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Methane emissions from the storage of liquid dairy manure: Influences of season, temperature and storage duration

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ABSTRACT

Methane emissions from livestock manure are primary contributors to GHG emissions from agriculture and options for their mitigation must be found. This paper presents the results of a study on methane emissions from stored liquid dairy cow manure during summer and winter storage periods. Manure from the summer and winter season was stored under controlled conditions in barrels at ambient temperature to simulate manure storage conditions. Methane emissions from the manure samples from the winter season were measured in two time periods: 0 to 69 and 0 to 139 days. For the summer storage period, the experiments covered four time periods: from 0 to 70, 0 to 138, 0 to 209, and 0 to 279 continuous days, with probing every 10 weeks. Additionally, at the end of all storage experiments, samples were placed into eudiometer batch digesters, and their methane emissions were measured at 20 °C for another 60 days to investigate the potential effect of the aging of the liquid manure on its methane emissions. The experiment showed that the methane emissions from manure stored in summer were considerably higher than those from manure stored in winter. CH_4 production started after approximately one month, reaching values of 0.061 kg CH_4 kg^{-1} Volatile Solid (VS) and achieving high total emissions of 0.148 kg CH_4 kg^{-1} VS (40 weeks). In winter, the highest emissions level was 0.0011 kg CH_4 kg^{-1} VS (20 weeks). The outcomes of these experimental measurements can be used to suggest strategies for mitigating methane emissions from manure storage.

1. Introduction

Climate change is the most important global challenge of our era, and it is a reflection of anthropogenic processes, especially of the increased emission of greenhouse gases (GHG) (Crowley, 2000). Considering the evidence that livestock and, in particular, dairy production systems make an important contribution to GHG emissions and to global warming mainly through the generation of methane (CH_4), the transformation of our production systems has become a priority, with a particular focus on reducing their GHG emissions (IPCC, 2001; Sommer et al., 2009; FAO, 2010; Wattiaux et al., 2019; Amon et al., 2020).

Livestock excreta constitute an important source of GHGs, especially CH_4, which is the largest contributor to global warming from the dairy sector and one of the most relevant gases, with an impact 28 times higher than that of carbon dioxide (CO_2) over a hundred-year period (IPCC, 2013). According to the EU annual GHG inventory report from 2019, within EU28+ ISL, (28 EU- countries+ Iceland), manure management CH_4 emissions decreased considerably, by 20% or 10.4 Mt CO_2-eq, in the period 1990 to 2017; Germany was one of the countries with the largest decrease in emissions mainly due to the decline in the number of animals in the first half of the 1990s in eastern Germany. CH_4 emissions from manure management depend on manure composition, storage conditions and manure treatment. There is a wide range of variability in these factors, contributing to the amount of CH_4 from manure stores including category and breed of animals, housing system, manure removal system and method of manure treatment, as well as the type and amount of feeding (Sommer et al., 2007; Umweltbundesamt, 2014; Loyon et al., 2016; Purath et al., 2017; Habtewold et al., 2018; Grossi et al., 2019).

The storage time on farms also depends on the land application times, which depend on field crops, crop rotations, fertilizer requirements and on the vegetation period. These factors

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determine the storage capacity required, resulting in on-farm retention times of up to nine months. This stage of the manure management process releases considerable amounts of CH_4 (Petersen et al., 2013; Purath et al., 2017; Petersen, 2018). Based on the fact that dairy production residues are a crucial part of the GHG emissions problem (FAO, 2010), effective treatment and management options to reduce the emissions of these residues would transform a problem into an opportunity by applying treatment and management options to reduce emissions (Sommer et al., 2013; Zucchella & Previtali, 2019; Treichel et al., 2020). To improve the production chain and use all available resources within the systems, the integration and application of new technologies such as manure treatment by means of anaerobic digestion (AD) for biogas production is a valid option for reducing the GHG footprint of farms (Rotz & Hafner, 2011).

It is well known that the temperature and storage time of liquid manure play a decisive role in the production of CH_4 (Husted, 1994; Hill et al., 2001; Sommer et al., 2004, Sommer et al., 2007; Baral et al., 2018). In the last 30 years, CH_4 -related studies have focused on storage conditions, housing systems, manure mitigation and management strategies, CH_4 production and codigestion. The target of research has turned to CH_4 emissions from manure storage, with a special emphasis on the drivers of the emissions process, including the effects of temperature and seasonal influences (Amon et al., 2001; Clemens et al., 2006; Elsgaard et al., 2016; Masse et al., 2008; Petersen, 2018; Petersen et al., 2013; Sommer et al., 2004; Moset et al., 2019; Rodhe and Ascue, 2009). Baral et al. (2018) identified temperature and VS concentration as the most relevant factors for CH_4 production but also stated that additional factors such as the methanogenic potential during storage must be considered. Additionally, Im et al. (2020) investigated the effect of storage temperature on CH_4 emissions from cattle manure stored at different temperatures (15–35 °C) for 80 d. Their findings reveal that both variables are closely related, indicating the highest CH_4 emissions at a storage temperature of 35 °C, while emissions are decreased by almost half at temperatures of 20 °C.

The winter and summer time periods in the study presented in this paper were chosen based on the typical manure spreading times in arable regions in temperate climate zones. At the beginning of the vegetation period, when soil moisture content allows traffic with heavy machinery, manure is applied to grass, cereals and rapeseed fields. Thus, at the beginning of spring, manure stores are largely emptied. Dairy cattle farm crop rotations typically have major portions of corn, as corn silage is an important part of animal diets. As a consequence, in April and May (depending on the region), a second phase of manure application is initiated when the fields are prepared for corn seeding.

Even if the general influence of temperature on CH_4 emissions is known, an explanatory model for a better understanding of the influence of season, temperature and storage duration on CH_4 formation during liquid manure storage is still missing. For that reason, the objective of the present study was to evaluate the dynamic changes in CH_4 emissions from dairy cow liquid manure under summer and winter conditions and to identify the threshold temperature at which CH_4 production increases between the winter and summer seasons. The following hypothesis was tested:

H1: Slurry stored under cool winter conditions has the same methane production after temperature rise in summer as slurry stored only under warm summer conditions.

2. Material and methods

2.1. Barn and manure sampling

Manure samples were collected at the experimental farm for Animal Breeding and Husbandry, LVAT Groß Kreutz, Brandenburg, Germany. Lactating German Holstein-Friesian dairy cows were fed maize and grass silage, hay and concentrates. The housing was a free-stall dairy barn with 1/3 slatted-floor, 2/3 solid-floor with straw and lime as beeding materials and a manure scraper removal system that is conveyed twice an hour via a slatted element to an intermediate storage tank below the slats. Washing water from the milking systems is mixed with the manure under the barn. The liquid manure is stored for no more than 24 h in a collecting pit. It is automatically stirred 3 times a day and mixed before sampling. The manure is usually pumped to a biogas plant daily. The manure was removed from the collection pit with a 5-L ladle and put into 12 60 L plastic barrels in May (summer sample). The same procedure was conducted for 6 barrels of fresh manure in October (winter sample). The barrels were always transported immediately from LVAT Groß Kreutz to DBFZ (Deutsche Biomasseforschungszentrum gemeinnützige GmbH), Leipzig, Saxony, Germany, so that the manure storage test setup at DBFZ could be filled with the manure samples. The manure storage tests were started on the same day that the samples arrived.

2.2. Manure storage test (barrel)

To quantify the emissions during manure storage, a study was carried out for two time periods: one long period starting in the summer season (S0, S1, S2, S3, S4) and one short period starting in the winter season (W0, W1, W2). Both periods ended in February of the following year. For both periods, the samples were collected at LVAT Groß Kreutz and stored at DBFZ under ambient temperature conditions to simulate on-farm manure storage conditions from May 2018 to February 2019 and October 2018 to February 2019. During manure storage, storage units of two 120 L barrels were connected with a gas hose. Four storage units were 50% filled for the storage period starting in May, and two additional storage units were filled for the storage period starting in October. After filling, the barrels were sealed gas-tight. To investigate changes in the CH_4 emission potential of the manure over the storage time, composite samples of the pair of barrels were taken at every 10th week of storage. Sampling was conducted after 10 weeks, 20 weeks, 30 weeks and 40 weeks of storage (S0, S1, S2, S3, S4) for the manure collected from the barn in May and after 10 and 20 weeks (W0, W1, W2) of storage for the manure collected from the barn in October. For each sample drawing, one storage unit was opened, thoroughly mixed and discarded after sampling. Fig. 1 visualizes the timetable of sampling for the summer and winter manure samples, including manure storage tests (barrels) and the subsequent measurement of the CH_4 emission potential at 20 °C (eudiometer).

Each storage unit was equipped with a TG05/Model No. 5 drum-type gas meter (Dr.-Ing. RITTER Apparatebau GmbH & Co. KG, Bochum, Germany) for the daily reading of the gas volume for the first 3 weeks (except weekends); after the first 3 weeks, the gas volume was read weekly. The gas volumes were standardized (dry gas, 273.15 K, 1013.25 hPa) The humidity of the gas (formed in the manure storage test) was calculated taking account of the measured ambient temperature by means of the Antoine equation (Strach, 2020a). It was assumed, that the biogas temperature in the gas sampling lines (approximately 3 m long) between barrel and gas meter equaled ambient temperature. The composition of the gas was determined daily using infrared and chemical sensors in a biogas analyzer CH_4, CO_2 0–100% accuracy max. ± 3.0%; H_2S 0–5000 ppm; Biogas-Analysator BM2000, Ansyco GmbH, Karlsruhe, Germany) for the first 3 weeks (except weekends); after the first 3 weeks, the gas composition was determined weekly. The process of measurement of gas quality took a few minutes. During the period of gas quality measuring, the inlet and outlet of the Biogas-Analysator BM2000 were connected to the headspace of the bar-

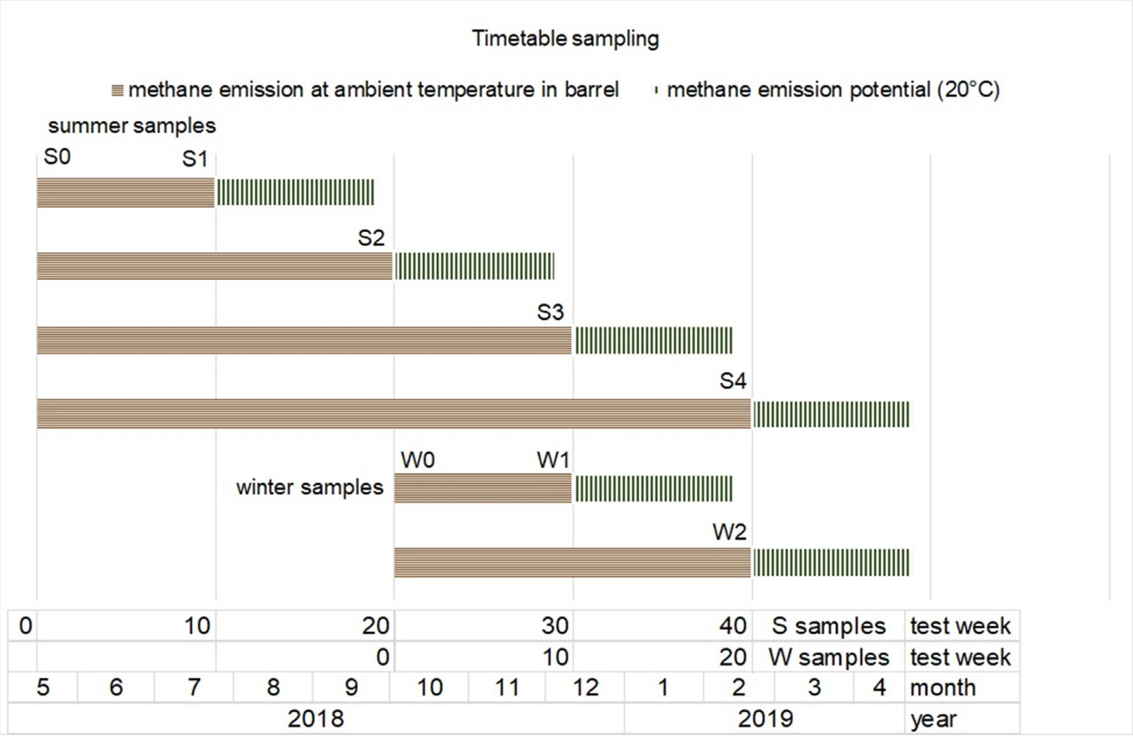

Fig. 1. Timetable for sampling for manure storage tests and methane emission potentials.

rels. The gas composition was corrected for the dilution within the headspace of the barrels. A temperature sensor (PT 100 Almemo, Ahlborn Mess- und Regelungstechnik GmbH, Holzkirchen, Germany) installed in the center of one barrel per storage unit was used for temperature measurements at 1 h intervals. All temperature sensors were connected to Almemo 2590-9 V5 data loggers (Ahlborn Mess- und Regelungstechnik GmbH, Holzkirchen, Germany). One additional temperature sensor measured the ambient temperature in the unheated and uninsulated storage room (garage) and was connected to a LT6-digi-GPRS data logger (A27083, 60.900.20/177, Umwelt- und Ingenieurtechnik GmbH, Dresden, Germany). The barrels were insulated with an aluminum laminated lamella mat made of 20 mm glass wool (SAINT-GOBAIN ISOVER G+H AG, Ludwigshafen, Germany) (Schumacher et al., 2020). The barrels were insulated to prevent or buffer frequent temperature fluctuations. It was assumed, that, the temperature fluctuations of the slurry during large-scale storage were also low due to the large volume of the slurry tanks. Fig. 2 shows the piping and instrumentation diagram of the manure storage test setups separately for the summer (Fig. 2a) and winter samples (Fig. 2b).

2.3. Methane emission potential at 20 °C (eudiometer)

To measure the CH_4 emission potential, fresh manure samples from the start of the experiments as well as the samples from every 10 weeks during the storage period (see Figs. 1 and 2) were placed into eudiometer batch tests without inoculum at a temperature of 20 °C for 60 days, following the method for the residual gas tests according to VDI 4630. 500 g of the manure samples to be tested were weighed into 1 L bottles, implemented in triplicate. The headspace of the filled bottles was then flushed with N_2 to expel excess oxygen from the system and create anaerobic test conditions. The manure storage test in barrels should give an insight into the effects of manure aging during the seasons and of fluctuating temperatures on CH_4 formation under pilot scale condictions mimicing commercial farm conditions. A saturated, acidified saline solution of the following composition was used as barrier fluid within the eudiometer:

- 150 ml sulfuric acid (conc.)
- 1000 g sodium sulfate decahydrate
- 5000 ml $H_2O_{dest.}$
- 10 ml methyl orange (0.1% in 20% alcoholic solution) was used as a pH indicator.

After being flushed with N_2, the bottles were connected to glass eudiometer tubes (greased ground joint), and the eudiometers were reset to zero. Gas was released via the gas valve at the upper end of the eudiometer tube until the pressure within the system had adjusted to the surrounding atmospheric pressure. The zero position was noted as the initial value in the test protocol, and the test was started in a water bath (incubation temperature of 20 ± 2 °C). Over the course of the test, the daily gas quantity produced was determined from the filling levels of the eudiometers. At the time of reading, the temperature and air pressure were documented separately to standardize the gas volumes. When a level of 250 ml of formed gas volume was reached, the eudiometers were reset to zero by opening the gas valve. The gas volumes were standardized (dry gas, 273.15 K, 1013.25 hPa). The humidity of the gas (formed in the CH_4 emission potential test at 20 °C) was calculated taking account of the measured room temperature by means of the Antoine equation (Strach, 2020a). The gas composition of the discharged biogas was analyzed by means of a biogas monitor equipped with infrared and chemical sensors (CH_4, CO_2, 0–100% accuracy ±0.5%; H_2S range 0–10000 ppm; Biogas-Analysator BM5000, Ansyco GmbH, Karlsruhe, Germany). The gas composition was corrected for dilution within the headspace volume of the bottles according to VDI guideline 4630.

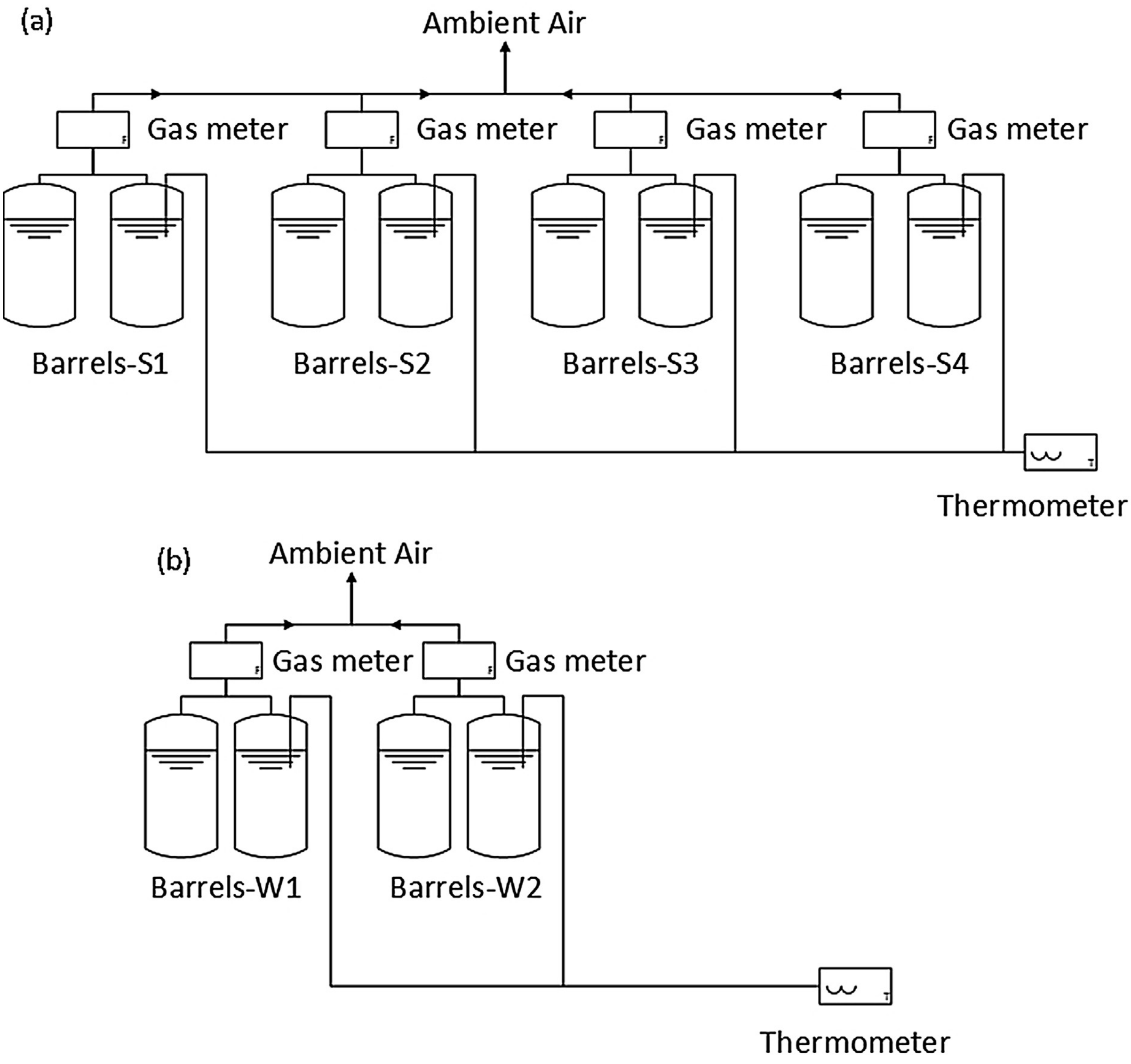

Fig. 2. Piping and instrumentation diagrams for summer (a) and winter (b) seasons.

2.4. Manure analysis

For the manure samples, pH, dry matter (DM), and volatile solids (VS) analyses were carried out.

The DM content was determined by oven-drying in a drying cabinet at 105 °C according to standard procedures (DBFZ, 2016). Subsequently, the samples were calcined in the muffle furnace for 30 min at 220 °C and then for 2 h at 550 °C for analyses of VS (Strach, 2020b). The pH value of the manure samples was measured using a measuring electrode Sentix 41 and pH device 3310 (together with an accuracy of ±0.3, WTW Wissenschaftlich-Technische Werkstätten GmbH, Weilheim, Germany).

2.5. Data analysis and modeling

In the eudiometer trials, the CH_4 production had to be adjusted for the mass loss of manure in the barrels during storage to make the various trials comparable on the base of initial mass (SO, WO) of VS. For this purpose, the mass at the start of the storage experiment was multiplied by the DM content and the organic DM content of the samples. The result was then divided by the mass at the end of storage multiplied by the DM content and the organic DM content of the samples at the end of the storage duration. The initial VS (VS_i) could be used as long as the analyses only refer to the storage experiments. During storage the VS content changes, and the different storage durations lead to different initial VS contents for the post-storage emission potential trials. A correction was necessary to be able to compare the emissions during storage with the remaining emission potential after storage. This resulted in correction factors of 0.77, 0.63, 0.66, and 0.61 for 10, 20, 30, and 40 weeks of storage starting in summer, respectively, as well as correction factors of 0.78 and 0.86 for 10 and 20 weeks of storage starting in winter, respectively. The remaining gas potential between the different storage variants S0-S4 and W0-W2 was compared with a one-way ANOVA with heterogeneous residuals between the storage variants. Post hoc multiple pairwise comparisons were then performed using a simulation approach for adjustment of p-values for multiple testing.

Since it could not be managed to measure gas production at the same time every day, the methane measurements were not evenly spaced in time. Therefore the modified Gompertz model (Zwietering et al., 1990) was used to estimate the parameters for the methane production function as prerequisites for further analyses. This allowed showing the evenly spaced daily methane production that was derived from the actual measurements in addition to the cumulative methane production. The estimated daily production values allowed to get daily fluxes despite not having evenly spaced daily gas production measurements that came in useful for the analyses relating to the daily ambient and manure temperatures. Originally developed to describe bacterial growth, this specific function is occasionally applied to describe cumulative gas production during discontinuous anaerobic degradation in the presence of a pronounced lag phase (Weinrich et al., 2020).

$$S(t) = S_{res}.e^{-e^{\left(\frac{Rm.e}{S_{res}}\right).(\lambda - t)+1}}$$

To depict the experimental results of the manure storage experiments, the total residual CH_4 potential S_{res} (mL g VS^{-1}), the maximum CH_4 production rate Rm (mL g VS^{-1} d^{-1}) and the specific lag phase duration λ (d) must be determined. The model implementations as well as the numeric parameter estimation (Nelder-Mead algorithm) were realized in the software environment MATLAB (The MathWorks, Inc., USA) by minimizing the squared differences between the measured and simulated cumulative CH_4 yields.

A cluster analysis and a canonical discriminant analysis were used to determine a temperature threshold for CH_4 emissions. In the first step, a cluster analysis was conducted with the daily average manure temperature and the daily CH_4 emissions. This created two clusters with (i) low temperature and low CH_4 emissions, and (ii) higher temperatures with predominantly medium to high CH_4 emissions. In a second step, the clustered data were put into a canonical discriminant analysis to create property functions for classification of data into the two clusters based on manure temperature and CH_4 emission. A data vector belongs to the cluster that produces a higher result when the values are plugged in the equation.

3. Results and discussion

3.1. Manure characteristics

The characteristics of the untreated manure are shown in Table 1. The % of volatile solids of the dry matter ($VS_{\%\ DM}$) and the dry matter % of the fresh matter ($DM_{\%FM}$) in the fresh liquid manure were determined. For the summer experiment, the values of $VS_{\%DM}$ are close to the data reported by Rodhe et al. (2009) and Le Riche et al. (2016), while the values for the dry matter ($DM_{\%FM}$), coincide with date reported by Petersen et al. (2012). The difference in dry matter content between the periods can be related to water consumption, which is higher in summer than in winter due to high temperatures, thus changing the consistency of the stored manure as a result of the increase in urine production (Krauß et al., 2016). The amount of water used in the dairy systems did not differ between winter and summer.

As mentioned by Petersen et al. (2016), manure storage systems are never fully emptied, indicating that the material remaining in the storage system functions as the inoculum for fresh material, triggering CH_4 production at an early stage. In the present study, no inoculum was present in the storage at filling. The physical properties of the fresh material are very important. Measurements of the current investigation are similar with the data reported in the literature, regarding liquid manure properties (Masse et al., 2008; Petersen et al., 2012; Sommer et al., 2004; Liu et al., 2018; Masse et al., 2003; Rodhe and Ascue, 2009; Sommer et al., 2009; Willén et al., 2016).

The concentrations of DM and VS were higher in the manure for the winter storage experiment, than for summer storage, this can be due to the concentration of excretion of manure with higher dry matter and less urine excretion in the winter period. Similar data was reported by Masse et al. (2003, 2008) illustrating the importance of the relationship between the diet composition (crude protein, dry matter, and neutral detergent fiber inter alia) and CH_4 emissions from manure.

Taking into account that temperature is an important variable in CH_4 production, we proceeded to monitor the temperature of the liquid manure and the ambient environment. In this way, we can demostrate the effects of seasonal temperature changes on CH_4 productivity. Hence, the emissions data obtained from stored manure can reflect emissions under natural conditions.

3.2. Methane emissions from stored liquid manure subjected to ambient seasonal temperatures

During this study, CH_4 emissions from stored liquid manure and their relationship to seasonal temperature changes were investigated. For this purpose, manure and ambient temperatures were monitored simultaneously in order to explore a correlation between CH_4 emissions and seasonal temperatures. The outcome of our experiments showed that the CH_4 emissions from manure stored were higher in summer in comparison to those from the winter trials, which is in line with the findings of other authors (Kupper et al., 2020; Petersen et al., 2013; Sommer et al., 2013; Sommer, 2007). The CH_4 production started after approximately one month (Fig. 3 summer samples), reaching values of 0.061 kg CH_4 kg^{-1} VS at the end of the 10 weeks and achieving a value of 0.131 kg CH4 kg^{-1} VS at the end of the 20 weeks. The highest level of emissions was observed at the end of the 30 weeks of retention with values of 0.148 kg CH_4 kg^{-1} VS. After the 30 weeks of retention, CH_4 emissions diminished until no CH_4 production was observed.

Fig. 3 shows the course of the mean daily CH_4 production rates for the whole storage period. Clearly, the CH_4 formation level corresponds very closely to the temperature curves. The CH_4 emissions reduction for the summer trials at the end of the experiment can be explained by multiple factors. One of these factors is the low temperatures at the end of the summer season; as illustrated in Fig. 3, the dependencies between the behavior of CH_4 production and temperature (ambient as well as manure) can clearly be observed. A decrease in temperature was accompanied by a decrease in CH_4 production to the extent that, when the temperature dropped below 5 °C, CH_4 production was absent or non-detectable. This behavior occurred towards the end of the experiment (between weeks 30 and 40).

Table 1
Characteristics of the manure samples for the summer and winter experiment.

Characteristics	Summer experiment				Winter experiment			
	Means	Std	Min	Max	Means	Std	Min	Max
pH	7.33	0.15	7.11	7.45	6.43	0.09	6.37	6.54
$DM_{\%FM}$	7.38	1.34	6.33	9.52	11.58	1.36	10.22	12.93
$VS_{\%DM}$	73.03	1.57	71.73	75.59	76.84	0.85	75.89	77.53

$DM_{\%\ FM}$ = Dry matter% of the fresh matter; $VS_{\%DM}$ = volatile solids of the dry matter

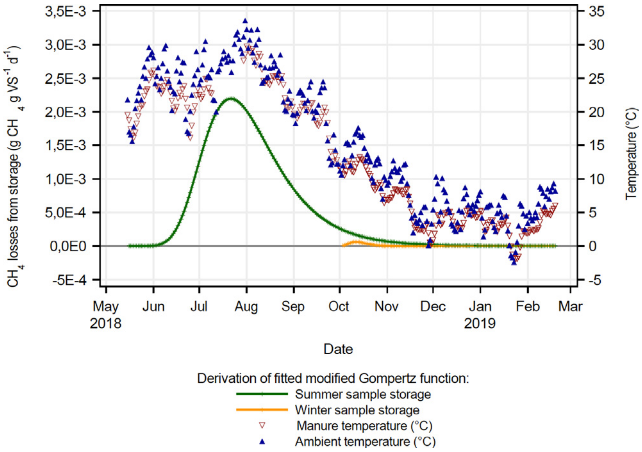

Fig. 3. Methane emissions from dairy liquid manure in the summer and winter seasons.

In the case of the winter trials, the CH_4 emissions were low over the duration of the experiment (0.0011 kg CH_4 kg^{-1} VS); suggesting that in the winter season, the emissions from manure stored on farms will likely be low. The low manure emissions can be related to the seasonally cold temperatures that prevent the start of the methanogenesis process, which optimally takes place at approximately 20 °C and causes the release of CH_4 (Husted, 1994; Sommer et al., 2004; Elsgaard et al., 2016). Microbial communities play an important role in methane formation. Some strains responsible for methane production are subject to different temperature levels. According to Im et al. (2020), methanogenic activity is inhibited by storing cattle manure at low temperatures. At low temperatures, the Methanolobus Psychrophilus strain increases its presence, Methanocullens spp and Methanosarcine spp are the major contributors to methanogenic activity, but it is the hydrogenotrophic species that dominate methane production (Barret et al., 2013; Im et al., 2020).

Our findings are similar to previous data reported in the literature; for example, Husted (1994) found values of 0.008 kg CH_4 kg^{-1} VS for annual emissions at 11.2 °C, while Sommer & Petersen (2000) found, over a short storage time of 9–12 weeks in the summer season, values of 0.001 kg CH_4 kg^{-1} VS. Rodhe & Ascue (2009) found 0.007 CH_4 kg^{-1} VS over 210 days in the summer and 0.004 kg CH_4 kg^{-1} VS for winter conditions with a storage period of 157 days, Petersen et al. (2016) reported 0.011 kg CH_4 kg^{-1} VS from slurry pits with retention times of 15 and 30 days. This value is lower than the value reported in our study, because the retention time is also shorter. Furthermore, Moset et al. (2019) published CH_4 emissions data related to temperature (20 °C − 35 °C) with a storage period of one year in which low temperatures and low CH_4 emissions are closely related. Amon et al. (2006), reported fluctuations over the course of one year in the net total CH_4 emissions during storage, with 4.046 kg CH_4 kg^{-1} VS under warm conditions (slurry temperature 17 °C for a storage time of 80 days). Similarly, Clemens et al. (2006) report substantially more CH_4 being emitted under summer conditions than under winter conditions and state that CH_4 production is temperature-sensitive and therefore is also susceptible to seasonal fluctuations. Meteorological conditions are summarized by Kupper et al. (2020), where temperature and the level of emission were related. Thiss assumption has been addressed before by Sommer et al. (2013). In their study, not only the air temperature but also the wind speed were related to the increase of GHG emissions including CH_4.

3.3. Effect of storage time on CH_4 emissions

The cumulative CH_4 emissions from the storage of liquid dairy cow manure during summer and winter were estimated by applying a modified Gompertz function. Fig. 4 shows the respective CH_4 losses for the summer and winter storage. During the summer season, a more intensive degradation of the volatile solids was observed, compared to that in the winter season. Summer manure had considerably lower dry matter content and was more dilute than winter manure, however, there was a considerable lag phase in the summer season before CH_4 production started. According to Masse et al. (2003) and Masse et al. (2008), the lag phase and the reduced methane production can be related to the dry matter content of manure, where CH_4 emissions from high dry matter manure are lower in comparison to dilute manure. Rennie et al. (2018) relate the lag phase to the design of the manure storage. The model parameters are shown in Table 2.

The respective CH_4 loss potentials for both experiments are shown in Fig. 4. CH_4 emissions from summer storage started approximately 4 weeks after the start; those from winter storage began directly after the start of the storage period. In the case of the summer trials, the highest emissions were reached between 15 and 25 weeks, and the cumulative gas volumes remained unchanged until the end of the experiment. This coincides with the daily CH_4 production rates displayed in Fig. 3. In the case of manure stored during the winter season, the CH_4 emissions were low and constant but did not show considerable production. Given the low temperatures, which reduced the intensity of the methanogenesis process, the VS in the raw materials are preserved and can be used later when conditions are favorable to activate the CH_4 production process; however, over the entire storage period, there were no substantial CH_4 emissions (Fig. 4). (Møller et al., 2004), found a loss of CH_4 from cattle manure after 30 days of storage. Likewise, Moset et al. (2019), found 1 L CH_4 kg^{-1} FM CH_4 emissions from stored manure at 20 °C.

In this study, we have demonstrated that the length of storage is a decisive factor in determining CH_4 emissions from slurry stores, especially during summer storage conditions when temperatures are above 15 °C. Even a short storage period can result in the emission of substantial amounts of CH_4 when the temperatures are above 15 °C, while longer storage periods under cold winter conditions emit little CH_4. These findings can be useful for designing CH_4 mitigation strategies such as long winter storage, short summer storage, cooling of slurry in the barn for ammonia and CH_4 mitiga-

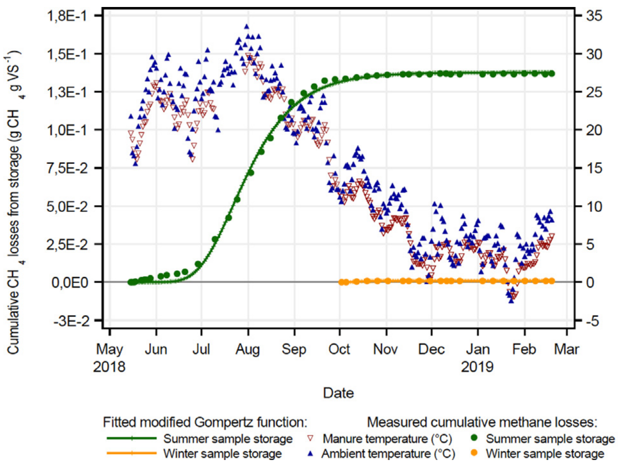

Fig. 4. Cumulative methane emissions from liquid manure stored over the summer and winter seasons.

Table 2
Estimated parameters from the modified Gompertz function of dairy cattle liquid manure from the winter and summer seasons.

Parameter	S (mL g^{-1} VS)(ml/g VS)	Rmax (mL g^{-1} VS d^{-1})	λ (d)	R2 (-)
Summer sample storage	191.116	3.049	45.056	1
Winter sample storage	1.295	0.086	4.460	0.99

S: the total residual methane emissions (mL g VS); Rm: the maximum methane emission rate (mL g^{-1}-VS d^{-1}); λ: the specific lag time (days).

tion. These strategies have the benefit of also supporting good agricultural practices for crop production in sustainable crop rotations that make optimum use of manure as a valuable fertilizer (Amon et al., 2006, 2020; Masse et al., 2008; Baral et al., 2018; Petersen, 2018).

3.4. Effects of dairy cattle liquid manure aging on the methane emission potential (20 °C)

To determine the effect of liquid manure aging on CH_4 emissions and to verify the results found in the previous experiment, subsamples were taken at a 10-week storage interval as shown in Fig. 1. The subsamples were stored at 20 °C for 60 days in a batch test without inoculum. The CH_4 production of each sample was measured. Individual CH_4 yields in Fig. 5 (green bars) show the CH_4 emission potential at 20 °C after the different storage periods (0, 10, 20, 30 and 40 weeks) (red bars). The findings obtained from the summer subsamples demonstrate that after a 10-week storage period, the potential for CH_4 production was the highest, at 0.1163 g CH_4 g^{-1} VS, but decreased gradually to 0.0326 g CH_4 g^{-1} VS at week 20, to 0.0160 g CH_4 g^{-1} VS at week 30, and finally to 0.0091 g CH_4 g^{-1} VS at week 40. This means that from week 20, there is a remaining potential of 28% compared to week 10, approximately 14% in week 30 and approximately 8% in week 40 of storage. The longer the retention period, the lower the potential for daily CH_4 emissions, but the higher the accumulated CH_4 emissions for the storage period. On the other hand, the results from the winter subsample showed a strong lag phase in which CH_4 production could not be activated during the 60 days of the experiment even though the temperature was a constant 20 °C. A lag phase of 250 days at 20 °C was reported by Masse et al. (2008) which was affected by the dry matter of manure. Also Rennie et al. (2018) reported a lag phase which they refer to the design of the storage facilities. The difference in methanogenesis processes between summer and winter is evident in this study and was likely influenced by the composition of the manure. More diluted manure produced more CH_4 than manure with a higher dry matter content. Manure dilution during the summer period can be related to the cow‘s increased water intake during the warm summer period (Masse et al., 2008; Krauß et al., 2016). We deduce that the low CH_4 production in the winter period was influenced by a multitude of factors including manure composition and low temperatures. Our initial hypothesis, that permanently low temperatures during the winter months do not inhibit long-term methanogenic processes was proven false. We showed that even under temperature conditions that were favorable for methanogenesis (20 °C eudiometer) CH_4 formation did not start again after slurry had been stored under cool winter conditions.

During storage, the manure temperature is influenced by a number of factors, including the climate and geographical location, daily/seasonal variations and the storage system. Arrus et al. (2006) and Blackwell et al. (2003) provided evidence regarding manure storage and its effect on CH_4 emissions; the findings suggest that the storage system design (aboveground systems and underground systems) has a strong influence, depending on the depth at which the manure is stored and the temperature range. In the same way, Rennie et al. (2018) reported that the temperature of manure is also influenced by storage design and management practices. Manure produced in summer and stored for a long time (up to 30 weeks) emits more CH_4 than manure produced and stored in winter, due to the fact that the methanogenesis activity is low at low ambient temperatures. Previous studies have found that the storage of liquid manure for long periods under warm conditions contributes to a greater share of the GHG emissions from dairy manure management, while the share from storage at low temperatures (below 10 °C) during winter is lower

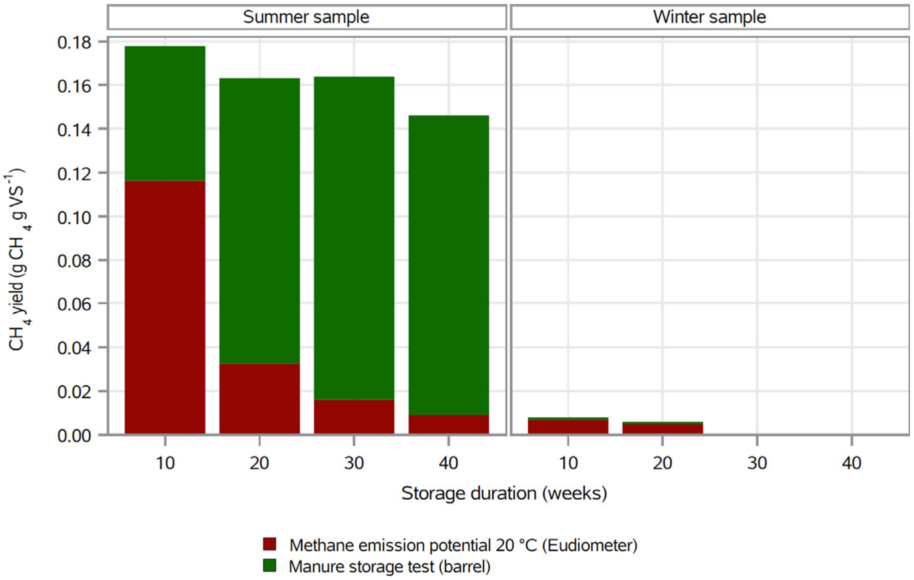

Fig. 5. Comparison of methane emissions at ambient temperature at various durations and their corresponding methane emission potential at 20 °C for 60 days.

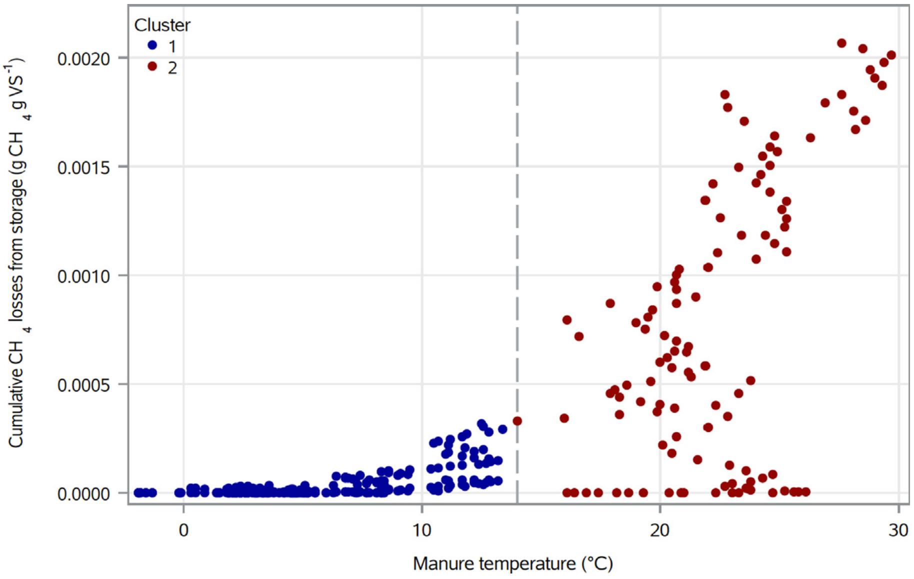

Fig. 6. Temperature threshold and methane emissions from liquid manure stored.

(Rodhe et al., 2009; Masse et al., 2003; Sommer, 2007). We confirmed these findings an added the important new finding, that CH_4 production stays at a low level after a cool storage period even if temperatures rise again.

The result of the cluster analysis is shown in Fig. 6. The follow-up discriminant analysis resulted in the following equations for the cluster 1 (low temperature) and the cluster 2 (mid-to-high temperature).

$$\begin{aligned} Cluster\ \ 1 &= -1.21452 + 0.46638\ \ manure\ \ temperature \\ &\quad - 1515\ \ methane\ \ emissions \end{aligned}$$

$$\begin{aligned} Cluster2 &= -19.46764 + 1.74503\ \ manure\ \ temperature \\ &\quad - 118.11757\ \ methane\ \ emissions \end{aligned}$$

If Cluster 1 > Cluster 2, then the data point is below the temperature threshold where CH_4 emissions stay low even when the manure is subsequently exposed to higher temperatures (20 °C). For the highest CH_4 emissions found in cluster 1 (0.000317174 g CH_4 g VS^{-1}) the temperature threshold is at 13.93 °C, given by the point where Cluster 1 = Cluster 2.

Our experiments demonstrated that the potential for CH_4 emissions from storage is markedly influenced by temperature. We identified the threshold temperature at which CH_4 production increases and under which CH_4 emissions are low. This factor is important and must be considered in order to accurately estimate and also limit CH_4 emissions from slurry stores. The highest levels of CH_4 production occurred during the first weeks of storage. The shorter the manure storage time is, the less CH_4 is released into the atmosphere. For the winter period, the emissions from stored manure are low because of the low temperatures. In general, this outline can contribute to improve the abatement strategies and their implication for national GHG inventories, according to the IPCC, 2019 refinement to the 2006 IPPC Guidelines.

4. Conclusion

In this paper, relevant findings about CH_4 emissions from liquid manure storage in the summer and winter season are presented. Our results show that if the temperature falls below a threshold value over a certain period of time, CH_4 production does not increase even when the temperature rises again. CH_4 production during winter, with temperatures below 13.93 °C, was consistently low. Even when the manure was subsequently stored at 20 °C, CH_4 emissions did not increase after the cold winter storage. These results show the complexity of analyzing the influence of variables such as temperature, storage duration and season on CH_4 emissions. Under summer conditions, CH_4 emissions from slurry stores without inoculum started after a month at a temperature of 20 °C, with a maximum production on the 100th day of storage and a subsequent decrease until day 150, when the CH_4 production was almost negligible. Consequently, it is necessary to build on this work and design additional detailed experiments to gain more in-depth understanding on the relationships of temperature, temperature sums, storage length and climate season and CH_4 emissions from slurry stores. These experiments shall also include microbiological analysis to identify the microbes that contribute to methane formation. This type of information will be helpful in estimating emissions, designing emission mitigation options and generating more accurate data for GHG inventories of livestock production. Improvement of inventory reporting plays a key role in determining relevant abatement strategies and their implications for national inventories.

Declaration of Competing Interest

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

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