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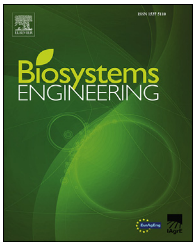

Research Paper

Non-linear temperature dependency of ammonia and methane emissions from a naturally ventilated dairy barn

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Ammonia (NH_3) and methane (CH_4) emissions from naturally ventilated dairy barns affect the environment and the wellbeing of humans and animals. Our study improves the understanding of the dependency of emission rates on climatic conditions with a particular focus on temperature. Previous investigations of the relation between gas emission and temperature mainly rely on linear regression or correlation analysis.

We take up a preceding study presenting a multilinear regression model based on NH_3 and CH_4 concentration and temperature measurements between 2010 and 2012 in a dairy barn for 360 cows in Northern Germany. We study scatter plots and non-linear regression models for a subset of these data and show that the linear approximation comes to its limits when large temperature ranges are considered. The functional dependency of the emission rates on temperature differs among the gases. For NH_3, the exponential dependency assumed in previous studies was proven. For methane, a parabolic relation was found. The emissions show large daily and annual variations and environmental impact factors like wind and humidity superimpose the temperature dependency but the functional shape in general persists.

Complementary to the former insight that high temperature increases emissions, we found that in the case of CH_4, also temperatures below 10 °C lead to an increase in emissions from ruminal fermentation which is likely to be due to a change in animal activity. The improved prediction of emissions by the novel non-linear model may support more accurate economic and ecological assessments of smart barn concepts.

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Nomenclature

SP	sampling point
THS	temperature-humidity sensor
LU	livestock unit (1 LU = 500 kg animal mass)
E	emission in g LU^{-1} h^{-1}
E_a	ammonia emission
E_m	methane emission
N	number of cows
m	average mass of a cow
C_i	gas concentrations inside
C_o	gas concentrations outside
Q	air exchange rate
A	animal activity
T	outdoor temperature
F	relative air humidity
W	wind speed
θ	wind direction
D	day of the year (cyclic with period 365.25)
H	hour of the day (cyclic with period 24)
μ, a, b, c, d, e, f, g, h, i	coefficients of the multilinear model
j, k	coefficients of the exponential model
l, n, p	coefficients of the parabolic model
q, r	coefficients of the linear model
ε	remaining model error

1. Introduction

Emissions from livestock production are a main concern to farmers, environmentalists and government representatives due to the negative impacts on the surrounding environment and the global climate that are associated with ammonia (NH_3) or greenhouse gases like methane (CH_4) (IPCC, 2013; Sutton et al., 2011a,b). Farming, particularly dairy farming, is regarded as one of the most important sources of these gaseous pollutants (FAO, 2006). In Germany, for example, according to the Federal Environment Agency about 95% of the NH_3 emissions and 54% of the CH_4 emissions are attributed to agriculture (Umweltbundesamt, 2013/2014). Cattle, which are typically housed in naturally ventilated buildings (NVB), cause about half of these NH_3 emissions and more than 90% of the CH_4 emissions. Different studies in moderate and cold climates have found average emission rates from naturally ventilated dairy buildings in the order of magnitude 1 g LU^{-1} h^{-1} NH_3 and 10 g LU^{-1} h^{-1} CH_4 with significant diurnal, seasonal and (inside and among buildings) spatial variations (Ngwabie, Vander-Zaag, Jayasundara, & Wagner-Riddle, 2014; Samer et al., 2011; Schrade et al., 2012).

The transport of pollutants, humidity and heat inside and out of NVB and thus the air exchange rate is mainly determined by the turbulent airflow (Rong, Liu, Pedersen, & Zhang, 2014; Saha et al., 2013; Schrade et al., 2012). Moreover, the production of polluting gases is affected by airflow, temperature and humidity inside the barn which strongly depend on the continuously changing weather conditions and are typically spatially heterogeneous and non-stationary (Amon, Amon, Boxberger, & Alt, 2001; Bjerg et al., 2013; Fiedler et al., 2013; Saha et al., 2014a,c, 2013,; Schrade et al., 2012). Long-term measurements of gas concentrations are needed to obtain statistically representative results for defined boundary conditions. The measurements must be spatially distributed and temporally highly resolved in order to obtain accurate emission factors. This highlights the necessity to better characterise the emission sources and their interrelation with different environmental factors at the barn scale to further increase also the accuracy of emission factors in general (i.e., averaged over a particular farm or region).

In the past decades, several authors investigated different aspects of the complex relation between climate conditions and emission rates. In this context, temperature is a common reference variable for the climate. Amon et al. (2001), for example, investigated NH_3 emissions from slurry-based and straw-based cattle houses and found strong variations in the course of the year and a linear correlation between indoor temperature and average emission (Amon et al., 2001). In the case of CH_4 the authors found, however, no significant linear correlation to the season or temperature. Schrade et al. (2012) investigated the dependency of NH_3 emission factors on external wind speed and temperature and found in both cases strong linear correlations in the log-transformed averaged emission values, which indicates that the underlying dependency is exponential (Schrade et al., 2012). Moreover, Saha et al. (2013) showed that the inflow in general, i.e. speed and direction of the incoming wind, strongly affects the spatial distribution of gas concentrations (Saha et al., 2013). The authors found a significant influence of wind, temperature and humidity on the log-transformed emission values of NH_3 and CH_4 in the temperature range between about 10 °C and 20 °C. Strong diurnal and seasonal variations were observed. In another study, Saha et al. considered again log-transformed emission values of NH_3 and CH_4 and showed that the prediction of the emissions can be improved if wind direction, time of the day and day of the year are included as cyclic variables in the modelling process in addition to temperature, humidity and wind speed (Saha et al., 2014a).

The previous studies mentioned above focused on linear relationships (in most cases Pearson correlation) between emission factors and climate conditions. In some cases, nonlinearity was considered indirectly via cyclic variables or log-transformed values, but non-linear modelling was not discussed (Saha et al., 2014a, 2013; Schrade et al., 2012). A low Pearson correlation, however, does not necessarily imply that there is no relation or interaction. In particular, in the case of non-monotonic functional relations (e.g., cycles or parabola) the Pearson correlation can be very low. In such cases, the linear approximation comes to its limits when a large range of the independent variable (temperature in our case) is considered.

The objective of this study is to investigate in detail the non-linear shape and monotonicity of the functional dependency between emissions (NH_3 and CH_4) and temperature for a wide range of outdoor temperatures in order to better understand and predict NH_3 and CH_4 emissions from a naturally ventilated dairy barn. In this context, we take up the study Saha et al. performed in 2014 and investigate a subset of the same data (Saha et al., 2014a). Since the authors found a complementary influence of temperature on the two gases, we further investigate the functional shape of the dependency of the emission values on temperature. First, we conduct the proposed multilinear regression analysis of different factors affecting NH_3 and CH_4 emissions in naturally ventilated dairy barns for the selected subset of data. Next, the functional shape of the temperature dependency is investigated with scatter plots and non-linear models are fitted accordingly. In this context, we investigate to what extent the accuracy of prediction can be improved by considering a non-linear instead of a linear temperature dependency, taking into consideration also a non-monotonic dependency. We discuss processes which can explain the observed non-linear functional relationships and argue how our results fit together with results from purely linear investigations.

2. Material and methods

2.1. Experimental barn

We used a subset of the data presented in a preceding study (Saha et al., 2014a). The data set is based on field experiments carried out at a commercial naturally ventilated dairy building, located in Mecklenburg-Vorpommern, northeast Germany (217 km north-west Berlin, 54°1′0″ N, 12°13′60″ E, and altitude 43 m above sea level). The dairy building is 96.15 m long and 34.20 m wide (Fig. 1a). The height of the sheet metal roof varies from 4.2 m at the sides to 10.7 m at the gable peak. The internal room volume of the barn is 25,499 m^3 (70 m^3 per animal), and was designed to accommodate 364 dairy cows in loose housing with free stalls. The building has an open ridge slot (0.5 m), space boards (11.5 cm width and 2.2 cm thickness of wood board having solid core and spaced by 2.5 cm) in the gable wall of the western side of the building and sheet metal wall of the eastern side. There is one gate (metal urethane core with thermal break; 4 m × 4.4 m) and 4 doors with adjustable curtains (where two doors are 3.2 m × 3 m, and two doors are 3.2 m × 4 m) in each gable wall. The long sidewalls are protected by nets and air is introduced via adjustable curtains.

2.2. Experiments

The experiments were conducted in four seasons (winter, spring, summer, and autumn) of the years 2010, 2011, and 2012. The experimental periods with date and seasons are shown in Table 1. They covered three winter and spring seasons and two summer and autumn seasons. During this study, the cows were milked thrice per day: at 6 a.m., 2 p.m. and 10 p.m. Each time it took approximately 4.5 h to complete a whole cycle. Average milk yield was 35 kg $day^{-1}cow^{-1}$.

Feed was given twice a day at 7 a.m. to all cows and 12 a.m. only to lactating cows of groups 2 & 4. Similar feeding strategies were followed throughout all experimental periods with an average feed consumption of 53.85 kg cow^{-1} day^{-1} (4.18 kg cow^{-1} day^{-1}crude protein) for the groups 1, 2, and 4, and 46.3 kg cow^{-1} day^{-1} (2.8 kg cow^{-1} day^{-1}crude protein) for group 3. A mixture of corn silage, grass silage, alfalfa and wheat straw was given. Feed mixing and spreading took approximately 1.5 h.

2.3. Emission measurements

Concentrations of different gases, including NH_3 and CH_4, were measured at about 2.7 m height. As in previous studies, measurements were carried out at eight points uniformly distributed inside and at four points outside the barn (Fig. 1b) for the specific periods mentioned in Table 1 (cf. Saha et al., 2014a, 2013). The sampling points outside the barn are 11 m (for the Southern point) and 3 m (for the other three points) away from the barn.

Gas concentrations were measured in a continuous sequence where each sampling point was assessed at intervals of approximately 12min (i.e. measurement duration each time about 1min per sampling point). The measurements were conducted using an infrared photo-acoustic analyser (INNOVA 1312, Innova AirTech Instruments, Ballerup, Denmark) at each of the twelve sampling points (SP) with detection thresholds of 0.4 ppm (CH_4) and 0.2 ppm (NH_3). Air from the sampling locations was drawn through twelve channels of a multiplexer (valve manifold) to the analyser using 3 mm (inner diameter) polytetrafluoroethylene (PTFE) tubes. The tubes had a length of 5 m to 50 m and a sufficiently long pumping interval ensured that air being analysed at any time originated from the sampling locations. The analyser has a repeatability of 1% and a range drift of 2.5% of the measured values (Saha et al., 2014a).

Simultaneously, temperature and relative air humidity were measured every minute using sensors (Comark Diligence EV N2003, Comark Limited, Hertfordshire, UK; temperature accuracy of ±0.5 °C for −25 °C to +50 °C, and RH accuracy of ±3% for −20 °C to +60 °C) positioned at four locations inside the building and at two locations outside the building (cf. THS in Fig. 1b). The high spatial and temporal resolution of the conducted long-term measurements resulted in more than $5 \cdot 10^6$ data points which was challenging for data management and storage and required a sound pre-processing of the data.

The emission E per livestock unit (LU, 1 LU = 500 kg animal mass) of the particular gases was calculated according to the CIGR definition (CIGR, 2002). It results from the equation:

$$E = Q^*(C_i - C_o^*500/(N^*m)). \tag{1}$$

Here, N is the number of cows in the barn; m the average mass of a cow accommodated in the building; C_i and C_o are the gas concentrations inside and outside the barn; $Q = A^*Q_{mean}$ is the air exchange rate estimated with the CO_2 balance method and adjusted for the animal activity A on an hourly basis (CIGR, 2002). The gas concentration C_i inside the barn is

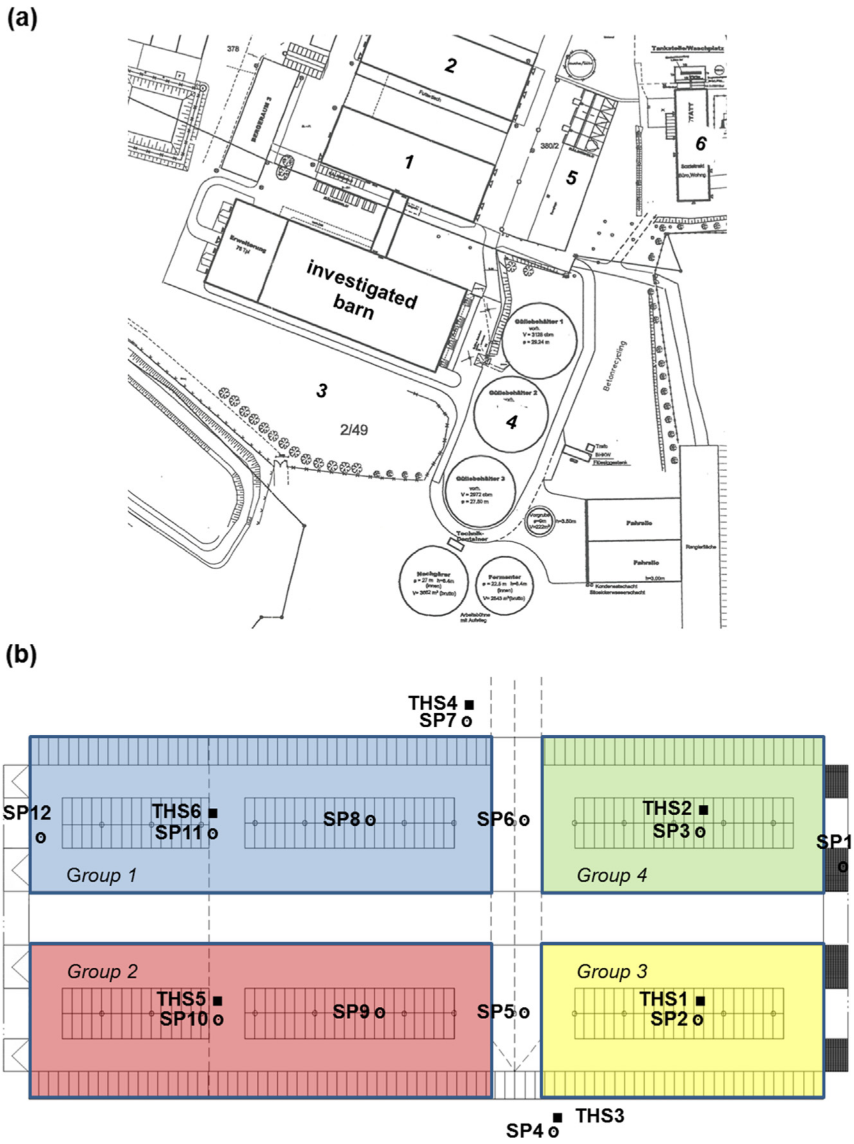

Fig. 1 – (a) Farmstead layout: (1) milking parlour, (2) dairy barn for young cattle, (3) open field, (4) manure tanks, (5) young stock housing, (6) workshop. (b) Plan view of the investigated barn and sensor positions. SP indicates a gas sampling point, and THS indicates a temperature-humidity sensor. Coloured areas indicate occupied zones with the four groups of animals.

Table 1 – Experimental periods and dairy cow conditions of the naturally ventilated dairy barn.

Experiment	Date		Season	Information about the cows		
	Start	End		Number of cows	Average mass [kg cow^{-1}]	Average milk yield [kg day^{-1} cow^{-1}]
1W	03/02/2010	28/02/2010	*winter*	353	680	36.1
2W	01/12/2010	31/12/2010	*winter*	347	678	32.1
3W	01/01/2011	25/01/2011	*winter*	347	678	32.1
1SP	01/03/2010	25/03/2010	*spring*	353	680	36.1
2SP	25/05/2011	31/05/2011	*spring*	359	665	35.0
3SP	24/05/2012	31/05/2012	*spring*	375	673	35.0
1S	16/06/2010	30/08/2010	*summer*	338	691	35.6
2S	01/06/2011	11/06/2011	*summer*	359	665	35.0
1A	01/09/2010	28/09/2010	*autumn*	338	691	35.6
2A	11/10/2011	15/11/2011	*autumn*	365	691	34.0

obtained by averaging the concentration values at all eight measurement points in the barn. Similarly, C_o is obtained by averaging over the four measurement points outside the barn. In addition to this spatial averaging, the concentration values were temporally averaged to obtain hourly values. According to CIGR, Q_{mean} could be estimated as the ratio between average CO_2 release rate of the cows and difference of indoor and outdoor CO_2 concentration (CO_2 balance method) (CIGR, 2002). Since direct measurements of the CO_2 release rates of more than 300 cows under conditions of practice are not feasible, we relied on an empirical equation given in literature (CIGR, 2002). The average release rate per cow for the measured indoor temperature and the average body mass and milk yield stated in Table 2 was estimated based on this equation (CIGR, 2002; Saha et al., 2014a).

Moreover, the relative animal activity *A* was taken from the literature where it is approximated by a sinusoidal equation (Saha et al., 2014a).

As an additional impact factor, ambient wind conditions were measured by a weather station (DALOS 515c-M, F&C Forschungstechnik & Computersysteme GmbH, Gülzow, Germany) located near the naturally ventilated dairy building (150 m east of the building). The wind measurement sensor of this station is located at a height of 2.5 m.

Further details of the experiments and emission calculation can be found in the preceding publication (Saha et al., 2014a).

2.4. Statistical analysis and modelling

We studied the influence of temperature on NH_3 and CH_4 emissions with different regression models. Model parameters were derived from two years of measurement data, whilst data from a third year were used for model validation (i.e., to determine the remaining model error). In the framework of this study, emission rates for the whole barn are considered which are calculated from the spatial averages of the concentration measurements at eight points inside the barn as described above.

2.4.1. Multilinear regression

Following the study of Saha et al. (2014a,b,c), we analysed and modelled the influence of outdoor temperature (*T*) on the NH_3 (E_a) and CH_4 emissions (E_m) considering relative air humidity (*F*), wind speed (*W*) and wind direction (θ) close to the barn (Saha et al., 2014a). Our modelling focused on environmental impact factors as independent variables. Management aspects like the times and intervals of milking, feeding and cleaning were generally kept constant (cf. Section 2.2 on experiment description) to avoid unwanted influences on NH_3 and CH_4 emissions. Thus, the impact of management factors can be neglected on larger time scales (e.g., seasons). Their influence on the daily cycle of the emissions is discussed qualitatively in this paper, but not directly included in the modelling process.

We performed a multi-linear regression on the logarithm of the emission rates where the daily and annual cycle was incorporated in the regression. The variables “day of the year” (*D*) and “hour of the day” (*H*) were considered as cyclic variables with periods of 365.25 and 24. Thus, they are included as arguments of trigonometric functions (sine and cosine). The analysis was performed with the R 3.1.0 software. The significance of impact factors is considered. Based on the contemporary literature we chose the following regression model:

$$\begin{aligned}\log E_{a/m} &= \mu + a\cdot\sin(H) + b\cdot\cos(H) + c\cdot\sin(D) + d\cdot\cos(D) + e\cdot T\\ &\quad + f\cdot F + g\cdot W + h\cdot\sin\theta + i\cdot\cos\theta + \varepsilon\end{aligned} \tag{2}$$

where E is the emission rate, μ is the intercept, *a* to *i* are the regression coefficients and ε is the remaining model error (Jammalamadaka & Lund, 2006; Saha et al., 2014a).

2.4.2. Additional analysis of the temperature dependency

We studied scatter plots of NH_3 and CH_4 emissions dependent on the outdoor temperature (*T*) for single hours of the day in order to investigate in detail the impact of outdoor temperature as crucial impact factor (cf. Fig. 2). Based on these plots we derived empirical models for the functional relation. For NH_3 we assumed, similar to the first analysis, an exponential dependency which we modelled with the following relation:

Table 2 – Regression effects of different variables with estimate and standard error of estimates for the mixed model of ammonia (E_a) and methane (E_m) emissions using a t-test[a].

Effect	$\log E_a$			$\log E_m$		
	Estimate	Error	t-Value	Estimate	Error	t-Value
Intercept	0.5887	0.0781	7.54	2.9923	0.0272	109.85
sin(H)	−0.3025	0.0127	−23.75	−0.1539	0.0044	−34.64
cos(H)	−0.7149	0.0136	−52.41	−0.2560	0.0048	−53.81
sin(D)	0.1440	0.0191	7.55	0.0897	0.0067	13.48
cos(D)	−0.2476	0.0245	−10.10	−0.0590	0.0086	−6.90
T	0.0181	0.0021	8.64	−0.0100	0.0007	−13.60
F	−0.0075	0.0008	−9.69	−0.0046	0.0003	−17.01
W	−0.0626	0.0082	−7.65	−0.0073	0.0029	−2.57
sin(θ)	−0.0970	0.0123	−7.87	−0.0420	0.0043	−9.77
cos(θ)	0.1054	0.0121	8.70	0.0146	0.0042	3.46

[a] The variables temperature (T), relative air humidity (F), wind speed (W), wind direction (θ), day of the year (D) and hour of the day (H) are considered in the mixed model. The degree of freedom in the model is 4551 in both cases. The significance level for the t-values is 0.0001, except for wind speed in the methane regression where the significance level is 0.05. The R^2 values for the fit are 0.66 (ammonia) and 0.61 (methane).

$$E_a = \exp(j + k\cdot T) + \varepsilon \tag{3}$$

Here j and k are regression coefficients and ε is the remaining model error.

For CH_4 we observed a non-monotonic behaviour in the data and, thus, we chose a regression with a polynomial of second order:

$$E_m = l + n\cdot T + p\cdot T^2 + \varepsilon \tag{4}$$

Here *l*, *n* and *p* are regression coefficients and ε is the remaining model error.

The model errors are compared to the results obtained with a purely linear model, which is usually the first order approximation in data analysis and modelling:

$$E_{a/m} = q + r\cdot T + \varepsilon \tag{5}$$

Here *q* and *r* are regression coefficients and ε is the remaining model error.

Finally, we compare the model prediction for CH_4 based on Eq. (2) with a prediction of a model that includes the parabolic temperature dependence:

$$E_m = \mu + a\cdot\sin(H) + b\cdot\cos(H) + c\cdot\sin(D) + d\cdot\cos(D) + e_1\cdot T + e_2\cdot T^2 + f\cdot F + g\cdot W + h\cdot\sin\theta + i\cdot\cos\theta + \varepsilon \tag{6}$$

where *E* is the emission rate, μ is the intercept, *a* to *i* are the regression coefficients and ε is the remaining model error.

3. Results

A large range of outdoor temperature values between −14 °C and 35 °C was observed. The indoor temperature followed the variation of outdoor temperature and was in the range of −9 °C and 36 °C (cf. Fig. 3). Indoor and outdoor temperature were highly correlated with a Pearson correlation coefficient larger than 0.98. The incoming wind ranged from 0 m s^{-1} to 6.4 m s^{-1} with varying directions. The effect of different climate factors on NH_3 and CH_4 emissions is shown in Table 2 and Fig. 4 (cf. preceding study Saha et al., 2014a). The multilinear regression yields, for both gases, the same sign for the dependency of the emission rate from daytime, season, air humidity, wind speed and wind direction. Both, the model for NH_3 and the one for CH_4 yield mainly negative regression coefficients. Only for *sin(D)* and *cos(θ)* were positive regression coefficients found for both gases. A disparate behaviour of both gases arises for the dependency from the temperature. The model yields a positive coefficient for NH_3, but for CH_4 a negative coefficient. The regression coefficients and the related significance values are shown in Table 2. In Fig. 4 the emissions estimated based on the 2010 and 2011 data are compared to measurements in 2012 for model validation. The estimated root mean square error of the regression model is 0.57 for NH_3 and 0.24 for CH_4 (considering the log-transformed emission values). Saha et al., however, noted that in both cases the errors are significantly smaller than for a model without cyclic variables (Saha et al., 2014a).

The disparate dependency of the emission rates on temperature for NH_3 and CH_4 is reflected in the scatter plots. Enhanced emission of both gases is observed for high temperature values. For low temperature values, as particularly observed in the winter measurements (Fig. 2 blue triangles), the temperature dependency of the emission rates of both gases is significantly different. The NH_3 emissions tend to zero for low temperature values (cf. Schrade et al., 2012). The CH_4 emissions, however, have a minimum around 10 °C and increase again for further decreasing temperature values.

The analysis of the temperature dependency of NH_3 and CH_4 emissions based on scatter plots shows clearly a nonlinear dependency. The functional shape is independent of the hour of the day, however, with varying degree of severity in the course of the day (cf. fit parameters in Table 3). For NH_3, the dependency is well approximated by an exponential function, while CH_4 shows a non-monotonic dependency on the temperature which can be approximated by a parabola. The root mean square error is, compared to a linear model, on average reduced by 0.5 for CH_4 and 0.7 for NH_3. This means a reduction in the error of 16% for CH_4 and as much as 47% for NH_3. The curve of the root mean square error dependent on the hour of the day is shown in Fig. 2.

If we finally add the parabolic dependency of the CH_4 emissions on temperature to multilinear regression model as in Eq. (6), the R^2 value increases from 0.61 to 0.69. This improvement is also visible in the model prediction for the 2012 data shown in Fig. 4.

The results presented here are based on spatial averages, whilst the spatial distribution of the concentration inside the barn is not homogenous and may vary significantly over time caused by the turbulent inflow of air and the partial absence of the animals in different areas of the barn (in groups during the milking times). However, the variations in the emission values calculated based on the spatially averaged concentrations show no significant dependency on the milking times (between 6 a.m. and 8 a.m. ca. 2–3 g LU^{-1} h^{-1} NH_3 and 13–15 g LU^{-1} h^{-1} CH_4; between 2 p.m. and 6 p.m. about 2–4 g LU^{-1} h^{-1} NH_3 and 10–20 g LU^{-1} h^{-1} CH_4; between 10 p.m. and 2 a.m. about 0–1 g LU^{-1} h^{-1} NH_3 and 7–10 g LU^{-1} h^{-1} CH_4; (cf. Saha et al., 2014a). This indicates that considering the impact of removing emission sources (i.e., taking cows out of the barn for milking) the effect on the overall emissions of the barn is averaged out at the considered time scales.

4. Discussion

4.1. *Uncertainty of emission measurements*

The accurate determination of the air exchange rate of a naturally ventilated dairy barn represents an unsolved problem, because the interaction between the various impact factors with their spatial and temporal fluctuations are insufficiently monitored by measurements. Currently there is no measurement method that can be marked as a solid reference (Ogink, Mosquera Losada, Calvet, & Zhang, 2013). Representative air volume flow measurements are sophisticated since an area-covering, simultaneous metrological assessment of the flow is impracticable due to the number and size of the openings. Since gas transport through the barn is mediated by the air flow, the ratio between gas concentrations at the

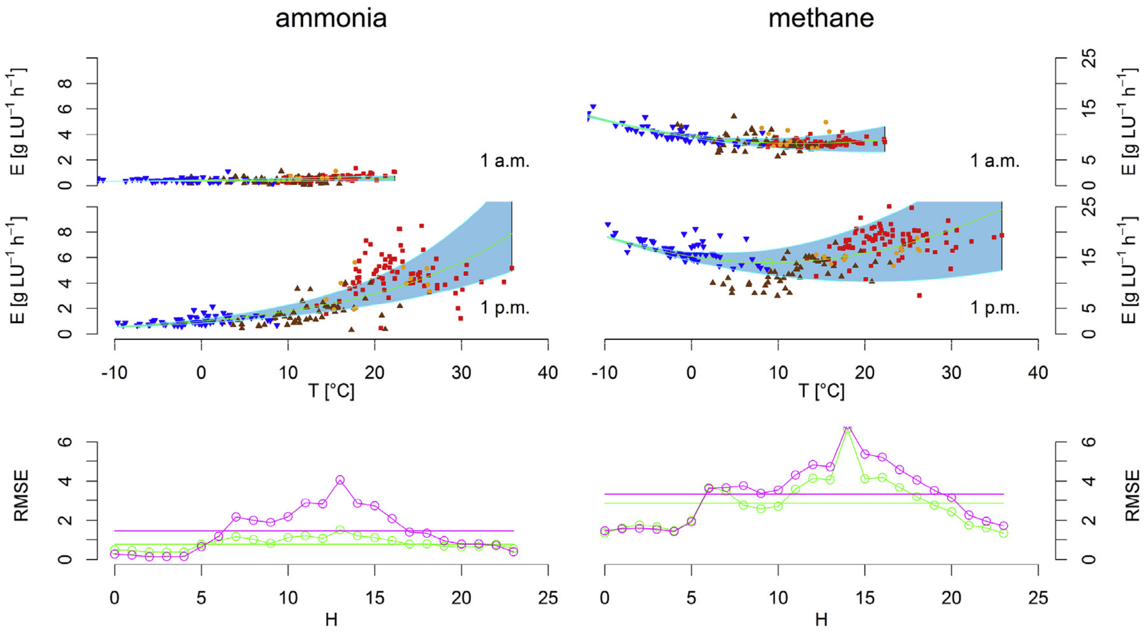

Fig. 2 – Scatter plots of gas emission rates E dependent on the temperature T are shown in the upper two rows for ammonia (left) and methane (right), exemplarily for 1 a.m. (i.e. H = 1) and 1 p.m. (i.e. H = 13). The colours indicate the different seasons of the measurements (winter blue, spring orange, summer red, autumn brown). The lower row shows the root mean square error (RMSE) for a linear (magenta) and the nonlinear model (green) in the course of the day.

inlets and outlets permits conclusions about the air exchange to be drawn. The advantage of estimating air exchange via mass balances, such as the CO_2 balance method used in this study, compared to tracer gas techniques is the options for continuous long-term measurements, since the reference gas is naturally injected and not environmentally harmful (Samer et al., 2011). A further advantage is the large number of tracer gas emitting sources (i.e., the dairy cows). The uncertainty in the position of these sources and in the individual emission rates (i.e., animal CO_2 production and activity data) affects the estimation of air exchange and emission rates.

Overall uncertainty of the air exchange and emission values is influenced by a range of impact factors (e.g., weather conditions, animal physiology and performance, barn

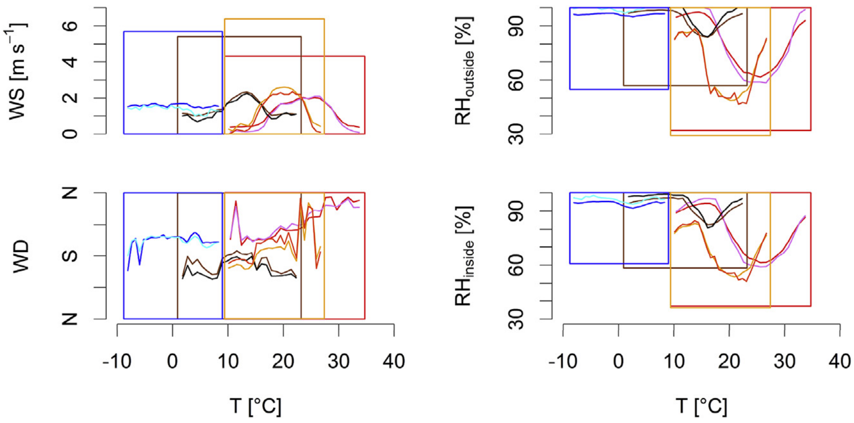

Fig. 3 – Range and average diurnal cycle of climatic variables measured in parallel with temperature T and gas concentrations. The colours indicate the different seasons of the measurements (winter blue, spring orange, summer red, autumn brown). The boxes show the maximal and minimal value of the temperature and the respective climatic variable observed for a season. The daily rhythm of the mean value in that season is shown in the same colour inside the box (hourly values starting at midnight). In addition, the daily rhythm of the median in each season is shown in dark orange (spring), pink (summer), black (autumn) and cyan (winter) to indicate the skewness of the distribution. In the case of wind direction, the estimation of mean and median incorporates modulo 360 operations to account for the cyclic character of the variable.

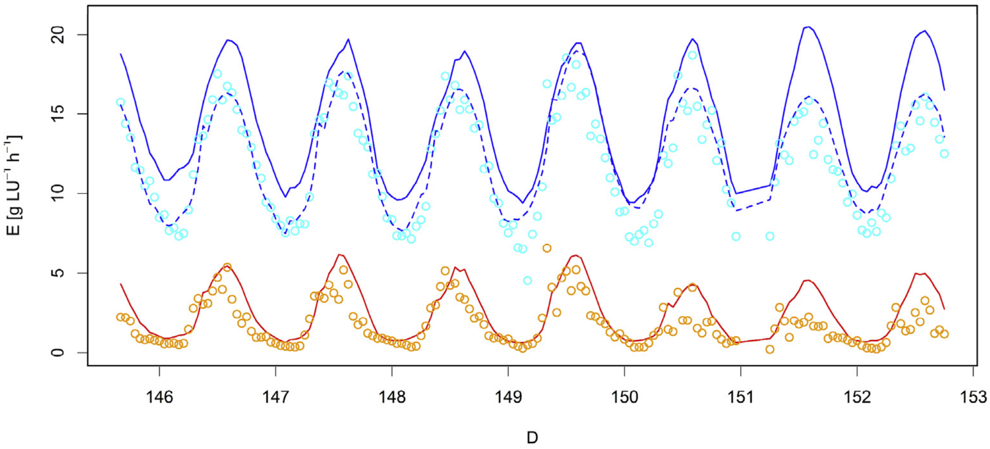

Fig. 4 – Gas emission rates of ammonia (lower curve) and methane (upper curves). Dots represent measurements from 2012 (D is the day of the year); solid lines represent model estimates based on the multilinear regression with the log-transformed emission values of 2010 and 2011 data. The dashed line shows the result of the regression for methane if we consider the not log-transformed emission values and include an additional T^2 term in the regression model as in Eq. (6).

management). Compared with a calibrated fan in closed barns, the estimation of the air exchange rate with the CO_2 balance method varies from −3% up to 17% (Ogink et al., 2013). This uncertainty can be attributed to the CO_2 production and release.

In addition, there is uncertainty attributed to the gas transport, measurement setup and barn geometry. Air exchange estimation from gas concentrations relies on a homogeneous dispersion of the gases and requires a uniform background concentration and continuous mixing of the whole barn air volume – preconditions which are typically not fully achieved in practice (Hempel et al., 2015). The actual air flow patterns and the resulting air exchange rates depend on the inflow conditions (wind speed and direction), the building geometry and on the size and position of the openings which change, for example, with curtain position (Saha et al., 2014b). The temperature difference between inside and outside measurements was, in our study, not essentially affected by the curtain position (see the strong linear correlation between inside and outside temperature persists even during the

Table 3 – Parameter estimates for model eqs. (3)–(5) for the different hours of the day. For q and r the first value refers to ammonia and the second refers to methane. All fitted parameters are rounded to two digits.

Time	Eq. (3)		Eq. (4)			Eq. (5)	
	j	k	l	n	p	q	r
12 a.m.	−0.67	0.02	9.79	−0.22	0.01	0.54/10.45	0.01/−0.13
1 a.m.	−0.91	0.01	9.27	−0.24	0.01	0.42/10.07	0.01/−0.14
2 a.m.	−1.04	0.01	9.03	−0.26	0.01	0.37/9.87	0.01/−0.15
3 a.m.	−1.23	0.01	8.81	−0.23	0.01	0.31/9.44	0.01/−0.14
4 a.m.	−1.28	0.02	8.60	−0.22	0.01	0.30/9.24	0.01/−0.14
5 a.m.	−1.21	0.02	8.63	−0.20	0.01	0.32/9.19	0.01/−0.12
6 a.m.	−0.51	0.04	9.28	−0.17	0.01	0.71/9.91	0.04/−0.07
7 a.m.	−0.13	0.06	10.91	−0.13	0.01	1.07/11.54	0.08/−0.02
8 a.m.	0.12	0.05	12.52	−0.22	0.01	1.38/13.69	0.12/0.00
9 a.m.	−0.03	0.05	13.27	−0.25	0.01	1.09/14.23	0.08/−0.02
10 a.m.	−0.18	0.04	14.13	−0.27	0.01	0.95/14.80	0.07/−0.04
11 a.m.	−0.14	0.05	15.22	−0.13	0.01	1.10/15.58	0.10/0.03
12 p.m.	−0.02	0.06	16.00	−0.11	0.01	1.20/16.27	0.12/0.05
1 p.m.	0.13	0.05	16.39	−0.10	0.01	1.35/16.61	0.13/0.05
2 p.m.	0.49	0.05	18.14	0.03	0.00	2.19/18.22	0.16/0.08
3 p.m.	0.29	0.05	16.52	−0.23	0.01	1.58/17.28	0.13/0.03
4 p.m.	0.17	0.04	16.50	−0.22	0.01	1.38/17.13	0.09/−0.02
5 p.m.	0.03	0.04	15.76	−0.21	0.01	1.14/16.32	0.07/−0.04
6 p.m.	−0.17	0.04	15.11	−0.25	0.01	0.93/15.71	0.05/−0.08
7 p.m.	−0.35	0.04	13.87	−0.23	0.01	0.79/14.49	0.05/−0.07
8 p.m.	−0.49	0.04	12.88	−0.25	0.01	0.67/13.65	0.04/−0.09
9 p.m.	−0.56	0.04	11.64	−0.22	0.01	0.61/12.40	0.04/−0.08
10 p.m.	−0.37	0.03	10.73	−0.20	0.01	0.75/11.44	0.03/−0.08
11 p.m.	−0.54	0.03	10.23	−0.24	0.01	0.61/10.99	0.02/−0.11

winter measurements). As a result, the uncertainty in the curtain position will contribute to the overall uncertainty of the emission values only by affecting the air flow. This means it can be attributed to the uncertainty in the inflow conditions.

Saha et al. (2014a,b,c) showed, for the same barn that was investigated in this manuscript, that for various inflow conditions the choice of the sensor positions can significantly affect the estimation of the air exchange rate resulting in relative differences of −49% up to 112% depending on the number and position of sampling points (Saha et al., 2014c). The uncertainty introduced by the gas measurement technology itself is considered to be small (Saha et al., 2014a). NH_3 has distinct absorption peaks and potential interferences between CH_4 and H_2O are compensated for by the instrument.

When estimating NH_3 or CH_4 emissions with the CO_2 balance method, the respective concentration difference of NH_3 or CH_4 is in the numerator while the CO_2 difference is in the denominator. Hence, measuring all three gases always simultaneously with the same measurement device and under the same boundary conditions reduces the flow- and device-related part of the uncertainty in the estimated emission value. As a result, the uncertainty in the estimated emission rate is mainly determined by the uncertainty in the CO_2 release (i.e., up to about 20% of the actual emission value).

Finally, the estimation of the confidence intervals for the model fits in Fig. 2 indicates that the uncertainty strongly depends on the actual temperature and increases with an increase in temperature. Up to 18 °C (i.e. almost 10 °C above the identified optimum) intervals are disjunct, while for temperatures above 18 °C, the confidence intervals for the fitting of the methane concentration are slightly overlapping.

In summary, we used the CO_2 balance method for estimating emission rates from a naturally ventilated barn. This method is considered a standard methodology and attributed uncertainties are between −3% and 17% (Ogink et al., 2013). The data on NH_3, CO_2 and CH_4 emissions gathered by the CO_2 balance method were then further analysed for their dependency on temperature and other climate parameters.

4.2. *Non-linear temperature dependency of ammonia*

NH_3 emissions are mainly caused by enzymatic, biochemical decomposition processes of excreta at the floor of the barn. It is well known that these processes depend on the air humidity, the local air flow at the floor surface (subject to the wind speed) and the temperature. The reaction kinetics, which determine the temperature dependency, follows Arrhenius law (Arrhenius, 1889). This implies an exponential relation, also observed in studies of NH_3 emissions in other barns, which is in accordance with our measurements (Schrade et al., 2012). Thus, for very low temperature values NH_3 emissions are predicted to tend towards zero, whilst never reaching exactly zero in reality. Schrade et al. (2012), for example, showed that winter emission are about 50%–75% lower than summer emissions, but still about 10 g LU^{-1} d^{-1} (cf. Figure 5 in Schrade et al., 2012). A similar decrease was found in our data. However, we observe a significantly lower dependency during the night, i.e. the approximation with a linear function is reasonable during that time. This is exemplified for two times (1 a.m. and 1 p.m.) in Fig. 2.

A possible explanation for the weak dependency in the night is a superposition of the temperature effect with other environmental impact factors such as wind and air humidity. Based on preceding studies, we expect higher wind speed to increase the NH_3 emissions (Bjerg et al., 2013). The reason for this assumption is the increased surface wind speed over the floor. During the night, wind speed was usually lower, as can be expected due to the night inversion (stable stratification of the atmosphere) which is related to the radiative loss of heat from the earth's surface during the night (McNaught & Wilkinson, 1997). Moreover, during almost calm periods thermo-induced convection processes may result in significantly different air flow patterns which affect the air exchange and emission rates. However, we observed only small temperature gradients between inside and outside. Largest differences were about 7 °C during winter nights. The dependency of incident wind speed on the hour of day, on the other hand, is much stronger in spring and summer than in winter (cf. Fig. 3). In addition, the openings of the naturally ventilated barn are often closed during the night, as shelter from extreme weather conditions (e.g., very low temperatures), particularly in winter. In this sense, the management actions enhance the general tendency. A quantitative evaluation of the management impact is not possible in the framework of this study. Nevertheless, a positive superposition of the effects of temperature and wind on the emission rate can be expected. In the daytime, temperature and wind speed are higher than at night and both yield increasing NH_3 emissions compared to the night. An increase of NH_3 emissions only caused by increasing external wind speed is, however, not proven by the multilinear regression in this case study.

Another crucial environmental impact factor is the air humidity. Huijsman, Holand, and Hendriks (2001) showed that higher relative air humidity leads to reduced volatilisation rates (Huijsman et al., 2001). In general, higher air humidity values are expected to yield reduced NH_3 concentrations, since NH_3 is highly water-soluble and will be absorbed by the water vapour in the air. This is, however, only true within a certain range and depends on the management strategies, since a drier floor also yields a decrease in NH_3 emissions. For the range of humidity values observed in this study, the decrease of NH_3 emissions with increasing air humidity becomes apparent in the negative coefficient for the relative air humidity in the multilinear regression model. Furthermore, we usually measure not only lower temperatures but also higher relative air humidity during the night. This means we can expect lower NH_3 emission during the night time than during the daytime.

4.3. *Non-linear temperature dependency of methane*

CH_4 emissions are mainly caused by the metabolism of the animals. According to Madsen et al. (2010) CH_4 production by high yielding cows (i.e., 600 kg body mass and 30 kg milk yield per day) is between 351 and 585 l day^{-1} (Madsen, Bjerg, Hvelplund, Weisbjerg, & Lund, 2010). This is about 12–21 g CH_4 LU^{-1} h^{-1} which corresponds well with the emission rates that we obtained in our long-term study. Moreover, various authors noted that about 80% of the CH_4 emissions associated with cattle are attributed to enteric/ruminal fermentation (Kirchgessner, Windisch, Müller, & Kreuzer, 1991; Ngwabie et al., 2014). Hence, they do not directly depend on climatic factors like temperature. However, there is an indirect dependency via the animal activity, metabolic rate and the ratio of performance versus conservation related metabolism (e.g., heat stress). Ngwabi et al. reported, for the temperature range 5 °C–15 °C, a negative correlation between daily animal activity and indoor temperature as well as between CH_4 emission and indoor temperature (Ngwabie, Jeppsson, Gustafsson, & Nimmermark, 2011; Ngwabie et al., 2014). Chagunda et al. showed that CH_4 emissions of ruminants are on average only half as high during resting phases as during phases of ruminating and feeding (Chagunda et al., 2013). Moreover, they found, for CH_4 measurements under simulated grazing conditions, a significant dependency on wind, humidity and pressure. A significant dependency on temperature was not proven in their study. This follows, however, from the investigated temperature range (14.4 °C–27.8 °C with 18.9 °C on average). Within a similar temperature range the temperature dependency in our study is also small and almost vanishing during the night (cf. Fig. 2). If we consider a larger temperature range, however, the non-linear dependency becomes obvious. The observed minimum of CH_4 emissions is around 10 °C which corresponds to the centre of the thermo-neutral zone of cows. Outside this zone, the milk yield is known to decrease while the conservative metabolism becomes more important. Our study shows that this comes with increasing emissions. At a first glance, the increase of emission for high temperature seems to contradict the results of the regression model which indicates a negative correlation between temperature and CH_4 emissions. Such a relationship was also found in an earlier study (Ngwabie et al., 2011). However, these regressions are only linear approximations. If one fits the scatter plot with a line in most cases a negative slope can be found for the temperature interval −10 °C to 40 °C which we consider in our study (for the case $H = 1$ in Fig. 2 this is particularly noticeable). Once nonlinearity is taken into account, an increase of emissions for higher temperatures is predicted.

The observed increase in CH_4 emissions when the temperature moves away from the optimum of 10 °C is, however, faster than initially expected from the literature. On the other hand, it has to be noted that most studies related to the thermo-neutral zone were performed some decades ago (Hahn, 1999; Kadzere, Murphy, Silanikove, & Maltz, 2002). In the meantime, the average milk yield of the cows has significantly increased. Gerber, Vellinga, Opio, and Steinfeld (2011) showed that this comes along with higher carbon dioxide and CH_4 emission per cow (Gerber et al., 2011). We suppose that in this context the sensitivity of the metabolism to temperature has also increased.

4.4. *Linear vs. non-linear model*

The lower panels in Fig. 2 illustrate that the consideration of a non-linear dependency between temperature and gas emissions yields a significant decrease in the model prediction error which is represented by the estimated root mean square error (RMSE).

As noted in the results section, for NH_3 the root mean square error in the considered temperature interval with an exponential model approach is on average reduced by 47% compared to a linear model. The largest decrease in the model prediction error is observed around noon. This corresponds well with the observation that emissions are much higher and non-linearity is more pronounced during the day. As discussed above, this is likely to be related to the superposition of the temperature effect with other environmental impact factors. Since the functional non-linear dependency is monotonic, a linear correlation analysis, however, still makes sense for NH_3 for a wide range of values of the independent variable temperature.

In the case of CH_4, the root mean square error in the considered temperature interval and with the parabolic model approach is on average reduced by 16% compared to a linear model. Largest differences in the prediction error of the linear and the non-linear model occur from late morning till noon time (8 a.m.–1 p.m.) and in the afternoon (3 p.m.–7 p.m.). These intervals correspond to periods with increased animal activity since they follow feeding times and fall together with milking cycles. This supports the assumption that non-linearity in the temperature dependency of CH_4 emissions is mainly related to the metabolism of the cows. Moreover, it highlights the necessity to consider non-linearity to improve the prediction of CH_4 emissions for different ambient temperatures particularly during phases of large animal activity. Since the non-linear dependency is not monotonic and has a minimum around 10 °C, a linear correlation analysis makes sense only for temperatures significantly higher or lower 10 °C. For a temperature interval which is symmetric around 10 °C no linear correlation must be expected.

5. Conclusions

The analysis of the temperature dependency of NH_3 and CH_4 emissions shows clearly a non-linear dependency. For NH_3 the dependency is monotonic. It is well approximated by an exponential function which was indirectly considered already in previous studies (e.g. (Schrade et al., 2012)). The monotonic shape of the functional dependency renders correlation analysis useful to assess the relation. CH_4 on the other hand shows a non-monotonic dependency on the temperature which can be approximated by a parabola. In this case, correlation analysis can reveal the relation only for specific temperature ranges where the dependency can be approximated by a linear function.

For both gases the non-linear dependency is particularly prominent during the daytime while during the night emissions are usually reduced and the functional dependency is masked by other impact factors. The amplification of NH_3 emission during the day can be related to higher wind speed and lower relative air humidity values compared to the night. The daily cycle of the CH_4 emissions might be related to animal activity, but more detailed studies are required to quantify this effect.

It was already known that lower indoor temperature reduces NH_3 emission, and it was assumed that temperature dependence of NH_3 emission follows an exponential function.

Our detailed analysis confirmed the validity of this exponential function.

In contrast to the findings for NH_3, we were able to show that, for CH_4 emissions from ruminal fermentation in dairy cows, the assumption of an exponential function can be made only above 10 °C. Below this value, emissions were not further reduced, but showed a distinct increase that would not be depicted by simple exponential functions. This increase is not due to a direct influence on methane formation – as is observed in slurry stores – but results from a change in animal behaviour, activity and metabolism induced by low temperatures.

The non-linear models developed in this paper reduce the model prediction error significantly. In particular, the improvement in the prediction of CH_4 emission by the novel non-linear model may support more accurate economic and ecological assessments of smart barn concepts in the future. To what extent cooling or heating is sensible as a tool for emission reduction, however, has to be investigated in detail in an additional study. Reliability of emission data can be increased by more sophisticated modelling and data analysis. In addition, it is essential to improve methodologies and technologies to assess emission rates from naturally ventilated livestock buildings.

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