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Analysis of the effect of air temperature on ammonia emission from band application of slurry☆

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A B S T R A C T

Field application of liquid animal manure (slurry) is a significant source of ammonia (NH_3) emission to the atmosphere. It is well supported by theory and previous studies that air temperature effects NH_3 flux from field applied slurry. The objectives of this study was to statistically model the response of temperature at the time of application on cumulative NH_3 emission. Data from 19 experiments measured with the same system of dynamic chambers and online measurements were included. A generalized additive model allowing to represent non-linear functional dependences of the emission on the temperature revealed that a positive response of the cumulative NH_3 emission on the temperature at the time of application up to a temperature of approximately 14 °C. Above that, the temperature effect is insignificant. Average temperature over the measuring period was not found to carry any additional information on the cumulative NH_3 emission. The lack of emission response on temperature above a certain point is assumed to be caused by drying out of the slurry and possible crust formation. This effect is hypothesized to create a physical barrier that reduce diffusion of NH_3 to the soil surface, thereby lowering the emission rate. Furthermore, the effect of the interaction between soil type and application technique and the effect of dry matter content of the slurry was derived from the model, and found to be significant on cumulative NH_3 emission predictions.

1. Introduction

Field application of liquid animal manure (slurry) is a significant source of ammonia (NH_3) emission to the atmosphere (Aneja et al., 2009). Ammonia emission should be mitigated as it contributes to nitrogen deposition, acidification, and particle formation (Aneja et al., 2009; Walker et al., 2006).

Over the last decades, extensive research has contributed to increased knowledge about the factors controlling and affecting the NH_3 emission and thereby which measurements can be used in order to mitigate these (Hafner et al., 2018; Sommer and Hutchings, 2001; Webb et al., 2010). It is well established that application technique and rate, slurry pH, dry matter (DM) content of the slurry, soil and crop type, climate conditions, and application timing are important parameters that affect NH_3 emission rate after field application of slurry (Bell et al., 2015; de Jonge et al., 2004; Hafner et al., 2019; Huijsmans et al., 2018; Martínez-Lagos et al., 2013; Misselbrook et al., 2005a; Rochette et al., 2008; Rodhe et al., 2004; Smith et al., 2000; Sommer and Olesen, 1991). Due to interactions between the parameters, it is challenging to determine the effects of the individual parameters on NH_3 emission.

The slurry DM content have been found to influence the NH_3 emissions, with higher emissions being observed from slurries with higher DM content (Huijsmans et al., 2018; Misselbrook et al., 2005b, 2005c; Smith et al., 2000; Sommer et al., 2006). The effect has been assigned to a reduction of slurry infiltration into the soil due to sealing of the soil pores (de Jonge et al., 2004; Sommer et al., 2003). Soil type and conditions also influences the slurry infiltration (Bell et al., 2015; Bussink et al., 1994; Huijsmans et al., 2018; Martínez-Lagos et al., 2013; Smith et al., 2000), and it has been found that the emissions after application by trailing hoses or trailing shoes interacts with the soil type (Pedersen et al., 2020b).

Timing of application include several factors, such as wind speed, rainfall rate, solar radiation and air temperature. The

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positive correlation between temperature in the measuring period and NH_3 emission has been recognized in several studies (Beauchamp et al., 1982; Bell et al., 2015; Génermont and Cellier, 1997; Hafner et al., 2018, 2019; Huijsmans et al., 2018; Martínez-Lagos et al., 2013; Sommer et al., 1991). Huijsmans et al. (2018) and Sommer and Olesen (1991) suggested that the temperature right after slurry application is the most important temperature, as the NH_3 emission potential is highest in this period. The effect of temperature on NH_3 emission is well supported by theory.

Theoretical calculations of NH_3 in the gas phase from a solution, shows that a 1 °C increase in temperature results in an approximately 13% increase in the gas-phase NH_3 (Hafner et al., 2018; Hafner and Bisogni, 2009) (Fig. 1). This relatively high increase in theoretical gas-phase NH_3 caused by small changes in temperature is the results of the equilibrium constant (determining the ratio between NH_4^+ and NH_3) and Henry's law constant (determining the ratio between NH_3 in solution and NH_3 in the gas phase) both are temperature dependent. Increasing temperature increase the potential for NH_3 loss due to a shift of the NH_4^+/NH_3 equilibrium in solution towards NH_3. Additionally, the amount of NH_3 in the gas phase compared to NH_3 in solution increase with temperature (Misselbrook et al., 2005a; Sommer et al., 2003).

As the parameters affecting NH_3 emission interact, the temperature effect anticipated from air-water equilibrium is not found in field experiments. Braschkat et al. (1997) and Misselbrook et al. (2005a) did not find the expected effect of temperature on cumulative NH_3 emission and both hypothesized that a surface crust formation of the slurry caused by drying counteracted it. A surface crust on the field-applied slurry is expected to increase the surface resistance of NH_3 transport with the results of a lower NH_3 transport from the slurry to the atmosphere (Sommer et al., 2003). Other studies also discuss the possible effect of crust formation and its mitigating effect on NH_3 emission (Hafner et al., 2018; Salazar et al., 2014; Sommer et al., 1991; Vandré et al., 1997).

The effect of temperature has been included in previous models. Génermont and Cellier (1997) developed the mechanistic Vol't Air model. In a sensitivity analysis, they found that a 2 °C or 4 °C increase in air temperature can increase NH_3 emission by 10% and 20%, respectively. These findings were contradicted by a sensitivity analysis of the Vol't Air model by Smith et al. (2009), who only found a 1% increase in cumulative NH_3 emission after an increase in air temperature of 5 °C. Neither Génermont and Cellier (1997) or Smith et al. (2009) provide all the model input parameters for their sensitivity analysis, so it is assumed that the differences regarding the temperature effect on cumulative emission are caused by differences in these. The first ALFAM model (Ammonia Loss from Field-Applied Manure) by Søgaard et al. (2002) predicted that 1 °C increase in temperature would increase the cumulative NH_3 emission by 2% (for illustrative example, see Figure S1 in supplementary materials). In the semi-empirical ALFAM2 model (Hafner et al., 2019), the emission has an increasing response to temperature that varies with the other predictor variables (for illustrative examples, see Figure S2 in supplementary materials). Increases of >40% can be observed when air temperature is increased by 5 °C (e.g. from 5 °C to 10 °C, TAN applied = 50 g kg^{-1} (as N), slurry DM = 6%, with other parameters set to reference conditions).

Field measurements are very limited in the number of replications possible and commonly the results have a high variation. As several parameters cannot be controlled but only observed during field measurements (e.g. parameters depending on application timing, and to some extend soil and slurry parameters) these will vary between experiments, making it difficult to make inter-comparisons. Furthermore, a high variation between test organizations has been observed in the ALFAM2 database (Hafner et al., 2018), which has to be considered when comparing results from different studies.

In the present study, data from 19 different experiments measured with the same system of dynamic chambers and online measurements are used to statistically separate the effect of temperature. The system, which is presented in detail by Pedersen et al. (2020b), allows for a high time resolution and relatively high reproducibility in NH_3 flux measurements. By using data measured with the same system, the high variation observed between test organizations recognized by Hafner et al. (2018) is removed. Furthermore, other factors linked to the timing of application (wind speed, rainfall rate, and solar radiation) will be constant in the wind tunnels throughout all experiments, giving a unique possibility to isolate the effect of ambient air temperature. The aim was to model the effect of temperature on cumulative NH_3 emission from band-applied slurry. The specific objectives were to (i) evaluate the effect of ambient air temperature on NH_3 emission from band-applied slurry, and (ii) Investigate the effect of DM and the interaction between soil type and application technique on cumulative NH_3 emission.

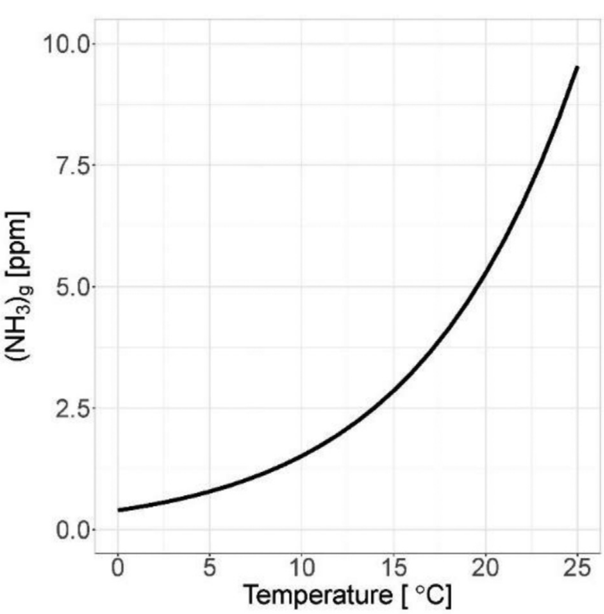

Fig. 1. Equilibrium gas phase NH_3 concentration for a solution with 0.1 M NH_4^+ and a pH of 7 at temperatures ranging from 0 to 25 °C.

2. Materials and methods

2.1. Ammonia measurements

Ammonia emission after field application of slurry was measured with a system consisting of nine wind tunnels. A detailed description and evaluation of the system is presented in (Pedersen et al., 2020b), and only a short description is given in the following. A stainless steel chamber (0.8 × 0.4 × 0.25 m) was used as the emission chamber. Air entered from a small air inlet and was passed through the chamber with a manually adjusted air exchange rate of 25 min^{-1}, corresponding to a calculated mean air speed of 0.33 m s^{-1}. The emission chamber was connected to a fan, motor, and frequency converter via a steel duct. Metal frames (0.29 × 0.67 m) was inserted into the soil for the tunnels to be mounted on, in order to control the amount of slurry in each plot, giving a plot area for each tunnel of 0.2 m^2. Ammonia concentration in the air entering the tunnels was measured with three background measurements, equally distributed among the tunnels. From each tunnel and the three background measurement points, air was drawn through heated PTFE tubing to a channel selection manifold. A cavity ring down spectroscopy (CRDS) instrument (G2103 NH_3 Concentration Analyzer, Picarro, CA, USA) was used to measure the NH_3 concentrations in the air stream from the channel selection manifold continuously. Different measuring intervals for each tube was used, ranging from five to 12 min (Table S1).

The air flow through the tunnels was constant and there was no precipitation or solar radiation inside the emission chambers. As these parameters were eliminated, it was easier to isolate the effect of temperature. The air flow inside the emission chamber has been found to be the most critical operating parameter (Eklund, 1992; Smith and Watts, 1994; Sommer and Misselbrook, 2016). Experiments evaluating the air turbulence at the soil surface (caused by air exchange) inside the emission chamber and at ambient conditions were used to select the air flow that gave a turbulence at the soil surface closest to ambient conditions at different combinations of temperature and wind speed. Details of the experiments are provided in (Pedersen et al., 2020b).

Recovery of NH_3 throughout the measuring system (from tube inlet on the tunnels to the CRDS instrument) was frequently tested, and always found to be minimum 90% within the measuring interval.

Average NH_3 emission flux F (g m^{-2} min^{-1}) in each measurement interval was calculated separately for each wind tunnel from the concentration C (g m^{-3}), the air flow q (m^3 min^{-1}) in the emission chamber, and the soil area covered by the wind tunnel A (m^2) (Equation (1)).

$$F_{NH3} = (C \cdot q)/A \tag{1}$$

Cumulative NH_3 emission was calculated using the trapezoidal rule (Burden and Faires, 2001).

During all of the experiments, ambient air temperature (2 m) was continuously logged with a weather station (Theis CLIMA, Göttingen, Germany with a Campbell CR10xB data logger, Campbell Scientific, INC, UT, USA). The temperature was logged and averaged in 10 min intervals. It has been tested that the temperature inside and outside of the tunnels only had minor differences (Pedersen et al., 2020a).

2.2. Data

The data used consisted of 108 observations from 19 different experiments. To obtain a relatively homogeneous dataset a set of criteria were used for data selection:

- Slurry: untreated pig or cattle slurry.
- Application techniques: trailing hoses or trailing shoes (Bomech B. V., Albergen, The Netherlands).
- Soil type: coarse sand, sandy loam, or loamy sand.
- Application rate [tonnes ha^{-1}] should be in within Danish standard practices.
- Minimum measuring period of 90 h.

These criteria meant that all data was used (3 treatments x 3 replicates (wind tunnels)) for some of the experiments, whereas for other experiments only one or two of the treatments were included.

The data can be found in Table 1. Additional information about soil, crops, and slurry for the individual experiments can be found in Table S1 in supplementary materials.

Parts of the data has been published in previous publications (Foldager et al., 2019; Pedersen et al., 2020a, 2020b), for detailed overview, see Table S2 in supplementary materials.

2.3. Model description

The NH_3 emission was modelled using a generalized additive model (Hastie, 1991; Hastie and Tibshirani, 1990; Venables and Ripley, 2002) defined with a Gamma distribution, and a logarithmic link function. The model contained three additive effects, one representing a combination of the soil type and application method, a second representing the dichotomized DM (≤ 4 or >4), and a third given by a smooth function of the air temperature at the time of slurry application estimated by a cubic B-spline. Additionally, the model contained an offset given by the logarithm of the total ammoniacal nitrogen (TAN) applied. This model is equivalent to describing the expected NH_3 emission per unit of applied TAN as a smooth function of the temperature at slurry application (not necessarily linear). The details are given below.

Denote by Y_{smdr} the random variable representing the total NH_3 emission observed at the r^{th} replicate (combination of wind tunnel and experiment) of the observation from the s^{th} soil type (s = coarse sand, loamy sand, sandy loam) that received the d^{th} DM content ($d = \leq 4, >4$) applied using the m^{th} method (m = trailing hoses, trailing shoes). According to the model, for the $smdr^{th}$ observation Y_{smdr} is Gamma distributed (see Jørgensen and Labouriau (2012)) and have expectation given by Equation (2).

$$\log[E(Y_{smdr})] = \mathrm{K}_{sm} + \mathrm{H}_d + f(\mathrm{T}_{smdr}) + \log(TAN_{smdr}) \tag{2}$$

Here the notation is constructed with the same indexing convention employed for defining Y_{smdr}, according to which K_{sm} is the additive effect of the combination of the s^{th} soil type and the m^{th} method; and H_d is the additive effect of the d^{th} DM content. The function f is an estimated cubic B-spline so that $f(\mathrm{T}_{smdr})$ is an additive regression term representing a possibly non-linear effect of the temperature at the time of application. Additionally, TAN_{smdr} is the known TAN applied to the $smdr^{th}$ observation, which enters in the model as an offset, and E is the expectation operator (*i.e.*, $E(X)$ denotes the expectation of the random variable X). Solving Equation (2) to $E(Y_{smdr})$ and passing the constant $1/TAN_{smdr}$ to inside expectation operator yields Equation (3).

$$E\left(\frac{Y_{smdr}}{TAN_{smdr}}\right) = exp(\mathrm{K}_{sm})exp(\mathrm{H}_d)g(\mathrm{T}_{smdr}) \tag{3}$$

Here the expected emission per TAN unit, $E\left(\frac{Y_{smdr}}{TAN_{smdr}}\right)$, is expressed as a smooth function $g(\cdot) = exp[f(\cdot)]$ (which is smooth because it is a composition of two smooth functions) that expresses the functional form of the regression term representing the temperature at the application; the exponential of the effects of the DM content and the combination of soil type and application method enter in the model as multiplicative factors which will be reported in Table 2. The model above was adjusted using the software R version 6.3.6; in particular, we used the R-package "gam" (Hastie and Tibshirani, 1990; Venables and Ripley, 2002), and the R-package "postHoc" (Labouriau, 2020) for performing post-hoc analyses. Model validation can be found in supplementary information, Section S4.

The potential of the mean temperature in the periods 0–6 h (Temp6h), 0–24 h (Temp24 h) and 0–90 h (Temp90 h) was assessed for predicting the total emission by using a graphical model (Abreu et al., 2010; Edwards et al., 2010; Lauritzen, 1999) as described below. In a graphical model, a group of variables in a study is represented as nodes of a graph with the following convention. Two nodes are connected by an edge (*i.e.*, a line) if, and only if, the conditional covariance between the two corresponding

Table 1
Data used for the statistical analyses. Each value of cumulative NH_3 emission is for one replicate (wind tunnel).

Experiment	Soil type[a]	Slurry DM [g kg^{-1}]	Application method[b]	Air temperature				TAN applied [kg N ha^{-1}]	Cumulative NH_3 emission [kg N ha^{-1}][c]
				At application	6 h average	24 h average	90 h average		
A	CS	≤4	TS	24.4	25.1	18.9	15.1	100	12.33; 15.12; 8.83
A	CS	≤4	TH	24.4	25.1	18.9	15.1	100	18.83; 31.91; 27.55
B	LS	≤4	TS	22.8	22.7	17.6	18.1	99	26.92; 27.39; 26.90
B	LS	≤4	TH	22.8	22.7	17.6	18.1	99	15.15; 19.53; 27.17
C	SL	≤4	TS	19.2	21.8	20.2	20.4	101	32.70; 29.09; 22.41
C	SL	≤4	TH	19.2	21.8	20.2	20.4	101	28.96; 30.10; 29.03
D	CS	>4	TH	8.3	8.2	7.8	11.3	102	10.59; 17.51; 10.55
E	CS	>4	TH	20.0	22.1	17.3	15.3	102	14.21; 19.50; 21.57
F	LS	>4	TS	15.2	15.8	12.8	15.0	98	21.17; 20.05; 20.39
F	LS	>4	TH	15.2	15.8	12.8	15.0	98	26.38; 27.47; 31.6
G	LS	>4	TS	22.8	22.6	17.0	16.9	99	23.81; 28.58; 28.96
G	LS	>4	TH	22.8	22.6	17.0	16.9	99	29.39; 32.58; 33.60
H	LS	>4	TS	15.7	15.9	14.7	15.8	95	26.08; 24.69; 28.20
H	LS	>4	TH	15.7	15.9	14.7	15.8	95	31.69; 29.08; 24.11
I	CS	≤4	TS	20.9	21.6	19.3	17.6	52	8.56; 9.56; 9.73
I	LS	≤4	TS	20.9	21.6	19.3	17.6	52	11.26; 11.58; 10.48
I	SL	≤4	TS	20.9	21.6	19.3	17.6	52	12.68; 15.27; 18.79
J	CS	≤4	TH	23.1	23.6	19.6	15.6	56	15.18; 14.13; 13.84
J	LS	≤4	TH	23.1	23.6	19.6	15.6	56	16.77; 17.53; 15.49
J	SL	≤4	TH	23.1	23.6	19.6	15.6	56	16.60; 16.41; 19.70
K	SL	≤4	TS	18.6	18.9	16.5	15.1	60	8.80; 11.62; 10.86; 12.48; 14.88; 10.85; 10.52; 12.81; 9.23
L	LS	>4	TS	21.3	21.7	17.9	15.5	62	9.46; 7.77; 8.24; 8.25; 7.23; 7.74; 8.25; 8.91; 6.94
M	CS	≤4	TS	15.0	15.3	12.2	12.2	65	10.43; 8.39; 7.23; 9.83; 10.83; 10.38; 9.17; 8.17; 9.21
N	SL	≤4	TH	5.9	6.8	7.8	5.3	99	2.21; 3.53; 4.42
N	SL	≤4	TS	5.9	6.8	7.8	5.3	99	3.19; 3.38; 3.12
O	SL	≤4	TH	8.4	8.0	5.6	3.5	51	2.47; 1.46; 2.17
P	LS	>4	TH	21.0	19.6	16.1	16.4	67	27.26; 28.68; 25.49
Q	SL	≤4	TH	10.9	7.1	6.6	6.9	106	31.56; 35.14; 27.65
R	SL	>4	TH	17.2	12.9	10.2	8.2	113	48.42; 45.95; 43.44
S	CS	>4	TS	21.5	19.6	14.6	12.0	59	32.54; 32.93; 29.51

[a] CS: coarse sand, LS: loamy sand, SL: sandy loam.
[b] TH: trailing hoses, TS: trailing shoes.
[c] Cumulative emission 90 h after application.

Table 2
Model parameters, exp(K_{sm}), (multiplicative factor of the combination of the s^{th} soil type and the m^{th} method) and H_d (additive effect of the d^{th} DM content), from Equations (2) and (3) with confidence intervals (95% coverage). Pairs containing a common letter do not statistically differ at a 5% significance level.

Combination of application method and soil type	Parameter exp(K_{sm}) and confidence interval (with 95% coverage)
Trailing shoes - Coarse sand	0.1494 (0.1262–0.1768) a
Trailing shoes - Loamy sand	0.1248 (0.1031–0.1509) a
Trailing shoes - Sandy loam	0.2109 (0.1748–0.2546) b
Trailing hoses - Coarse sand	0.177 (0.1398–0.224) b
Trailing hoses - Loamy sand	0.1702 (0.1415–0.2047) b
Trailing hoses - Sandy loam	0.2693 (0.2244–0.3233) c
Slurry DM > 4 [g kg^{-1}]	1.498 (1.2564–1.7861) d

variables given the other variables is different from zero. The absence of an edge connecting two nodes indicates that the corresponding two variables are conditionally non-correlated given the other variables. According to the theory of graphical models, if a variable, say E, is isolated from a group of other variables, say T6, T24 and T60, in a graph representing a graphical model (in the sense that it is not possible to connect the nodes of E to any of the nodes representing T6, T24 or T60 by a sequence of edges), then the variables T6, T24 and T60, do not carry any information on the variable E (see Whittaker (1990)). We consider a graphical model constructed with the following four variables: the mean temperature in the periods 0–6 h, 0–24 h and 0–90 h and the emission adjusted for the effects of the soil type, application method, temperature at application and slurry DM. The graphical model was estimated by searching for the graph that minimizes the Bayesian or Schwartz Information Criterion (BIC), using the R-package "gRapHD" (see Abreu et al. (2010)). Moreover, we tested for the presence of edges using a bootstrap version of the conditional test described in Anderson (2003).

3. Results

There is a significant positive response of the cumulative NH_3 emission to the temperature at application when the temperature varies from 5 °C to approximately 14 °C (Fig. 2). Thereafter, no increase in the emission is observed when the temperature increases (Fig. 2). Indeed, according to the model, increasing the temperature at application from 5 °C to 10 °C or 15 °C results in a predicted 5-

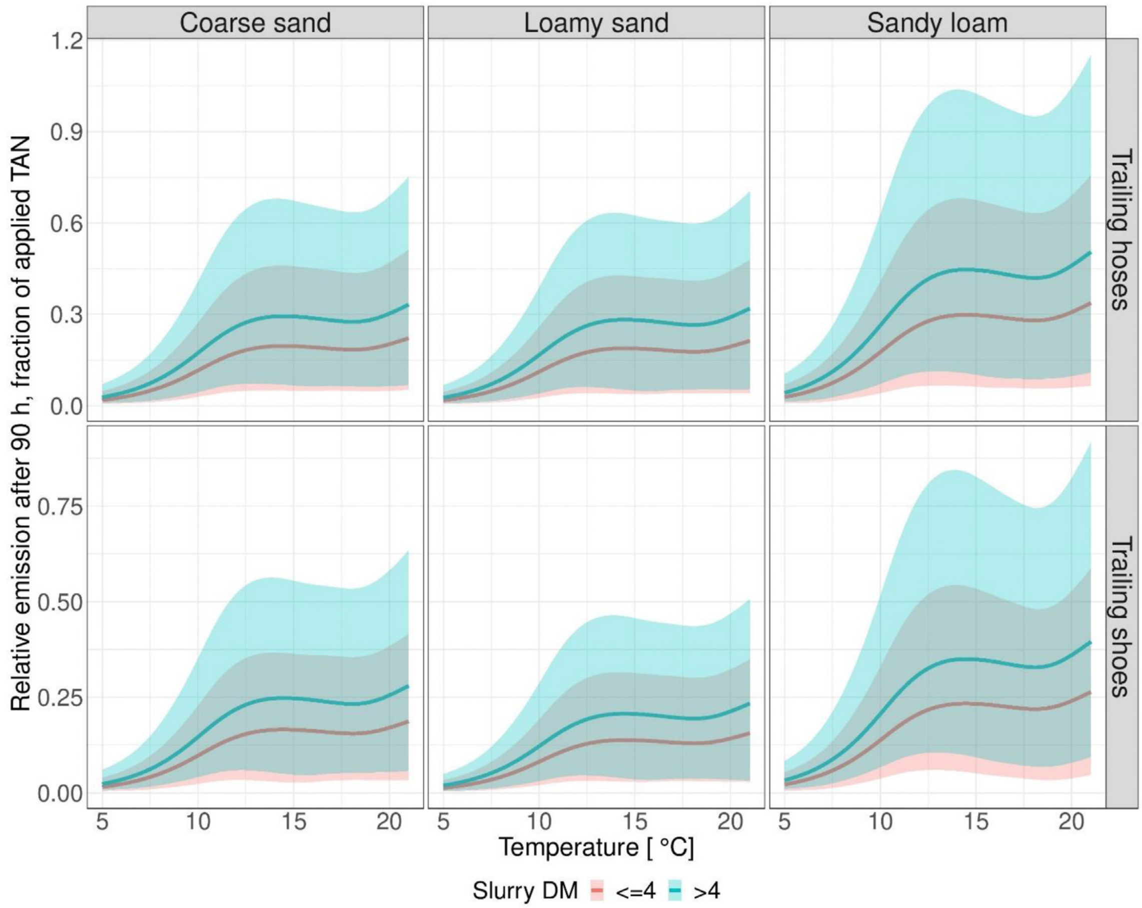

Fig. 2. Model predictions of cumulative NH_3 emission at temperatures between 5 °C and 21 °C after application of untreated pig or cattle slurry on coarse sand, loamy sand or sandy loam by trailing hoses or trailing shoes. Pointwise confidence region with 90% coverage is displayed as highlighted bands.

fold and 10-fold increase in NH_3 emission respectively (fraction of applied TAN). An additional increase from 15 °C to 20 °C does not increase the predicted NH_3 emission additionally.

The model predicts that application by trailing shoes decrease the NH_3 emission by 18.5% (95% coverage CI, 13.8%–23.2%), 36.4% (95% coverage CI, 33.6%–39.2%) and 27.7% (95% coverage CI 23.5%–31.9%) relative to trailing hoses for coarse sand, loamy sand, and sandy loam respectively (Table 2). Note that we detected a significant statistical interaction between soil type and application technique ($P < 0.0001$) so that the differences between the soil type effects are not the same when different application techniques are used. The NH_3 emission from sandy loam is significantly higher than coarse sand and loamy sand ($P < 0.0001$) for both application techniques. The effect of DM on NH_3 emission was found to be significant, with the emission being 50% lower on average for slurries with DM $\leq$ 4 g kg^{-1} compared to slurries with DM > 4 g kg^{-1}.

Fig. 3 displays a graphical model constructed with the adjusted emission and the mean temperature in the periods 0–6 h, 0–24 h and 0–90 h. The graph was inferred by searching for the graph that minimizes the BIC. Additionally, all the possible vertices in the graph were tested and it was found that the corresponding conditional correlations to each of the vertices present in the graph were significantly different from zero ($P < 0.05$). Moreover, each of the conditional correlations related to the vertices not present in the graph was not significantly different from zero ($P < 0.05$). The node representing the adjusted emission is isolated from the other three nodes (in the sense that no edges are connecting the node representing the adjusted emission to any of the other nodes). This result indicates that none of the three mean-temperature-related variables carries information on the emission that is not already contained in the temperature at application (which enters in the adjustment of the emission).

4. Discussion

4.1. Model evaluation

The present study is an observational study, as no attempt was made to control temperature in the wind tunnels. The experiments were performed in order to investigate the effects of other parameters (e.g. soil type, application technique, slurry treatment) on NH_3 emission, and were therefore not designed optimally for statistical modelling of the effect of air temperature on cumulative NH_3 emission. This was partially accounted for by selecting observations from all experiments that meet the chosen criteria, thereby making the dataset more homogeneous. The observed temperatures were not evenly distributed and in some areas only a few observations were made. Consequently, the results should be interpreted as trends and indications. The trends are significant, but not precise. The DM levels are highly confounded with slurry type. All slurries with DM $\leq$ 4 g kg^{-1} are pig slurry, and all but two of slurries with a DM content of >4 g kg^{-1} are cattle slurry.

The plateau observed (Fig. 2) fluctuates slightly. It is assumed

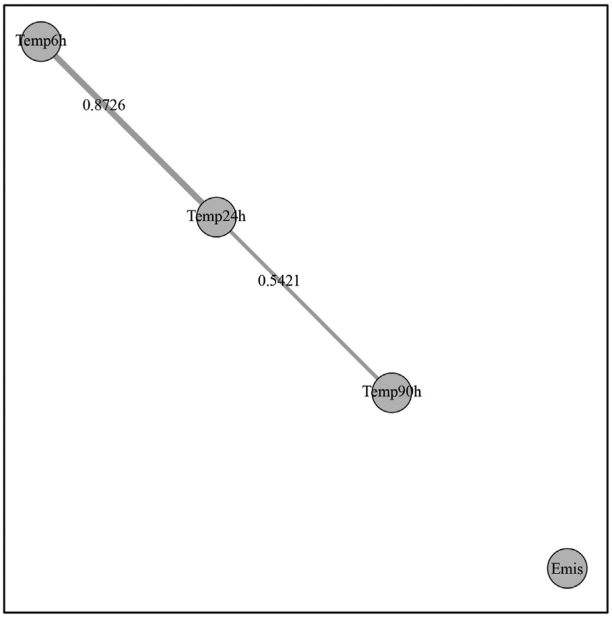

Fig. 3. Representation of the graphical model for the adjusted emission and the mean temperature observed in the periods 0–6 h, 0–24 h and 0–90 h, labelled "Emis", "Temp6h", "Temp24h" and "Temp90h", respectively. Two nodes are connected by a vertice (a line in the figure) if, and only if, the conditional covariance between the two corresponding variables, given the other variables, is different than zero. The graph was estimated by searching for the graph that minimizes the BIC. The numbers over the lines are the estimated conditional correlations between the respective variables; the thickness of the lines are proportional to the conditional correlation.

that this is caused by sparse data and unevenly distributed temperature observations. Therefore, it is suggested that there is a positive response on cumulative NH_3 emission of the temperature at application time, but at a certain temperature the emission increase levels off. Hereafter the temperature effect is small or not present. Due to the sparsity of the data, the exact point of the beginning of the plateau could not be determined based on the present study. Note that generalized additive models are data driven, so there is no assumption of the particular form of the function relating the NH_3 emission and temperature. This allowed us to detect the presence of the plateau, which might not have been detected if dependences had been determined beforehand, as can be the case with mechanistic and semi-empirical models.

4.2. Effect of temperature

A positive correlation between air temperature and cumulative NH_3 emission was determined, but only in the span from approximately 5 °C–14 °C, thereafter no additional increase in cumulative NH_3 emission is observed with an increase in temperature. It is generally assumed and modelled that there is a positive correlation between NH_3 emission and temperature, but a lack of correlation has also been observed, e.g. by Braschkat et al. (1997) and Misselbrook et al. (2005a). The lack of correlation has usually been ascribed to drying out of the surface leading to crust formation (Braschkat et al., 1997; Hafner et al., 2018; Misselbrook et al., 2005a; Salazar et al., 2014; Søgaard et al., 2002; Sommer et al., 1991; Vandré et al., 1997).

The theoretical exponential correlation between temperature and NH_3 emission can be described by Henry's law constant and the equilibrium constant (Fig. 1). Both of these describe the chemical processes in a liquid and are not applicable in a slurry that has a high DM content. When the surface of the field-applied slurry dries out the DM content at the surface increase and crust formation can take place creating a porous layer. It is hypothesized that the dry porous layer hinders the aqueous phase diffusion of NH_4^+ to the soil surface (Sommer et al., 2003) and that the porous diffusion of NH_3 in the desiccated surface layer is relatively slow, which in combination creates a physical barrier. This phenomenon is assumed to cause the plateau observed in the model (Fig. 2). Braschkat et al. (1997) did not see any differences in NH_3 emission from field applied slurry at 8 °C and 20 °C and hypothesized that a crust formation at 20 °C depressed the NH_3 emission, which is in agreement with the results from the present study.

The change in slurry DM at the surface and crust formation does not only depend on air temperature and slurry DM, but also on air flow right over boundary layer of the slurry as well as solar radiation. The air temperature inside the NH_3 emission chambers has been tested, and was found not to differ from ambient air temperature (Pedersen et al., 2020a). The air flow and solar radiation are different in the wind tunnel than under ambient conditions. The air flow has been selected based on experiments, so that the average turbulence is close to the ambient one under a range of ambient air temperatures and ambient wind velocities (Pedersen et al., 2020b). The slurry applied in the tunnels is not exposed to any solar radiation, which has been found to have an effect on NH_3 emission (Sommer et al., 2001, 2003). While it is not possible to quantify and account for the different environmental conditions inside the tunnels compared to ambient conditions, the conditions has been equal throughout all experiments. This provides the advantage that air speed and solar radiation can be eliminated as explanatory variables for the NH_3 emission in the present study.

Further research should be carried out in order to investigate the effect of temperature on slurry surface drying and crust formation of the field applied slurry, and the effect of these on NH_3 emission. Methods should be developed for quantification of these physical changes in the slurry surface over time after application. Additionally, the effects of air velocity/turbulence over the slurry surface on the slurry surface drying out and crust formation should also be considered and assessed. Determining the effect of slurry surface drying out and crust formation on NH_3 emission and the parameters affecting this can be used to improve current and future models of NH_3 emission from field-applied slurry.

The temperature right after application was found to be an explanatory variable in the model, whereas mean temperatures in the periods 0–6 h, 0–24 h and 0–90 h (the whole measuring period) after application was not found to carry any additional information on the total NH_3 emission that was not already explained by the model. The importance of the temperature at the time of application has been found in earlier studies (Beauchamp et al., 1982; Sommer et al., 1991; Sommer and Olesen, 1991), and the present study underlines the importance of reporting this in NH_3 emission studies. The importance of the temperature at application could indicate the initiation of a crust formation takes place relatively rapidly after slurry application. The speed of crust formation is assumedly also linked to temperature, where higher temperatures lead to a more rapid crust formation, counteracting the higher emission potential at higher temperatures.

4.3. Interaction between soil and application technique and effect of dry matter

The model of the present study show that the reduction effect of trailing hoses and trailing shoes depends on the soil type (Table 2 and Fig. 2). Application by trailing shoes significantly lower the NH_3 emission on coarse sand and loamy sand, whereas application by trailing shoes on sandy loam results in NH_3 emission that is not significantly different from application by trailing hoses on coarse sand and sandy loam. Application by trailing hoses on sandy loam gives significantly higher NH_3 emission than the other combinations (Table 2). These results confirm the findings in a previous study by Pedersen et al. (2020b) where some of the data included in the statistical model of the present study is presented. The present study includes data from several experiments not included in Pedersen et al. (2020b), thereby further validating the conclusions. The decrease in NH_3 emission by applying slurry by trailing shoes instead of trailing hoses was found to be 19 ± 12% on average by Pedersen et al. (2020b). The reductions found in the present study of 18.5% (95% coverage CI, 13.8%–23.2%) for coarse sand, 36.4% (95% coverage CI, 33.6%–39.2%) for loamy sand and 27.7% (95% coverage CI 23.5%–31.9%) for sandy loam, are in the same range, but on average higher.

A reduction in NH_3 emission from application by trailing shoes instead of trailing hoses has been found in previous studies (Misselbrook et al., 2002; Webb et al., 2010; Wulf et al., 2002), but the dependency of the effect of application technique on soil type has only previously been systematically evaluated by Pedersen et al. (2020b).

Several studies ascribe slurry DM as an important parameter for NH_3 emission after field application of slurry (Braschkat et al., 1997; de Jonge et al., 2004; Hafner et al., 2019; Sommer et al., 1991). The effect is assigned to a decreased slurry infiltration into the soil at higher slurry DM levels. The predicted DM effect on NH_3 emission in ALFAM2 model are in the same range as found in the present study, but it is difficult to make a direct comparison as the present study groups the DM in two categories, high (>4 g kg^{-1}) and low (≤4 g kg^{-1}).

5. Conclusion

The results from this study shows that after field application of slurry there is a positive response on the cumulative NH_3 emission with increasing air temperature at application in the range of approximately 5 °C–14 °C. At higher temperatures no clear increase in NH_3 emission with increasing temperatures is observed. These results contradict the general assumption and models, which may overestimate NH_3 emission during warm periods. The importance of the initial temperature on NH_3 emission should be considered to a higher extend when discussing NH_3 emission results, and the temperature at application should always be reported. The emission plateau at higher temperature is hypothesized to be a result of the slurry surface drying out and crust formation, but more research and techniques quantifying the physical changes are needed in order to make definitive conclusions.

The present study highlights the effect of slurry DM on NH_3 emission where higher DM contents of the slurry yields in higher cumulative NH_3 emission. The results underline the importance of the interaction between the soil type and application technique. Based on this, soil type should always be taken into account when low emission application technologies, such as trailing shoes, are considered as an NH_3 mitigation strategy.

Author statement

Johanna Pedersen: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Writing – Original Draft, Writing – Review & Editing, Visualization, Project administration. Tavs Nyord: Conceptualization, Investigation, Writing – Review & Editing, Supervision, Funding acquisition. Anders Feilberg: Resources, Conceptualization, Writing – Review & Editing, Supervision, Funding acquisition. Rodrigo Labouriau: Methodology, Software, Validation, Formal analysis, Data Curation, Writing – Original Draft, Writing – Review & Editing, Visualization.

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envpol.2021.117055.

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