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Methane emissions during storage of different treatments from cattle manure in Tianjin

Jiajun Wang[1,2], Chiqing Duan[1,2], Yaqin Ji[1,2,*], Yichao Sun[3]

1. *College of Environmental Science and Engineering, Nankai University, Tianjin 300071, China. E-mail: xiaomei506@hotmail.com*
2. *State Environmental Protection Key Laboratory of Urban Ambient Air Particulate Matter Pollution Prevention and Control, Tianjin 300071, China*
3. *Institute of Environment and Ecology, Tianjin Academy of Environmental Sciences, Tianjin 300191, China*

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Abstract

Many studies on methane emissions from animal manure have revealed that animal manure is a major source of methane emissions to the atmosphere that can have negative consequences for people, animals and environment. In general, the release of methane can be influenced by the type of feed taken by animals, temperature, manure characteristics and so on. This study aimed at quantifying and comparing methane release from dairy manure with different piling treatments. Four treatments were designed including manure piling height 30, 45, 60 cm and adding 6 cm manure every day until the piling height was 60 cm. Static chamber method and gas chromatography were adopted to measure the methane emissions from April to June in 2009. Methane emission rates of all four manure treatments were low in the first week and then increased sharply until reaching the peak values. Subsequently, all the methane emission rates decreased and fluctuated within the steady range till the end of the experiment. Wilcoxon nonparametric tests analysis indicated that methane emission rate was greatly influenced by manure piling height and manner. There were no significant relationships between methane emission rates and the temperatures of ambience and heap. However, regression analysis showed that the quadratic equations were found between emission rates of all treatments and the gas temperature in the barrels.

Key words: dairy manure storage; methane emissions; different piling treatments

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Introduction

Methane (CH_4) which directly contributes to the global warming is an important greenhouse gas (GHG). CH_4 has a global warming potential 23 times that of CO_2 (Trine et al., 2006). A major change in atmosphere in recent years is the concentration of methane (IPCC, 2001). In the past 200 years, the atmospheric concentration of CH_4 has increased by 115% (Kyu-Hyun et al., 2006). Meanwhile, methane may contribute about 15%–17% to the greenhouse effect over the next 50 years (IPCC, 1992).

Worldwide agriculture plays a significant role in greenhouse effect (Amon et al., 2001). Methane, ammonia and nitrous oxide gases are produced from the decomposition of the animal wastes, the produced gases are subsequently volatilized and emitted to the outdoor environment (Blanes-Vidal et al., 2008). In recent years, with the increasing living standard and the change in diet structure the total amount of livestock and its manure has on the rise rapidly (Lu et al., 2008). Stored animal manure becomes the major source of atmospheric methane emission (Lu et al., 2007; National Research Council of the National Academies, 2003; Yamulki, 2006). The total methane emission from worldwide manure is 20–30 Tg/yr (You et al., 2008). It is estimated that livestock manure has contributed 5% to the total emission of CH_4 in the 1990s (Sven, 2006).

Recent works have shown that GHG emissions from farmyard manure were significantly influenced by manure characteristics during storage (Petersen et al., 1998). This article concentrates on the quantification of methane emissions from solid manure stores and investigating the influence of manure treatment and air temperature in buckets on methane release. Static chamber-GC method was adopted to measure the methane emissions. The results can not only provide the basic data for the research on methane emissions from the manure storage, assess and monitor the effect of system (dairy manure with different piling height treatments), but also serve as references for building the list of GHGs for China.

1 Materials and methods

1.1 Experimental design

Fresh dairy cattle manure used in the experiment was fecaluria (excreta) mixture containing a little sand. Manure

* Corresponding author. E-mail: jiyaqin@nankai.edu.cn

sample was obtained from the Holstein dairy cows (8–9 months old, approximate 300 kg weight) of the conventional dairy farmyard located in Qingguang Town, Beichen District of Tianjin, China. The following four different treatments were included in this experiment: manure piling height 30 cm (I), 45 cm (II), 60 cm (III) and adding 6 cm manure every day until the piling height was 60 cm (IV). The piling area of each treatment was 706.5 cm^2 in total (the cross-sectional area of the buckets). Each treatment was stored in replicate, resulting in eight chambers. The duration of the storage experiment was seven weeks from April to June 2009.

Static chamber-GC method was adopted by using laboratory simulating to analyze the methane emission from stored dairy manure of different piling treatments. The homogenized manure was filled into eight replicated 67.12 L cylindrical buckets made of polyethylene (95 cm in height, 30 cm in inner diameter and 31.5 cm in outer diameter). The buckets were all covered by air-tight lids and sealed with the panels of 45 cm × 45 cm at the bottom. A hole of 4 mm diameter was made on each lid to maintain the gas pressure in the bucket. To mix the air in the bucket thoroughly, a 3-V electric fan (10.00 cm (height) × 4.20 cm (width) × 3.20 cm (diameter)) was placed vertically inside the lid. At the beginning of the investigations, the volume of the closed chambers used for the determination of methane emission rates varied from 24.73 to 45.92 L. And it increased during the storage period because of evaporation. In the flank of the barrel, a hole (1 cm in diameter) was drilled at a distance of 20 cm from the top of bucket. This hole was attached with a tube whose other end was clamped air-tightly outside the barrel as an outlet for gas sampling. On each lid, two screwed outlets (both 25 mm in diameter) were made at 10 cm below the manure surface and in the middle of the manure pile for temperature measurements and manure sample collections. Figure 1 shows the experimental facility. To avoid the effect of precipitation on the experiment, the buckets were put in the laboratory with the door and windows open during the investigations.

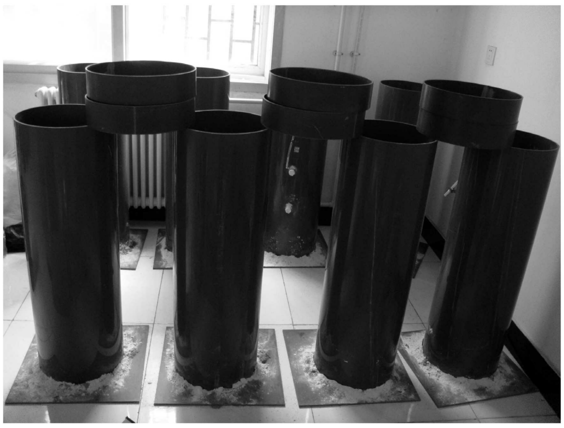

Fig. 1 Design of the experimental facility for quantifying methane emissions from manure storage.

1.2 Methane collection and analysis

1.2.1 Methane collection

In view of variability in methane emissions it was necessary to have frequent sampling to obtain reliable data (Amon et al., 2006). The gas samplings were taken at 9:00–10:00 in the morning and analyzed in time every day.

The manure storage buckets were closed and ventilated by fans only during measurements (Berg et al., 2006). According to the variability of the methane concentration in the chamber, the methane emission rates can be calculated (Møller et al., 2004). After each measurement the lids were removed to guarantee the manure exposed to natural conditions.

The process included the following steps. During each measurement, the lid was closed and gas sample was collected from each treatment at 0, 30 min by a 50-mL glass syringe through the connecting tube and transferred (under atmospheric pressure) into 0.5-L aluminum foil gas collecting bags to store. At the same time, the temperatures of ambient atmosphere and the gas in the buckets were measured. The temperatures at 10 cm below the manure surface and in the middle of the manure were measured daily.

1.2.2 Methane analysis

CH_4 gas was analyzed by means of gas chromatography (GC-6820N, Agilent Inc., USA) with flame ionization detector (FID), equipped with a HP-5MS capillary column (30 m × 0.32 mm × 0.25 μm). Operating temperature were 80°C for the column, 150°C for the injector and 200°C for the detector. The carrier gas was nitrogen (99.999%). The purging gas was high purity nitrogen (10 mL/min) and the duration of purging was 0.75 min. The total injection time was 3.5 min. Every time, 1 mL gas sample was injected manually. Two parallel injections were measured. The equipments were calibrated with a CH_4 calibration gas (the concentration of 12.43 mg/m^3, under the condition of 101.325 kPa) at the beginning and end of the sample measurements. According to the peak area in chromatogram, the percentage content of methane in the air samples can be calculated by the external standard method.

The methane emission rates from the manure were calculated by Eq. (1) (Sommer and Møller, 2000):

$$F = \frac{\rho \times V \times (\frac{dc}{dt}) \times \frac{273}{273+T}}{m} \tag{1}$$

where, F (mg/(kg·hr)) represents the emission rate of methane; ρ (0.717 kg/m^3) is methane density on standard condition; V (m^3) is the volume of the headspace in bucket; $\frac{dc}{dt}$ shows the methane concentration variance in the bucket; T (°C) is the average gas temperature in the bucket during gas sampling; m (kg) represents the mass of the dairy manure used in each treatment. In addition, statistical data analysis was carried out with the software package SPSS, Version 11.5.

1.3 Chemical composition analysis of manure

Some researches put forward that manure chemical characteristics affected methane emission (National

Research Council of the National Academies, 2003; You et al., 2008). During the period of manure storage, water content of the manure decreased and some other characteristics also changed. So the characteristics of the fresh manure were concerned (Lu et al., 2008).

After manure being homogenized, about 500 g fresh manure samples were drawn and frozen at 4°C for characteristics analysis. In order to show the changes during the storage period, manure samples from 10 cm under the surface were also taken after seven weeks storage to analyze its density, pH, dry matter content (DM), volatile solid (VS), ash, total nitrogen (TN), total phosphorus (TP), ammonia nitrogen (NH_3-N) and total organic carbon (TOC) through the conventional analytical techniques. In this experiment, the density of the manure was determined by cutting ring method (Lu et al., 2007, 2008). Moisture content was measured by vacuum drying method (GB8575-88). Manure pH was measured with a pH meter (pHS-25) in samples (Külling et al., 2002). DM was analyzed by heating samples in an electric oven at (105 ± 2)°C for 24 hr. VS and ash were analyzed by heating samples in a muffle furnace at 550°C for 4 hr. Manure contents of TN and TP were determined by sulfate-hydrogen peroxide heating digestion method (NY/T297-1995) and vanadium ammonium molybdate spectrophotometry (NY/T298-1995) respectively. NH_3-N was measured by formaldehyde method (GB/T3600-2000). TOC was determined by thermal potassium dichromate oxidation-capacity method.

2 Results and discussion

2.1 Chemical composition

The density of the dairy cattle's fresh manure used in this experiment was 1121.68 kg/m^3. The analytic results of pre- and post-manure storage experiment are shown in Table 1. After seven weeks, DM and VS of all four different treatments decreased while ash, TN, TP, NH_3-N and TOC increased. The C/N ratios of treatments III and IV were slightly higher while that of treatments I and II were similar to the fresh manure. Except treatment I, pH values of other treatments decreased a little. It means the manure samples were acidified slightly.

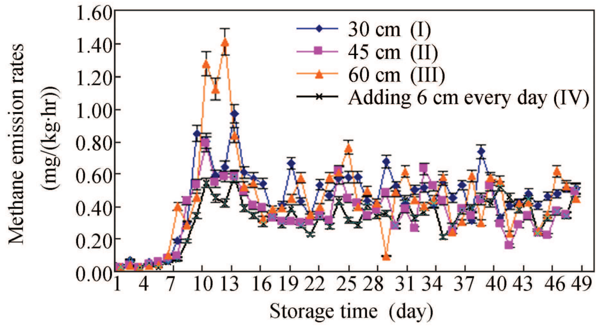

Fig. 2 Methane emission rates from different treatments of dairy cattle manure.

2.2 Tendency of methane emission rate

Figure 2 shows that the four different treatments have the similar tendency on methane emission rates.

Methane emissions after storage experiment were small with all treatments in the first week. And then the methane emission rates peaked after 10 days of storage, thereafter they decreased and ranged from 0.2 to 0.6 mg/(kg·hr). The maximum methane emission rates of all four treatments (I, II, III, IV) were 0.9746, 0.7838, 1.4323 and 0.5790 mg/(kg·hr), respectively. The peak emission rate of treatment III was the maximum while that of treatment IV was the minimum. Average methane emission rates observed from all the treatments were 0.4446, 0.3351, 0.4405 and 0.3052 mg/(kg·hr), respectively. Totally, the emission rates of four different dairy manure treatments decreased and stayed steadily after the peak emissions.

Methane formation is a strictly anaerobic process. Previous studies showed that the anaerobic conditions generally promoted methane production (National Research Council of the National Academies, 2003; You et al., 2008). At the beginning, low methane emission rates observed in all treatments presumably resulted from the aerobic conditions and low ambient temperature. From day 2 to day 8 of the storage, manure pilings of all treatments expanded palpably due to fermenting. As an example, the piling height of treatment III increased by 20%. After that, as a result of microbial decomposition and evaporation, the piling height of the treatments decreased and the anaerobic condition formed gradually during the storage. Due to the microbial decomposition of the organic material contained in manure under the steady anaerobic conditions and increasing temperature inside the heap, methane emission

Table 1 Characteristics of the dairy manure used

	Fresh manure	After seven weeks			
		30 cm (I)	45 cm (II)	60 cm (III)	Adding 6 cm every day (IV)
Density (kg/m^3)	1121.68	–	–	–	–
Moisture content (%)	63.78	–	–	–	–
pH	8.00	8.07 ± 0.01	7.83 ± 0.05	7.92 ± 0.05	7.97 ± 0.10
DM (g/kg wet basis)	234.17	195.77 ± 11.75	203.87 ± 5.84	204.19 ± 4.53	167.69 ± 8.00
VS (g/kg wet basis)	712.15	694.58 ± 18.88	709.32 ± 5.40	694.40 ± 5.02	670.39 ± 6.54
Ash (g/kg wet basis)	287.85	305.42 ± 18.88	290.68 ± 5.40	305.60 ± 5.02	329.61 ± 6.54
TN (g/kg dry basis)	19.10	20.50 ± 0.10	20.15 ± 0.15	20.10 ± 0.06	20.55 ± 0.55
TP (g/kg dry basis)	2.10	7.75 ± 0.10	5.55 ± 1.25	6.30 ± 0.25	7.40 ± 0.60
NH_3-N (g/kg dry basis)	0.50	1.25 ± 0.05	1.39 ± 0.06	1.25 ± 0.05	1.58 ± 0.10
TOC (g/kg dry basis)	49.50	51.15 ± 0.05	50.60 ± 4.50	54.80 ± 0.10	57.25 ± 1.15
C/N ratio	25.92	24.95 ± 1.29	25.13 ± 2.42	27.26 ± 0.24	27.86 ± 0.19

Table 2 Results of Wilcoxon Signed Ranks Test

Index	I–II	I–III	I–IV	II–III	II–IV	III–IV
Z	–4.963[a]	–5.418[a]	–5.206[a]	–3.979[a]	–1.757[a]	–2.677[b]
Asymp. sig. (2-tailed)	0.000	0.000	0.000	0.000	0.079	0.007

[a] Based on positive ranks; [b] based on negative ranks.

rates increased over the first 13 days of storage. And then the crusts formed on the surface of the heap which decreased the wind speed over the heap and lower gas escape, resulting in the subsequent decline in methane concentration (Blanes-Vidal et al., 2008).

2.3 Effect of piling treatment on methane emission

Some works reported that a large-scale compost heap increases the emission rates of methane while a smaller pile is adverse to methane emissions (Fukumoto et al., 2003). However, the different results of this experiment may be explained by the crusts formed on the surface which decreased the wind speed over the heap and lower gas escape, influencing methane emissions (Blanes-Vidal et al., 2008). Wilcoxon nonparametric test was applied for a correlation analysis between different piling treatments and methane emissions. The results are shown in Table 2.

The results showed no significant difference ($P > 0.05$) between treatment II and IV but a clear and significant difference ($P < 0.05$) in methane emissions between other different piling treatments, namely treatment I and II, I and III, I and IV, II and III, and III and IV which proved that piling height had an obvious effect on methane emissions. Although the final piling height of treatment III and IV were both 60 cm, the significant difference was also found between them, it is likely because 60 cm piling height of treatment IV was reached gradually and methane was easily emitted from the center of the piling manure within the first ten days.

2.4 Effect of temperature on methane emission

Many studies have revealed that temperature had a strong influence on both the short- and long-term methane emissions of animal manure. The amount of methane produced during the manure stores was mainly affected by the ambient and heap temperatures, which influenced the growth of the bacteria responsible for methane formation (Gupta et al., 2007). The heap will stay warmer than the ambient air temperature as temperature drops in the fall, and will stay colder than the ambient air temperature as temperature rises in the spring (Gupta et al., 2007).

The methane emission rates of manure increased with the rising temperature. A significant relationship was found between temperature and methane emission rate of dairy manure (Lu et al., 2007). Husted (1994) also pointed out that methane emissions correlated with heap temperature, which was possibly owing to differences in animal husbandry practices and environmental conditions. However, Mangino et al. (2001) observed an insignificant correlation between ambient air temperature and manure heap temperature, which may be due to the high porosity inside the heap. The low dependency of CH_4 emission on heap temperature might be due to compaction, height, age, moisture and type of feed taken by animals (Mangino et al., 2001).

As the temperature of the atmosphere rose gradually, the gas temperature in the bucket also has a similar tendency. But insignificant correlation was observed between methane emission rate and ambient temperature in this study. Also, no clear relationship was found between the heap temperature and methane emission rate of the manure. This consequence was not consistent with that concluded by Yamulki (2006). However, Fig. 3 shows methane emission rates closely followed the gas temperatures measured in the barrels. Therefore regression analysis allows us to obtain the relationships between

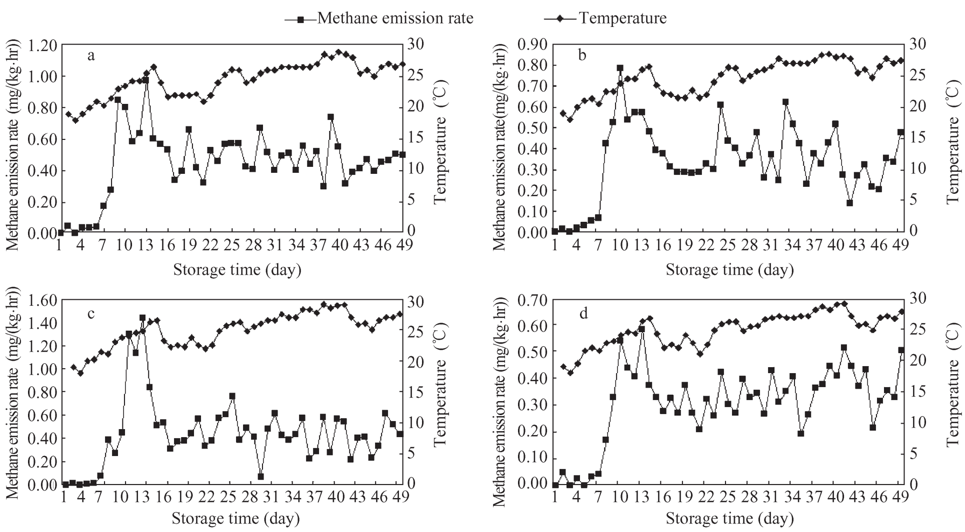

Fig. 3 Relationships between methane emission rates and the gas temperature in the buckets during the sampling period. (a) treatment I; (b) treatment II; (c) treatment III; (d) treatment IV.

them. The optimalizing equations are shown as follows:

$$Y \text{ (treatment I)} = 0.0026X + 0.0006X^2 \quad (R^2 = 0.8652, F = 0.0000) \tag{2}$$

$$Y \text{ (treatment II)} = 0.0008X + 0.0005X^2 \quad (R^2 = 0.8326, F = 0.0000) \tag{3}$$

$$Y \text{ (treatment III)} = 0.0137X - 0.0002X^2 \quad (R^2 = 0.5664, F = 0.0000) \tag{4}$$

$$Y \text{ (treatment IV)} = -0.0126X + 0.0010X^2 \quad (R^2 = 0.9102, F = 0.0000) \tag{5}$$

where, X (°C) is the gas temperature in the barrel and Y (mg/(kg·hr)) is the methane emission rate. The F values of the curve models were all much smaller than 0.05, which revealed that they were reliable.

2.5 Methane cumulative emission fluxes

In order to assess the cumulative effect of methane production, the methane cumulative emission fluxes of the manure with different piling treatments in the seven weeks experiment are shown in Fig. 4. It reveals that the tendencies of cumulative emission fluxes from four treatments were similar. The cumulative emission fluxes of all four different treatments (I, II, III, IV) were 516.8274, 388.4145, 512.7871 and 352.8619 mg/kg, respectively. In other words, treatment I had the maximum cumulative emission fluxes whereas treatment IV had the minimum.

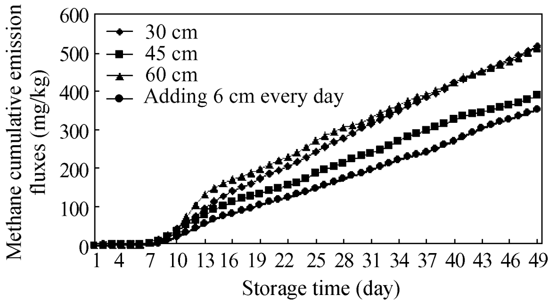

Fig. 4 Methane cumulative emission fluxes of dairy manure with different piling treatments.

3 Conclusions

Methane release from dairy manure with different piling treatments were investigated by the static chamber-GC method from April to June. The manure chemical analysis results of pre- and post-manure storage experiments indicated that DM and VS of all four different treatments decreased while ash, TN, TP, NH_3-N and TOC increased, and the manure samples were acidified slightly. The methane emissions from all four different dairy manure treatments were low at the beginning and then increased sharply until reaching the peak values. Subsequently, all the methane emission rates decreased and fluctuated in the steady range till the end. Furthermore, Wilcoxon nonparametric tests showed that piling height and manner impacted on the methane emission rates from manure. The quadratic relationships were found between the emission rates of all treatments and the gas temperature measured in the barrels by regression analysis. Additionally, other factors affecting methane formation and gaseous concentrations of the manure, such as water content, pH values, the covering style of manure, ventilation flow, air velocity over the manure space and other site-specific factors also should be researched further.

Acknowledgments

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