated by the use of the empirical equation of Kochler et al. (2007), Eq. 11.

$$EP = ETP - ETP * (1 - e^{exkg * LAI}) \quad (10)$$

$$r_{c,pen} = \begin{cases} r_{c,pen} & | LAI < 1 \\ r_{c,pen} / LAI & | 1 < LAI < 2 \\ r_{c,pen} / 2 - r_{c,pen} / 6 * ((LAI - 2) / 4) & | LAI > 2 \end{cases} \quad (11)$$

where $exkg$ is the extinction coefficient (0.5) for global radiation and leaf area index (LAI) is the leaf area index [square metre per square metre]. The extinction coefficient thereby was estimated by minimisation of the difference between the LAI

values, measured by LAI-3100 and the LAI values, estimated from the transformed Lambert–Beer law and the canopy closure data. For higher LAI values ($LAI > 1$), LAI was determined using the LAI-2000 (LI-COR LAI-2000 metre; LI-COR, Inc., Lincoln, NE, USA). All LAI-2000 values have been multiplied by a coefficient (1.22), resulting out of a linear regression between LAI-3100 and LAI-2000 values.

Soil Ammonium not being available for NH_3 volatilisation from the slurry liquid is the flux into the soil. In this model, three different subfractions exist: (1) infiltration of the liquid phase into the soil, (2) nitrification and (3) incorporation by ploughing. These three paths were investigated in specific experiments. Conclusions and implementation of the function will be presented in the results chapter.

2.1.4 Modelling Environment

The model was implemented in the environment of ModelMaker version 4 (Cherwell Scientific Ltd., UK). The time step of the model was a 10-min interval using Euler integration. The meteorological input data air temperature, soil temperature, wind speed, precipitation and global radiation were also logged every 10 min. Parameters of slurries were applied liquid amount, applied ammonium amount, pH value and dry matter. The vegetation height as well as the LAI was set to a constant value for each modelling run of 3 days. One resistance parameter β for all slurry types was parameterised with the simple Marquardt procedure in ModelMaker.

2.2 Experiments

2.2.1 Experimental Design and Study Sites

The measurements of NH_3 loss were carried out in a multiplot designed field trial. Each plot in the field trial was 12×12 m. In addition to the (for Northern Germany) typical continuous maize (*Zea mays* L.) cropping (for silage production) alternative biogas crop rotations with wheat (*Triticum aestivum* L.) and rye grass (*Lolium perenne* L.) were established. All crops in the rotations were planted every year in four replications with four nitrogen levels in separate doses (as total N = mineral N + organic N). NH_3 losses were

determined only in the highest N level to minimise the influence of adjacent plots. For wheat and maize, the maximum N levels were 120 and 180 kg N ha⁻¹, applied in three and two doses, respectively. The application of maize was split as the hilly landscape made a homogenous application of 180 kg N⁻¹ impossible, especially considering the small plot size of 12×12 m. For grass, the measured N levels were 120 and 140 kg N ha⁻¹ applied. As a result, the NH₃ losses were determined in different crop canopies (bare soil, cut rye grass, different growth stages of wheat and maize). In total, three different N application levels were tested, and 13 measurement trials (Table 1) were carried out. The slurries were applied with trail hoses which were specially constructed for the small plots with a range of 6 m to guarantee a homogenous application, for details see Gericke et al. (2011).

Measurements were carried out from March 2007 to August 2008 on fields of the research farms Hohenschulen and Karkendamm (both Christian-Albrechts University of Kiel) in Schleswig-Holstein, Northern Germany. The location Karkendamm is typical for the region, outwash plain with sandy soils. Hohenschulen represents the eastern hilly region with loamy soils. Both locations are characterised by a maritime climate with an annual average temperature of 9°C and an annual mean precipitation of 760 mm. The average temperature during the experimental years was slightly above these long-time values.

2.2.2 Meteorological Data

On both study sites, weather stations were installed including two-cup anemometers. One was mounted on a height of 0.2 m (Thies First Class anemometer Thies GmbH, Göttingen, Germany) and another one at 2 m (Thies economy; Thies GmbH, Göttingen, Germany). Air temperature and air pressure were measured at a 1.5-m height with a Thermo Hygro Sensor Standard (Wilmers Messtechnik, Hamburg, Germany), soil temperature in a depth of 5 cm with a soil temperature sensor economy (PT100, Wilmers Messtechnik, Hamburg, Germany). Furthermore, the global radiation was determined with a CM3 (Kipp & Zonen, Delft, Netherlands). The sensors of the weather station were connected to a WILOG NDL 485 (Wilmers Messtechnik, Hamburg, Germany). The

data were measured internally every 10 s and were averaged every 10 min.

2.2.3 Soils

According to the modelling approach, only the characteristics of the soil slurry surface have a potential effect on the NH₃ loss process. The texture of the plough layer in Karkendamm was sandy (clay content ~3%). The characteristic parameters of the top layer were a pH(CaCl₂) of 6.1, a high C_{org} content of 6.3% (moor outskirts) and a cation exchange capacity slightly above 70 mmol c kg⁻¹.

The soil texture in Hohenschulen varied due to the hilly landscape. The most common texture of the plough layer was loamy sand (clay content ~12%). The pH (CaCl₂) of 6.7 as well as the cation exchange capacities clearly above 100 mmol c kg⁻¹ was higher than in Karkendamm, but the C_{org} content was lower (3.0%).

2.2.4 Organic Fertiliser

In the field studies, two types of mono-fermented and one co-fermented biogas slurry was applied. The mono-fermented one used in 2007 consisted of maize (90% w/w) and cereals (10% w/w). This biogas slurry had an atypical pretreatment (hydrolytical cleavage) before the fermentation process, which meant that its viscosity was lower compared to other biogas slurries. The second mono-fermented slurry used in 2008 originated from 100% maize substrate. The co-fermented biogas slurry contained pig slurry (50% w/w) and maize (50% w/w), temporarily cattle slurry. For better comparison, unfermented pig slurries were also tested. Samples of all slurries were taken at every application date. Next to the parameters, dry matter, total nitrogen content and NH₃ content, the pH value (pH metre HI1291 D, Hanna Instruments), as well as the pH buffer capacity (Sommer and Husted 1995) was determined. For the analysis of slurry mineral N, slurry was extracted with a 2-M KCl (pH 1) solution (1:4 w/v) for 1 h. These extracts were then filtered with Whatman 602 filter paper and were immediately analysed. The concentrations of NH₄⁺ in slurry extracts were measured using a TRAACS 800 autoanalyzer (Bran and Luebbe, Hamburg, Germany). Slurry viscosity was measured with a HAAKE Viscotester 71, Thermo Scientific, USA. The characteristics of the organic fertilisers are shown in Table 2.

Table 2 Properties of the organic fertilisers applied in the field experiments (standard deviations in brackets)

Fertiliser	Year	Number	Dry matter Percent	Total N kg N m ⁻³	TAN kg N m ⁻³	pH –	Buffer capacity mol H ₃ O ⁺ ΔpH ⁻¹	Viscosity mPa
Mono-ferment	2007	6	3.64 (0.32)	2.97 (0.14)	1.75 (0.30)	7.56 (0.09)	0.0724 (0.0032)	27 (8)
Mono-ferment	2008	7	5.06 (1.91)	3.31 (0.36)	1.95 (0.15)	7.56 (0.09)	0.0718 (0.0174)	271 (114)
Co-ferment	2007	5	5.46 (1.25)	3.31 (0.34)	1.82 (0.24)	7.50 (0.23)	0.0981 (0.0069)	300 (313)
Co-ferment	2008	7	5.59 (1.51)	3.88 (0.43)	2.01 (0.21)	7.69 (0.22)	0.0684 (0.0094)	249 (165)
Pig	2007	6	7.23 (1.91)	4.05 (0.43)	2.72 (0.18)	6.94 (0.14)	0.0661 (0.0059)	46 (33)
Pig	2008	7	5.06 (0.65)	3.84 (0.28)	2.65 (0.26)	7.04 (0.24)	0.0704 (0.0055)	31 (18)

2.2.5 NH₃ Loss Measurements

Appropriate for the measurement of NH₃ emissions in factorial field trials, a combination of modified passive samplers as employed in the Standard Comparison Method (Vandre and Kaupenjohann 1998; Wulf et al. 2001, 2002) and a variant of an open dynamic chamber method (Pacholski et al. 2006) was used (Gericke et al. 2011). The ammonium concentrations in the passive sampler solution were measured with an ammonium electrode (Orion 4 Star, Thermo Orion).

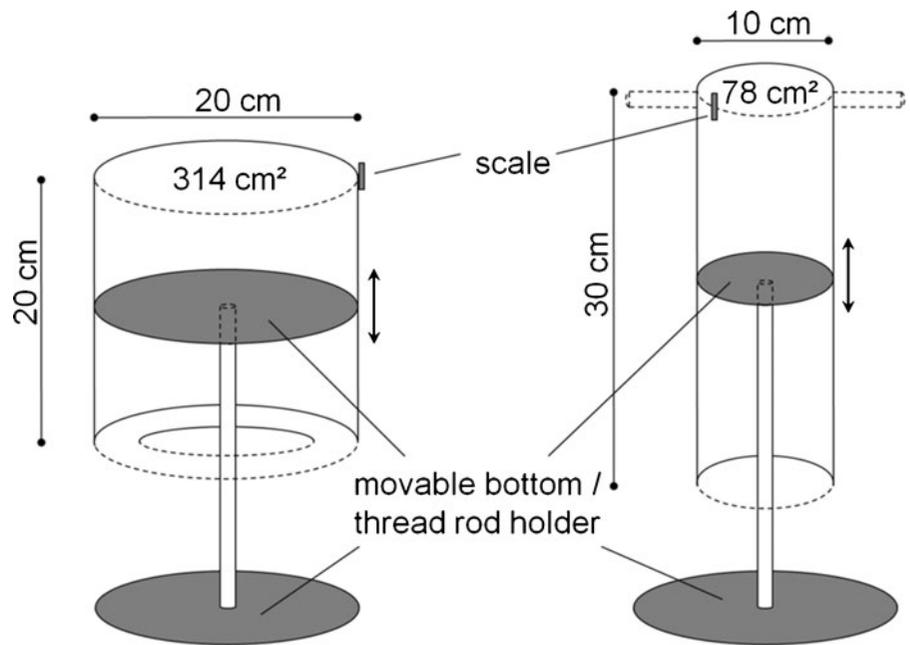
2.2.6 Interaction of Biogas Slurries with Soil

Infiltration During the fermentation process, the input material is decomposed resulting in better infiltration qualities of fermented animal slurries and lower NH₃ emissions after field applications, as compared to raw slurries (Sommer and Jacobsen 1999). In general, the fermentation has the same effect on plant material. However, the combination of plant material and animal slurries or solely plant material, results in higher viscosities of biogas slurries than viscosities of animal slurries. Our own measurements showed that biogas slurries can have up to 60 times higher viscosity than thin pig slurries (Ni et al., under review). The assumption was that such high viscosities would reduce the infiltration into the soil. To quantify this effect, two infiltration experiments were carried out to determine the infiltration depths of total TAN after the spreading of biogas slurries. Infiltration was investigated on a sandy (location Karkendamm) and on a loamy sandy soil (location Hohenschulen) at two different water contents. One experiment was carried out in the field after harvest in autumn 2007 (higher water content), the other experiment in the laboratory

1 month later (lower water content). For the laboratory experiments, undisturbed soil samples, for each of the three fertiliser types in four replications ($n=4$), were taken with self-constructed soil corers (see Fig. 3) and were stored for 1 week in a greenhouse at a constant temperature of 20°C. Organic fertilisers (mono-fermented, co-fermented and pig slurry) were applied by hand onto bare soil (field and laboratory) with a rate of 6 L m⁻², which corresponds to the highest nitrogen level used in the NH₃ emission field trials. Water was additionally applied as a reference. The combination of highest nitrogen level and bare soil represents the situation with the greatest potential TAN infiltration depths. After 1 h and after 5.5 h, ten 5-mm slices (total depth, 5 cm) were sampled with self-constructed soil samples and were frozen afterwards. Previous test infiltration experiments with brilliant blue (results not presented here) showed that the main infiltration process was completed in this time span. The water content (drying 24 h at 105°C) as well as the ammonium content was measured. Ammonium content was determined by extracting with 1.0 M potassium chloride, shaking for 30 min and centrifuging for 10 min at 2,500 rpm. The ammonium concentration in the extract was measured with an ammonium electrode (Orion-4-Star, Thermo Scientific, USA).

Incorporation The most important plant material for fermentation in Germany is maize followed by cereals and grass (UBA German Federal Environment Agency 2008). Thus, the main part of the biogas slurries used under practical conditions are applied to bare soil and are incorporated after a few hours according to the maize fertilisation practice in Germany. It was, therefore, necessary to implement incorporation events into the model. For this purpose, a field experiment

Fig. 3 Self-constructed soil sampler based on “Mitscherlich” flower pots (*left*) and steel tubes (*right*); thread rods were mounted with screw nuts to the iron plates used as movable bottoms as well as pedestals; soil cores were pulled out taking into consideration the magnetic scale; soil slices were cut with standard putty knives



was carried out at the experimental fields in Hohenschulen (loamy sand) at the end of April 2008. The applied organic fertilisers were mono-fermented biogas slurry, co-fermented biogas slurry and pig slurry. All fertilisers were tested for the highest N level applied (180 kg N ha^{-1}) and, in addition, for the co-fermented biogas slurry for all N levels (0, 60, 120, and 180 kg N ha^{-1}). The fertilisers were applied with trail hoses and were incorporated with a harrow (incorporation depth $\sim 30 \text{ cm}$). Soil slurry surface samples (thickness = 1 cm) were taken from four plots in four plot stripes ($n=4$), shortly after biogas slurry application ($\sim 10 \text{ min}$) and immediately after incorporation. The soil samples were analysed for NH_4 content and gravimetric water content. Ammonium and water content was determined with the same procedures as described above.

Nitrification The ammonium in biogas slurries, which infiltrates in the soil, is transformed to nitrate. This results in decreasing ammonium content. Prior studies showed that several hours after the application of animal slurries, nitrification rates were very low, but after several days increased exponentially (Lin et al. 2004). For the quantification of the nitrification process a laboratory trial was carried out. Undisturbed soil samples were taken with self-constructed samplers at Hohenschulen (loamy sand) in spring 1 week after ploughing. Organic fertilisers were applied by hand

onto bare soil at a rate of 6 L m^{-2} (corresponding to the highest N level used in field trials) in ten pots (diameter = 20 cm). During the first 3 days three times a day (morning, midday, evening) three samples from one pot (three slices, each 1 cm) were taken. At the fourth day the tenth pot (midday) was investigated. No replications were done because (a) preparation of 1 cm slices is very time consuming and (b) results of Lin et al. 2004 should only be confirmed for biogas slurries. The pH value was determined ($n=3$) immediately after the sampling with 5 g soil in a 0.01-M calcium chloride solution with a pH metre (HI1291 D, Hanna Instruments). Afterwards, the soil samples were frozen and nitrate concentrations were determined by the Lufa ITL GmbH (Sarstedt). Initial nitrate concentrations are in the range of 2 g kg^{-1} dried soil.

Ammonium Adsorption in Soil For testing the assumption that only ammonium not infiltrating into soil plays a role in the NH_3 emission process ammonium adsorption in soil was determined by an ammonium adsorption isotherm. In this laboratory study 5 g of fresh and sieved soil ($<2 \text{ mm}$) was suspended in 20 mL CaCl (0.01 mol) of ammonium solution with increasing ammonium concentration ($0.1; 0.2; 0.5; 1; 2; 5; 10; 20; 40; 60; 100; \text{ and } 200 \text{ mmol NH}_4^+ \text{ L}^{-1}$). After shaking for 1 h , the suspension was centrifuged at $2,500 \text{ rpm}$, and the supernatant ammonium concentration was determined

in the supernatant solution by means of an ammonium electrode (Orion 4 Star, Thermo Orion).

Acidity Buffering in Slurry Solution In order to compare the pH buffering behaviour of the biogas slurries as compared to the animal slurries and to test the applicability of the implemented empirical pH algorithm, the pH changes depending on the addition of acidity was tested in the laboratory. For that purpose, acidity was added stepwise (ten times 0.1 mL HCl (15% v/v), later on 0.5 mL until a pH of <4 was reached) in 100 mL of fresh slurry. Under stirring, pH values were determined by a pH metre HI1291 D, Hanna instruments.

2.2.7 Statistics

Statistical analyses (regression, ANOVA and correlation analyses) of the field trials were carried out with the statistic software R (version 2.6.1, 2004) and Sigma Plot (version 10).

For the evaluation of the model performance, three different methods were chosen. First, the root mean square error (RMSE, Eq. 12) was used as an absolute measure for the comparison of observed and simulated cumulated NH_3 losses.

$$\text{RMSE} = \sqrt{\frac{(O - S)^2}{n - p}} \quad (12)$$

where O is the observed NH_3 loss, S is the simulated NH_3 , n is the number of sampling points and p is the number of estimated parameters in the model.

Secondly, the modelling efficiency (Eq. 13) is where a negative result represents an unacceptable modelling run.

$$\text{ME} = 1 - \frac{\sum_{i=1}^n (O_i - S_i)^2}{\sum_{i=1}^n (O_i - \bar{O})^2} \quad (13)$$

where O and S represent the observed and simulated values, n represents the number of observed and simulated values, and \bar{O} is the observed average.

Lastly, a linear regression analysis between the observed and simulated cumulated NH_3 losses was carried out.

The sensitivity analysis of the model was executed in the environment of ModelMaker version 4 (Cherwell

Scientific Ltd., UK). For all validation runs and the co-fermented slurry, the parameters dry matter, temperature, wind speed, pH, air humidity and ammonium content were varied as presented in Table 3.

3 Results

3.1 Infiltration

In total, average ammonium contents in soil (0.5–5 cm) ranged from 26% to 34% of the applied ammonium (Table 4). A statistical analysis showed no significant differences for the sandy soil and only weak effects ($p=0.02$) for the pig slurry (13% soil moisture) and the co-ferment (16% soil moisture), considering the loamy sand. Differences in terms of TAN between the locations were also not observed ($p=0.53$). Furthermore, no significant differences between the two sampling events for all slurries were detected.

A noteworthy higher level of NH_3 concentration after the application of biogas slurries was not observed for depths >20 mm ($p>0.05$), neither for the sandy soil nor for the loamy sandy soil. However, the pig slurry with low viscosity infiltrated deeper into the loamy sand, and higher TAN amounts could be observed down to a depth of 50 mm. The infiltration depth was probably even higher, but could not be detected due to a maximum sampling depth of 5 cm.

3.2 Effect of Ploughing on NH_4^+ Contents in the Surface Soil

No significant differences after application (high application rate) in terms of all parameters investigated (soil moisture, TAN) were detected (Table 5). After

Table 3 Parameters and margins of deviation used in the sensitivity analysis

Model parameter	Unit	Range	Increment
Temperature	°C	±10	1
pH	–	7–8	0.1
Dry matter	%	0–10	1
Wind	m s^{-1}	±2	0.2
Air humidity	%	±10	1
Ammonium			kg ha^{-1}
–20	2		

Table 4 Fraction of applied TAN (pig=162 kg ha⁻¹, co-ferment=96 kg ha⁻¹, mono-ferment=120 kg ha⁻¹ infiltrated in the top soil (0.5–5 cm, n=4), 5.5 h after application of 6 L m⁻² slurry/biogas slurry, in brackets the standard deviations

Soil	Sand		Loamy sand		Mean
	21	14	16	13	
∅ grav. [%]					
Mono-ferment	0.37a (0.06)	0.19a (0.06)	0.25b (0.08)	0.23ab (0.10)	0.26 (0.08)
Co-ferment	0.31a (0.12)	0.25a (0.07)	0.42a (0.12)	0.19b (0.06)	0.29 (0.09)
Pig	0.33a (0.11)	0.32a (0.13)	0.21b (0.06)	0.35a (0.03)	0.30 (0.08)
Mean	0.34 (0.10)	0.25 (0.09)	0.29 (0.09)	0.26 (0.06)	

Letters a and b indicate significance level (Anova, Tukey post hoc test)

grav. % percent by weight

ploughing, the TAN content of the soil slurry surface of the plot, which was applied with the co-fermented slurry, was slightly higher, whereas the soil moisture of the pig slurry plots was lower. The mean ammonium content of the soil slurry surface (application rate=180 kg N ha⁻¹) was lowered after incorporation by 66–80% of the initial amount, whereas the mean water content was reduced only by 40–50% (Table 5). Weak differences ($p<0.05$) between the co-fermented treated plots could be seen but only after incorporation.

3.3 Nitrification

The vertical nitrate distributions in the nitrification trial were in accordance with the results of the infiltration experiments. Biogas slurries infiltrated only into the upper two centimetres of the soil. Hence, nitrate concentrations in the third centimetre were very low. In

all of the soil layers sampled, the nitrate concentrations were very low during the first 48 h (<5 mg kg per soil); afterwards an exponential increase of nitrate concentrations could be observed (see Fig. 4). Thus, an exponential function was fitted ($r^2=0.97$) to the data (0–0.01 m).

3.4 NH₄⁺ Adsorption Capacity in Soil

Ammonium adsorption experiments showed that at both locations (sand and loamy sand) up to 100% ammonium was adsorbed in the range of concentrations used in the field trials. Exemplarily, the ammonium adsorption isotherm of Karkendamm (sand) is shown in Fig. 5.

3.5 Buffer Capacity

The laboratory experiments showed that the buffer capacities of the substrates pig slurry, mono-ferment

Table 5 Ammonium content, water content (n=4) in the soil slurry surface (0.01 m) before and after the incorporation, in brackets the standard deviations, soil pH=6.7, initial gravimetric water content=17% standard deviations in brackets

Fertiliser	N level, kg N ha ⁻¹	After application	After incorporation	Incorporation	After application	After incorporation	Incorporation,
		NH ₄ ⁺ ppm g DM soil ⁻¹	NH ₄ ⁺ pm g DM soil ⁻¹	NH ₄ ⁺ Percentage	Water, grav. %	Water, grav. %	liquid Percentage
Mono-ferment	180	37.9a (16.5)	7.4b (2.8)	80*	59.9 a (11.8)	30.7a (4.3)	49*
Pig	180	35.2a (4.7)	7.8b (2.8)	78***	46.6a (3.9)	23.3b (2.5)	50***
Co-ferment	180	41.8a (13.9)	14.1a (4.0)	66**	59.2a (9.2)	35.3a (4.5)	40**
	120	26.3a (5.8)	6.9b (2.4)	74*	43.9a (5.9)	27.2b (0.9)	38*
	60	11.4b (3.5)	0.7c (0.4)	94*	44.2a (18.8)	16.1c (0.6)	64*

Letters a, b and c indicate significance level (Anova, Tukey post hoc test)

grav. % percent by weight

* $p<0.05$; ** $p<0.01$; *** $p<0.001$ (t test)

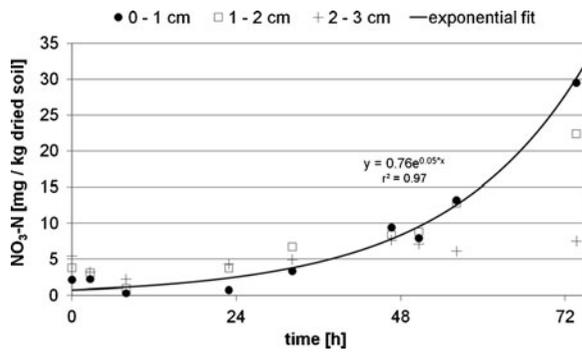


Fig. 4 Nitrate concentrations in different soil depths after application of 6 L m⁻² mono-fermented slurry, corresponding to 120 kg NH₄⁺-N per hectare, data of the first layer could be significantly fitted by an exponential function ($a^*e^{b^*x}$, $p_a < 0.001$, $p_b < 0.001$)

and co-ferment were in the same range (Fig. 6). Linear estimation (coefficient of determination always >0.92) resulted in buffer capacities of 0.71 mol H₃O⁺ per pH unit for the biogas slurries and 0.70 mol H₃O⁺ per pH unit for the pig slurry ($n=7$). In contrast, the variability for the biogas slurries (mono-ferment=0.015, co-ferment=0.031) were bigger than that for pig slurry (0.005).

3.6 Modelling Results

3.6.1 Parameterisation

Soil infiltration experiments showed that the average ammonium content in soil (0.5–5 cm) ranged from 26% to 34% of the applied ammonium. Considering that in the soil slurry surface (0–5 mm, which could not be measured exactly) ammonium will also be adsorbed in the soil, the fraction of ammonium in the

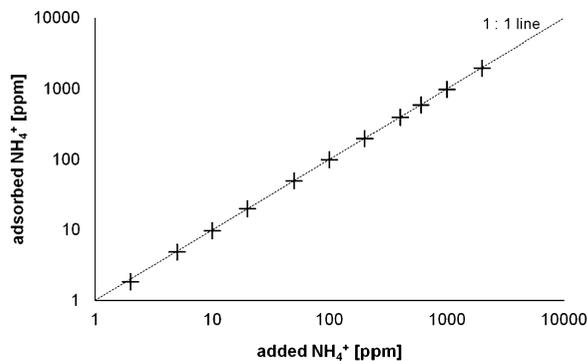


Fig. 5 Ammonium adsorption isotherm measured for the top soil of the location Karkendamm (sandy soil)

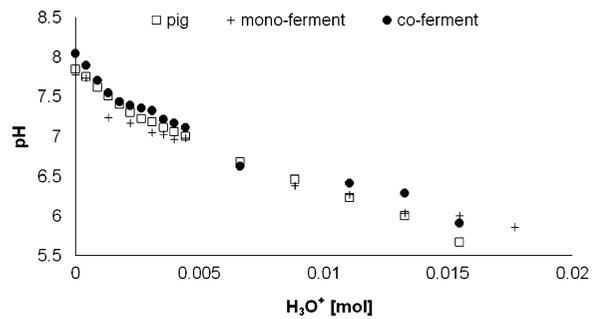


Fig. 6 Buffer behaviour of slurries collected in July 2008; buffer capacity was estimated by linear regression with 0.076, 0.098 and 0.082 mol H₃O⁺ per pH unit for pig slurry, mono-ferment and co-ferment

soil phase is probably higher than 34%. Thus, the percentage of TAN in the model, which does not take part in the volatilisation process due to infiltration, was set to 40% of the applied TAN for all fertilisers and all soil types. At an application rate of 6 L m⁻², 40% corresponds to 0.67% per 0.1 mm slurry liquid applied. For rain events, it was equally assumed that 0.67% per 0.1 mm liquid as well as of TAN applied is washed down to a depth <5 mm. We decided to use only one reduction factor because a statistical analysis showed only occasionally differences between the slurries.

Since no clear trend could be observed from the ploughing experiments, in the model the TAN content in the upper layer after incorporation was set to 25% of the TAN applied, the water content was reduced to about 50% for all slurry types.

Nitrification pot experiments showed that the nitrification processes in the soil slurry surface (0–1 cm) could be described adequately by exponential fitting. The derivative of this exponential function was implemented in the model for the calculation of the nitrification rates (Eq. 14) considering all slurry types. This applied for the simulation time of 3 days and assumed that the TAN amount of the slurry liquid on the soil slurry surface is not limited in this time span.

$$\frac{dnitrate}{dt} = \alpha^* \varepsilon^* e^{\varepsilon^* t} \tag{14}$$

Where t is the time [10 min], nitrate is the nitrate N in soil [milligrammes per kilogramme], α and ε are empirical constants.

The best results obtained by the original parameterisation of the atmospheric resistances by Sommer and

Olesen (2000) were with $\beta_0=0$ or $\beta_1=0$ and a small β_0 . Our best approach resulted in β_0 as well as $\beta_1=0$. Thus, only one atmospheric resistance parameter (β_2) in Eq. 8 was used for the parameterisation of the model by fitting the model to the experimental data, as shown in Eq. 15.

$$r_c = \beta^*(1 - \theta_{\text{surface}}) \quad (15)$$

For each of the two experimental years, one early, one mid and one late application trial ($n=18$) of each slurry type was used in the parameterisation (Table 1). Every trial was parameterised separately because a simultaneous parameterisation could not be done in our modelling environment. The resulting mean value of $\beta=833$ [-] was used for the validation of the remaining application trials ($n=19$; Table 1). During parameterisation, three of the 18 modelling runs could not be estimated adequately, the overall RMSE of the cumulated NH_3 emission endpoints for parameterisation resulted in $1.80 \text{ kg N ha}^{-1}$ excluding three outliers. The corresponding mean error (ME) was 0.48.

3.6.2 Validation Runs

The results of the validation runs in comparison with the cumulated NH_3 losses measured at the end of a measurement campaign are presented in Fig. 7. The

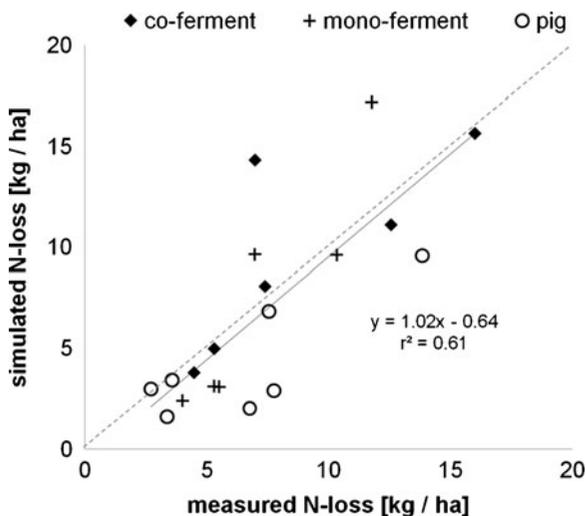


Fig. 7 Simulated NH_3 emissions (cumulated endpoints) in relation to measured losses in the field experiments (p intercept >0.5 , p gradient <0.001)

validity of the linear fit was evaluated with $r^2=0.61$, with an intercept close to 0 ($p>0.5$) and a slope close to 1 ($p>0.001$), but three of the seven pig simulation runs underestimated the NH_3 losses and two of the 12 biogas runs overestimated the emissions.

The most cumulated N losses in the validation runs were in the range of the standard deviations of the replicated NH_3 field measurements. Moreover, time courses of cumulated NH_3 losses in the validation runs showed daily fluctuations (Fig. 8, left graph) as well as the effect of rain events (Fig. 8, right graph, rain events during the first two measurement days) in close agreement to measured data.

The RMSE analysis of the validation runs resulted in an arithmetic mean of $1.95 \text{ kg N ha}^{-1}$ (27% of average measured cumulated NH_3 losses), including two outliers for the biogas slurries with 5.2 and 5.5 kg N ha^{-1} . Without these two outliers, the RMSE decreased to $1.56 \text{ kg N ha}^{-1}$. An analysis of the pig slurry simulations showed either very good agreement ($0.1\text{--}1.7 \text{ kg N ha}^{-1}$) or relatively high RMSEs of 3.9 kg N ha^{-1} . The RMSE results showed a close relationship to the ME values. In general, the model simulation showed a performance with an overall ME of 0.21 including outliers and 0.49 without outliers. However, outliers, identified in the RMSE analysis, showed unacceptable results of $\text{ME} < 0$. The regression analysis of time courses of NH_3 emissions always indicated a model performance with an overall mean r^2 of 0.96 and no outliers. Statistical results are summarised in Table 6.

3.7 Sensitivity Analysis

The dominant driving factors of the models were temperature and pH. Following a change of $+1^\circ\text{C}$, the NH_3 emissions will increase by 1% of the applied TAN, with a change of $+0.1$ pH units, the NH_3 volatilisation will increase by about 1.6% of the applied TAN. Other model input parameters have minor influences on the emissions (see Fig. 9).

The higher the dry matter content is, the higher the ammonium concentration in the slurry liquid. This effect resulted in an increase in emissions by 0.03% of the applied TAN per 1% dry matter. A comparable effect was detected for an increase of the air humidity. In accordance with the analysis of the measurement data, increasing air humidity showed that the evaporation level decreased and the drying of the surface

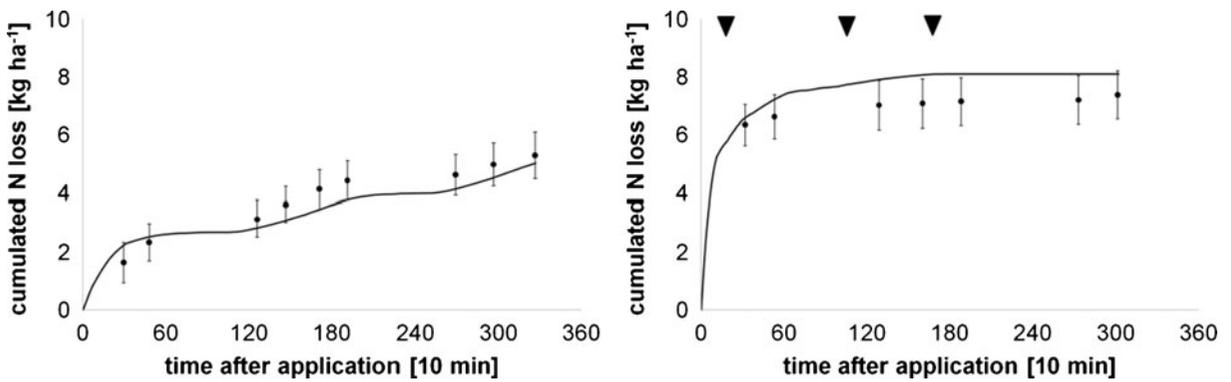


Fig. 8 Comparison of measured data (co-ferment, rye grass) in the field under different environmental conditions with simulated NH₃ loss; symbols represent measured data with standard

deviation (left 19 May 2008, right 3 July 2008), solid lines are simulated NH₃ losses, triangles indicate rain events (in total 20 mm)

liquid was delayed (0.11% increase per percent of air humidity). The influence of wind speed showed no clear positive or negative trend because the evaporation model as well as the atmospheric model includes this parameter. The higher the wind speed, the higher the NH₃ volatilisation due to air exchange, as well as the evaporation, which in turn reduces NH₃ volatilisation due to drying out the slurry on the soil surface (increase of resistance). A reduction in the ammonium content resulted in a change of -0.04% per kilogramme NH₄-N. As determined in the field measurement, changes in the NH₃ emission between different ammonium levels occurred after the first day. This implies that a decrease in the applied ammonium amount will increase the relative NH₃ emissions because most of the NH₃ volatilisation took place during the first day. Sommer and Olesen (2000)

showed that approximately 50% volatilised during the first day. In the sensitivity analyses, a reduction by 10 kg of ammonium per hectare resulted in an increase of the relative NH₃ losses of 7% of applied TAN.

4 Discussion

The aim of this work was to develop a simple but mainly mechanistic model which can describe the main processes of NH₃ volatilisation after the application of biogas waste for a large variety of conditions. This would prove useful in order to analyse the main factors controlling NH₃ losses in crop rotations fertilised with biogas residues and different slurry types. The model is based on the

Table 6 Statistical analysis results (RMSE, ME and the r^2 of the linear regression between measured and simulated values) comparing simulated and observed cumulated losses

Statistic parameter	RMSE [kg N ha ⁻¹]			ME [-]			Regression [-]		
	Mono-ferment	Co-ferment	Pig	Mono-ferment	Co-ferment	Pig	Mono-ferment	Co-ferment	Pig
04/11/07	1.5	–	0.3	-0.40	–	0.48	0.92	–	0.95
05/22/07	0.9	1.5	3.9	0.94	0.88	-0.80	0.96	0.94	0.94
06/06/07	5.2 ^a	0.6	3.9	-0.76	0.98	0.21	0.97	0.98	0.96
03/17/08	–	0.4	1.4	–	0.93	-0.40	–	0.94	0.99
05/19/08	1.8	0.5	3.9	0.02	0.90	-1.58	0.96	0.98	0.97
06/03/08	1.6	5.5 ^a	1.7	0.54	-4.19	0.46	0.97	0.98	0.98
07/03/08	1.7	0.8	0.1	0.17	0.90	0.99	0.95	0.99	0.99
Overall mean	1.95			0.21			0.96		

^aOutlier

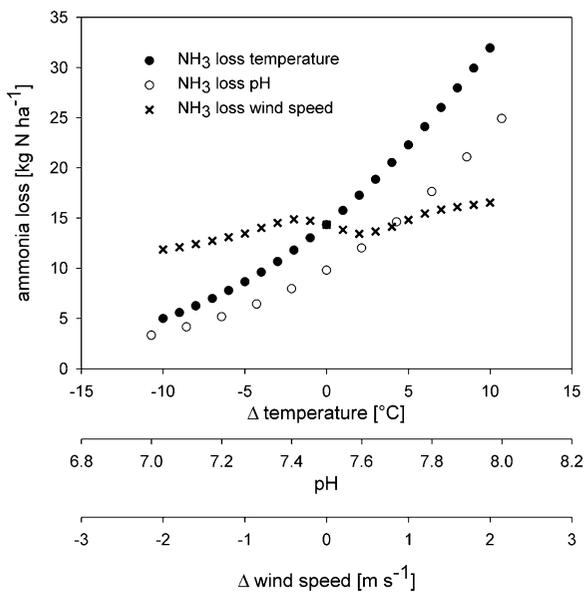


Fig. 9 Effect of temperature, pH and wind speed on simulated NH_3 volatilisation on the basis of the application date 6 June 2008 ($17.1\text{ }^\circ\text{C}$, 3.9 m s^{-1})

existing knowledge of the main processes controlling NH_3 emissions but designed to be compatible with our experimental data, especially in terms of model parameterisation. In its complexity, it may be regarded on an intermediate level between more complex approaches (Genermont and Cellier 1997 or Wu et al. 2003) and simple, empirical Michaelis–Menten-type models (Søgaard et al. 2002).

The results from a sensitivity analysis of the model (Fig. 9) are in good agreement with NH_3 emission measurements. A statistical analysis by Søgaard et al. (2002) of several field experiments showed a similar effect of the temperature (2% per 1°C) for example, but he could not test the effect of pH. Duan and Xiao (2000) investigated positive and negative effects on the NH_3 emission and could show that the pH had the strongest positive effect as also shown by our analysis. In contrast, the wind speed in our model had only a slight positive effect although Sommer et al. (1991) and Søgaard et al. (2002) showed a considerable effect on NH_3 emissions. However, our results are confirmed by studies of Beauchamp et al. (1978), Thompson et al. (1990) and Bussink et al. (1994), which investigated no or only a slight positive effect. Sommer and Hutchings (2001) assumed that the wind speed is often high enough, so that other factors control the NH_3 emissions. Since the wind

speed in the maritime regions of our field experiments is by trend higher than in continental regions, we agree with this argumentation.

The tested NH_4^+ adsorption isotherms showed almost complete sorption of NH_4^+ in the range of ammonium application levels in both soils used for the model parameterisation. This results in an implicit assumption that ammonium which infiltrates in the soil plays no role in the NH_3 volatilization process.

The pH function implemented in this study (Eq. 4) was developed for pH dynamics measured after application of pig slurry. The pH buffer curves from laboratory studies for biogas and pig slurries determined showed very similar dynamics for all tested slurries which proves the applicability of the pH algorithms for a wide range of organic slurries. Both assumptions are also positively supported by the good agreement of model runs with measured NH_3 loss dynamics.

No significant differences in the infiltration behaviour of TAN from different slurries with respect to volatilisation process were determined in our experiments. The deeper infiltration of pig slurry at Hohenschulen with loamy sand, without a significant effect on the ammonium content in the soil slurry surface layer (0–5 mm), can be explained by preferential flow through macropores in this highly structured soil and the low viscosity of the slurry, which was also observed during pretests with brilliant blue. However, this process could not increase the NH_3 amount in soil depths from 0.5 to 5 cm, only the distribution was deflected. In certain specific cases, the slurry liquid leaked out of the pots (sand) after a few seconds, so it is probable that preferential flow through macropores caused leaking deeper than 5 mm here. The expected effect of the viscosity on slurry infiltration was not confirmed at last. The infiltration results are probably transferable to other soil types with comparable ammonium adsorption and infiltration behaviour. It is possible, however, that soils with higher pH values, not typical for arable land in Germany, can react in a different way, so that a model adaption could be necessary for such soils. In addition, infiltration of slurries in very fine textured, clayey soil can differ from those in the range of soil conditions covered in this study. A first test of the model for clayey soils in the marsh region of Northern Germany showed that infiltration can be slightly reduced (by about 5% $\text{NH}_4\text{-N}$ applied)

compared to the results presented in this study. However, the simplifying assumption that soil water dynamics is not to be explicitly covered by an NH_3 loss model from field applied slurries is strongly confirmed by our recent investigations.

NH_3 volatilisation from biogas slurries normally takes place within 3 to 5 days of application. The largest amount will be emitted during the first day (Søgaard et al. 2002). Nitrification experiments of the surface layer showed that there is a lag phase or only a small conversion during the first 2 days and quantitatively relevant nitrification started only on the third day. Hence, the implementation of one nitrification curve for all slurries and soil conditions was sufficient.

The linear regression analysis between measured and modelled time courses of NH_3 losses always showed correlation values above 90%, whereas the RMSE and ME displayed outliers. Thus, the model reflects the NH_3 volatilisation kinetics or changes for all situations in an adequate way, and only in a few cases, the volatilisation dynamics were negatively or positively offset. The performance of the validation resulted in a mean RMSE of 1.95 kg ha^{-1} , corresponding to 27% of the measured NH_3 losses, and was only slightly higher than the standard deviations of the field measurements reflecting that the model covers the main processes of NH_3 volatilisation.

The outliers were limited to one slurry type out of several model runs for different slurries under identical environmental conditions. In no case did all simulated emissions from certain slurry types at a single application trial showed unsatisfactory results (e.g. RMSE in kilogrammes N per hectare on 6 June 2008, 1.6 for mono-ferment, 5.5 for co-ferment and 1.7 for pig slurry). Thus, the deviations are due to the slurry properties and not to the emission subprocesses based on environmental conditions. As shown by the sensitivity analysis, slurry pH has the strongest effect on NH_3 volatilisation (1.6% of applied TAN per 0.1 pH). It is very likely that either the pH model or the measurement of the pH caused the outliers. As mentioned in the introduction, a variety of NH_3 emission models for application of animal slurries were developed. Many authors noted problems with the modelling of the pH dynamics. The tested pig slurry had a pH around 7.0, close to the pH threshold value, above which a significant volatilisation com-

mences (Freney et al. 1983). This might indicate a necessary correction of the pH model in the parameters. Vandre and Clemens (1996) observed a pH increase in animal slurries caused by CO_2 volatilisation after application. Our measurements rarely showed such a pH increase. However, this effect could also explain the underestimation. The two outliers were observed for application dates in summer. The measured emissions (approximately 6 kg N ha^{-1}) were very low under such environmental conditions and especially in comparison to application dates in spring. Hence, the simulated $\sim 14 \text{ kg N ha}^{-1}$ (see Fig. 7) from a total ammonium application rate of 88 kg ha^{-1} was quite realistic. Analytical errors in the determination of the slurry properties are a possible reason for the single outliers. An example for the uncertainty of measured input parameters is the determination of nitrogen contents with two established methods using subsamples of the same sample, and results showed sporadic deviations up to 30%.

The model performance of the parameterisation was comparable to the validation. Remarkably, parameterisation was not as good as the validation, which, to a certain extent, can be explained by the outliers. The smaller parameterisation dataset had one more outlier. On the other hand, this would not account for the discrepancy as the parameterisation of the parameter β was done separately for every trial and slurry type, and finally, one mean value was calculated. A more satisfactory procedure would have been the simultaneous parameterisation of all trials. However, this could not be carried out due to the restraints of the modelling environment. Furthermore, it is questionable if this method of action would actually be successful when applied to other modelling environments, which often use the same optimisation procedures. Even the parameterisation of single trials was time consuming and often unstable.

5 Conclusion

Infiltration measurements in Northern Germany showed no significant quantitative effect of the different infiltration depths of different slurries on the related NH_3 volatilisation process. Simulations without a specific soil compartment, but including evaporation, pH and atmospheric compartment therefore showed good results, providing estimates for the

cumulated NH_3 emission after the application of biogas and animal slurries with trail hoses to bare soil as well as to different crops used in biogas crop rotations. Simulations using a more complex soil model/model approach showed no better correlation between experimental data and simulated data than those presented in our study. Our model calculations showed that temperature and slurry pH are the main drivers for NH_3 volatilisation in the model. The modelling approach for NH_3 emissions after the field application of the organic fertilisers presented in this paper could easily be used as simulation models in comprehensive system models of agro-ecosystems.

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