Methane emissions from liquid manure storage – influence of temperature, storage time, substrate type and anaerobic digestion

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Contents

1. Summary

This report consists of 2 parts. The first part looks at the influence of anaerobic digestion on the emission potential of manure and the second part looks at the influence of storage temperature, time and manure origin on methane emission.

The ultimate biogas yield of manure (B_o) and the residual gas production (B_{res}) has been determined in commercial co-digestion biogas plants and in laboratory biogas digesters with cattle manure. Assuming that the methane conversion factor for the digested and non-digested substrate is the same the average influence of anaerobic digestion has been calculated to a reduction of 86 % of Bo in both co-digestion and cattle manure based biogas plants. Hydraulic retention time and digestion temperature plays a role for the reduction and increasing retention time and thermophilic temperature will increase the reduction potential. Using crops will have a negative impact on the reduction.

Methane (CH_4) emission derived from slurry storage are presented and compared to the IPCC (2006) estimations. For this purpose 6 different dairy cattle manure (CM) and three different pig manures (PM) were analyzed and stored at 4 different temperatures (10°C, 15°C, 20°C, 35°C). Important differences on slurry composition and CH_4 emissions and the response to the temperature were shown between animal category (cattle and pig). Different CH_4 emission factors should be used for pig and cattle manure. In fact, the used IPCC default values for slurry storage in the Danish's national inventory would lead to an overestimation which would be pronounced in cattle manure but less evident in pig manure. In addition, an alternative model to estimate CH_4 emission of slurry storage based on slurry category (cattle and pig), temperature and storage time is presented in our work. The model shows a good correlation in the range 10-20°C for cattle manure. However, more data are needed in order to better parameterize the model for pig slurry.

2. Methane yield and methane emissions from undigested and digested substrate as affected by operating conditions of biogas plants

2.1 Introduction

The environmental benefits of using manure and organic waste in biogas plants are very high due to the combined effect of production of methane as a non-fossil fuel, and the corresponding reduction in the emissions of methane to the atmosphere from unwanted anaerobic degradation during slurry storage and application on the fields (Sommer et al. 2004). The corresponding reduction in methane emissions depends on several factors such as operating conditions of the biogas plant and substrate characteristics. However the knowledge about potential variation among commercial biogas plants is scarce and knowledge about the influence of the substrate characteristics originating from the feeding of the animal are not known. The ultimate biogas yield of manure (B_o) during indefinite anaerobic digestion is the value that together with a methane conversion factor (MCF) is used to determine the amount of methane emitted during storage of untreated manure. Precise knowledge of B_o thus is a pre-requisite to predict methane emission without anaerobic digestion or after anaerobic digestion. The ultimate methane potential of the digested material after anaerobic digestion (AD) is often termed residual gas production (B_{res}). If it is assumed that the methane conversion factor for the digested and non-digested substrate is the same the influence of anaerobic digestion can be calculated by knowing the ultimate yield on a volumetric basis before and after digestion and the reduced emission can be calculated as the difference between B_o and B_{res} times the MCF value. However this assumption will only be true for substrates handled like manure which is not the case for crops and some types of waste. The aim of the present study has been to find B_o and B_{res} values of a range of different substrates mono-digested at mesophilic and thermophilic conditions and mixed substrates from commercial biogas plant.

2.2 Results and discussion

Commercial biogas plants

To calculate the ultimate gas yield (B_o) of the different biogas plants on a weight basis the following model was used:

$$B_{o(w)} = B_{p(w)} + B_{res(w)}$$

Where B_P is the actual gas-production measured in practice at the plant as an average for the month of sampling in terms of Nm^3 CH_4/ton of substrate added and $B_{res(w)}$ is the ultimate gas yield of the digested material leaving the last digester with gas collection. The subscript $_w$ indicates that the calculations are done in terms of weight.

In table 1 the results from the study of 15 biogas plants is shown. It can be seen that there is a big difference between the different plant. The average reduction is 2,7 L CH_4/kg substrate.

Table 1: Emission from storage with and without biogas (+/-AD). For the calculation and a MCF value of 10% has been used.

		HRT	**Bo**	**Bp**	**Bres**	**Emission**			**Reduction**
						-AD	+ AD	Reduced by AD	%
Anlæg	Temp	Days				L CH4/kg substrate			
A	Meso	70,8	44,2	42,5	1,7	4,42	0,17	4,25	96,13
B	Thermo	27,7	23,3	20,4	2,9	2,33	0,29	2,04	87,46
C	Meso	29,5	24,8	21,7	3,1	2,48	0,31	2,17	87,65
D	Thermo	17,5	27,7	20,9	6,8	2,77	0,68	2,09	75,40
E	Thermo	38,0	31,9	27,5	4,4	3,19	0,44	2,75	86,17
F	Thermo	29,5	25,2	20,0	5,2	2,52	0,52	2,00	79,39
G	Thermo	30,3	20,7	16,3	4,4	2,07	0,44	1,63	78,64
H	Meso	99,2	28,1	24,3	3,8	2,81	0,38	2,43	86,55
I	Thermo	43,1	59,0	52,1	6,9	5,90	0,69	5,21	88,33
J	Meso	26,6	50,5	45,6	4,9	5,05	0,49	4,56	90,32
K	Meso	23,2	28,6	21,7	6,9	2,86	0,69	2,17	75,84
L	Thermo	27,7	19,3	16,6	2,7	1,93	0,27	1,66	86,09
M	Thermo	69,0	21,8	18,9	2,9	2,18	0,29	1,89	86,64
N	Thermo	44,7	28,4	25,2	3,2	2,84	0,32	2,52	88,89
O	Thermo	55,0	35,2	33,0	2,2	3,52	0,22	3,30	93,77
Average		42,1	31,2	27,1	4,1	3,1	0,4	2,7	85,8

In general there is a high reduction in the volumetric calculated Bo value for all the tested commercial biogas plants with an average reduction around 86%. If it is assumed that the MCF value is equal in the digested and none-digested substrate the reduction in emission can be estimated to the same value. However this can only be concluded for the manure since the use of other substrates as crops and industrial waste will not lead to the same results. For crops there will be no emission of methane in a reference scenario without biogas and the emission coming from the digestate will lead to an emission that were not present before. Thus the use of crops will instead of an reduction lead to an increase in emission. In the tested plants a very small amount of crops has been used (<1%) and for the moment the negative emission from crops can be neglected. In the case of industrial waste most of it will behave like manure since in a situation most of it would be stored and handled like manure and in the case of wastes that are faster degradable than manure then influence will be higher.

HRT plays an important role for both the residual gas production and the reduction in Bo value. The influence of HRT are illustrated in figure 1.

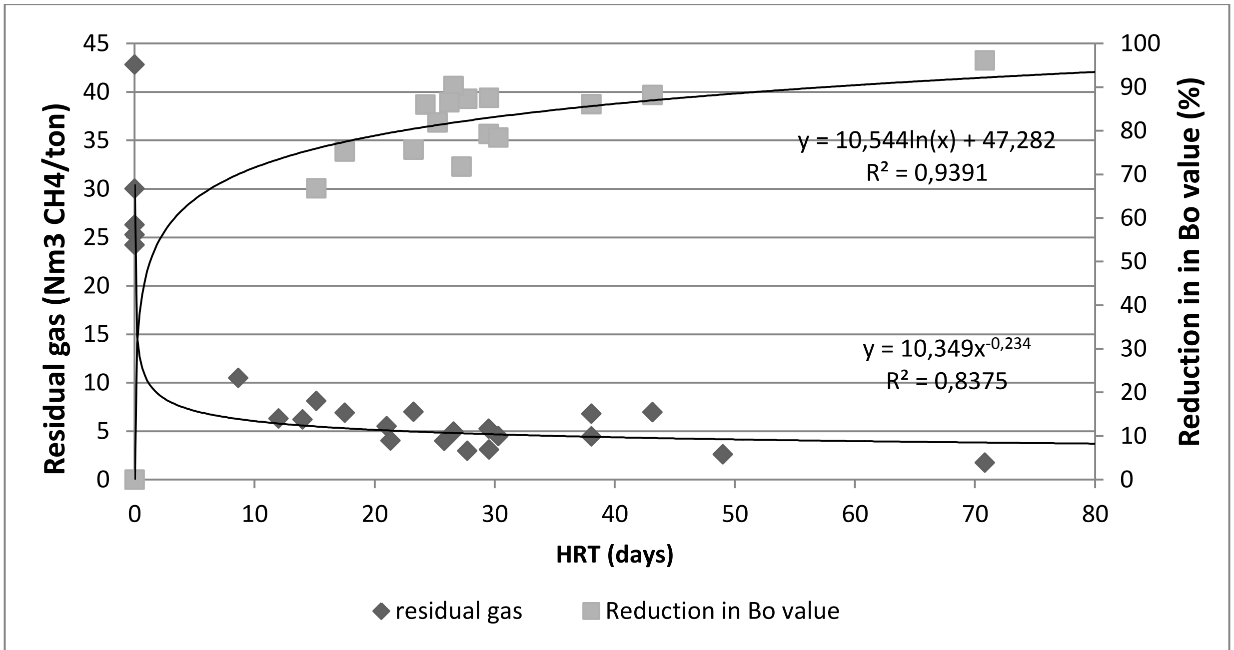


Figure 1: Influence of HRT on residual gas and reduction in Bo value.

Cattle manure

The experiments were performed in batch assay using 0.5 L infusion bottles with the method described by Møller et al. (2004). The incubations were done in triplicate. The slurry derived from an experiment with 54 Holstein cows. First all cows were feed a total mixed ration (standard) with 55% of dry matter from forage for one week. Thereafter the cows were allocated on three experimental diets with different enteric methane emission potential. The experimental diets were total mixed ration with a forage content of 60% of dry matter. The diets were maize silage as only forage and concentrate with a low fat content (maize), maize silage as only forage and concentrate supplemented with crushed rape seed (maize+fat), and grass-clover silage with low digestibility as only forage and concentrate with low fat content (grass) (table 2). The slurry was collected from slurry tanks for each ration fed cow group and was preserved at a constant temperature of 15ºC in four different containers until use in biogas digesters. Anaerobic digestion was conducted both in thermophilic (50ºC) and mesophilic (35ºC) conditions in 8 intermittently stirred medium scale (7 liter) continuous digesters (CSTR). Batch assays was also run with inoculum, at thermophilic (50ºC) and mesophilic (35ºC) temperatures to determine the ultimate methane yield at an extended incubation period.

Table 2: Chemical composition of the standard diet and three experimental diets

	Standard	Maize	Maize+fat	grass
Ash [g/kg DM]	73	57	55	73
Protein [g/kg DM]	175	172	164	192
Fat [g/kg DM]	34	21	56	24
Starch [g/kg]	ND	261	229	110
NDF [g/kg DM]	306	350	342	365

Table 3: Emission from storage with and without biogas (+/-AD) for cattle manure from cows fed different diets. For the calculation and MCF value of 10% has been used.

		HRT	Bo	Bp	Bres	Emission			Reduction
						-AD	+ AD	Reduced by AD	%
Diet	Temp	Days				L CH4/kg manure			
Maize	Meso	20	27,1	23,7	3,4	2,71	0,34	2,37	96,13
Maize+fat	Meso	20	32,8	29,2	3,5	3,28	0,35	2,92	87,46
Grass	Meso	20	18,0	14,5	3,6	1,80	0,36	1,45	87,65
Standard	Meso	20	22,7	18,2	4,5	2,27	0,45	1,82	75,40
Maize	Thermo	20	27,1	24,1	3,0	2,71	0,30	2,41	86,17
Maize+fat	Thermo	20	32,8	29,4	3,4	3,28	0,34	2,94	79,39
Grass	Thermo	20	18,0	15,3	2,7	1,80	0,27	1,53	78,64
Standard	Thermo	20	22,7	19,6	3,1	2,27	0,31	1,96	86,55
Average		20	25,2	21,8	3,4	2,5	0,3	2,2	85,8

3. Methane emission from animal slurry storage

3.1 Introduction

Protocols for estimating methane (CH_4) emissions from manure management have been set out by the Intergovernmental Panel on Climate Change (IPCC, 2006), and Denmark, like most European countries, uses the IPCC tier2 methodology (Nielsen et al., 2014). This protocol estimates CH_4 emission using volatile solids (VS) excreted by the animals, CH_4 conversion factor (MCF) and ultimate CH_4 yield (B_0). Denmark´s National Inventory (Nielsen et al., 2014) uses national values to calculate VS excreted, a MCF of 10% for liquid/slurry management and the default values provided by the IPCC (2006) for B_0 (240 L CH_4 kg VS^{-1} for dairy manure and 450 L CH_4 kg VS^{-1} for pig slurry). Nevertheless, IPCC (2006) recommends expanding the representativeness of the default values using specific country values, especially for livestock in tropical regions and when varying diet regimen. In addition, the application of these equations to sequential and concatenated slurry management strategies results difficult because time is not considered.

The objective of this report is to evaluate CH_4 emission from slurry storage and comparing the results with the IPCC (2006) estimates. For this purpose 6 different dairy cattle manures (CM) and three different pig manures (PM) were analyzed and stored at 4 different temperatures (10°C, 15°C, 20°C, 35°C). In addition, an alternative model to estimate CH_4 emission of slurry storage based on slurry category (cattle and pig) as affected by temperature and storage time is developed.

3.2 Materials and Methods

3.2.1. Slurry and inoculum

Cattle slurry

For the cattle manure category, 6 different slurries were used (Table 1). CM1, CM2 come from dairy commercial farms located close to Thorsø in central Jutland. The other four (CM3, CM4, CM5, and CM6) belong to groups of animals subjected to experimental diets carried out at Research Centre Foulum (Aarhus University, Denmark). CM3 corresponds to feces obtained from 1 animal fed with the control diet described in Brask et al. (2013), and CM4, CM5, and CM6 are described in Hellwing et al. (2014).

In the experiment carried by Hellwing et al. (2014) (CM4, CM5, CM6), the slurry was obtained from with 54 Holstein cows. Firstly, all cows were feed a total mixed ration (standard) with 55% of dry matter from forage for one week. Thereafter the cows were allocated on three experimental diets. The experimental diets were total mixed ration with a forage content of 60% of dry matter. The diets were maize silage as only forage and concentrate with a low fat content (maize), maize silage as only forage and concentrate supplemented with crushed rape seed (maize+fat), and grass-clover silage with low digestibility as only forage and concentrate with low fat content (grass) (Hellwing et al. 2014). The slurry was collected from slurry tanks for each ration fed cow group and was preserved at a constant temperature of 15ºC in four different containers until use.

Pig slurry

Three different pig slurries belonging to three different physiological states: fattening pigs, sows with piglets and piglets from 7 to 20 kg (Table 4) were used in this animal category. The three pig slurries were collected from commercial farm located close to Thorsø in central Jutland (Denmark).

Table 4: Characterization and origin of cattle and pig slurries used in this study, (CM: Cattle manure, PM: Pig manure)

Name	Characteristics	Origin
CM1	CM from dairy cows	Commercial dairy farm Thorsø
CM2	CM from dairy cows	Commercial dairy farm Thorsø
CM3	CM from dairy cows fed a diet based on rapeseed cake	Research Center Foulum
CM4	CM from dairy cows fed a diet based on maize	Research Center Foulum
CM5	CM from dairy cows fed a diet based on maize high in fat	Research Center Foulum
CM6	CM from dairy cows fed a diet based on grass	Research Center Foulum
PM1	Fattening pig slurry	Commercial fattening pig farm
PM2	Sows + piglets slurry	Commercial fattening pig farm
PM3	Piglets 7-20 kg	Commercial fattening pig farm

3.2.2. Analysis

Chemical composition

Fresh samples from each slurry were analyzed for: total solids (TS) and volatile solids (VS) according to APHA (2005); total ammonia (TAN) was determined using photometric kits (kit number 1.14555.0001, Spectroquant® kit, Merk, USA); volatile fatty acids (VFA) were determined using a gas chromatograph (5560-D of APHA, 2005) equipped with a flame ionization detector (HP 68050 series Hewelt Packard); pH was measured from fresh samples using a pH-meter Portamess® 911 pH (Knick, Germany).

In addition, fresh samples from each slurry were taken at the beginning of the experiment, dried (48 hours at 60°C) and milled using a mill with a 0.8 mm of diameter (CyclotecTM 1093, Foss, North America). Fiber fractions (neutral detergent fiber (NDF), acid detergent fiber (ADF) and lignin (ADL)) were analyzed from the dried milled samples. Fiber fractions were determined according to the Van Soest procedure (Van Soest, 1991). From these fractions, hemicellulose, cellulose and lignin were calculated. The hemicellulose content was calculated as the difference between NDF and ADF, cellulose content was calculated as the difference between ADF and ADL, and lignin content was assumed to be equal to ADL.

Methane production

From each slurry, ultimate methane yield (B_0) at 35°C, and CH_4 emission at 4 different temperatures (10°C, 15°C, 20°C and 35°C), were determined. Both analyses were performed in triplicate in a batch assay using 0.5 L infusion bottles with the method described by Møller et al. (2004). In addition to the incubation temperature, the main differences between B_0 and CH_4 emission analyses were the use of inoculum and the incubation time.

For the B_0 determination mesophilic inoculum from the mesophilic post digester placed at the Biogas plant of Foulum (Aarhus University, Denmark) was introduced in each infusion bottles together with the slurry with an inoculum: substrate ratio of approx. 1:1, based on VS. Incubation time for the B_0 analysis was 90 days.

For measurement of CH_4 emission, approximately 200 gr of slurry were introduced in each infusion bottles and incubated at different temperatures during 225 days. Methane emission was considered as the cumulative CH_4 emission produced in the bottles without inoculum at each time and storage temperature.

Periodically, the total volume of biogas produced per bottle was measured. The measurement of biogas volume was done by inserting a needle connected to a tube with inlet to a column filled with acidified water (pH<2) through the butyl rubber. The biogas produced was calculated by the water displaced until the two pressures (column and headspace in bottles) were equal. The biogas was sampled and analyzed for CH_4, carbon dioxide (CO_2) and hydrogen sulphide (H_2S) content and the volume corrected at standard temperature and pressure (0 °C and 760 mmHg). The cumulative CH_4 production at each measurement was calculated in both experiments in terms of L CH_4 per Kg VS.

3.3. Model parameterization and statistical analyses

The equation to estimate MCF as a function on time and temperature was modelled by assimilating experimental data to equation provided by IPCC (2006) to estimate CH_4 emission. Methane emission and B_0 were obtained from experiments. Methane conversion factor was calculated by using the individual experimental data (CH_4 emission and B_0) at each time and temperature data (Eq 1).

Methane emission (L CH_4 Kg VS^{-1}) = B_0 (L CH_4 Kg VS^{-1}) x MCF (%) (Eq. 1)

In the proposed model, the effect of time was considered by using a modification of Gompertz equation (Lo et al., 2010) (Eq. 2).

$BMP_t = B_0 \exp\{-\exp[\mu m\, e / B_0 (\lambda - t) + 1]\}$ (Eq. 2)

Where BMP_t denotes the cumulative CH_4 yield (L CH_4 $kgVS^{-1}$) at time (t) expressed in days; B_0 is the ultimate CH_4 yield (L CH_4 $kgVS^{-1}$); µm: Volumetric rate of methane production [LCH_4 $kgVS^{-1}$ d^{-1}], e: Euler's number, ʎ: duration of the lag phase (days).

Arrhenius function was used (Eq. 3) to consider temperature, as in Sommer et al. (2004).

$$k = \exp\left[lnA - \frac{E}{RT}\right] \qquad \text{(Eq. 3)}$$

Where k is the rate constant of a chemical reaction, A: Arrhenius parameter [L CH_4 (Kg VS d^{-1})], E: apparent activation energy[kJ mol^{-1}], T: Temperature [K] and R: gas constant [kJ K^{-1} mol^{-1}].

Equation 4 shows the proposed model to estimate CH_4 emission in terms of time and temperature.

$$CH_4 \text{ emission} = B_0 \text{ x } \exp\left[-exp\left[\frac{\mu_m \times e}{B_0} \times [ʎ - t] + 1\right]\right] \times \exp\left[lnA - \frac{E}{RT}\right] \qquad \text{(Eq. 4)}$$

Specific experimental data (CH_4 emission and B_0) were used in the parameterization of the model. The parameters μ_m, ʎ, A and E were estimated for each animal cathegory (Cattle and pig) by applying non-linear regression modelling in R language/environment source version 2.1.4.1 (R Development Core Team, 2008) by using lme4 package (Bates et al. 2012).

3.4 Results and Discussion

3.4.1. Analysis

Table 5 shows chemical composition of the slurries used. As shown, CM showed higher TS, VS and lower ash content than PM. In addition, CM showed a higher fiber content than PM, especially cellulose and lignin, probably due to differences on diet composition between these two animal categories.

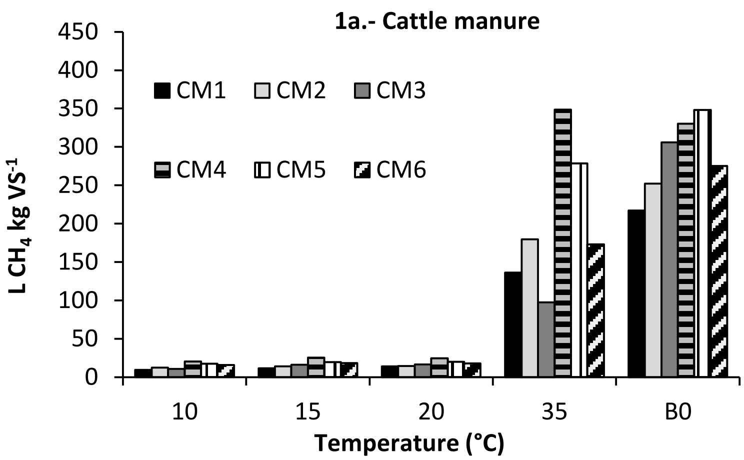
Table 5: Chemical composition of the slurries used.

	TS [%]	Ash [%TS]	VS [%TS]	Cellulose [%TS]	Hemicellulose [%TS]	Lignin [%TS]	Protein [% TS]	VFA [%TS]	[l]VS_{Unex} [%TS]
CM1	9.44	19.55	80.45	22.57	16.97	11.25	5.67	4.15	19.84
CM2	7.03	17.53	82.47	25.14	16.41	10.70	10.31	4.30	15.61
CM3	14.82	14.08	85.92	15.54	19.12	19.95	11.83	2.04	17.44
CM4				31.90	32.29	6.38	15.63		
CM5				27.25	29.57	7.62	16.88		
CM6				25.44	20.86	8.19	18.75		
PM1	5.25	34.77	65.23	10.68	12.39	3.20	13.479	4.69	20.79
PM2	7.18	24.65	75.35	18.12	17.95	5.24	10.21	2.15	21.68
PM3	5.18	24.83	75.17	17.77	17.24	4.75	9.20	2.36	23.85

[l]VS_{Unex}: Unexplained volatile solids. It was calculated as VS-(fiber + protein +VFA) all of them expressed in terms of % of VS

As shown in Table 5, higher unexplained VS was obtained in PM compared to CM, this could mean a higher fraction of volatile compounds and lipids are present in PM, probably caused by a higher fat content in pig diets than in cattle diets. Sommer et al. (2004) distinguished between degradable and non-degradable VS in slurry organic matter. These authors found that degradable VS were higher in PM than in CM. Although in this work we didn't calculate these VS fractions, the higher unexplained VS in PM would support Sommer et al. (2004) results, and it could indicate a higher biodegradable VS in PM compared to CM.

Figure 1 shows B_0 and total cumulative CH_4 emission at different temperatures in both animal categories tested. In average PM showed a higher B_0 value than CM in the slurries tested.



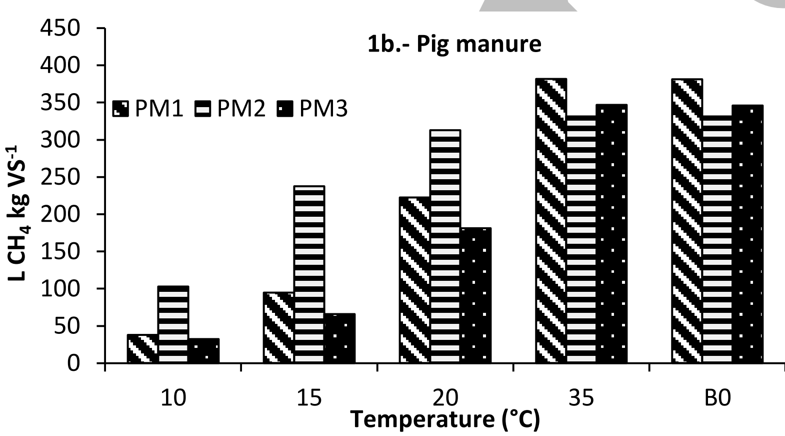


Figure 2. Methane emission and ultimate methane yield (B_0) obtained in cattle (1a) and pig slurries (1b) used in this study. CM1, CM2 and CM3 are dairy cattle manure from a commercial farm, CM4, CM5, CM6 are CM obtained in Foulum from different diets based on maize low fat, maize high fat and grass, respectively. PM1, is pig manure obtained from a commercial fattening pig farm. PM2, pig manure obtained from sow and piglets and PM3 pig manure obtained from piglets between 7 and 20kg.

IPCC (2006) uses 240 L CH_4 kg VS^{-1} as B_0 default value for CM in Europe and North America, however in the present study a high variation range on B_0 was observed among different CM tested in this work. The lowest B_0 (217 L CH_4 kg VS^{-1}) was obtained in CM1 and the highest B_0 (348 L CH_4 kg VS^{-1}) was obtained in CM5, which was obtained from diets based on maize with a high fat content. Therefore, fat content on diets could increase B_0 of its derived manure; Møller et al (2014) also found important increases on B_0 of faeces obtained from animal fed high fat levels.

IPCC (2006) B_0 default value in Europe is 450 L CH_4 kg VS^{-1} for fattening pig and breeding swine. Results obtained in this works showed a lower B_0 than what was reported in IPCC (2006), which might be caused by the fact that B_0 default value reported by IPCC refers to VS from fresh feces, and in our study, B_0 was obtained from slurry (feces + urine + water) collected from the pit of a commercial farm, with an approximately storage time of 2 weeks. Although a small B_0 variability was found within PM, the highest B_0 (381 L CH_4 kg VS^{-1}) was observed in manure from fattening pigs, followed first by sows with piglets and then piglets (346 and 331 L CH_4 kg VS^{-1}, respectively).

Higher CH_4 emissions were obtained in PM (Figure 1b) than in CM (Figure 1a) at all temperature tested, especially at psychrophilic range (10-20°C). the MCF values determined in CM at psychrophilic temperatures were very stable and lower than 8% in all CM manures tested. However, MCF default values provided by IPCC (2006) in Tier 2 for liquid animal manure storage in dairy cattle in cool climates (with a temperature range variation between 10-15°C) is between 10 and 27% depending of temperature and the establishment or not of a natural crust cover and thus much higher than indicated by our study.

From an emission point of view it's important to compare the overall CH_4 emission and not merely the MCF. Since the B_0 of CM obtained in this work was higher than reported by IPCC (2006), this fact would counteract the lower MCF obtained in our work and thus reduce the difference. In general a higher variation was found among CM used. In the cool climate range (10-15°C), maximal CH_4 emission in our work was 38.86 L CH_4 Kg VS^{-1}, obtained from CM4 after 225 days storage at 15°C. At 15°C, minimal CH_4 emission was obtained in CM1 (11.8 L CH_4 Kg VS^{-1}). According to IPCC (2006) the estimated CH_4 emissions at 15°C for liquid dairy slurry with and without natural crust are 40.8 L CH_4 Kg VS^{-1} and 64.8 L CH_4 Kg VS^{-1}, respectively. Therefore, IPCC default values were only similar to CM4 (cattle manure from dairy cows fed a diet based on maize). In the others CM used, an overestimation in the calculation of the CH_4 emission is evident by using IPCC default values. These results support the hypothesis that the use IPCC default for CM could lead to an overestimation of the country specific CH_4 emission from slurry storage in cool climates (Husted 1994, Dustan 2002 and Sommer et al., 2000).

At 20°C, maximal CH_4 emission obtained in our study was 57.5 L CH_4 Kg VS^{-1}, achieved from CM3 after 225 days storage and minimal CH_4 emission was obtained in CM1 (13.9 L CH_4 Kg VS^{-1}). By using IPCC (2006) methodology CH_4 emissions at 20°C for liquid dairy slurry with and without natural crust are 62.4 L CH_4 Kg VS^{-1} and 100.8 and L CH_4 Kg VS^{-1}, respectively. Therefore, according to the results obtained in our study the use IPCC default for CM could lead to an overestimation of the country specific CH_4 emission from slurry storage not only in cool climates, but also in the in the range 10-20°C. At 35°C however, CH_4 emission from CM increased exponentially reaching between 40 and 100% of the B_0 (between 103 to 330 L CH_4 Kg VS^{-1}). These values are more similar, or even higher than the range reported by the IPCC (2006) for temperate and warm countries (120-192 L CH_4 Kg VS^{-1}).

In PM the CH_4 emissions were significant higher at low temperatures than the emissions obtained in CM. In fact, at 15°C around 20% of B_0 was reached in all PM used. IPCC (2006) uses the same MCF for CM and PM, but according to our results, slurry behaved very differently depending on animal category and therefore we would recommend that different MCF values should be used for different animal categories.

Methane emission from pig slurry at 15°C ranged from 65.8 (sows with piglets) to 94.7 (piglets) L CH_4 Kg VS^{-1}. The CH_4 emission using IPCC methodology for liquid market swine slurry with and without natural crust are 51 L CH_4 Kg VS^{-1} and 81 L CH_4 Kg VS^{-1}, respectively. Therefore in cool climates, the estimation of CH_4 emission by using IPCC methodology results in values that are closer to our values than is the case for CM. In temperate and warm climates, the calculation of CH_4 emission from PM storage by using IPCC default values could lead to an underestimation of the country specific CH_4 emission.

3.4.2. Parameterization

Figure 3a shows the normal QQ plot for the model obtained using all cattle manure data. As shown, the distribution of the values conforming the QQ plot using all cattle manure data doesn't follow a straight line intercepting the y axis at 0 and having slope 1; as it is required to show that the distribution of the standardised residuals of two distributions (experimental data and estimated data) follows a normal distribution (Ritz and Streibig, 2008). This could be explained by the high difference in CH_4 emission between psychophrilic (5 and 20°C) and mesophilic (35°C) conditions. In fact, when these two temperature ranges are separated in two different models the respective QQ plots improved considerably (Figure 3.b and 3.c).

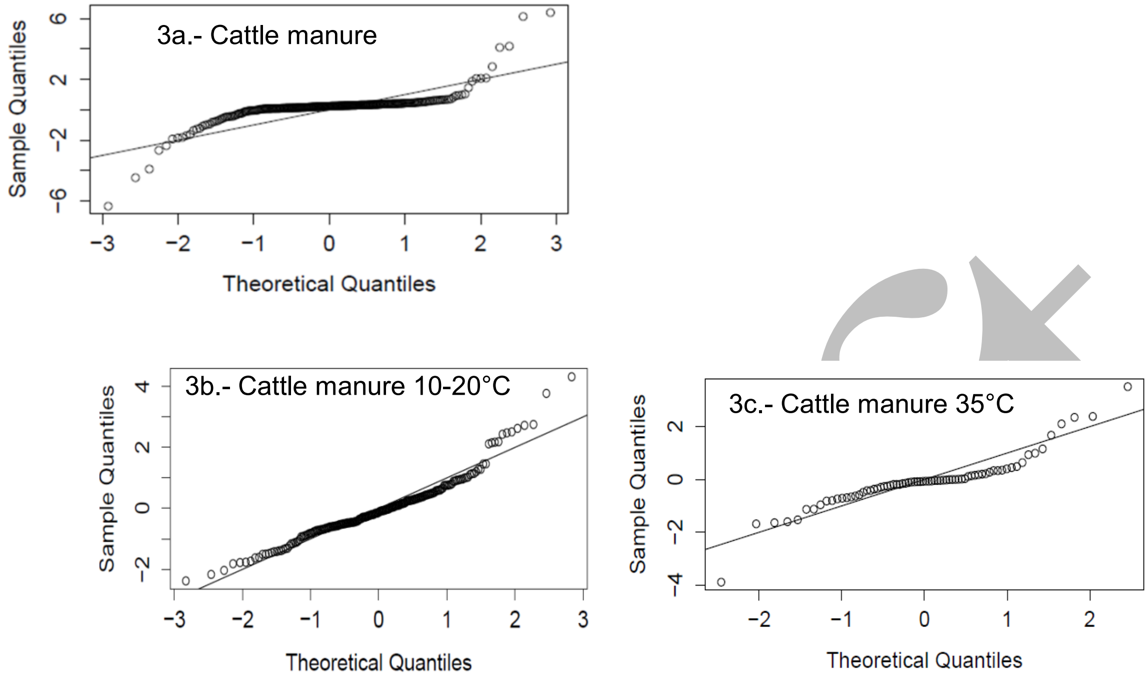


Figure 3. Normal QQ-plot and the reference line with intercept 0 and slope1 for the none linear models obtained in cattle manure

Table 3 shows the calculated parameters, their respective statistical significance and the model correlation. Arrhenius values were not estimated for cattle manure at mesophilic range since only one temperature (35°C) was used in this range.

The models obtained in our study results in a higher E value when all data from cattle manure are used than when all data from pig manure were used. According to Schütz et al. (1990), E is an empirical value which describes the temperature response of the reaction, in this case, the response of CH_4 production to temperature. When a high effect from temperature is observed in the model, as is the case in the complete cattle manure model, a high E can be expected. The higher E value obtained in the total CM model compared to the total PM model could indicate that CM needs higher energy to initiate anaerobic degradation, and therefore as shown in Figure 1, very low CH_4 emissions can be expected at low temperatures in CM. On this regard, Husted (1994) observed that slurry with a high content of bedding material (high solids content) higher energy was needed to initiate anaerobic degradation (higher E).

Table 6. Calculated parameter values, their respective statistical significance and the model correlation

Animal category	Range	E [kJ mol^{-1}]	ln A [ln (L CH_4 (Kg VS $d)^{-1}$)]	µm [L CH_4 (Kg VS $d)^{-1}$]	ʎ [d]	Correlation
CM	Total CM	92.0 ± 6.41***	35.7 ± 2.51***	5.3 ± 0.57***	28.5 ± 1.93***	0.812
	10-20°C	16.7 ± 0.22***	4.1 ± 0.91***	4.8 ± 0.31***	-1.9 ± 1.29	0.875
	35°C	-	-	2.8 ±0.33***	23.5 ± 4.06***	0.728
PM	Total PM	4.5 ± 0.27***	16.3 ± 1.08***	7.7 ± 1.17***	2.0 ± 2.5	0.808
	Fatt + sows	61.2 ± 2.14***	22.7 ± 0.84***	9.3 ± 0.80***	6.3 ± 1.22***	0.961
	Piglets	27.0 ± 2.87***	9.5 ± 1.16***	6.8 ± 1.50***	0± -2.74	0.841

When different models are built for each temperature range (psychrophilic and mesophilic), E in the psychrophilic range was lower than the E in the complete CM model. The very stable and low CH_4 emission obtained in cattle manure during psychrophilic temperature range explains the low E obtained. The parameters estimated for the Gompetz model results in a lower µ and a higher ʎ at mesophilic range (35°C) compared to the psycrophilic range (10-20°C), problably because microorganisms in the CM need more time to establish at this temperature range.

When using all data into the model in the case of PM it didn't show a good model performance as shown in the QQ plot (Figure 4.a). However in this case, separating temperatures ranges didn't improve the model (data not shown), probably because in PM the composition and origin of the pig manure were too different. In fact, slurry from piglets showed a very different response to temperature compared to slurries coming from fattening pigs and sow with piglets (Figure 2.b). For this reason in this slurry category, two models were built using all temperatures tested (from 5°C to 35°C), one for fattening pigs and sows with piglets and the other for piglets. However, the model comprising fattening pigs and sows with piglets showed a poorer model (Figure 4b) than the model with slurry from piglets (Figure 4a), meaning that probably specific model for each physiological stage of the animal should be used. For this reason, more data in pig slurry belonging to the same animal category are needed in order to better parameterize the model.

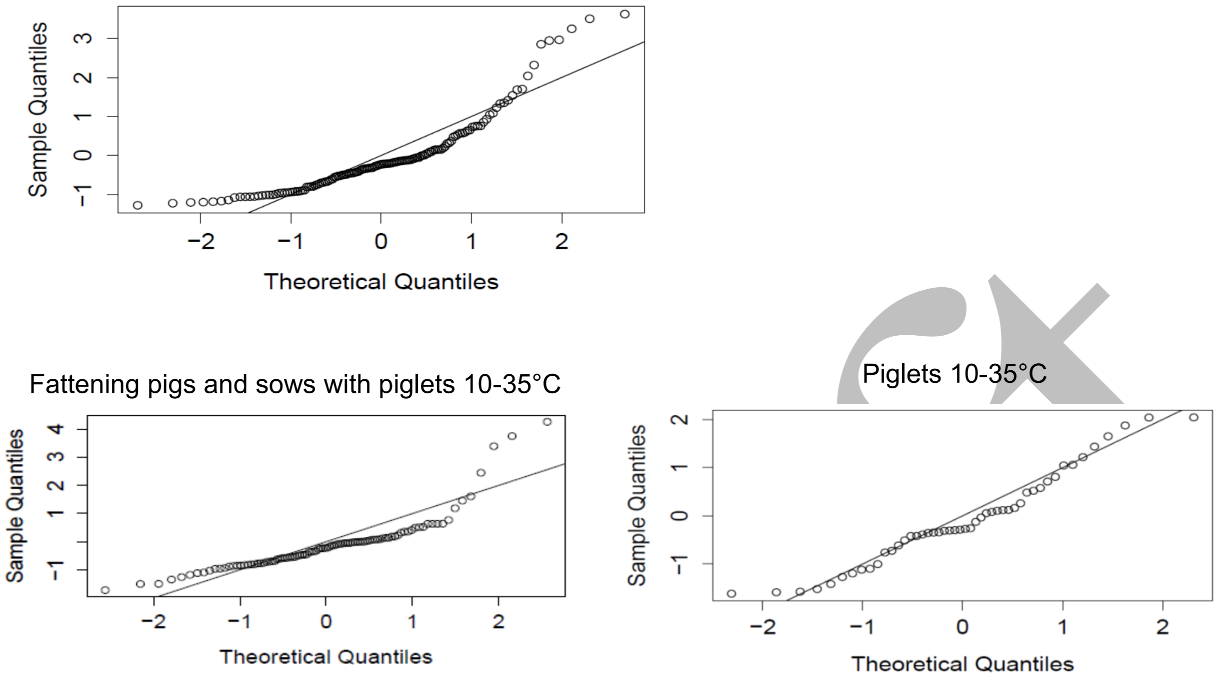


Figure 4. Normal QQ-plot and the reference line with intercept 0 and slope1 for the no lineal models obtained in pig manure

The pig model (Table 6), showed a lower E when all data from pig were used in the pig model, compared with the models obtained for different animal categories. However μ_m was very similar within the models in pig manure. The lag phase was only statistical significant (P<0.001) in the fattening pigs and sows with piglets model. In this case λ was lower than in CM model.

Several works in literature have used Arrhenius equation to estimate CH_4 emissions from wetlands and slurry storage at different temperatures (Safley and Westerman, 1990; Westerman, 1993; Macdonald et al., 1998; Sommer et al., 2004). In these works, a wide range of E values are estimated (from 28.54 kJ mol^{-1} in Westerman, 1993 to 112.7 kJ mol^{-1} in Sommer et al., 2004). Different estimates on E can be explained not only by the above mentioned differences in manure composition (Husted 1998), but also by different incubation times. Westerman (1993) thus showed how E of methanogenesis decreases with incubation times in wetlands.

In the Inventory of U.S. Greenhouse Gas Emissions and Sinks (USEPA, 2014) specific methods to estimate GHG emissions are provided. In this report, monthly CH_4 emissions for liquid/slurry, anaerobic lagoon, and deep pit systems are calculated in a methodology similar to IPCC (2006) (Tier 2), the main difference is the effect of temperature. In this case, CH_4 emission are estimated as the product of VS produced on a monthly basis, B_0 and a factor (f), which describes the effect of monthly air temperature on CH_4 emissions according to Arrhenius equation, based on Safley and Westerman (1990) and Mangino et al., (2001) recommendations. In those works, a constant E of 15.175 kcal mol^{-1}

(63.53 kJ mol^{-1}) is used. In order to simplify the model, Søren O. Petersen (personal communication) also suggested the use of a constant E (81.0 kJ mol^{-1}) for all slurry categories. This value is very similar to that found in this work for the complete CM model (Table 3), and very different to those obtained in the complete pig model, probably because as stated before, temperature response of the CH_4 emission of CM and PM is very different.

3.4.3 Conclusions and recommendations

Important differences on slurry composition and CH_4 emission between animal category (cattle and pig) were observed. Cattle manure showed higher TS, VS, fibre and E than PM. PM shows a higher unexplained VS (presumably the biodegradable fraction) and CH_4 emission than CM, especially at lower temperatures (10-20°C). This might explain the different responses to the temperature that was observed in the two categories of animals with regard to CH_4 emissions. Therefore, we recommend to use different MCF value for different animal categories to estimate the CH_4 emission during storage

The MCF values calculated from CM between 10 and 20°C were in the same level and lower than 8% for all CM manures tested. This value is lower than the current value used in Denmark's national inventory (10%) based in IPCC (2006) recommendations. The use of IPCC default values to estimate CH_4 emission from CM thus could lead to an overestimation of the country specific CH_4 emission from slurry storage in the range 10°C to 20°C. At higher temperatures and for PM, the calculated CH_4 emissions by using IPCC (2006) default values are closer or even lower than the experimental data obtained in this work.

A model to estimate CH_4 emission considering storage time and temperature has been developed in our work. This model shows a good correlation for CM in the temperature range between 10°C and 20°C. However, some difficulties to build a single model for each animal category were found. Cattle manure needed a high E to start methanogenesis which resulted in very different results for psycrophilic (10°C) and mesophilic (35°C) temperature ranges. In PM, the response to temperature differs among the three different slurries used and we suggest to extend the amount of data to better parameterize the model.

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