



Implications of seasonal and daily variation on methane and ammonia emissions from naturally ventilated dairy cattle barns in a Mediterranean climate: A two-year study

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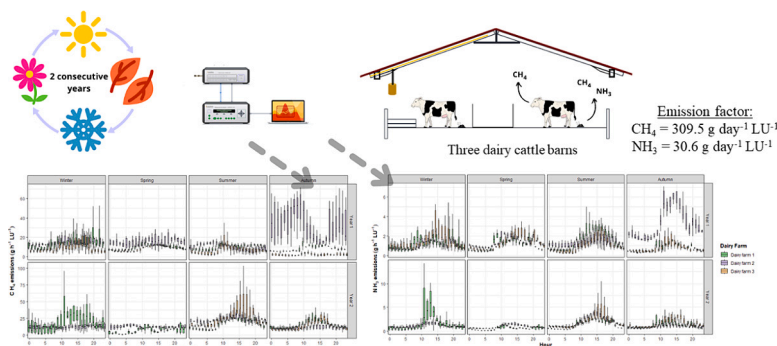
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HIGHLIGHTS

- Daily and seasonal CH₄ and NH₃ emissions were assessed in two consecutive years.
- Both emissions increased in daytime and varied among seasons.
- High intra-hour variability was observed during daytime for both gases.
- NH₃ emissions presented an emission peak in the middle day in all seasons.
- The CH₄ and NH₃ emission factors were 309.5 and 30.6 g⁻¹ day⁻¹ LU⁻¹.

GRAPHICAL ABSTRACT



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ABSTRACT

Seasonal and daily variations of gaseous emissions from naturally ventilated dairy cattle barns are important figures for the establishment of effective and specific mitigation plans. The present study aimed to measure methane (CH₄) and ammonia (NH₃) emissions in three naturally ventilated dairy cattle barns covering the four seasons for two consecutive years. In each barn, air samples from five indoor locations were drawn by a multipoint sampler to a photoacoustic infrared multigas monitor, along with temperature and relative humidity. Milk production data were also recorded. Results showed seasonal differences for CH₄ and NH₃ emissions in the

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Natural ventilation
Seasonality

three barns with no clear trends within years. Globally, diel CH₄ emissions increased in the daytime with high intra-hour variability. The average hourly CH₄ emissions (g h⁻¹ livestock unit⁻¹ (LU)) varied from 8.1 to 11.2 and 6.2 to 20.3 in the dairy barn 1, from 10.1 to 31.4 and 10.9 to 22.8 in the dairy barn 2, and from 1.5 to 8.2 and 13.1 to 22.1 in the dairy barn 3, respectively, in years 1 and 2. Diel NH₃ emissions highly varied within hours and increased in the daytime. The average hourly NH₃ emissions (g h⁻¹ LU⁻¹) varied from 0.78 to 1.56 and 0.50 to 1.38 in the dairy barn 1, from 1.04 to 3.40 and 0.93 to 1.98 in the dairy barn 2, and from 0.66 to 1.32 and 1.67 to 1.73 in the dairy barn 3, respectively, in years 1 and 2. Moreover, the emission factors of CH₄ and NH₃ were 309.5 and 30.6 (g day⁻¹ LU⁻¹), respectively, for naturally ventilated dairy cattle barns. Overall, this study provided a detailed characterization of seasonal and daily gaseous emissions variations highlighting the need for future longitudinal emission studies and identifying an opportunity to better adequate the existing mitigation strategies according to season and daytime.

1. Introduction

The mutual effect between agriculture and climate change requires actions to mitigate the negative impacts of the first, and adaption measures to improve the sector's resilience to climate risks to suppress the demand for a projected worldwide population growth of 9.7 billion by 2050 (FAO and GDP, 2018; Munidasa et al., 2021). Milk and dairy products are essentials in a balanced diet playing an important role in food security, being the reduction of environmental footprint, particularly of methane (CH₄) and ammonia (NH₃) emissions, a priority for the dairy cattle sector (McGarr-O'Brien et al., 2023).

Methane is the second largest greenhouse gas (GHG) in terms of radiative forcing, with a global warming potential (GWP) of 28 in relation to carbon dioxide (CO₂) (IPCC, 2014), and is a precursor to tropospheric ozone, a harmful pollutant for human, crop production and ecosystems (Mar et al., 2022). According to EEA (2020), enteric fermentation is responsible for 81% of the total CH₄ emissions from the agriculture sector, with dairy cows contributing nearly 40%. Enteric CH₄ is primarily formed in the rumen by methanogens during microbial fermentation of fibrous feedstuffs, being mainly released by eructation and representing 2–12% loss of feed energy for the cow (Johnson and Johnson, 1995). Its production varies with diet composition, breed, and lactation stage, among others (Benchaar and Hassanat, 2020; Hossein-Zadeh, 2022; Palangi et al., 2022).

Manure management including housing, storage, and application to croplands accounts for the great majority of NH₃ from the livestock sector (Sajeew et al., 2018). At the animals' barn floor, the urinary urea is hydrolyzed by fecal urease activity, forming ammonium ion (NH₄⁺)/NH₃. The NH₃ volatilization process is correlated with pH, air temperature, and velocity, driving the mass transfer process of NH₃ from liquid manure to the surface and the air (Sigurdarson et al., 2018; Tong et al., 2020). Additionally, nitrous oxide (N₂O) can also be formed during incomplete nitrification/denitrification processes of NH₃ into N₂ (den Toorn et al., 2021). Moreover, atmospheric NH₃ is the main source of NH₄⁺ (an aerosol constituent), the precursor of secondary particles (components of PM_{2.5}), and upon deposition, can cause severe impacts on human health and the environment (Pan et al., 2018; Zilio et al., 2020).

Gaseous emissions vary among dairy cattle barns due to architectural characteristics, feeding and manure management systems, and climate parameters, among others (D'Urso et al., 2021; Poteko et al., 2019). Measurements of gaseous emissions are not only crucial to derive country-specific emission factors (EFs) and to characterize emissions at different levels but also to allow the definition of appropriate mitigation strategies (Tedeschi et al., 2022; VanderZaag et al., 2014). Several European countries have been monitoring GHG and NH₃ emissions from naturally ventilated dairy cattle barns as Germany (Hempel et al., 2020; Saha et al., 2014; Schmithausen et al., 2018; Wu et al., 2016), Italy (Baldini et al., 2016), Poland (Mazur et al., 2021; Rzeznik et al., 2016), Denmark (Wu et al., 2012; Zhang et al., 2005), and Sweden (Ngwabie et al., 2011; Ngwabie et al., 2009), while in many others, including in Portugal, no available published data are reporting on-farm GHG emission from naturally ventilated dairy cattle barns.

In this context, the current work aimed to measure CH₄ and NH₃ emissions from three naturally ventilated dairy cows' barns, and to identify seasonal and daily gaseous emissions variations. We hypothesize that the outcomes of this work will contribute data to improve the Mediterranean and European EFs of CH₄ and NH₃ for dairy cattle barns in the future.

2. Material and methods

2.1. Measurement sites

Measurements were conducted over two years in three dairy cattle barns located at Vila do Conde, in the Northwest (NW) of Portugal. All three barns were of free stall type housing with cubicles and naturally ventilated by large openings on the side walls, open ridges on the roof, and ceiling fans ensuring the air re-circulation. The free-stall zones had solid concrete floors and a cubicle system with bedding sawdust in the lying area. In all barns, the manure handling system equipped with an automatic scrapper removed the manure from the inside buildings to the outside manure pit. The detailed characterization of the dairy barns is presented below, and the dairy effective is described in Table 1.

The first dairy cattle barn (dairy barn 1) had approximately 846 m² with 3.60 m eave height and 5.07 m ridge height, and Northeast-Southwest (NE-SW) orientation (Fig. 1). The NW side had large openings, the NE and SW sides open doors, and the Este River was located at approximately 50 m of the NW side. The ceiling fans were scheduled to work at temperatures above 24 °C. The barn floor was cleaned every 3 h in the feed alley, and every 1 h in the remaining area to an outside manure pit with southern exposure, connected to a manure lagoon on the North (Fig. 1). The animals were milked at a milking parlor and fed a total mixed ration twice per day, during early morning and late afternoon.

The second cattle barn (dairy barn 2) had approximately 1600 m² with 4.38 m eave height and 6.59 m ridge height, and NE-SW orientation (Fig. 1). The NW side presented large openings with an open door on the Southern side and a passage to other cattle barn on the SW side. The ceiling fans were scheduled to work at temperatures above 25 °C. The manure scrap system removed the manure floor every 2 h to two concrete manure pits, one on the Southern side and another on the NW side of the barn. The animals were milked with a robotic milking system with customized frequency for each cow, and fed a total mixed ration twice per day, during early morning and late afternoon, supplemented with a concentrate at the milking robot.

The third cows' barn (dairy barn 3) had approximately 960 m² with 4.38 m and 4.92 m eave height in the Southern hall and the Northern hall, respectively, and 7.13 m ridge height, and with East-West (E-W) orientation (Fig. 1). The Southern side was closed by a grid and the Northern side presented large openings, with ceiling fans schedule to work at temperatures above 22 °C. The manure scrap system removed the manure every 3 h to a cement manure pit located on the W side of the barn. The animals were milked at a milking parlor and fed a total mixed ration delivered once per day, during the late afternoon.

2.2. Measurement periods and sampling methodology

Measurements of CO₂, CH₄, and NH₃ concentrations covered all seasons of two consecutive years, 2016/2017 (year 1) and 2017/2018 (year 2). The measurement periods of each season, the number of animals in the barn, the milk yield (kg day⁻¹), and average days in milk are presented in Table 1. In each measurement period the diet was sampled and chemically analyzed (Tables S1 to S3).

Gas concentrations were measured in five indoor points at each dairy barn, by a Teflon tubes system (3 mm inner diameter) equipped with a polytetrafluoroethylene membrane (1.0 μm pore size, Whatman, Ome, Japan), to protect them from dust. Sampling points were 2.5 m above the floor and located on the opposite wall of the feed alley in dairy barn 1 and above the feed alley in dairy barns 2 and 3. The air samples were collected at intervals of 2 min per sampling point by a multipoint (model INNOVA 1409–12, Lumasense Technologies, Ballerup, Denmark) connected to a photoacoustic gas-monitor (model INNOVA 1412i-5, Lumasense Technologies). The gas analyzer was calibrated by the manufacturer before the beginning of the study, being operated in a mode for compensation of water interference and cross-interference and equipped with an optical filter for water vapor (filter type SB0527, Lumasense Technologies) and the detection limits for NH₃ (filter type UA0973, Lumasense Technologies), CO₂ (filter type UA0982, Lumasense Technologies) and CH₄ (filter type UA0969, Lumasense Technologies) were, respectively, 152.1, 2947.1 and 286.4 μg m⁻³.

For each experimental date, indoor and outdoor temperatures (°C) and relative humidity (%), RH) were assessed in 10 min intervals using sensors (CS215, Campbell Scientific, Leicestershire, UK) and recorded in a micrologger (CR3000, Campbell Scientific).

2.3. Data pre-processing

Data pre-processing methodology applied to gases concentration, temperature, and RH time series included three steps: i) data preparation; ii) missing data identification; and iii) missing data interpolation.

The gases concentrations recorded from the five sampling points were hourly averaged, and hourly missing data was interpolated using the Seasonally Split Missing Values Imputation model associated with Kalman filtering smoothing. The missing data of indoor temperature was firstly interpolated for 10 min intervals following the same methodology described above, and subsequently hourly averaged.

The gaseous concentrations and indoor temperature were used for emission calculation and were analyzed on a 24 h basis as described in Section 2.4.

2.4. Ventilation rate and gases emission calculation methodology

The ventilation rate and gaseous emission were calculated according to the guidelines established by CIGR (2002). The hourly CO₂, CH₄, and NH₃ concentrations from the five indoor points were averaged to represent the indoor concentration in each dairy cows barn, following the methodology described in several research works (Hempel et al.,

2020; Saha et al., 2014; Schmithausen et al., 2018).

The ventilation rate (Q , m³ h⁻¹) was calculated by the indirect CO₂ mass balance method as follows in Eq. (1):

$$Q = \frac{CO_{2 \text{ prod}}}{(CO_{2 \text{ inside}} - CO_{2 \text{ outside}})} \times N \quad (1)$$

where CO_{2 prod} is the estimated CO₂ production rate per animal (g h⁻¹), N is the animal number in the barn (Table 1), CO_{2 inside} and CO_{2 outside} the average CO₂ concentration of the indoor and outdoor gas (g m⁻³), respectively (CO_{2 outside} = 0.80 g m⁻³), (WMO, 2019).

The CO₂ production rate excreted is related to the heat produced (Heat_{prod}) per cow depending on several factors, from feed intake or animal activity to the housing type (CIGR, 2002). Thus, the CO₂ production rate was calculated using the Eq. (2):

$$CO_{2 \text{ prod}} = \frac{0.185 \times \text{Heat}_{\text{prod}} \times A}{1000} \quad (2)$$

where Heat_{prod} is multiplied by the relative animal activity (A) and by the 0.185 factor. The Heat_{prod} is calculated from the multiplication of the total heat production (ϕt) by the corrected factor for the temperature inside the building (CF), as follows in Eqs. (3)–(6):

$$\text{Heat}_{\text{prod}} = \phi t \times CF \quad (3)$$

$$\phi t = 5.6 \times (m)^{0.75} + 1.6 \times 10^{-5} \times (p)^3 + 22y \quad (4)$$

$$CF = 1000 \times \left(4 \times 10^{-5} (20 - T_i)^3 + 1 \right) \quad (5)$$

$$A = 1 - a \times \sin \left[(2 \times \pi / 24) \cdot (h + 6 - h_{\min}) \right] \quad (6)$$

where variable m in Eq. (4) represents the average mass of the cow (kg cow⁻¹), p the days after insemination (days), and y the milk yield (kg day⁻¹, Table 1). The variable A in Eq. (6) follows the sinusoidal dromedary model for diurnal variation (CIGR, 2002). The constant a expresses the amplitude concerning the constant 1, and h_{\min} indicates the minimum activity of the day (hours after midnight).

Following CIGR (2002) parameters for dairy cows in cubicles, our study considered $a = 0.22$, and $h_{\min} = 2.9$, for the three dairy cattle barns.

The emission rate (E_t , g h⁻¹) was calculated as followed in Eq. (7):

$$E_t = Q \times (C_i - C_o) \quad (7)$$

where Q (m³ h⁻¹) is the ventilation rate calculated in Eq. (1), and C_i and C_o (g m⁻³) are the average indoor and outdoor concentrations, respectively. Cows numbers were expressed in livestock unit (LU), considering that one dairy cow was 1.2 LU (NREAP, 2013), with the emission rate converted to LU calculated following Eq. (8):

$$E = \frac{E_t \times 1.2}{N \times m} \quad (8)$$

Table 1

Description of cow's number and milk production parameters of dairy farms in the respective measurement period.

| Year | Season | Date | | Number of cows | | | Milk yield (kg cow ⁻¹ day ⁻¹) | | | Days in milk | | |
|------|--------|------------|------------|----------------|--------|--------|--|--------|--------|--------------|--------|--------|
| | | Start | End | Barn 1 | Barn 2 | Barn 3 | Barn 1 | Barn 2 | Barn 3 | Barn 1 | Barn 2 | Barn 3 |
| 1 | Winter | 07/12/2016 | 26/01/2017 | 162 | 95 | 60 | 34.6 | 37.8 | 31.4 | 157 | 160 | 190 |
| 1 | Spring | 10/03/2017 | 18/04/2017 | 158 | 99 | 61 | 34.7 | 37.8 | 33.3 | 177 | 178 | 182 |
| 1 | Summer | 13/07/2017 | 26/08/2017 | 159 | 97 | 64 | 32.4 | 37.2 | 32.4 | 194 | 183 | 195 |
| 1 | Autumn | 25/10/2017 | 21/11/2017 | 162 | 100 | 65 | 34.6 | 39.0 | 30.8 | 157 | 162 | 183 |
| 2 | Winter | 22/12/2017 | 19/01/2018 | 165 | 101 | 71 | 35.1 | 38.8 | 32.0 | 144 | 165 | 173 |
| 2 | Spring | 14/04/2018 | 01/05/2018 | 167 | 101 | 70 | 36.4 | 38.6 | 32.5 | 158 | 168 | 186 |
| 2 | Summer | 14/08/2018 | 11/09/2018 | 160 | 101 | 71 | 31.2 | 37.7 | 31.2 | 178 | 160 | 189 |
| 2 | Autumn | 18/10/2018 | 17/11/2018 | 164 | 101 | 69 | 33.2 | 37.1 | 32.0 | 164 | 162 | 173 |

2.5. Statistical analysis

Statistical analysis was performed using the R software version 4.0.5 (The R foundation for statistical computing). The model included the fixed effects of barn, season, and year, and the random residual error. The experimental unit was the hourly average of the five sampling points. The Kruskal-Wallis test was employed to compare the seasons in each dairy barn and the years of measurement, and Dunn’s *post hoc* test was used for the respective multiple comparisons (* $p < 0.05$, ** $p < 0.01$, and *** $p < 0.001$ were the adopted levels of significance). In this analysis, inter quartile range (IQR) filtering was applied to identify and remove outliers in the dataset (Kannangara et al., 2018). This method involves identifying data points that fall below $Q1 - 1.5 \times IQR$ or above $Q3 + 1.5 \times IQR$, where $Q1$ is the first quartile and $Q3$ is the third quartile of the data distribution.

3. Results

3.1. Gas concentrations, ventilation rate and climate parameters

Average daily CH_4 concentrations varied among dairy barns between years and seasons (Fig. 2, Table S4). Indeed, daily CH_4 concentrations ($g\ m^{-3}$) ranged from 0.001 to 0.030 and from 0.002 and 0.038 in years 1 and 2, respectively, with dairy barn 3 differing from the others in year 1 ($p < 0.001$), and dairy barn 2 differing from barns 1 and 3 in year 2 ($p < 0.05$, Table S4, Fig. 2). Significant differences were observed between autumn and summer ($p < 0.001$) and winter and summer ($p < 0.001$) in dairy barn 1, between summer and winter ($p < 0.01$) and autumn and summer ($p < 0.001$) in dairy barn 2, and between autumn and spring ($p < 0.001$) and autumn and summer ($p < 0.001$) in dairy barn 3, in years 1

and 2, respectively (Tables S5 and S6).

Average daily NH_3 concentrations varied among dairy barns between years and seasons (Fig. 2). In fact, daily NH_3 concentrations ($g\ m^{-3}$) varied from 2.8×10^{-5} to 0.0020 and from 0.0002 to 0.0024 in years 1 and 2, with dairy barn 3 differing from the others ($p < 0.001$), and barn 1 differing from barn 2 in year 1 ($p < 0.05$), and dairy barn 2 differing from barns 1 and 3 in year 2 ($p < 0.001$ and $p < 0.01$, respectively, Table S4, Fig. 2). Significant differences were observed between winter and summer ($p < 0.05$) and summer and autumn ($p < 0.001$) in dairy barn 1, between winter and spring ($p < 0.001$), winter and autumn ($p < 0.05$) and spring and summer ($p < 0.01$) in dairy barn 3 in year 1 (Table S5). Moreover, between winter and summer ($p < 0.001$), winter and autumn ($p < 0.05$), and spring and summer ($p < 0.001$) in dairy barn 1, between winter and summer ($p < 0.05$), spring and summer ($p < 0.01$), and summer and autumn ($p < 0.001$) in dairy barn 2, and between summer and autumn ($p < 0.01$) in dairy barn 3, in year 2 (Table S6).

Average daily indoor temperatures were similar between dairy barns in year 1 ($p > 0.05$) and in year 2 dairy barn 1 differed from 2 ($p < 0.05$ Table S7, Fig. 2). Besides, ranged from 13 °C to 22 °C and 12 °C to 18 °C in dairy barn 1 (winter and summer, $p < 0.001$, and autumn and summer, $p < 0.01$), from 13 °C to 22 °C and 15 °C to 18 °C in dairy barn 2 (spring and summer, $p < 0.001$, and winter and spring, $p < 0.01$, respectively), and from 8 °C to 20 °C and 14 °C to 21 °C in dairy barn 3 (winter and summer, $p < 0.001$, and summer and autumn, $p < 0.001$), during year 1 and 2, respectively (Fig. 2, Tables S8 and S9). Moreover, indoor temperature differed between summer and autumn in dairy barns 1 and 2 ($p < 0.001$ and $p < 0.01$, respectively), and winter and autumn in dairy barn 3 ($p < 0.01$) during year 1 (Table S8).

Average daily indoor RH was similar between dairy barns in years 1

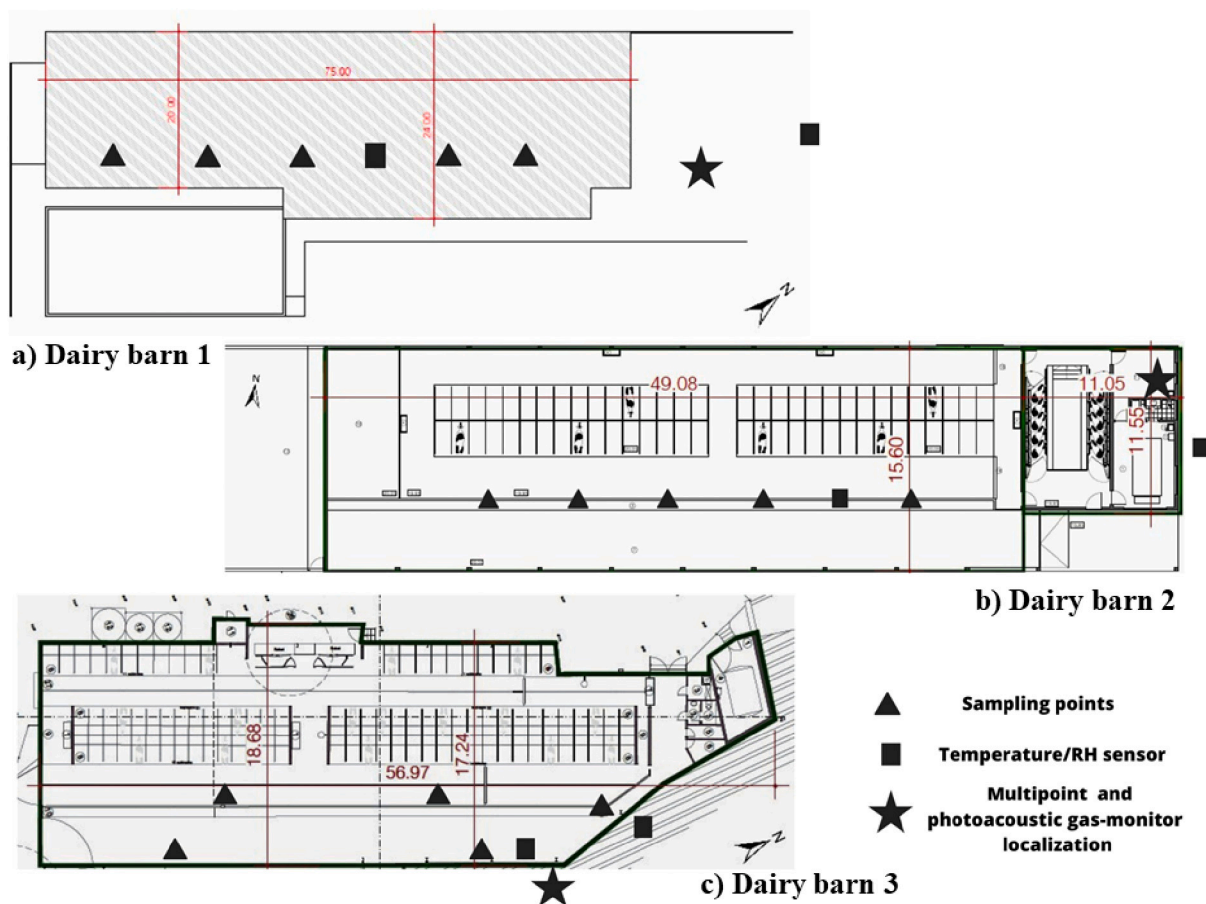


Fig. 1. Schematic representation of the three cattle barns.

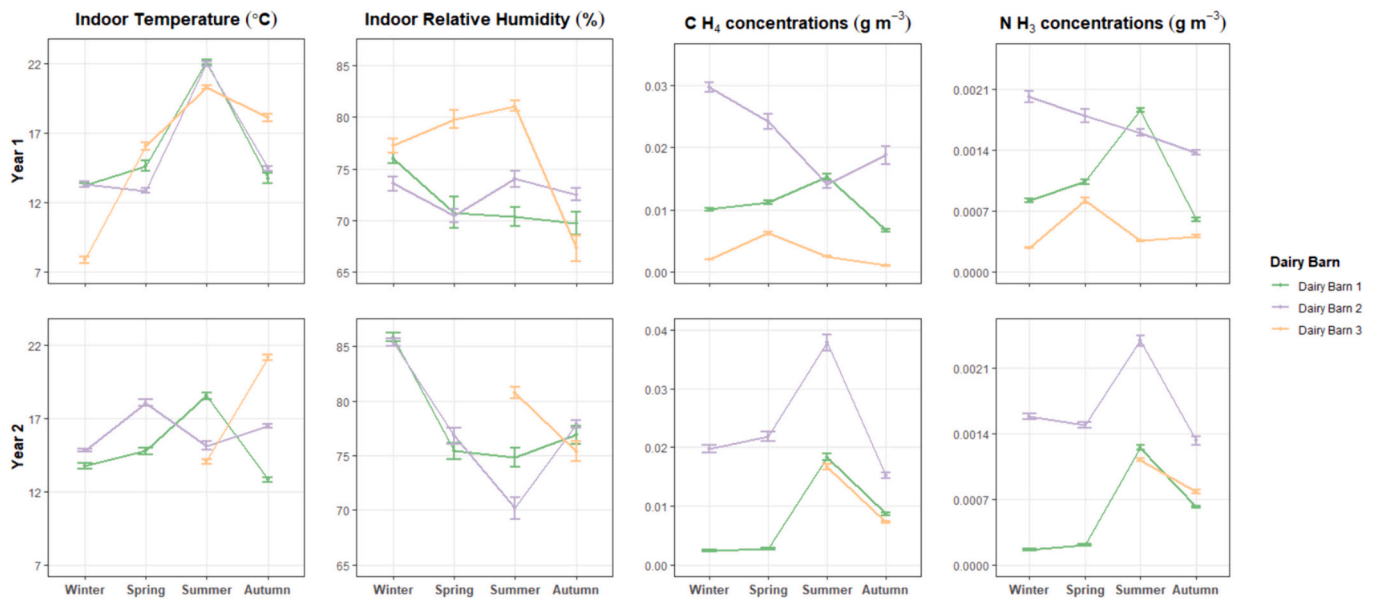


Fig. 2. Environmental parameters and daily average CH₄ and NH₃ concentrations in all barns, in year 1 and year 2. Vertical bars represent the standard error of the mean. CH₄, methane and NH₃, ammonia.

and 2 ($p > 0.05$, Table S7). Differences in indoor RH in year 1 were only identified in dairy barn 3 between summer and autumn ($p < 0.05$, Table S8), while during year 2 varied from 75% in spring to 86% in winter in dairy barn 1 ($p < 0.01$), 70% in summer to 85% winter in dairy barn 2 ($p < 0.001$), 75% in autumn to 81% in summer in dairy barn 3 ($p < 0.05$, Table S9, Fig. 2).

The average daily ventilation rate in the dairy barn 3 differed from dairy barns 1 and 2, in year 1, while dairy barn 2 differed from dairy barns 1 and 3, in year 2 ($p < 0.001$, Table S4, Fig. 3). Besides, hourly

ventilation ranged from 830 to 1258 g h⁻¹ LU⁻¹ in the dairy barn 1 (summer and autumn, $p < 0.001$), 479 to 2543 g h⁻¹ LU⁻¹ in the dairy barn 2 (winter and autumn, $p < 0.001$), and 1513 to 3475 g h⁻¹ LU⁻¹ in the dairy barn 3 (spring and winter, $p < 0.001$, Table S5) in year 1 (Fig. 3). In dairy barn 1, ventilation rate differed among seasons, varying from 7101 in winter to 1007 g h⁻¹ LU⁻¹ in summer ($p < 0.001$) and to 1878 g h⁻¹ LU⁻¹ in autumn ($p < 0.01$), in year 2 (Tables S5 and S6).

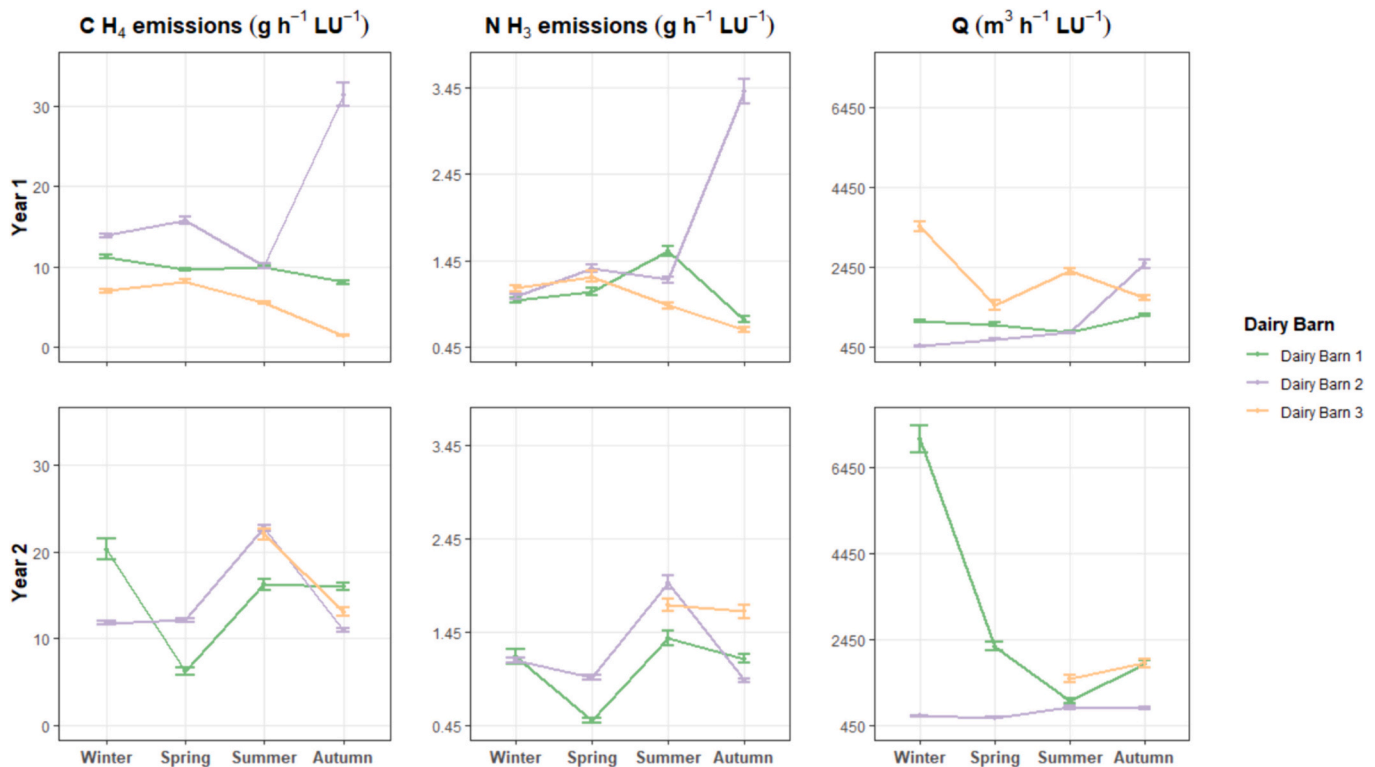


Fig. 3. Hourly average CH₄ and NH₃ emissions and ventilation rate in all barns, in year 1 and year 2. Vertical bars represent the standard error of the mean. CH₄, methane, NH₃ and ammonia, Q, ventilation rate.

3.2. Daily patterns and 24-hour profile of methane emissions

Generally, average hourly CH₄ emissions in years 1 and 2 were lower than 25 g h⁻¹ LU⁻¹, except in the autumn of year 1 at barn 2 that was higher than 30 g h⁻¹ LU⁻¹. Diel CH₄ emissions increased during the daytime and presented high intra hour variability from 9 a.m. to 7 p.m. (Fig. 4). This pattern is particularly marked in the winter and autumn of years 1 and 2, in the spring of year 1 and summer of year 2, nonetheless in the autumn of year 1 in dairy barn 3 emissions followed the opposite pattern (Fig. 4). In more detail, average hourly CH₄ emissions were significantly different among all dairy barns in year 1 contrarily to year 2 (Table S10, Fig. 3). Besides, hourly CH₄ emissions varied from 8.1 to 11.2 g h⁻¹ LU⁻¹ and 6.2 to 20.3 g h⁻¹ LU⁻¹ in dairy barn 1 (autumn and winter, $p < 0.001$ and spring and winter, $p > 0.05$), from 10.1 to 31.4 g h⁻¹ LU⁻¹ and 10.9 to 22.8 g h⁻¹ LU⁻¹ in dairy barn 2 (summer and autumn, $p < 0.001$, autumn and summer, $p < 0.001$), and from 1.5 to 8.2 and 13.1 to 22.1 g h⁻¹ LU⁻¹ in dairy barn 3 (autumn and spring, $p < 0.001$, and autumn and summer, $p < 0.001$), in years 1 and 2, respectively (Fig. S1, Tables S11 and S12).

Furthermore, daily CH₄ emissions presented seasonal intraday variation in dairy barns (Fig. S1). In dairy barn 1, daily variability was low in all seasons, except in the first days of winter in year 1, while in year 2 the winter season presented the highest daily variability followed by summer (Fig. S1). In dairy barn 2, the winter season showed the highest daily variability, contrary to autumn and spring in year 1, while in year 2 daily variability was globally low (Fig. S1). In dairy barn 3, the daily variability was low in year 1, particularly in the autumn season, with some exceptions in specific days of winter and summer (Fig. S1).

3.3. Daily patterns and 24-hour profile of ammonia emissions

Globally, average hourly NH₃ emissions in years 1 and 2 were lower than 2.45 g h⁻¹ LU⁻¹, except in the autumn of year 1 at barn 2. Diel NH₃ emissions were consistently higher with high variability during the daytime (8 a.m. to 8 p.m.) compared to the nighttime, which showed lower variability in most seasons.

In particular, average hourly NH₃ emissions in dairy barn 2 differed from 3 ($p < 0.001$), and barn 1 from barn 3 in year 2 ($p < 0.05$ Table S10). Moreover, hourly NH₃ emissions varied from 0.77 to 1.56 g h⁻¹ LU⁻¹ and from 0.50 to 1.38 g h⁻¹ LU⁻¹ in dairy barn 1 (autumn and summer, $p < 0.001$ and spring and summer $p < 0.01$), from 1.04 to 3.40 g h⁻¹ LU⁻¹ and from 0.93 and 1.98 g h⁻¹ LU⁻¹ in dairy barn 2 (winter and autumn, $p < 0.001$, and autumn and summer $p < 0.001$), from 0.66 to 1.32 g h⁻¹ LU⁻¹ and 1.67 and 1.73 g h⁻¹ LU⁻¹ in dairy barn 3 (autumn and winter, $p < 0.001$, and autumn and summer, $p > 0.05$), in year 1 and year 2, respectively (Tables S11 and S12).

Daily NH₃ emissions variability in dairy barn 1 was higher at the beginning of the winter and autumn when compared to the remaining

seasons. In year 2 daily variability was globally greater, with the highest emissions identified in the winter and summer (Fig. S2). In dairy barn 2, the winter season presented the highest daily variability and summer the lowest in year 1, while the daily variability was higher in summer and lower in the autumn in year 2 (Fig. S2). In dairy barn 3, daily variability differed within each season of year 1 and was higher in the summer compared to autumn in year 2 (Fig. S2).

Besides, diel NH₃ emissions were particularly high and with high variability during the daytime (8 a.m. to 8 p.m.) in the winter in dairy barns 1 and 2 (years 1 and 2), in the spring in barns 1, 2, and 3 (year 1), and barn 2 (year 2), in the summer in barn 3 (year 1), and barn 2 and 3 (year 2) and in the autumn in dairy barn 2 (years 1 and 2) (Fig. 5). Additionally, NH₃ emissions in the autumn in the dairy barn 2 presented the highest and greater variability compared to the remain measurement periods in year 1 (Fig. S2).

4. Discussion

4.1. Seasonal and daily variation of CH₄ emissions

The three dairy cattle barns studied had a solid concrete floors, the manure pit was only located outside, and floor cleaning frequency ranged between 1 and 3 h in all barns, suggesting that the great majority of CH₄ measured in this study was from enteric fermentation (Ngwabi et al., 2014). Indeed, the anaerobic degradation of manure stored in manure pits located underneath animals barn or outside were estimated to represent 24% of total CH₄ emissions from livestock (Vechi et al., 2022). Besides, the barns were naturally ventilated by large open windows and passages, leading to the greater influence of the outdoor climate parameters on the indoor conditions. In our study, daily CH₄ emissions varied among seasons similar to Tabase et al. (2023), while Saha et al. (2014) only found the influence of one season (autumn) in CH₄ emissions. Interestingly, Cortus et al. (2015) and Huang and Guo (2017b) identified variations of CH₄ concentrations among seasons, however with no variation in CH₄ emissions. A possible explanation for the contrasting results observed may be the sliding windows, the curtains, and the high density of fans of the barns studied by these authors, ensuring stability of indoor parameters and constant ventilation.

Diet composition strongly modulates CH₄ production from enteric fermentation, with forage-based diets known to promote acetate whereas starch-rich diets favor propionate production, which provides a sink for H₂, resulting in less CH₄ emission in the rumen (Wang et al., 2023). In our study, although the chemical composition of diets was similar among dairy barns, dairy barn 2 differed from the other barns by including alfalfa in the cows' diet. Despite this difference, no effect on CH₄ emissions was detected. Thus, our results suggest an opportunity to increase farm self-sufficiency using this high-quality protein source, with no detrimental effects on CH₄ emissions (Gislon et al., 2020).

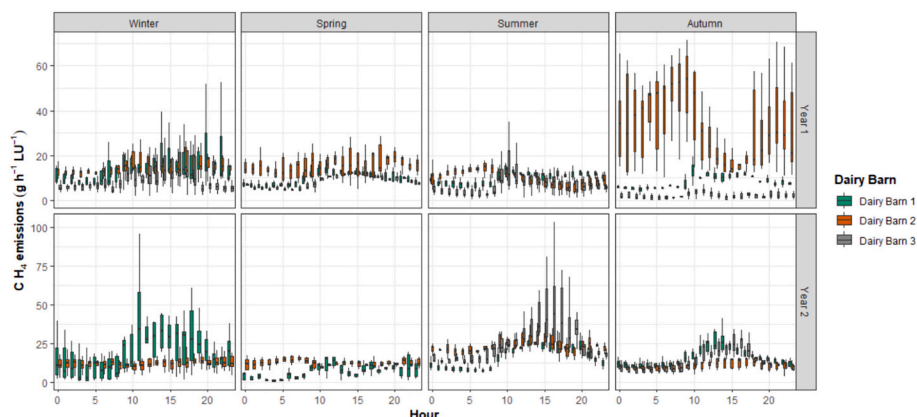


Fig. 4. Diel variations of CH₄ emissions in all barns, in year 1 and year 2.

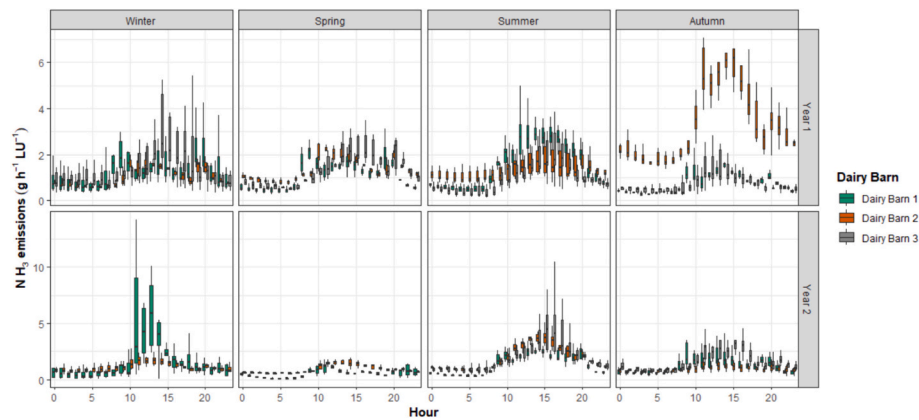


Fig. 5. Diel variations of NH_3 emissions in all barns, in year 1 and year 2.

Besides, genetics, animal activity, and climate parameters such as ambient temperature and RH can cause stress in dairy cows and account for the changes in dry matter intake, drinking frequency, feed efficiency, and rumination time with consequent reduction in milk production and affecting CH_4 emission patterns, not only seasonally but also daily (Antanaitis et al., 2023; Islam et al., 2021).

In general, the results of this study showed higher diel CH_4 emissions during daytime similar to Saha et al. (2014) and Joo et al. (2015a), with higher intra hour variability from 9 a.m. to 7 p.m. in all seasons, maybe due to the greater animal activity during the daytime compared to nighttime (Ngwabie et al., 2014). Moreover, an increase of CH_4 emissions up to 2 h after feeding followed by a decrease in the values until the next meal has been described in the literature (Blaise et al., 2018; Crompton et al., 2011; Hollmann et al., 2013). In this study, this pattern was not identified in all measurements, despite the different feeding systems of the studied dairy barns. Moreover, diel CH_4 emissions increased in the early morning for dairy barns 1 and 2, roughly matching the first (of two) feed distributions; dairy barn 3, which only had one feed distribution (at late afternoon), presented the same behavior. Despite the differences in feeding distribution, the chemical composition of the cow's diet was similar among the three dairy barns studied in all periods. Thus, these results may be more related to cow's feeding behavior than to differences in feeding distribution as proposed by Muñoz-Tamayo et al. (2022). During the daytime is also possible to identify smaller CH_4 emissions peaks in all dairy barns, except during the spring of year 1 in dairy barns 1 and 3. A larger second CH_4 emission peak in late afternoon was detected only in the winter of years 1 and 2 in the dairy barn 1, and the spring and autumn of year 1 in the dairy barn 2. In the other seasons, the CH_4 emissions decreased at nighttime, however in dairy barn 2 the emissions decreased slower when compared to dairy barns 1 and 3 possibly due to concentrate delivering in robot milking.

Feeding rate and time spent eating is expected to be higher after diet delivery, however, despite one feed delivery in late afternoon, CH_4 emissions in the dairy barn 3 increased during the daytime, following a similar pattern to dairy barn 2, highlighting the higher animal's activity during the daytime compared to nighttime (Ngwabie et al., 2011).

4.2. Seasonal and daily variation of NH_3 emissions

The correlation between NH_3 emissions and temperature has been described in several studies as positive (Poteko et al., 2019; Qu et al., 2021; Sanchis et al., 2019) or negative (Hempel et al., 2016; Tabase et al., 2023). Similarly, the correlation between NH_3 emissions and RH is also still uncertain being described as positive (Tabase et al., 2023) and negative (Hempel et al., 2016; Qu et al., 2021; Saha et al., 2014).

In dairy barn 1 in year 1, the average NH_3 emissions were different between summer and autumn, as well as indoor temperature while RH did not differ significantly. The same behavior was observed in the dairy

barn 2 between summer and autumn, and in the dairy barn 3 between winter and autumn, in year 1.

Manure decomposition in the floor is the main emission source of NH_3 from dairy cattle barns, particularly the hydrolysis of the urinary-urea by urease enzyme produced from fecal bacteria, whose activity depends on pH, temperature, urinary urea content, and barn floor characteristics (Fangueiro et al., 2023; Pedersen et al., 2022). Although the results of the present study suggest the effect of temperature and RH on NH_3 emissions in some seasons, it also highlights the impact of other parameters on NH_3 emissions. Significant differences between seasons were identified in indoor temperature but were not identified in NH_3 emissions, such as in dairy barn 1 in winter and summer for both years, and in dairy barn 2 in winter and summer and winter and autumn, or in dairy barn 3 in winter and summer and summer and autumn, in years 1 and 2, respectively.

Furthermore, the daily variation in NH_3 emissions showed consistency, increasing with high variability during the daytime, from 8 a.m. to 8 p.m. Daily variances in NH_3 emissions from ventilated dairy barns were also described in the study of Saha et al. (2014) and of Huang and Guo (2017a). It is also possible to identify in this study, for all periods, a peak in the middle of the day, with small variations on the specific hour of said peak among the different seasons. The highest outdoor temperature in the middle of the day may be an additional explanation for this emission peak. Contrarily to the present study, D'Urso et al. (2021) found two distinct emission peaks, the first during cleaning between 7 a.m. and 8 a.m. and the second after milking. Interestingly, in this study, the three dairy cows' barns studied differed in the milking system; however, all presented the same consistent emission peak. These results are in line with the findings of Rodrigues et al. (2022), who described higher cumulative N-NH_3 emissions (g kg^{-1} excreta, total N, and organic soluble N) at 12 h when compared to 8 h and 17 h. Therefore, a possible higher urease activity occurred in the middle of the day, with excreta characteristics favoring volatilization of NH_3 .

4.3. Emission factors and strategies to mitigate CH_4 and NH_3 emissions from dairy cattle barns

The Intergovernmental Panel on Climate Change (IPCC) provides guidance on methods to estimate emissions from livestock (IPCC, 2006). Thus, many studies have been conducted to enhance the national emission inventories in different countries. Besides, databases can be established to compile EFs from different inventories to a more comprehensive understanding of variations among animal categories, livestock barns, and regions, among others (Hassouna et al., 2023). Considering the seasonal and daily variation of CH_4 and NH_3 emissions previously reported in naturally ventilated dairy cattle barns, the present study suggests that national EFs should be derived from *in loco* campaigns and include correction factors for accurate assessment of

Table 2
Selected literature values of average NH₃ and CH₄ emission factors from dairy cattle barns.

| Country | Measurements | Emission factors (g day ⁻¹ LU ⁻¹) | | Reference |
|-------------|-------------------------|--|-----------------|-----------------------|
| | | CH ₄ | NH ₃ | |
| Portugal | All | 309.5 | 30.6 | Present study |
| Germany | All | 308.4 | – | Hempel et al. (2020) |
| Canada | All | 259.2 | – | Huang and Guo (2017a) |
| Poland | Spring, summer & autumn | 283.2 | 19.0 | Rzeznik et al. (2016) |
| USA-WA | Spring, autumn & winter | – | 21.6 | Joo et al. (2015b) |
| Denmark | Winter & summer | 205.7 | 12.2 | Rong et al. (2014) |
| Germany | All | 330.2 | 56.2 | Saha et al. (2014) |
| Switzerland | All | – | 36.4 | Schrade et al. (2023) |
| Denmark | Spring, autumn & winter | 304.9 | 80.0 | Wu et al. (2012) |
| Portugal | All | – | 43.7 | Pereira et al. (2010) |

climate, animal, and housing variables.

The EF of CH₄ observed in this study was 309.5 g day⁻¹ LU⁻¹, which was in line with the results reported in the literature for dairy cattle barns (Table 2). The EF of CH₄ reported in Central Europe were between 283.0 and 330.0 g day⁻¹ LU⁻¹ (Hempel et al., 2020; Rzeznik et al., 2016; Saha et al., 2014), in Northern Europe between 205.7 and 304.0 g day⁻¹ LU⁻¹ (Rong et al., 2014; Wu et al., 2012), and Canada between 259.2 and 313.2 g day⁻¹ LU⁻¹ (Huang and Guo, 2017a; Ngwabie et al., 2014). Despite some research works varied in the measurement periods making comparisons between studies difficult, the differences among EFs can be mainly related to climate conditions and the architectural characteristics of cattle barns (Huang and Guo, 2017a; Vecchi et al., 2022).

There are several effective strategies developed to reduce CH₄ emissions from dairy cattle barns, from nutritional to herd management, without impairing animals' performance (Arndt et al., 2022; den Toorn et al., 2021; FAO, 2023). Feed additives for enteric CH₄ reduction, such as 3-nitrooxypropanol have been intensively studied in the last years, with results reporting a 28 to 32% decrease in CH₄ emissions (Hristov et al., 2022). However, the length of effectiveness is still the major obstacle to feed additives due to the ruminal microbial resistance development (Loh et al., 2020). Besides, the effect of 3-nitrooxypropanol on dry matter intake, rumen fermentation parameters, and microbial composition must be explored in the future (Alemu et al., 2023). Also, high-quality forages, lower forage to concentrate ratio and increased feeding levels are known approaches to decrease CH₄ emissions (Arndt et al., 2022; Lileikis et al., 2023). Besides, improvement of barn conditions to control temperature and RH such as higher fan density or sprinklers could reduce heat stress of cows known to affect CH₄ production (Gisbert-Queral et al., 2021).

Reducing the age at first calving and enhancing animal health also decrease CH₄ emissions (Fresco et al., 2023). Besides, genetic improvement of traits linked to CH₄ production can also be considered as a long-term mitigation approach towards breeding for low-emitters cows (van Breukelen et al., 2023). These available strategies can be applied in the production systems studied in the present research.

The EF of NH₃ in this study was 30.6 g day⁻¹ LU⁻¹ which was within the range described in the literature (Table 2). Studies performed in Central Europe reported average NH₃ emissions between 19.0 and 80.0 g day⁻¹ LU⁻¹ (Pereira et al., 2010; Rzeznik et al., 2016; Saha et al., 2014; Schrader et al., 2023), in Northern Europe between 12.2 and 80.0 g day⁻¹ LU⁻¹ (Rong et al., 2014; Wu et al., 2012), in United Kingdom of 23.1 g day⁻¹ LU⁻¹ (Misselbrook et al., 2015) and 21.6 g day⁻¹ LU⁻¹ in Washington state of United States of America (Joo et al., 2015b).

Different sustainable options are available to minimize NH₃ emissions from livestock such as feeding strategies, floor design, and manure management at the barn, storage, treatment operations, and when applied to soil (Bittman et al., 2014; Fangueiro et al., 2023). A decrease of 1% of the protein content of the animal feed was suggested to reduce up to 15% of the total NH₃ emissions from barn if a balanced amino acid supply is granted (Bittman et al., 2014). Inclusion of some ingredients (such as sunflower oil or red clover silage) and amino acids supplementation can improve N retention while reducing N emissions (Broderick, 2018; Doranalli and Mutsvangwa, 2011; Tan et al., 2021). Besides, the determination of dairy cow's metabolizable protein requirements, or shift from urine to fecal excretion of N are important strategies used to improve N use efficiency and reduce N emissions (Huhtanen and Ahvenjärvi, 2022; Weiss et al., 2009). Differences in cow's stages of lactation within dairy barns could be addressed in the future, particularly the manure management in the housing floor, where cumulative N–N₂O emissions (g kg⁻¹ total N, and ammoniacal-N) and cumulative N–NH₃ (g kg⁻¹ excreta, and total N) differed between stages of lactation (Rodrigues et al., 2022). The decrease of manure surface area in the barn floor, rapid removal of urine, separation of urine and feces or urine drainage are recommended techniques to decrease NH₃ emissions from the animal's barn (Bittman et al., 2014). Studies on the effect of floor type on NH₃ emissions showed a reduction of 46% with grooved floors and 35% with grooved floors without perforations when compared to slotted floors (Swierstra et al., 2001). Besides, a solid floor with a 3% of inclination and a V-shaped can reduce NH₃ volatilization by 21% and 50%, respectively, when compared to a slatted floor (Bram et al., 1997). Moreover, to ensure an optimal barn climatization roof insulation and/or automatically controlled natural ventilation are recommended techniques that can reduce 20% of NH₃ volatilization (Bittman et al., 2014).

5. Conclusion

The seasonal differences found for CH₄ and NH₃ emissions in the three dairy barns indicate the climate parameter's effect on dairy barns, in which open windows and large openings do not ensure the stability of indoor temperature and RH and constant ventilation among seasons. Diel CH₄ and NH₃ emissions increased during the daytime with higher intra hour variability, when compared to nighttime. This fact may reflect the higher animal activity during the day, being also in this period of the day where mitigation approaches must be mainly focused, such as barn climatization and cleaning frequency.

The EFs for CH₄ and NH₃ were 309.5 and 30.6 g day⁻¹ LU⁻¹, being in line with the literature on the topic and several mitigation strategies can be adopted to reduce gaseous emissions at the barn level. The insight of this study provides a better understanding of daily and seasonal CH₄ and NH₃ emissions variations from naturally ventilated dairy cattle barns. These variations should be further explored in future works and considered in the definition of mitigation plans in the short- and long-term.

CRedit authorship contribution statement

Ana R.F. Rodrigues: Writing – review & editing, Writing – original draft, Investigation, Formal analysis. **Maria Eduarda Silva:** Writing – review & editing, Supervision, Formal analysis. **Vanessa F. Silva:** Writing – review & editing, Formal analysis. **Margarida R.G. Maia:** Writing – review & editing. **Ana R.J. Cabrita:** Writing – review & editing. **Henrique Trindade:** Writing – review & editing, Supervision, Conceptualization. **António J.M. Fonseca:** Writing – review & editing, Supervision, Resources, Funding acquisition, Conceptualization. **José L. S. Pereira:** Writing – review & editing, Supervision, Resources, Conceptualization.

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.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2024.173734>.

References

- Alemu, A.W., Gruninger, R.J., Zhang, X.M., O'Hara, E., Kindermann, M., Beauchemin, K. A., 2023. 3-Nitrooxypropanol supplementation of a forage diet decreased enteric methane emissions from beef cattle without affecting feed intake and apparent total-tract digestibility. *J. Anim. Sci.* 101 <https://doi.org/10.1093/jas/skad001>.
- Antanaitis, R., Dzermeikaite, K., Bepalovaitė, A., Ribelyte, I., Rutkauskas, A., Japertas, S., Baumgartner, W., 2023. Assessment of ruminating, eating, and locomotion behavior during heat stress in dairy cattle by using advanced technological monitoring. *Animals* 13. <https://doi.org/10.3390/ani13182825>.
- Arndt, C., Hristov, A.N., Price, W.J., McClelland, S.C., Pelaez, A.M., Cueva, S.F., Oh, J., Dijkstra, J., Bannink, A., Bayat, A.R., Crompton, L.A., Eugene, M.A., Enahoro, D., Kebreab, E., Kreuzer, M., McGee, M., Martin, C., Newbold, C.J., Reynolds, C.K., Schwarm, A., Shingfield, K.J., Veneman, J.B., Yanez-Ruiz, D.R., Yu, Z.T., 2022. Full adoption of the most effective strategies to mitigate methane emissions by ruminants can help meet the 1.5 degrees C target by 2030 but not 2050. *Proc. Natl. Acad. Sci. USA* 119. <https://doi.org/10.1073/pnas.2111294119>.
- Baldini, C., Borgonovo, F., Gardoni, D., Guarino, M., 2016. Comparison among NH₃ and GHGs emissive patterns from different housing solutions of dairy farms. *Atmos. Environ.* 141, 60–66. <https://doi.org/10.1016/j.atmosenv.2016.06.047>.
- Benchaar, C., Hassanat, F., 2020. Frequency of diet delivery to dairy cows: effect on nutrient digestion, rumen fermentation, methane production, nitrogen utilization, and milk production. *J. Dairy Sci.* 103, 7094–7109. <https://doi.org/10.3168/jds.2020-18199>.
- Bittman, S., Dedina, M., Howard C.M., Oenema, O., Sutton, M.A., (eds), 2014, Options for Ammonia Mitigation: Guidance from the UNECE Task Force on Reactive Nitrogen, Centre for Ecology and Hydrology, Edinburgh, UK.
- Blaise, Y., Andriamandroso, A.L.H., Beckers, Y., Heinesch, B., Muñoz, E.C., Soyeurt, H., Froidmont, E., Lebeau, F., Bindelle, J., 2018. The time after feeding alters methane emission kinetics in Holstein dry cows fed with various restricted diets. *Livest. Sci.* 217, 99–107. <https://doi.org/10.1016/j.livsci.2018.07.004>.

- Braam, C.R., Smits, M.C.J., Gunnink, H., Swierstra, D., 1997. Ammonia emission from a double-sloped solid floor in a cubicle house for dairy cows. *J. Agric. Eng. Res.* 68, 375–386. <https://doi.org/10.1006/jaer.1997.0215>.
- Broderick, G.A., 2018. Utilization of protein in red clover and alfalfa silages by lactating dairy cows and growing lambs. *J. Dairy Sci.* 101, 1190–1205. <https://doi.org/10.3168/jds.2017-13690>.
- CIGR, 2002. Climatization of animal houses. In: Working Group Report on: Heat and Moisture Production at Animal and House Levels. Denmark, Research Centre Bygholm, Danish Institute of Agricultural Sciences, Horsens.
- Cortus, E.L., Jacobson, L.D., Hetchler, B.P., Heber, A.J., Bogan, B.W., 2015. Methane and nitrous oxide analyzer comparison and emissions from dairy freestall barns with manure flushing and scraping. *Atmos. Environ.* 100, 57–65. <https://doi.org/10.1016/j.atmosenv.2014.10.039>.
- Crompton, L.A., Mills, J.A.N., Reynolds, C.K., France, J., 2011. Fluctuations in methane emission in response to feeding pattern in lactating dairy cows, in: D. Sauvant, J. Van Milgen, P. Faverdin, N. Friggens (Eds.), Modelling nutrient digestion and utilisation in farm animals, Wageningen Academic Publishers, Wageningen, pp. 176–180.
- den Toorn, S.I.A., Worrell, E., van den Broek, M.A., 2021. How much can combinations of measures reduce methane and nitrous oxide emissions from European livestock husbandry and feed cultivation? *J. Clean. Prod.* 304, 14. <https://doi.org/10.1016/j.jclepro.2021.127138>.
- Doranalli, K., Mutsvangwa, T., 2011. Feeding sunflower oil to partially defaunate the rumen increases nitrogen retention, urea-nitrogen recycling to the gastrointestinal tract and the anabolic use of recycled urea-nitrogen in growing lambs. *Br. J. Nutr.* 10, 1453–1464. <https://doi.org/10.1017/S0007114510005155>.
- D'Urso, P.R., Arcidiacono, C., Valenti, F., Cascone, G., 2021. Assessing influence factors on daily Ammonia and greenhouse gas concentrations from an open-sided cubicle barn in hot Mediterranean climate. *Animals* 11, 17. <https://doi.org/10.3390/ani11051400>.
- EEA, 2020. Annual European Union greenhouse gas inventory 1990–2018 and inventory report 2020.
- Fanguiero, D., Merino, P., Pantelopoulou, A., Pereira, J.L.S., Amon, B., Chadwick, D.R., 2023. The Implications of Animal Manure Management on Ammonia and Greenhouse Gas Emissions, in: T. Bartzanas (Eds.), Technology for Environmentally Friendly Livestock Production, Springer International Publishing, Cham, pp. 99–136.
- FAO, 2023. Methane emissions in livestock and rice systems – Sources, quantification, mitigation and metrics, Rome.
- FAO, GDP, 2018. Climate Change and the Global Dairy Cattle Sector – The Role of the Dairy Sector in a Low-Carbon Future, Rome, 36 pp.
- Fresco, S., Boichard, D., Fritz, S., Lefebvre, R., Barbey, S., Gaborit, M., Martin, P., 2023. Comparison of methane production, intensity, and yield throughout lactation in Holstein cows. *J. Dairy Sci.* 106, 4147–4157. <https://doi.org/10.3168/jds.2022-22855>.
- Gisbert-Queral, M., Henningsen, A., Markussen, B., Niles, M.T., Kebreab, E., Rigden, A.J., Mueller, N.D., 2021. Climate impacts and adaptation in US dairy systems 1981–2018. *Nature Food* 2, 894–901. <https://doi.org/10.1038/s43016-021-00372-z>.
- Gislon, G., Colombini, S., Borreani, G., Crovetto, G.M., Sandrucci, A., Galassi, G., Tabacco, E., Rapetti, L., 2020. Milk production, methane emissions, nitrogen, and energy balance of cows fed diets based on different forage systems. *J. Dairy Sci.* 103, 8048–8061. <https://doi.org/10.3168/jds.2019-18134>.
- Hassouna, M., van der Weerden, T.J., Beltran, I., Amon, B., Alfaro, M.A., Anestis, V., Cinar, G., Dragoni, F., Hutchings, N.J., Leytem, A., Maeda, K., Maragou, A., Misselbrook, T., Noble, A., Rychla, A., Salazar, F., Simon, P., 2023. DATAMAN: a global database of methane, nitrous oxide, and ammonia emission factors for livestock housing and outdoor storage of manure. *J. Environ. Qual.* 52, 207–223. <https://doi.org/10.1002/jeq2.20430>.
- Hempel, S., Saha, C.K., Fiedler, M., Berg, W., Hansen, C., Amon, B., Amon, T., 2016. Non-linear temperature dependency of ammonia and methane emissions from a naturally ventilated dairy barn. *Biosyst. Eng.* 145, 10–21. <https://doi.org/10.1016/j.biosystemseng.2016.02.006>.
- Hempel, S., Willink, D., Janke, D., Ammon, C., Amon, B., Amon, T., 2020. Methane emission characteristics of naturally ventilated cattle buildings. *Sustainability* 12, 4314. <https://doi.org/10.3390/su12104314>.
- Hollmann, M., Powers, W.J., Fogiel, A.C., Liesman, J.S., Beede, D.K., 2013. Response profiles of enteric methane emissions and lactational performance during habituation to dietary coconut oil in dairy cows. *J. Dairy Sci.* 96, 1769–1781. <https://doi.org/10.3168/jds.2012-6039>.
- Hossein-Zadeh, N.G., 2022. Estimates of the genetic contribution to methane emission in dairy cows: a meta-analysis. *Sci. Rep.* 12 <https://doi.org/10.1038/s41598-022-16778-z>.
- Hristov, A.N., Melgar, A., Wasson, D., Arndt, C., 2022. Symposium review: effective nutritional strategies to mitigate enteric methane in dairy cattle. *J. Dairy Sci.* 105, 8543–8557. <https://doi.org/10.3168/jds.2021-21398>.
- Huang, D., Guo, H., 2017a. Diurnal and seasonal variations of greenhouse gas emissions from a naturally ventilated dairy barn in a cold region. *Atmos. Environ.* 172, 74–82. <https://doi.org/10.1016/j.atmosenv.2017.10.051>.
- Huang, D.D., Guo, H.Q., 2017b. Diurnal and seasonal variations of odor and gas emissions from a naturally ventilated free-stall dairy barn on the Canadian prairies. *J. Air Waste Manage. Assoc.* 67, 1092–1105. <https://doi.org/10.1080/10962247.2017.1329172>.
- Huhtanen, P., Ahvenjärvi, S., 2022. Review: problems in determining metabolisable protein value of dairy cow diets and the impact on protein feeding. *Animal* 16, 100539. <https://doi.org/10.1016/j.animal.2022.100539>.
- IPCC, 2006. Guidelines for National Greenhouse Gas Inventories, Japan.

- IPCC, 2014. Climate Change 2014: Synthesis Report. Contribution of Working Groups I, II and III to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change. Geneva, Switzerland.
- Islam, M., Kim, S.H., Son, A.-R., Ramos, S.C., Jeong, C.D., Yu, Z., Kang, S.H., Cho, Y.I., Lee, S.S., Cho, K.K., 2021. Seasonal influence on rumen microbiota, rumen fermentation, and enteric methane emissions of Holstein and Jersey steers under the same total mixed ration. *Animals* 11, 1184. <https://doi.org/10.3390/ani11041184>.
- Johnson, K.A., Johnson, D.E., 1995. Methane emissions from cattle. *J. Anim. Sci.* 73, 2483–2492. <https://doi.org/10.2527/1995.7382483x>.
- Joo, H.S., Ndegwa, P.M., Heber, A.J., Ni, J.Q., Bogan, B.W., Ramirez-Dorransoro, J.C., Cortus, E., 2015a. Greenhouse gas emissions from naturally ventilated freestall dairy barns. *Atmos. Environ.* 102, 384–392. <https://doi.org/10.1016/j.atmosenv.2014.11.067>.
- Joo, H.S., Ndegwa, P.M., Wang, X., Heber, A.J., Ni, J.Q., Cortus, E.L., Ramirez-Dorransoro, J.C., Bogan, B.W., Chai, L., 2015b. Ammonia and hydrogen sulfide concentrations and emissions for naturally ventilated freestall dairy barns. *Trans. ASABE* 58, 1321–1331. <https://doi.org/10.13031/trans.58.11267>.
- Kannangara, M., Dua, R., Ahmadi, L., Bensebaa, F., 2018. Modeling and prediction of regional municipal solid waste generation and diversion in Canada using machine learning approaches. *Waste Manag.* 74, 3–15. <https://doi.org/10.1016/j.wasman.2017.11.057>.
- Lileikis, T., Nainiene, R., Bliznikas, S., Uchokis, V., 2023. Dietary ruminant enteric methane mitigation strategies: current findings, potential risks and applicability. *Animals* 13, 2586. <https://doi.org/10.3390/ani13162586>.
- Loh, Z.H., Ouwerkerk, D., Klieve, A.V., Hungerford, N.L., Fletcher, M.T., 2020. Toxin degradation by rumen microorganisms: a review. *Toxins* 12, 664. <https://doi.org/10.3390/toxins12100664>.
- Mar, K.A., Unger, C., Walderdorff, L., Butler, T., 2022. Beyond CO2 equivalence: the impacts of methane on climate, ecosystems, and health. *Environ. Sci. Pol.* 134, 127–136. <https://doi.org/10.1016/j.envsci.2022.03.027>.
- Mazur, K., Roman, K., Wardal, W.J., Borek, K., Barwicki, J., Kieronczyk, M., 2021. Emission of harmful gases from animal production in Poland. *Environ. Monit. Assess.* 193, 341. <https://doi.org/10.1007/s10661-021-09118-7>.
- McGarr-O'Brien, K., Herron, J., Shaloo, L., De Boer, I.J.M., De Olde, E.M., 2023. Characterising sustainability certification standards in dairy production. *Animal* 17 (7), 100863. <https://doi.org/10.1016/j.animal.2023.100863>.
- Misselbrook, T.H., Gilhespy, S.L., Cardenas, L.M., 2015. Inventory of Ammonia Emissions from UK Agriculture, Department for Environment Food & Rural Affairs, London, United Kingdom.
- Munidasas, S., Eckard, R., Sun, X.Z., Cullen, B., McGill, D., Chen, D.L., Cheng, L., 2021. Challenges and opportunities for quantifying greenhouse gas emissions through dairy cattle research in developing countries. *J. Dairy Res.* 88, 3–7. <https://doi.org/10.1017/s0022029921000182>.
- Muñoz-Tamayo, R., Ruiz, B., Blavy, P., Giger-Reverdin, S., Sauvant, D., Williams, S.R.O., Moate, P.J., 2022. Predicting the dynamics of enteric methane emissions based on intake kinetic patterns in dairy cows fed diets containing either wheat or corn. *Animal - Open Space* 1, 100003. <https://doi.org/10.1016/j.anopen.2021.100003>.
- Ngwabie, N.M., Jeppsson, K.H., Nimmermark, S., Swensson, C., Gustafsson, G., 2009. Multi-location measurements of greenhouse gases and emission rates of methane and ammonia from a naturally-ventilated barn for dairy cows. *Biosyst. Eng.* 103, 68–77. <https://doi.org/10.1016/j.biosystemseng.2009.02.004>.
- Ngwabie, N.M., Jeppsson, K.H., Gustafsson, G., Nimmermark, S., 2011. Effects of animal activity and air temperature on methane and ammonia emissions from a naturally ventilated building for dairy cows. *Atmos. Environ.* 45, 6760–6768. <https://doi.org/10.1016/j.atmosenv.2011.08.027>.
- Ngwabie, N.M., VanderZaag, A.C., Jayasundara, S., Wagner-Riddle, C., 2014. Measurements of emission factors from a naturally ventilated commercial barn for dairy cows in a cold climate. *Biosyst. Eng.* 127, 103–114. <https://doi.org/10.1016/j.biosystemseng.2014.08.016>.
- NREAP, 2013. Decree number 81/2013 of 14 June regarding new regime to perform the livestock activity. *Diário da República*, editor. 113, Portugal, pp. 3304–3329.
- Palangi, V., Taghizadeh, A., Abachi, S., Lackner, M., 2022. Strategies to mitigate enteric methane Emissions in Ruminants: a review. *Sustainability* 14, 13229. <https://doi.org/10.3390/su142013229>.
- Pan, Y., Tian, S., Zhao, Y., Zhang, L., Zhu, X.f., Gao, J., Huang, W., Zhou, Y., Song, Y., Zhang, Q., 2018. Identifying ammonia hotspots in China using a national observation network. *Environ. Sci. Technol.* 52, 3926–3934. <https://doi.org/10.1021/acs.est.7b05235>.
- Pedersen, J., Feilberg, A., Nyord, T., 2022. Effect of storage and field acidification on emissions of NH₃, NMVOC, and odour from field applied slurry in winter conditions. *J. Environ. Manag.* 310, 114756. <https://doi.org/10.1016/j.jenvman.2022.114756>.
- Pereira, J., Misselbrook, T.H., Chadwick, D.R., Coutinho, J., Trindade, H., 2010. Ammonia emissions from naturally ventilated dairy cattle buildings and outdoor concrete yards in Portugal. *Atmos. Environ.* 44, 3413–3421. <https://doi.org/10.1016/j.atmosenv.2010.06.008>.
- Poteko, J., Zähler, M., Schrade, S., 2019. Effects of housing system, floor type and temperature on ammonia and methane emissions from dairy farming: a meta-analysis. *Biosyst. Eng.* 182, 16–28. <https://doi.org/10.1016/j.biosystemseng.2019.03.012>.
- Qu, Q.B., Groot, J.C.J., Zhang, K.Q., Schulte, R.P.O., 2021. Effects of housing system, measurement methods and environmental factors on estimating ammonia and methane emission rates in dairy barns: a meta-analysis. *Biosyst. Eng.* 205, 64–75. <https://doi.org/10.1016/j.biosystemseng.2021.02.012>.
- Rodrigues, A.R.F., Maia, M.R.G., Miranda, C., Cabrita, A.R.J., Fonseca, A.J.M., Pereira, J.L.S., Trindade, H., 2022. Ammonia and greenhouse emissions from cow's excreta are affected by feeding system, stage of lactation and sampling time. *J. Environ. Manag.* 320, 115882. <https://doi.org/10.1016/j.jenvman.2022.115882>.
- Rong, L., Liu, D.W., Pedersen, E.F., Zhang, G., 2014. Effect of climate parameters on air exchange rate and ammonia and methane emissions from a hybrid ventilated dairy cow building. *Energ. Buildings* 82, 632–643. <https://doi.org/10.1016/j.enbuild.2014.07.089>.
- Rzeznik, W., Mielcarek, P., Rzeznik, I., 2016. Pilot study of greenhouse gases and ammonia emissions from naturally ventilated barns for dairy cows. *Pol. J. Environ. Stud.*, 25, pp. 2553–2562. <https://doi.org/10.15244/pjoes/63660>.
- Saha, C.K., Ammon, C., Berg, W., Fiedler, M., Loebis, C., Sanfteleben, P., Brunsch, R., Amon, T., 2014. Seasonal and diel variations of ammonia and methane emissions from a naturally ventilated dairy building and the associated factors influencing emissions. *Sci. Total Environ.* 468–469, 53–62. <https://doi.org/10.1016/j.scitotenv.2013.08.015>.
- Sajeew, M.E.P., Winiwarter, W., Amon, B., 2018. Greenhouse gas and Ammonia emissions from different stages of liquid manure management chains: abatement options and emission interactions. *J. Environ. Qual.* 47, 30–41. <https://doi.org/10.2134/jeq2017.05.0199>.
- Sanchis, E., Calvet, S., Prado, A., Estellés, F., 2019. A meta-analysis of environmental factor effects on ammonia emissions from dairy cattle houses. *Biosyst. Eng.* 178, 176–183. <https://doi.org/10.1016/j.biosystemseng.2018.11.017>.
- Schmithausen, A.J., Schiefeler, I., Trimborn, M., Gerlach, K., Sudekum, K.H., Pries, M., Buscher, W., 2018. Quantification of methane and Ammonia emissions in a naturally ventilated barn by using defined criteria to calculate emission rates. *Animals* 8 (5), 75. <https://doi.org/10.3390/ani8050075>.
- Schrade, S., Zeyer, K., Mohn, J., Zähler, M., 2023. Effect of diets with different crude protein levels on ammonia and greenhouse gas emissions from a naturally ventilated dairy housing. *Sci. Total Environ.* 896, 165027. <https://doi.org/10.1016/j.scitotenv.2023.165027>.
- Sigurdarson, J.J., Svane, S., Karring, H., 2018. The molecular processes of urea hydrolysis in relation to ammonia emissions from agriculture. *Rev. Environ. Sci. Biotechnol.* 17, 241–258. <https://doi.org/10.1007/s11157-018-9466-1>.
- Swierstra, D., R. Braam, C., C. Smits, M., 2001. Grooved floor system for cattle housing: ammonia emission reduction and good slip resistance. *Appl. Eng. Agric.*, 17, pp. 85–90. <https://doi.org/10.13031/2013.1929>.
- Tabase, R.K., Naess, G., Larring, Y., 2023. Ammonia and methane emissions from small herd cattle buildings in a cold climate. *Sci. Total Environ.* 903, 166046. <https://doi.org/10.1016/j.scitotenv.2023.166046>.
- Tan, P., Liu, H., Zhao, J., Gu, X., Wei, X., Zhang, X., Ma, N., Johnston, L.J., Bai, Y., Zhang, W., Nie, C., Ma, X., 2021. Amino acids metabolism by rumen microorganisms: nutrition and ecology strategies to reduce nitrogen emissions from the inside to the outside. *Sci. Total Environ.* 800, 149596. <https://doi.org/10.1016/j.scitotenv.2021.149596>.
- Tedeschi, L.O., Abdalla, A.L., Alvarez, C., Anuga, S.W., Arango, J., Beauchemin, K.A., Becquet, P., Berndt, A., Burns, R., De Camillis, C., Chara, J., Echazarreta, J.M., Hassouna, M., Kenny, D., Mathot, M., Mauricio, R.M., McClelland, S.C., Niu, M.T., Onyango, A.A., Parajuli, R., Pereira, L.G.R., del Prado, A., Trier, M.P., Uwizeye, A., Kebreab, E., 2022. Quantification of methane emitted by ruminants: a review of methods. *J. Anim. Sci.* 100, 1–22. <https://doi.org/10.1093/jas/skac197>.
- Tong, X., Zhao, L., Heber, A.J., Ni, J.-Q., 2020. Mechanistic modelling of ammonia emission from laying hen manure at laboratory scale. *Biosyst. Eng.* 192, 24–41. <https://doi.org/10.1016/j.biosystemseng.2020.01.004>.
- van Breukelen, A.E., Aldridge, M.N., Veerkamp, R.F., Koning, L., Sebek, L.B., de Haas, Y., 2023. Heritability and genetic correlations between enteric methane production and concentration recorded by GreenFeed and sniffers on dairy cows. *J. Dairy Sci.* 106, 4121–4132. <https://doi.org/10.3168/jds.2022-22735>.
- VanderZaag, A.C., Flesch, T.K., Desjardins, R.L., Balde, H., Wright, T., 2014. Measuring methane emissions from two dairy farms: seasonal and manure-management effects. *Agric. For. Meteorol.* 194, 259–267. <https://doi.org/10.1016/j.agrformet.2014.02.003>.
- Vecchi, N.T., Mellqvist, J., Scheutz, C., 2022. Quantification of methane emissions from cattle farms, using the tracer gas dispersion method. *Agric. Ecosyst. Environ.* 330, 107885. <https://doi.org/10.1016/j.agee.2022.107885>.
- Wang, K., Xiong, B., Zhao, X., 2023. Could propionate formation be used to reduce enteric methane emission in ruminants? *Sci. Total Environ.* 855, 158867. <https://doi.org/10.1016/j.scitotenv.2022.158867>.
- Weiss, W.P., Willett, L.B., St-Pierre, N.R., Borger, D.C., McKelvey, T.R., Wyatt, D.J., 2009. Varying forage type, metabolizable protein concentration, and carbohydrate source affects manure excretion, manure ammonia, and nitrogen metabolism of dairy cows. *J. Dairy Sci.* 92, 5607–5619. <https://doi.org/10.3168/jds.2009-2248>.
- WMO, 2019. Greenhouse gas bulletin - The State of Greenhouse Gases in the Atmosphere Based on Global Observations through 2018. Geneva, Switzerland.
- Wu, L.S., Koerckamp, P., Ogink, N.W.M., 2016. Temporal and spatial variation of methane concentrations around lying cubicles in dairy barns. *Biosyst. Eng.* 151, 464–478. <https://doi.org/10.1016/j.biosystemseng.2016.10.016>.
- Wu, W., Zhang, G., Kai, P., 2012. Ammonia and methane emissions from two naturally ventilated dairy cattle buildings and the influence of climatic factors on ammonia

- emissions. *Atmos. Environ.* 61, 232–243. <https://doi.org/10.1016/j.atmosenv.2012.07.050>.
- Zhang, G., Strøm, J.S., Li, B., Rom, H.B., Morsing, S., Dahl, P., Wang, C., 2005. Emission of Ammonia and other contaminant gases from naturally ventilated dairy cattle buildings. *J. Biosyst. Eng.* 92, 355–364. <https://doi.org/10.1016/j.biosystemseng.2005.08.002>.
- Zilio, M., Orzi, V., Chiodini, M.E., Riva, C., Acutis, M., Boccasile, G., Adani, F., 2020. Evaluation of ammonia and odour emissions from animal slurry and digestate storage in the Po Valley (Italy). *Waste Manag.* 103, 296–304. <https://doi.org/10.1016/j.wasman.2019.12.038>.