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Research Paper

Assessment of the biochemical methane potential of in-house and outdoor stored pig and dairy cow manure by evaluating chemical composition and storage conditions

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ABSTRACT

Biogas production is a suitable option for producing energy from dairy and pig manure types. During manure storage, organic matter degradation results in methane emissions decreasing the potential biogas yield. The present research advances the understanding of the biochemical methane potential (BMP) and the chemical characteristics of manure collected year-round from sequential stages of the liquid manure management chain of commercial dairy cow and pig farms. To this end, manure samples from six livestock farms in Germany were analyzed. The results showed that changes in chemical composition during storage led to a 20.5% decrease in the BMP of dairy manure from the barn to outdoor storage. For fattening pig manure samples, there was a 39.5% decrease in the BMP from intermediate to outdoor storage. An analysis of BMP according to manure age showed that pig manure degrades faster than dairy manure; the importance of promptly feeding manure to the biogas plant in order to avoid significant CH_4 emission losses and reduction in energy producing capacity was highlighted. The best BMP predictors for dairy manure were the contents of dry matter, volatile solids and lignin, whereas best BMP predictors for pig manure were dry matter and volatile fatty acid (VFA) content. Prediction models performed well for samples from outdoor storages; refinements for predicting BMP of less aged samples presenting lower chemical variability would be necessary.

1. Introduction

In 2018, methane in the atmosphere reached levels 2.6 times higher than the preindustrial level (Saunois et al., 2020). The Intergovernmental Panel on Climate Change (IPCC)'s sixth assessment report states that atmospheric CH_4 caused a 0.5 °C global temperature increase until 2019 compared to 1850–1900 levels (IPCC, 2021). Anthropogenic CH_4 contributes 0.97 Wm^{-2} to planetary heat storage, while CO_2 contributes 1.68 Wm^{-2} (Stocker, 2014). CH_4, with a nine-year atmospheric lifetime (Prather et al., 2012), has a GWP 79.7 times higher than CO_2 over 20 years time scale and 27 times higher over 100 years (IPCC, 2021). In addition, CH_4 emissions correspond to only 3.9% w/w of the yearly CO_2 emissions (Saunois et al., 2020). Reducing anthropogenic CH_4 emissions can lower their concentrations and global warming impact, which meets IPCC near-term strategy urging significant reductions by 2030–2040. Leveraging this strategy, the European Union (EU) aims to cut CH_4 emissions by 50% from 2020 to 2050, reducing global temperature change by 0.18 °C until 2050 (EU, 2020).

Primary anthropogenic CH_4 sources include agriculture (40%; 32% from manure and enteric fermentation, 8% from rice cultivation), fossil fuels (35%), and waste (20%) (UNEP-CCAC, 2021). A recent assessment has shown that emissions from enteric fermentation and manure management increased their contributions from 102 $TgCH_4yr^{-1}$ in 2000–2006 to 115 $TgCH_4yr^{-1}$ in 2017[1] (Jackson et al., 2020). Meat production increased 46% from 236.4 million tons in 2000 to 346.1 million tons in 2018, with pig meat at 35% (Ritchie & Roser, 2017); 690 million tons of dairy milk (81% of global production) were made in 2019 (OECD et al., 2020). Therefore, changes in the livestock sector are needed to achieve emission reductions consistent with temperature increases below the 2 °C targets proposed by the Paris Agreement.

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[1] Tg means teragrams a unit of mass equivalent to one trillion grams.

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A range of emission mitigation technologies is available for manure management systems that may, additionally, provide extra revenue streams for farmers, such as their applications as fertilizer and for biogas generation. The biogas resulting from manure is a renewable energy source; the digestate that remains after anaerobic digestion is usable as a valuable fertilizer. According to the EU's long-term decarbonization strategy, the annual production of biogas should increase four or five times by 2050 relative to the 2020 levels. Cooperation among farmers and communities will be essential for maximizing the potential of biogas production from diffuse sources in agriculture and for reaching the proposed target (EU, 2020).

Manure management systems (MMSs) are designed for storing and transporting large volumes of biomass types from animal barns to outdoor storages, and from there to the fields. Manure storage is needed in order to apply manure during vegetation to create a cleaner and healthier environment for livestock and to meet regulations regarding nitrogen losses in agriculture (EEC, 1991). According to the German National Inventory, liquid manure (slurry) systems were used on 52.37% of dairy farms and 77.79% of pig farms in 2019 (German Environment Agency, 2021). Anaerobic degradation is a sequence of biochemical processes that lead to CH_4 production during manure storage (Amon et al., 2007). The sequence is composed of hydrolysis, acidogenic fermentation, hydrogen-producing acetogenesis, and methanogenesis. The strictly anaerobic process leads to the degradation of organic matter and the production of mainly CH_4 and CO_2. These processes are accelerated in anaerobic digestion (AD), where conditions for anaerobic degradation are optimised.

Chemical composition of in organic matter plays vital roles in potential CH_4 production, and the contents of the different components may be used that predict the potential of feedstock for biogas production. Previous studies have highlighted the importance of the chemical composition of manure to biogas production. Amon et al. (2007) verified that significant protein content in dairy manure is associated with higher CH_4 yields during anaerobic digestion than those of samples with less protein. In comparison, lignin content tends to reduce the specific CH_4 yield. However, predictions of CH_4 production potential of manure depends on the anaerobic degradation occurring before treatment, as determined by animal and manure management practices (Triolo et al., 2011), as well as storage conditions (Clemens et al., 2006; Wood et al., 2012).

Dairy manure has a lower content of biodegradable carbon than pig manure, reducing the biochemical methane potential (BMP). In a study by Triolo et al. (2011), the differences between pig and dairy cow manure were evident due to the higher content of organic nitrogen in dairy manure than in pig manure. In contrast, in pig manure, most nitrogen is in the form of total ammonia nitrogen (TAN). The lignocellulose contents were higher in cow manure than in pig manure, mainly due to the differences in their diets. The studies by Triolo et al. (2011) and Amon et al. (2007) presented mathematical models aimed at predicting the BMP from the manure chemical composition.

In a recent review, Raposo et al. (2020) presented different mathematical models to predict BMPs from different feedstock (energy crops, food and crop wastes, municipal solid waste, and manure). The researchers verified that proteins and lipids positively affect the CH_4 potential, whereas nonstructural carbohydrates present different impacts on BMP, depending on the feedstock. Regarding fibers, anaerobic digestion can degrade a limited fraction of lignin. Usually, hemicellulose positively impacts BMP, differing from cellulose, which commonly harms CH_4 potential due to the effect of crystallinity and the combined effect with lignin.

To our knowledge, this study is the first to assess the BMP and the chemical characteristics of manure collected year-round from sequential stages of the liquid manure management chain of commercial dairy cow and fattening pig farms, and to model the BMP according to the manure management stages and the chemical composition. Accurately estimating the CH_4 potential from animal manure is critical for designing successful climate change mitigation measures. Although many feedstocks have been studied regarding the BMP, there is a need for documenting the effect of manure storage conditions on CH_4 potentials and chemical composition. In addition, understanding the progressive degradation of organic matter along the manure management chain is relevant for the potential mitigation of the environmental impacts of livestock systems. The aims of this work are (1) to characterize the chemical compositions and BMPs of liquid dairy cow and fattening pig manure samples from different stages on the manure management chain (MMC) and (2) to model BMP according to the manure composition along the MMC of cattle and pig slurry systems.

2. Materials and methods

2.1. Dairy cow manure and fattening pig manure

Dairy cow manure samples were collected form four farms, and fattening pig manure samples were collected from two farms. All farms offered the possibility to collect manure samples from the barn and from outdoor facilities. Table 1 shows the main characteristics of the dairy and pig farms that contributed to this study, including information about the herd, feeding, housing and storage, and manure management are available. The manure management systems of the farms exhibit typical traits for Germany, as liquid manure systems are predominant on dairy cattle and pig farms: manure is typically stored inside the barn and moved to an outside store at regular intervals (German Environment Agency, 2021). Three dairy farms are located in Brandenburg (DE01, DE02 and DE04), while one is in Lower Saxony (DE03). They all have Friesland-Holstein cows stabled in freestall barns. This breed and this housing system are common in Germany (59% and 81% of the dairy farms, respectively) (Tergast et al., 2022). Regarding the fattening pig farms (DE05 and DE06) they are all located in Brandenburg and they have full or partial slatted floors as the vast majority of German pig farms, which is consistent with slurry management (Rohlmann C, 2022).

For both animal categories the sample collection was performed in different positions along the MMC. For dairy farms, barn samples were collected from the walking alley while operating scrapers, which allowed the collection of feces and urine from the walking alley. Samples from the pumping pit in the dairy farms were collected using a 1-m long sampling device (Stainless Steel Zone Sampler, Hartwig Instruments BV, Rotterdam, The Netherlands). Samples were collected from different depths in the pit and mixed before packing. The same instrument was used for collection of samples from outdoor storage. Since the outdoor storage tanks were high and wide, samples from the top or bottom layers were collected depending on the level of slurry in the tank at the visiting time.

Samples collected in pig farms varied according to the design of the manure management system. On farm DE05, the manure was stored under a barn in pits with a pull-plug system that were emptied approximately every three months; samples were collected using a bucket positioned in the outlet stream every minute during discharge to outdoor storage. On farm DE06, the samples were collected under the slatted floor using a pump (Unistartk/K 2001-B, ZUWA-Zumpe GmbH, Laufen, Germany). Pig manure samples were collected from outdoor storage by following the same procedure as that for cow manure. Samples collected under the slatted floor of pig farms are referred to as barn samples, and samples collected from the pumping pit in pig farms are referred to as intermediate-storage samples.

At every spot, 5-liter samples were collected. Immediately after collection, the samples were stirred, placed in cooling boxes and transported to the biogas laboratory at the Leibniz Institute for Agricultural Engineering and Bioeconomy in Potsdam, Germany. In the laboratory, 1-L subsamples were stored frozen at −18 °C for physical–chemical analyses and BMP tests.

Table 1

Characteristics of the dairy cow and fattening pig farms where manure samples were collected.

Dairy cow farms						Fattening pig farms			
	Units						Units		
Farm ID	[-]	DE01	DE02	DE03	DE04	Farm ID	[-]	DE05	DE06
Herd Info									
Animal breed	[-]	Friesland–Holstein	Friesland–Holstein	Friesland–Holstein	Friesland–Holstein	Annual production	pigs/ year	500	1000
Number of milking cows in barn	head	205	380	112	350	Average weight at delivery	kg	120	130
Feeding									
Grass silage	%FM	4	29.3	37	50	Dry or wet feeding	[-]	Dry	Dry
Maize products	%FM	61	36.1	41	27	Feed ration	[-]	Rye, triticale, barley, soybean meal, rapeseed meal, peas, and sunflower meal	Barley/husked (35%), rye (20.6%), wheat (31%), soybean meal (9.3%), and soybean hulls (4.1%)
Roughage and byproducts	%FM	25	9.1	4	10				
Concentrates and minerals	%FM	0	8.3	17	6				
Other	%FM	10	17.2	–	7				
Housing characteristics									
Barn dimensions (length × width)	m	38.8 × 17.65, 35 × 71.5	19 × 75, 19 × 33, 25 × 60	42 × 53	23 × 75, 43 × 75	Barn dimensions (length × width)	M	17 × 64 + 17 × 64	76 × 16
Bedding type in the lying boxes	[-]	Straw and lime	Barley straw	no	Straw (barley/rye) and lime (2%)	Bedding type in the lying boxes	%	50	100
Manure collection system	[-]	Pumping pit and scrapers	Pumping pit, ring channels and scrapers	Pumping pit, ring channels and scrapers	Pumping pit and scrapers	Manure collection system	[-]	Pit	Pit
Manure management	[-]	Stored before field application	Stored before field application	Stored before field application	Stored before field application	Manure management	[-]	Stored and field applied	Stored and field applied
Outdoor Storage									
Manure storage conditions	[-]	Liquid with crust	Liquid with tent and solid crust	Liquid with crust	Liquid with crust	Manure storage conditions	[-]	Liquid with crust (clay additive)	Liquid with crust
Storage type	[-]	Glassed steel	Glassed steel	Concrete	Metal and concrete	Storage type	[-]	Metal	Concrete
Storage period	[-]	November to April	November to April	November to April	November to May	Storage period	[-]	November to April	November to April
Average diameter	m	24	25.7	33	25.1 and 23.5	Average diameter	m	14.6	15
Height	m	7	4.2	6	5,	Height	m	6	5

2.2. Physical–chemical analysis

Electrical conductivity, pH, and sample temperature were measured immediately after collection with an electrical conductivity meter, pH meter (Multiline P3 pH/LH, WTW, Weilheim, Germany) and thermometer (Hamster ET2, Elpro, Buchs, Switzerland), respectively. The pH value was obtained by immersing the electrode (Sen Tix 81, WTW, Weilheim, Germany) (DIN38404). The frozen samples were gently defrosted before the chemical analysis and batch anaerobic digestion tests occurred. To determine the dry matter (DM) content, samples were dried at 105 °C to a constant weight, followed by dry combustion at 550 °C to determine the ash and volatile solids (VS) content in a muffle furnace (CWF 1100, Carbolite Gero GmbH & Co. KG, Neuhausen, BW, Germany) (VDLUFA, 2006). The contents of volatile fatty acids (VFAs) (C_2, C_3, C_4, C_5, and C_6) and alcohols (C_1, C_2, C_3, and C_4) were verified by cold-water extraction and gas chromatography (Agilent Technologies Inc., Santa Clara, CA, USA), including a PERMABOND FFAP capillary column (Machery-Nagel GmbH & Co. KG, Düren, Germany) and a flame ionization detector (VDLUFA, 2006).

An elemental analyzer was used to assess the contents of hydrogen, nitrogen, sulfur and carbon (Vario EL, Elementar Analysensysteme GmbH, Hanau, Germany); this determination adopted the principle of raw catalytic combustion under high temperatures and oxygen supply (VDLUFA, 2006). Crude protein was determined by multiplying elemental N by 6.25. Analyses of neutral detergent fiber (NDF) and acid detergent fiber (ADF) were conducted according to Van Soest et al. (1991) using the Ankom 2000 fiber analyzer system with filter bag technology (Ankom Technology Corp., Macedon, NY, USA) (VDLUFA, 2012a). The content of acid detergent lignin (ADL) was measured gravimetrically after adding 72% sulfuric acid to the bag from ADF analysis for 3 h, drying the sample, and incinerating the sample in a muffle furnace at 600 °C for 2.5 h (VDLUFA, 2012b, 2012c). The amounts of the different fibrous fractions were assessed as follows: cellulose was determined by calculating the difference between ADF and ADL, and hemicellulose was determined as the difference between ADF and NDF. Lignin was defined as ADL by assuming that the fraction of lignin-bound nitrogen was insignificant. The crude fat level was verified according to the Weibull–Stoldt method using the AnkomXT10-Extractor (Ankom Technology Corp., Macedon, NY, USA).

Total ammonia nitrogen (TAN) was converted to ammonia by magnesium oxide, collected by steam distillation (Vapodest 20 Gerhardt, Apeldoorn, The Netherlands), and then transferred to a distillation receiver containing boric acid (VDLUFA, 2006). Chemical oxygen demand (COD) analyses were conducted by following standard methods (DIN38409-2, 1987). More details about the physical and chemical parameters are found in (Hilgert et al., 2022).

2.3. Biochemical methane potential tests

BMP tests were performed to evaluate the CH_4 production potential of the collected manure samples according to the standard procedure VDI (2016). The inoculum was a mixture of digestate from laboratory anaerobic digestion batch experiments and digestate from two commercial biogas plants running with crop residues, animal manure, and energy crops as feedstock. The inoculum had methanogenic microorganisms adapted to mesophilic temperature conditions. The digestate was sieved (mesh size 3 mm) to avoid large particles, stored in a tank at 37 °C and stirred once a week. The inoculum was not standardized over several batches; therefore, a possible effect of the inoculum on CH_4 production could not be fully ruled out. Hence, blank samples were included to evaluate this influence, as well samples with cellulose tested the activity levels of the microorganisms.

The experimental setup used 100-mL glass syringes filled with inoculum and substrate in quantities that guaranteed volatile solids ratios of approximately 2; the ratio was controlled by weighing (Precision balance EG4200-2NM, Kern & Sohn GmbH, Balingen, Germany). The glass syringes were closed; so that the piston movement displaced the air inside, ensuring anaerobic conditions. Silicone paste (Silicon paste medium viscous, Carl Roth GmbH + Co. KG, Karlsruhe, Germany) was applied between the piston and the syringe to avoid leakages during handling and measurement of gas production. Five replicates were set up for each manure sample.

The samples were incubated at 37 °C. To evaluate the volume of gas produced during incubation, the piston displacement was recorded at least 4 times per week. The biogas volume produced by the blank samples was subtracted from the measured gas production of each sample. Biogas production was expressed in norm liters per kg of volatile solids ($L_N\ kg_{VS}^{-1}$); that is, the volume of biogas production was based on normal conditions, which included a dry gas temperature of 273 K and pressure of 1013 mbar (VDI 4630., 2016). The gas composition (CH_4 and CO_2) was measured twice per week in the first 14 days and once per week in the following days (for CH_4: Advanced Gasmitter, Sensors Europe GmbH, Erkrath, Germany; for CO_2: MonoGas Analyzer, Pronova Analysentechnik GmbH & Co. KG, Berlin, Germany). Standard gas (60% CH_4 and 40% CO_2, Air Liquide Deutschland GmbH, Düsseldorf, Germany) was used to verify the calibration of the equipment every time the gas composition was measured. The agitation of the batches occurred during volume and gas composition measurements. The completion of the BMP tests respected the stopping criteria of the VDI procedure (i.e., daily biogas production during three consecutive days was lower than 0.5% of the total biogas produced until that time) (VDI 4630., 2016). Depending on the sample, the stopping criteria were reached after 45 and 70 days.

2.4. Data analysis

2.4.1. Dry matter correction

The VFA content was expressed as acetic acid equivalents following division by factors based on molarity. To account for the losses of volatile components during sample processing, a methodology from Weissbach and Kuhla (1995) was used to include the VFA content in the calculation of the DM.

In order to account for the dry matter loss from dairy cow manure during storage, the dry matter content of outdoor storage samples was corrected based on the ash content of manure samples collected in the barn. The assumption considered was that the ash content during storage is constant (Larney et al., 2005).

2.4.2. Kinetics analysis

Kinetic analyses were performed to extract the degradation parameters of the samples using a first-order differential Eq. (1) and a modified Gompertz equation Eq. (2). The first-order differential equation was used to model the degradability of substrates which allowed the estimation of the substrate degradation constant k.

$$y(t) = y_m \bullet \left(1 - e^{(-k_1 t)}\right) \tag{1}$$

where $y(t)$ is the cumulative specific CH_4 yield at time t $\left(L_N CH_4 kg_{VS}^{-1}\right)$, y_m is the maximum specific CH_4 yield at a theoretically infinite digestion time $\left(L_N CH_4 kg_{VS}^{-1}\right)$, t is the time $(days)$ and k is the first-order decay constant (day^{-1}).

The modified Gompertz equation allowed the estimation of the lag phase time (λ) and the maximum specific CH_4 production rate (R_m) (Zwietering et al., 1990). The curve obtained had a fixed inflection point and was asymmetric around the inflection point (Herrmann et al., 2016; Lo et al., 2010; Morais et al., 2021). The negative lag times estimated from this equation were assumed to be 0 (Dalgaard & Koutsoumanis, 2001).

$$y(t) = y_m \bullet exp\left\{-exp\left[\frac{R_m \bullet e}{y_m} \bullet (\lambda - t) + 1\right]\right\} \tag{2}$$

where $y(t)$ is the cumulative specific CH_4 yield at time t, $\left(L_N CH_4 kg_{VS}^{-1}\right)$, y_m is the maximum specific CH_4 yield at a theoretically infinite digestion time $\left(L_N CH_4 kg_{VS}^{-1}\right)$, R_m is the maximum specific CH_4 production rate $\left(L_N CH_4 kg_{VS}^{-1} day^{-1}\right)$, λ is the lag phase ($days$), and t is the time ($days$).

To evaluate the effect of storage time on the BMPs of the manure samples, the average storage time was estimated based on the last time the storage was emptied before the day of sample collection. The period in days was divided by two to estimate the average storage time. Eq. (1) and Eq. (2) were adapted to more accurately represent the obtained information, in Eq. (1) essentially turning the subtraction of the terms inside the brackets into an addition, and in Eq. (2) by removing the negative sign of the double-exponential term. By comparing the Akaike Criteria for these curves, the best fit was determined. Furthermore, the parameters derived from these equations were assessed to confirm if they retained the same significance as those used in BMP curves.

2.4.3. *Statistical analysis*

Statistical data analysis was performed using R software (R Core Team, 2022). The significance levels of differences in the physicochemical compositions and the kinetic parameters from the manure samples at different positions on the manure management chain were verified by Welch's analysis of variance (ANOVA). When significant effects were identified, the Games–Howell post hoc test, using a 0.05 p-level, was applied for multiple mean comparisons. A principal component analysis (PCA) was carried out with the y_m and the chemical components as input to explore possible positive and negative relationships.

Descriptive statistics using multilevel multiple linear regression tests were performed to develop mathematical models for predicting the potential y_m of livestock manure samples from the storage systems. The chemical component contents of the samples and the stage of storage where the samples were collected, were used as predictors. Statistical techniques to reduce the number of predictors were used. Graphical representations of these analyses are given in the Supplementary Material. To verify which manure chemical components could explain most of the sample variability, PCA and correlation coefficients were calculated for barn as well as intermediate and outdoor storage systems to reduce the collinearity of the variables. If two predictors were strongly correlated (correlation higher than 0.7), the presence of both in a model could decrease the model significance, and one of them was chosen based on higher correlation with the principal components and potential to simplify the model. After predictor selection, a stepwise regression using Akaike information criterion was performed to select the model that showed the best fitting with the obtained BMPs. To identify and exclude outliers, Cook's distance was used to estimate the influence of a data point when performing a least-squares regression analysis. Interactions between lignin and other chemical components were tested to verify whether the interaction had some influence on the BMP. The obtained models were validated by plotting the results against the obtained kinetic parameters.

3. Results and discussion

3.1. *Manure chemical characteristics*

Table 2 shows the samples' physicochemical parameter means and the significant differences when present for pig and cow manure specimens in different stages on the MMC. For dairy manure, the average dry matter contents were higher for barn storage samples than for outdoor storage samples (F = 9.67 and p = 0.004), which could be explained by the dilution and degradation of organic matter during storage. For pig manure, dry matter was lower for barn samples relative to outdoor storage (F = 9.13 and p = 0.012), which may have been caused by the

Table 2

Kinetic parameters for CH_4 production and chemical characteristics of dairy cow manure and fattening pig manure samples. y_m is the maximum specific CH_4 yield at a theoretically infinite digestion time from the Gompertz equation $\left(L_N CH_4 kg_{VS}^{-1}\right)$, R_m is the maximum specific CH_4 production rate from the Gompertz equation $\left(L_N CH_4 kg_{VS}^{-1} day^{-1}\right)$, λ is the lag phase from the Gompertz equation ($days$) *and* k *is the first-order decay constant from the first-order differential equation* (day^{-1}). *The significance levels of the Games–Howell test results are reported with the letters a, b and c.*

	DM (%)	VS (%$_{DM}$)	pH	EC (µS/cm)	VFAs (%$_{DM}$)	TAN (mg/kg$_{FM}$)	XP (%$_{DM}$)	XF (%$_{DM}$)	NFC (%$_{DM}$)	Lig (%$_{DM}$)	Cel (%$_{DM}$)	Hem (%$_{DM}$)	C/N	CH_4 content (%)	y_m – Gompertz	R_m - Gompertz	λ - Gompertz	K - EDO
Dairy cow manure																		
Kinetics parameters for CH_4 production and chemical characteristics of dairy cow manure collected from barn storage systems																		
Mean	**9.59^a**	**81.08^a**	**6.87**	**12.04^b**	**6.59^a**	**1306.4**	**16.67^a**	**1.91**	**14.77**	**8.06**	**19.79^a**	**19.87^a**	**16.79**	**61.69**	**277.52^a**	**21.56^a**	**0.46**	**0.13**
SE	**0.37**	**1.04**	**0.08**	**0.55**	**0.38**	**82.26**	**0.4**	**0.13**	**0.69**	**0.24**	**0.34**	**0.45**	**0.32**	**0.33**	**4.87**	**0.53**	**0.09**	**0.03**
Kinetic parameters for CH_4 production and chemical characteristics of dairy cow manure collected from outdoor storage systems																		
Mean	**8.16^b**	**61.78^b**	**6.89**	**14.22^a**	**4.09^b**	**1310.25**	**12.45^b**	**1.79**	**13.15**	**6.88**	**13.66^b**	**13.83^b**	**17.29**	**63.13**	**223.69^b**	**13.89^b**	**n.a.**	**0.09**
SE	**0.3**	**3.88**	**0.1**	**0.69**	**0.96**	**55.77**	**0.69**	**0.12**	**0.93**	**0.49**	**1.11**	**1.02**	**0.69**	**0.61**	**7.7**	**1.45**	**n.a.**	**0.01**
Fattening pig manure																		
Kinetics parameters for CH_4 production and chemical characteristics of fattening pig manure collected from barn storage systems																		
Mean	**1.12^a**	**58.72**	**7.27**	**16.43**	**2.83**	**1546.5^a**	**19.42**	**2.73^b**	**22.61^a**	**2.56^b**	**3.89**	**7.53^b**	**11.87**	**70.57**	**312.66^a**	**22.76^a**	**0.36**	**0.09^a**
SE	**0.12**	**2.26**	**0.05**	**1.28**	**0.77**	**134.89**	**0.76**	**0.48**	**1.18**	**0.4**	**0.64**	**1.38**	**0.58**	**1.11**	**20.66**	**2.47**	**0.41**	**0.01**
Kinetics parameters for CH_4 production and chemical characteristics of fattening pig manure collected from intermediate storage systems																		
Mean	**4.00^{ab}**	**70.79**	**7.07**	**17.71**	**7.13**	**2573.8^{ab}**	**18.58**	**5.56^a**	**14.07^b**	**5.85^a**	**9.29**	**17.44^a**	**13.65**	**71.25**	**230.26^b**	**15.42^{ab}**	**0.86**	**0.08^{ab}**
SE	**1.02**	**3.4**	**0.15**	**1.31**	**3.05**	**528.51**	**1.09**	**0.43**	**0.46**	**0.73**	**1.61**	**2.09**	**1.69**	**1.55**	**10.88**	**2.77**	**0.39**	**0.01**
Kinetics parameters for CH_4 production and chemical characteristics of fattening pig manure collected from outdoor storage systems																		
Mean	**2.68^b**	**60.14**	**7.4**	**15.37**	**1.82**	**2238.7^b**	**18.81**	**3.64^b**	**14.30^b**	**5.85^a**	**6.29**	**11.26^{ab}**	**11.97**	**69.5**	**165.73^c**	**9.20^b**	**n.a.**	**0.06^b**
SE	**0.42**	**2.65**	**0.05**	**2.26**	**0.39**	**106.29**	**0.79**	**0.22**	**1.27**	**0.95**	**1.16**	**1.6**	**1.6**	**1.07**	**16.98**	**1.51**	**n.a.**	**0.01**

problem of obtaining representative samples, especially for pig manure, where the nonhomogeneous nature has a tendency to cause natural stratification during storage (Ndegwa & Zhu, 2003). VS concentrations of cow manure for barns and outdoor storage were significantly different ($F = 22.125$ and $p < 0.001$), consistent with organic matter degradation during storage. This difference was verified in the study of Browne et al. (2015), where dairy slurry specimens were stored at 9 °C and 20 °C for 26 weeks. The VS concentrations based on fresh matter decreased by 5% and 17% for the specimens stored at 9 °C and 20 °C, respectively. The differences in VS among the sampling positions were not significantly different for pig manure.

Although the average pH values of cow and pig manure samples did not present significant differences among the storage systems, there was a pH increase with increasing storage time. This result was in agreement with the studies performed by Sommer & Husted (1995) and Teixeira Franco et al. (2018), where the manure pH value tended to increase with a decrease in VFA concentration explained by conversion into CH_4 and the release of CO_2. For cow manure, the VFAs seemed to degrade according to the progress in the MMC ($F = 5.24$ and $p = 0.032$). The abovementioned study by Browne et al. (2015) showed that the VFA concentration in 20 °C stored dairy cow slurry markedly decreased from the 17th week; the VFA concentration of manure stored for 26 weeks at 9 °C remained relatively constant. The VFAs in pig manure did not present significant differences among the storage systems ($F = 1.864$ and $p = 0.233$); however, the concentrations tended to decrease from intermediate storage to outdoor storage. These results confirmed the hypothesis of organic matter degradation because acetogens degraded VFAs to acetate, CO_2, and hydrogen, which were further converted by methanogens to CH_4 and CO_2 (Gerardi, 2003). This finding was in line with the results of Teixeira Franco et al. (2018), in which stored cow manure with low total solids (TS) content and relatively high pH levels leads proliferates methanogenic consumption and, consequently, VFA consumption.

The TAN content for dairy manure was similar among the storage systems ($F = 0.001$ and $p = 0.973$). For pig manure, the TAN content from the barn sample was lower than that of the samples from the other storage systems ($F = 7.912$ and $p = 0.0169$), while the protein content showed similar values for all the storage systems ($F = 0.231$ and $p = 0.798$). In contrast, the protein contents of dairy manure samples presented significant decreases ($F = 27.64$ and $p < 0.001$) from barn storage to outdoor storage, suggesting at some degradation during storage.

The content of crude fat (X_F) was not significantly different between the cow manure storage systems ($F = 0.566$ and $p = 0.458$). For pig manure, the samples from the intermediate storage had higher contents of X_F than the contents from the other storage systems ($F = 10.191$ and $p = 0.007$).

The content of nonfiber carbohydrate (NFC) was low in dairy manure samples from both stages ($F = 1.851$ and $p = 0.184$), showing that the digestive process of the cattle removed most of the easily digestible carbon. For pig manure, the barn samples had higher contents of NFC than the outdoor and intermediate storage samples ($F = 21.842$ and $p < 0.001$). Regarding the fiber content, in cow manure, the contents of hemicellulose ($F = 27.38$ and $p < 0.001$) and cellulose ($F = 27.66$ and $p < 0.001$) were lower in the outdoor samples than in the barn samples. The lignin contents in cow manure samples was not significantly different ($F = 4.053$ and $p = 0.055$) between the sampling storage systems, agreeing with studies by Susmel & Stefanon (1993), Gerardi (2003) and Muhammad Nasir & Mohd Ghazi (2015), who showed that lignin was a challenging component to degrade by anaerobic microbial communities. For pig manure, samples from the barn presented lower values for lignin ($F = 10.181$ and $p = 0.005$) and hemicellulose ($F = 7.310$ and $p = 0.013$) than those from the other sampling positions. This fact agrees with the results from other cow manure studies and could show the difficulties of degrading lignin by microorganisms. The cellulose contents in pig manure samples exhibited significant differences among the storage systems ($F = 5.249$ and $p = 0.035$); however, the post hoc analysis revealed no significant differences. The C/N ratio did not present significant differences between the storage systems for cow manure ($F = 1.37$ and $p = 0.2469$) and pig manure ($F = 0.458$ and $p = 0.650$).

3.2. Biochemical methane potentials

The comparisons of the maximum y_m showed that barn samples have a higher BMP than aged samples, and this was true for cow manure ($F = 36.38$ and $p < 0.001$) as well as pig manure ($F = 14.342$ and $p < 0.001$). Degradation of organic matter by anaerobic microorganisms during storage possibly decreased the CH_4 production potential through emissions to the atmosphere. There was a 20.4% decrease in the y_m for dairy cow manure from the samples collected in the barn storage system relative to those collected in the outdoor storage system. The study by Browne et al. (2015) observed a similar decrease in the specific CH_4 yield of stored dairy cow manure at 20 °C after 18 weeks of storage. For fattening pig manure, there were 47.1% decreases in the y_m values, showing a faster degradation of organic matter in pig manure than in cow manure. This sharp decrease in the CH_4 potential for pig manure during storage was in agreement with the study by de Buisonjé & Verheijen (2014) who stored pig manure for different periods and verified a 74% decrease in the CH_4 potential when comparing pig manure samples stored for 32 and 120 days.

The cow manure samples from barns presented higher maximum production rates (R_m) values than the outdoor samples ($F = 24.64$ and $p < 0.001$). A similar behavior was seen for pig manure, i.e., with samples from the barn storage system presenting higher rates than those from the outdoor storage system ($F = 10.412$ and $p = 0.006$). The difference was probably due to samples from the outdoor storage system being more degraded than the barn samples. Additionally, the trend for the decay constant, showed a decreasing tendency according to the position on the manure management chain for both animal manure types. However, no significant differences appeared in the cow manure samples ($F = 2.39$ and $p = 0.141$), whereas for pig manure the samples from the barn had a higher decay constant than those from outdoor storage ($F = 4.269$ and $p = 0.046$). The lag-phase evaluation suggested a shorter lag-phase periods for older samples, but there were no significant differences with both animal categories (cow $F = 2.11$ and $p = 0.163$) (pig: $F = 0.605$ and $p = 0.560$). The analyses of the differences between different seasons and farms were not significant for either of the animal manure types.

3.3. Effect of storage time (or aging) on BMP

Fig. 1 and Fig. 2 show BMPs from dairy cow and fattening pig manure samples, respectively, plotted against the average storage time. For both manure types there is evidence for a fast decrease in the BMP at the beginning of the storage and declining rates with increasing storage time, agreeing with the rates presented in Table 2, and with the observations of de Buisonjé & Verheijen, (2014). Also, Gopalan et al. (2013) conducted an analysis of the average BMPs of beef feedlot manure samples. The researchers found that fresh samples (<8 h old) had BMPs of 350 mL CH_4 g_{VS}^{-1}, pad samples (aged between 3 and 8 weeks) had BMPs of 270 mL CH_4 g_{VS}^{-1}, and stockpile samples (aged between 8 and 12 months) had BMPs of 140 mL CH_4 g_{VS}^{-1}. Similarly, Hashimoto et al. (1981) demonstrated a decrease in the BMPs of beef cattle manure samples with increasing storage time. Specifically, the BMP for fresh manure was 260 mL CH4 g_{VS}^{-1}, and the BMP for manure aged between 6 and 8 months was 210 mL CH_4 g_{VS}^{-1}.

The faster decrease in pig manure could be related to the higher content of NFC compared to cow manure; since in cattle this component is already digested in the rumen and gut (Amon et al., 2007). The study of Feng et al. (2018), in which the CH_4 emissions from cattle and pig manure specimens were measured in storages prior to digestion, showed that the degradation was more intense for pig manure samples. Another reason can be related to the controlled environmental temperature in the

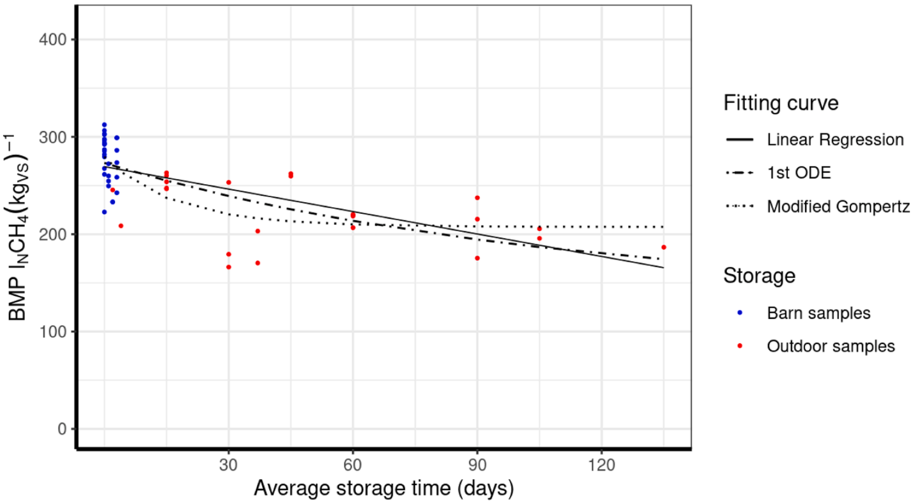

Fig. 1. BMPs of dairy cow manure samples collected from barn and outdoor storage systems by considering the storage time. Outliers were excluded based on Cock's distance.

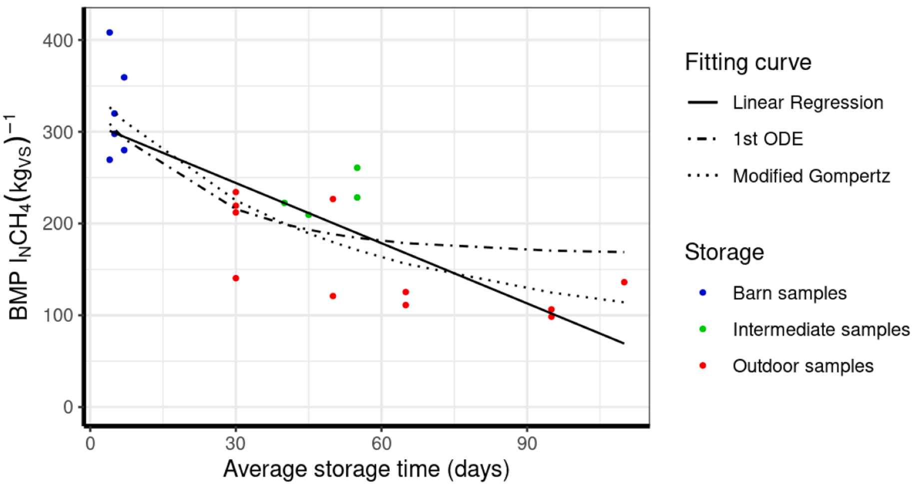

Fig. 2. BMPs of fattening pig manure samples from barn, intermediate and outdoor storage systems by considering the storage time. Outliers were excluded based on Cock's distance.

pig barns of approximately 20 °C, which will increase in the activity of microorganism involved in the degradation of organic matter (Hilgert et al., 2022).

Manure samples from different stages in the manure management process could undergo changes in chemical composition and CH_4 potential in two phases. The initial phase was marked by a high TS content that caused the bacteria to hydrolyze fibers to produce VFAs, producing mainly acetic acid; this phenomenon decreased the pH values to levels that could inhibit the methanogens. The second phase occurred when manure was stored in a more liquid-like setting, and it was characterized by an increase in methanogen growth and VFA consumption, breaking down VFAs into CH_4 and CO_2. The literature confirmed this process for both pig and cow manure types (Conn et al., 2007; Teixeira Franco et al., 2018).

The adapted Modified Gompertz Equation presented the best fitting criterial for both animal categories when compared with the adapted first-order equation and linear regression. More details on the goodness of fit of the non-linear and linear analysis are presented in the Supplementary Material. Despite the good fitting, it is evident that the curve fitting is limited due to variations in samples and conditions from different barns, such as feeding, housing, manure storage, and management systems. Additionally, uncertainties regarding precise storage times and factors influencing storage (e.g., temperature) contribute to these limitations.

Furthermore, non-linear models are generally effective in representing biological degradability of organic matter (Herrmann et al., 2016). Concerning the rate parameter (R_m cow: 4.1, R_m pig: 0.25) of the adapted Modified Gompertz Equation they are lower in comparison to those in BMP tests (Table 2), since storage takes place at lower temperatures and without the addition of inoculum. Compared with the results by Hilgert et al. (2022), where fresh manure samples were stored at different temperatures for 90 days, the rates of methane production during storage are higher than those obtained by the fitting curves. Future studies with broader sample size and further investigations regarding residual BMP may confirm the significance of other parameters.

3.4. Principal component analysis (PCA): Relationships between y_m and chemical components

A separate PCA was performed for each animal category, and samples from different positions in the manure management chain were included. The results of these analyses are presented in Fig. 3 and Fig. 4. The position of the vector for each individual component describes its

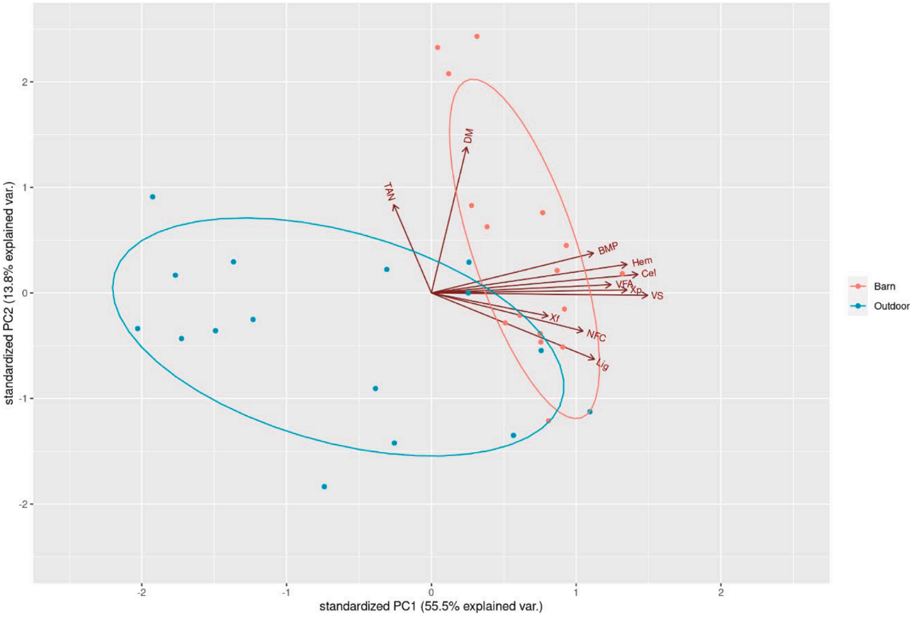

Fig. 3. PCA between BMP and the chemical components for dairy cow manure samples collected in the barn and outdoor storage systems.

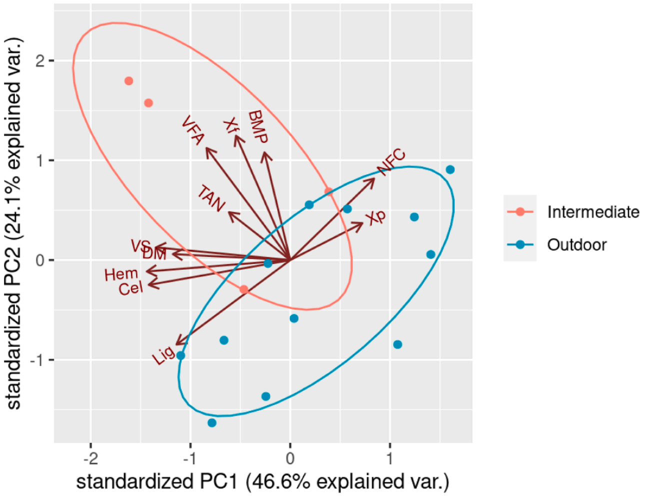

Fig. 4. PCA between BMP and the chemical components for fattening pig manure samples collected in the intermediate and outdoor storages.

association with the other variables. Components with correlation indices exceeding 0.7 with the PCs were highly correlated, and components with correlations below −0.7 were strongly negatively correlated. As shown in Fig. 3 and Fig. 4, each dot represented a sample, and ellipses delimit samples from the different positions in the MMC. For this analysis, fresh and pumping pit dairy cow samples were grouped as barn storage samples. For pig manure, in Fig. 4, only samples from intermediate and outdoor storage systems were considered due to the aforementioned difficulties of sampling in barns.

In Fig. 3, two principal components of dairy cow manure explained 69.3% of the total variation (55.5% and 13.8%, respectively). The components that were highly correlated with PC1 were volatile solids (0.99), hemicellulose (0.89), VFAs (0.82), cellulose (0.94), crude protein (X_p) (0.89) and lignin (0.74). BMP also presented a high correlation with PC1 (0.74); the analysis showed that samples with highly correlated with PC1 tended to have higher BMPs, besides dry matter was strongly correlated with PC2 (0.92). As in the previous sections, this analysis indicated that barn storage samples tended to have higher CH_4 potentials than outdoor storage samples, as indicated by the ellipses in the graphs.

This analysis was partially in agreement with a review performed by Raposo et al. (2020), stating that many models predicting CH_4 potentials from the initial chemical composition of different feedstocks (for instance, energy crops and animal manure) revealed that the contents of hemicellulose and X_p were positively related to BMP. The content of volatile solids was a good indicator of organic matter but not clearly positively related to BMP. The contents of lignin and cellulose were reported to be negatively related to the BMP. The studies by Amon et al. (2007) and Triolo et al. (2011), in which models predicted methane potentials, showed lignin was negatively correlated with BMP. Cellulose content was negatively correlated with methane potential for animal manure according to a study by Triolo et al. (2011).

Fig. 4 shows the principal components to explain the variances in the fattening pig manure samples. PC1 explains 46.6% of the variance, and PC2 explains 24.1% of the variance. The correlation analysis with PC1 revealed strong correlations with the contents of hemicellulose (-0.97), cellulose (-0.96), volatile solids (-0.91) and dry matter (-0.79). Regarding PC2, the correlated components were (X_f) (0.84) and VFAs (0.76). When identifying the samples from each stage of storage, samples from the intermediate storage tended to have a tendency for higher BMP and organic component levels, such as X_f and VFAs; samples from the outdoor storage tended to have higher contents of lignin, X_p and NFC. The content of crude fat was often related to high BMPs in substrates relative to protein or carbohydrate contents (Raposo et al., 2020).

3.5. *Predicting y_m from stored dairy cow manure*

Details about the PCA and the correlation matrix for selecting the chemical components as predictors for y_m for dairy cow manure are shown in the Supplementary Material. For barn samples, the main principal components explained 54.2% of the variability; the contents of volatile solids, X_p, lignin, and hemicellulose were the chemical components most correlated with the main principal components. The correlation matrix for the barn samples showed that all components were strongly correlated with y_m, which could have occurred because of the low variability levels between the samples; many of them were collected under similar conditions. A strong negative correlation was found between the dry matter and lignin content (-0.73), indicating that samples with lower dry matter levels had higher lignin contents. A positive correlation was seen between the volatile solids contents and the NFC, indicating that for these samples, NFC were important components of the volatile solids contents.

For the outdoor storage samples of dairy cow manure, the main principal components presented 74.6% of the sample variability. The highest correlations occurred between PC1 and volatile solids (-0.99), VFA (-0.88), X_p (-0.90), NFC (-0.81), lignin (-0.84), cellulose (-0.95) and hemicellulose (-0.91). For PC2, the dry matter content presented a strong correlation (0.88). By analyzing the correlation matrix, it was possible to verify that the content of volatile solids was strongly correlated with many of the organic components; X_f was an exception, possibly because the content of fat in dairy manure was low.

According to the results from the PCA, the components initially selected to be part of the model were volatile solids, X_p, lignin, hemicellulose, and dry matter. After the stepwise analysis, the obtained models are presented in Eqs. (3) and (4).

$$y_{m(dairybarn)} = 347.2 + 2.96DM - 1.2VS + 0.22Lig \tag{3}$$

$$y_{m(dairyoutdoor)} = 275.8 - 11.71DM + 3.2VS - 21.43Lig \tag{4}$$

The model predicting y_m for dairy cow barn samples had a significant intercept ($p = 0.01$), which could be explained by the low variability levels of the barn samples, whereas the predictors have low significance ($p > 0.05$). However, the predictors for y_m from the outdoor dairy manure samples were statistically significant, and the dry matter content negatively influenced the BMP ($p < 0.05$). At an advanced degradation state, dry matter was mainly composed of lignin and ash, both being nondegradable components, because a high dry matter content was related to a low BMP. Lignin negatively affected the CH_4 potential of the sample ($p < 0.001$), as in the models presented in the studies by Amon et al. (2007) and Triolo et al. (2011). The content of volatile solids positively impacted the CH_4 potentials of the outdoor samples ($p < 0.001$), likely because more organic material was available for degradation by anaerobic digestion.

Fig. 5 shows a graph where the maximum BMP values obtained from the kinetic model are plotted against the models presented in Eq. (3) and Eq. (4). The multiple R-squared value of the model is 0.829, and the adjusted R-squared value is 0.775, indicating that the multiple regression equations could reasonably explain the variation in the CH_4 yields from the manure samples. Interactions between lignin and other chemical components were analyzed to verify whether the presence of lignin could prevent the degradation of other organic components, for instance, cellulose ($p = 0.980$), hemicellulose ($p = 0.732$), VFAs ($p = 0.075$), X_f ($p = 0.246$), X_p ($p = 0.253$), and NFC ($p = 0.843$). The results of these analyses were not significant for the model presented in Eq. (3) and Eq. (4).

3.6. Predicting y_m from stored fattening pig manure

A statistical analysis of the chemical components as predictors for y_m for fattening pig manure is shown in the Supplementary Material. For the intermediate storage samples, the main principal components explained 91.5% of the variability, and all the chemicals were strongly related to the principal components. Due to the small sample size, many chemical components established strong correlations in the correlation matrix. The final selection determined the contents of dry matter, VFAs, hemicellulose and lignin as the main predictors for the BMPs of the intermediate storage samples.

For the fattening pig manure outdoor storage samples, the main principal components presented 74.4% of the sample variability. The highest correlations were found between PC1 and dry matter (0.73), volatile solids (-0.82), NFC (-0.79), lignin (0.99), cellulose (0.95) and hemicellulose (0.97); for PC2, VFA (0.77) and X_f (0.94) presented strong correlations. After analyzing the correlation matrix for outdoor storage pig manure samples, the predictors selected were the contents of lignin and X_f.

Following this selection, a stepwise regression resulted in the position and the content of dry matter and VFA being the variables that best predicted y_m for fattening pig manure. The model equations are shown in Eq. (5) and Eq. (6) for intermediate and outdoor samples, respectively.

$$y_{m(pigintermediate)} = 222.02 - 6.76DM + 4.94VFA \tag{5}$$

$$y_{m(pigoutdoor)} = 186.78 - 30.9DM + 30.21VFA \tag{6}$$

The model predicting y_m for fattening pig manure from the intermediate storage samples had a significant intercept ($p < 0.01$) that was explained by the low variability of the intermediate storage system. Other predictors for samples from the intermediate storage systems were not significant ($p > 0.05$). By evaluating the model for the outdoor storage system samples, the contents of dry matter and VFAs were significant ($p < 0.05$). This result could be the effect of the larger sample size and the higher variability levels of the samples because they came from two different farms.

Fig. 6 shows a comparison between the BMP values obtained from the kinetic model plotted against the data obtained from the models presented in Eq. (5) and Eq. (6). The multiple R-squared value of the model is 0.696, and the adjusted R-squared value is 0.527, indicating that the multiple regression equations poorly explained the variations in the CH_4 yields from the pig manure samples. Additionally, for the obtained model, interactions between lignin and other chemical components were analyzed; however, these analyses revealed no significant

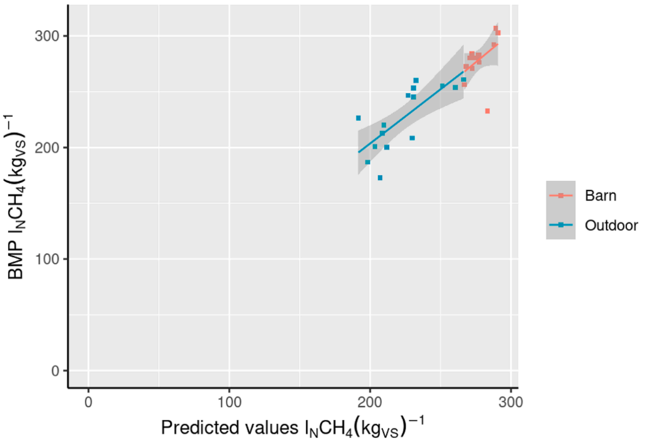

Fig. 5. Validation of the model to predict CH_4 production potential from manure management from dairy farms (Multiple R^2: 0.829, adjusted R^2: 0.775, $p < 0.001$).

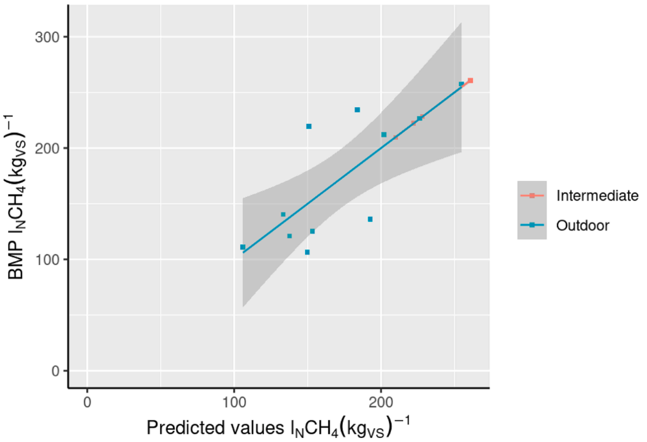

Fig. 6. Validation of the model to predict CH_4 production potential from manure management from fattening pig farms (Multiple R^2: 0.696, adjusted R^2: 0.527, $p = 0.032$).

results for the model presented in Eq. (5) and Eq. (6), for instance, with cellulose ($p = 0.334$), hemicellulose ($p = 0.199$), VFAs ($p = 0.434$), X_f ($p = 0.087$), X_p ($p = 0.105$), and NFC ($p = 0.410$).

The analysis of the models for the different animal manure types showed different intercepts for the samples from the less aged manure relative to the older samples, suggesting that important degradation of the organic matter occurred during storage. This phenomenon was in accordance with the strategy of exporting manure as soon as possible to biogas facilities to avoid losses in potential CH_4 sources to the atmosphere (de Buisonjé & Verheijen, 2014; Browne et al., 2015; Møller et al., 2022).

4. Conclusions

This study investigates the BMP of dairy cow and fattening pig manure samples from sequential stages of the liquid MMS of commercial farms, examining changes in the chemical compositions of these samples to evaluate organic matter degradation during storage. An empirical model is proposed to predict stored animal manure BMP. Results show significant organic matter degradation during storage, led to CH_4 emissions, with a up to 20.5% decrease in BMP for dairy manure and 39.5% decrease for fattening pig manure. The loss of degradable organic matter was twice as high in pig manure compared to dairy manure. The study suggests rapidly transferring manure to biogas facilities to maximize energy yield and minimize CH_4 emissions. The model highlights the importance of lignin for dairy manure and VFAs for pig manure in predicting BMP. Further refinement of the model is needed for better short-term stored manure BMP prediction.

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.wasman.2023.05.031.

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