

GASEOUS EMISSIONS FROM MANURE AS AFFECTED BY MICROBIAL-BASED ADDITIVE AND TEMPERATURE

Raimundas Matulaitis, Violeta Juškienė, Remigijus Juška
Institute of Animal Science, Lithuanian University of Health Sciences (LUHS)
R. Žebenkos 12, LT-82317 Baisogala, Radviliškis Distr., Lithuania
Tel. +370 42265383; e-mail: ramatulaitis@gmail.com

Abstract. This experiment was conducted to investigate ammonia (NH₃), methane (CH₄), hydrogen sulfide (H₂S), carbon dioxide (CO₂), carbon monoxide (CO) and nitric oxide (NO) emissions during the storage of untreated pig and cattle liquid manure at different temperatures and to assess the effect of the microbial-based additive for the volatilization of these gasses.

Dynamic chamber method and infrared or electrochemical detection were employed using laboratory simulation to analyze the gas emissions from pig and cattle liquid manure. Twenty-four buckets were filled with fresh manure. To half of the buckets the microbial-based additive was added. The samples were stored for a period of 29 days at 5±1, 15±1 and 25±1 °C temperatures.

The present study showed that under the same storage conditions, the use of the additive did not change the manure characteristics and did not result in significant differences between the emission rate of measured gases from the untreated manure and from manure+additive for both pig and cattle. Nevertheless, the use of the microbial-based additive has a tendency to reduce ammonia emission from pig manure, contrariwise, it has the potential to increase the emissions of CH₄, CO and NO of pig and cattle manure. In this experiment, the temperature and the type of manure were the main factors significantly related to the emission rates of investigated gases.

Keywords: gas emission, additive, manure, pig, cattle

MIKROBIOLOGINIO PRIEDO IR TEMPERATŪROS POVEIKIS DUJŲ EMISIJAI IŠ MĖŠLO

Raimundas Matulaitis, Violeta Juškienė, Remigijus Juška
Gyvininkystės institutas, Lietuvos sveikatos mokslų universitetas
R. Žebenkos g. 12, LT-82317 Baisogala, Radviliškio r.; tel. +370 422 65 383; el. paštas: ramatulaitis@gmail.com

Santrauka. Šio darbo tikslas buvo išmatuoti mikrobiologinio priedo poveikį amoniako (NH₃), metano (CH₄), vandenilio sulfido (H₂S), anglies dioksido (CO₂), anglies monoksido (CO) ir azoto oksido (NO) emisijai iš skystojo kiaulių bei galvijų mėšlo esant skirtingai aplinkos temperatūrai.

Bandymas atliktas laboratorinėmis sąlygomis. Dujų emisija matuota iš kiaulių ir galvijų skystojo mėšlo dinaminės kameros metodu bei infraraudonųjų spindulių arba elektrochemine detekcija. Tyrimui naudotas šviežias mėšlas, išdalintas į dvidešimt keturis indus. Į pusę indų įpilta mikrobiologinio priedo. Mėginiai inkubuoti 29 dienas pastovioje 5±1, 15±1 ir 25±1 °C temperatūroje.

Bandymas parodė, kad tomis pačiomis kiaulių ir galvijų mėšlo laikymo sąlygomis patikimo skirtumo tarp mėšlo sąvybių bei matuotos dujų emisijos iš natūralaus mėšlo, ir mėšlo su priedu nebuvo. Vis dėlto, mikrobiologinis priedas turėjo tendenciją mažinti amoniako emisiją iš kiaulių mėšlo ir priešingai – didinti CH₄, CO ir NO emisiją iš kiaulių bei galvijų mėšlo. Šio bandymo metu temperatūra ir mėšlo rūšis buvo pagrindiniai veiksniai, statistškai patikimai susiję su tirtų dujų emisija.

Raktažodžiai: dujų emisija, priedas, mėšlas, kiaulės, galvijai.

Introduction. Stored animal manure becomes the source of ammonia (NH₃), methane (CH₄), hydrogen sulfide (H₂S), carbon dioxide (CO₂), carbon monoxide (CO), nitric oxide (NO) and other gases including malodour. It was estimated that livestock manure contributed to 5 % of the total emission of CH₄ in the 1990s (Sommer, 2006). Livestock excreta accounts for more than 80 % of NH₃ emissions from European agriculture (EMEP/EEA, 2009). Ammonia and methane emissions are related with serious environmental problems. NH₃ contributes to eutrophication and acidification of soils and also indirectly contributes to N₂O emissions by increasing the N-cycling in natural

ecosystems (Dinuccio et al., 2008). CO₂, CH₄ and N₂O are greenhouse gases affecting the global environment and climate change. Hydrogen sulphide and ammonia are certainly odourants associated with livestock production. Carbon monoxide has a negative impact on health. Nitric oxide is involved in the formation of ozone, which near the surface of the Earth can have an adverse effect on human health and plant growth (EMEP/EEA, 2009).

There are wide possibilities for managing livestock wastes and reduction of gas emission to the atmosphere. But use of some effective methods is limited, primarily due to the high cost and expertise required to operate these mechanized systems effectively, especially on small

farms. Therefore, attention has been focused on treatment methods that alleviate associated problems. One treatment approach that appears to fit these criteria is livestock waste additives. There exist many commercially available additives to manures for reducing odour and other gases emission (Van der Stelt et al., 2007; Sasaki et al., 2006; McCrory, Hobbs, 2001). The results of some studies are promising. Sasaki et al. (2006) found a quicker depression of ammonia emission from the compost pile after use of microbiological additive. Wang et al. (2009) study indicated that feed supplementation with BioPlus 2B® can reduce manure NH₃ emission (but not H₂S and mercaptan emission) in growing pigs without impacting growth performance. Lee et al. (2007) attained about 88.3 % and 70 % NH₃ and H₂S emissions suppression from swine manure, after use of aqueous foam, containing microorganisms, monocalcium phosphate and the Yucca extracts. At 4 °C storage temperature and no mixing, a significant decrease of 34 % in NH₃ volatilization was observed, when Agri-mest® and Effective Microorganisms® were applied to manure in combination (Van der Stelt et al., 2007). Park et al. (2006) found NH₃, H₂S and odour emissions suppression from swine manure after use of cover made of aqueous foam. Furthermore, emissions of odorous compounds were better controlled by incorporating odour-degrading bacteria into the aqueous foam. The study of Amon et al. (2005) indicated that NH₃ emission was considerably reduced by 11 % through the addition of effective microorganisms (EM), but an increase of CH₄ and CO₂ emissions by 32 % and 3 % were detected.

According to McCrory and Hobbs (2001) microbial-based digestive additives may offer a long-term control solution of odour and ammonia emissions from livestock wastes. But currently, their use cannot be recommended because of lack of investigations. Besides, the results of different studies are not consistent. It is questionable if all commercially available additives can reduce manure gas emissions. Also, it seems, that microbial-based additives can help to decrease individual gas emission at the same time increasing emissions of other gases. Thus, to determine if the commercially available microbial-based digestive additives indeed decrease the polluting gas emissions from livestock manure, the further experiments should be made.

This experiment was conducted to investigate NH₃, CH₄, H₂S, CO₂, CO and NO emissions during the storage of untreated pig and cattle liquid manure at different temperatures and to assess the effect of the microbial-based additive for the volatilization of these gasses.

Materials and methods

Experimental design. The trials were carried out at the Institute of Animal Sciences of the Lithuanian University of Health Sciences.

Fresh pig and cattle liquid manure were collected from two commercial farms. The same day manure was homogenized and twenty-four 2.1 l buckets were filled with 1.0 l of manure. Twelve buckets were filled with pig manure, other twelve with cattle manure. The samples were stored in open buckets in three temperature

controlled rooms, which were kept at 5±1, 15±1 and 25±1 °C. On the next day, 20 ml of the microbial-based digestive additive were added to half of the buckets and 20 ml of deionised water, to the other half of buckets. The same additions were repeated after 6, 14 and 20 days of the experiment. Two replicates of each sample were tested (for untreated pig manure, untreated cattle manure, pig manure with the additive and cattle manure with the additive), thus a total of 8 buckets were used per climate room. The gas measurement period extended for 29 days.

Additive. The microbial-based digestive additive used in the current experiment is comprised of a mixture of: *Bacillus subtilis* var natto, *Bifidobacterium animalis*, *Bifidobacterium bifidum*, *Bifidobacterium longum*, *Lactobacillus acidophilus*, *Lactobacillus buchneri*, *Lactobacillus bulgaricus*, *Lactobacillus casei*, *Lactobacillus delbrueckii*, *Lactobacillus fermentum*, *Lactobacillus plantarum*, *Lactococcus lactis*, *Lactococcus lactis* subsp. *Diacetylactis*, *Rhodopseudomonas palustris*, *Rhodopseudomonas sphaeroides*, *Saccharomyces cerevisiae*, *Streptococcus thermophilus*, molasses, sea saline, rice-brans, flours of minerals, mixture of different herbs and algae. It contains at least 5.4×10^6 cfu/ml of lactic acid bacteria and 1.4×10^4 cfu/ml of yeast. The pH of the product is 3.26-3.60, moisture content – 94.86 %.

Measurement of gases. The dynamic chamber method and gas measuring devices (Dräger X-am 7000, Dräger Pac III, M40) were applied for laboratory simulation to analyze the gas emission from the stored manure. Until and after each gas concentration measurement, the samples of manure were stored in open buckets, as described in studies of Wang et al. (2010) and Dinuccio et al. (2008). At the beginning of the measurements, each bucket was closed with an airtight lid provided with two ports for air inlet and outlet (Fig. 1). The air outlet port was connected with a gas measuring device, sampling pump and a flow meter. The headspace (chamber) between the manure surface and the lid was then ventilated by pumping air to create a 0.015 m³/h air flow rate through the dynamic chamber.

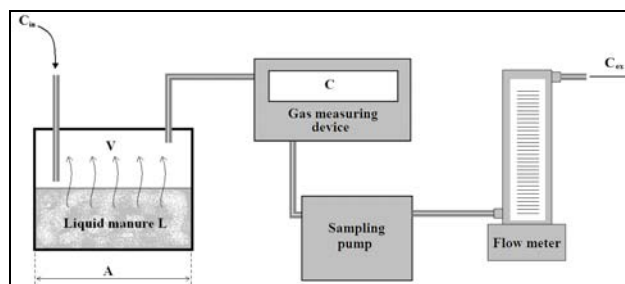


Fig. 1. Schematic diagram of the gas measuring system

Gas measurements were carried out 1–2 times per week. Gas emission rate from the manure under standard conditions (25 °C and 100 kPa) were calculated by Eq. (1):

$$F = Q V M p (C_{ex} - C_{in}) R^{-1} (T + 273)^{-1} A^{-1} \quad (1)$$

where, F (mg m⁻² h⁻¹) – represents the emission rate of NH₃, CH₄, H₂S, CO₂, CO or NO gases; Q (m³ h⁻¹) – the air

flow rate through the chamber; V (m^3) – the volume of the headspace in the bucket; M (g mol^{-1}) – gas mole mass; p (kPa) – gas pressure; C_{in} (ppm) – gas concentration of air inlet into the chamber; C_{ex} (ppm) – gas concentration of air outlet from the chamber; R ($8.314 \text{ J K}^{-1} \text{ mol}^{-1}$) – gas constant; T ($^{\circ}\text{C}$) – gas temperature; A (m^2) – the surface area of manure.

Analysis of manure. At the beginning and at the end of the investigation period the samples were analyzed for pH, total solids (TS), ash, volatile solids (VS), total Kjeldhal nitrogen (TKN) and total ammonia nitrogen (TAN) through conventional analytical methods. The manure pH was measured with a pH meter (HI 98128). The total solids content was determined after drying in an electric oven at $105 \pm 2^{\circ}\text{C}$ for 24 h. (Peters (ed.) et al., 2003). Volatile solids and ash content were determined

after burning TS in a muffle furnace at 550°C for 4 h. The total nitrogen was measured by the Kjeldahl method, the total ammonia nitrogen in the manure – by distillation and a FOSS Tecator™ device. All analyses were carried out in duplicate, and values are given as average of the two results.

Statistical analysis. Statistical analysis was conducted by using the software package Statistica (version 7.1). Significant differences in results were investigated using the ANOVA procedure. A significance level of $P=0.05$ was applied. Assumption of equal variance of different groups was tested using Bartlett's test prior to analysis.

Results

Composition of manure. The analytical results of pre- and post- manure storage experiment are shown in Table 1.

Table 1. Composition of manure at the beginning and the end of the experiment

Measurement time:		At the beginning of experiment	At the end of experiment					
Storage temperature ($^{\circ}\text{C}$):		-	5		15		25	
Type of manure:		Fresh manure	Untreated manure	Manure+ additive	Untreated manure	Manure+ additive	Untreated manure	Manure+ additive
Type of animal:		Pig						
Analysis:	pH	8.83	9.00	8.62	7.98	7.41	7.44	7.26
	TS (%)	14.92	18.22	17.00	14.01	13.57	15.50	14.39
	VS (%)	12.49	14.55	13.90	11.28	10.98	12.38	11.42
	Ash (%)	2.44	3.67	3.10	2.73	2.60	3.13	2.97
	TKN (g/kg)	7.33	8.62	8.60	6.93	6.17	6.09	6.18
	TAN (g/kg)	4.34	4.03	4.10	3.54	3.49	3.26	3.11
Type of animal:		Cattle						
Analysis:	pH	8.40	9.23	9.05	8.27	7.87	7.92	7.82
	TS (%)	10.84	13.23	12.53	10.33	9.64	9.99	9.79
	VS (%)	9.24	11.18	10.63	8.45	7.39	8.34	8.20
	Ash (%)	1.59	2.05	1.90	1.88	2.25	1.65	1.59
	TKN (g/kg)	3.47	4.85	4.92	3.59	3.85	3.64	3.79
	TAN (g/kg)	0.84	2.33	2.56	1.97	2.01	1.61	1.70

Over the storage period water evaporation occurred in all samples and it caused the relative increase of total solids (TS), volatile solids (VS) and ash amounts in some samples taken for chemical analysis. However, because of differences in the degradation rate of organic matter, the changes of TS and VS in the samples were not equal. At the end of experiment, TS and VS increased for pig and cattle manure stored at 5°C , also TS increased for pig manure stored at 25°C , but for all other treatments TS and VS decreased. After manure storage period, TS and VS were higher for all untreated manure by 2–14 % compared with the manure+additive. At the end of the experiment, the ash content of all manure samples taken for chemical analysis were higher than in the fresh manure which was analyzed at the beginning of the experiment. The changes of pH values, showed quite similar tendencies as TS and VS. pH value increased for pig and cattle manure stored at 5°C , but for all other samples it decreased. pH were slightly lower in all samples of manure+additive compared with untreated manure. At the end of the experiment the TKN increased

for all treatments except for pig manure stored at 15 and 25°C . TAN changed differently for pig and cattle manure. I. e. it decreased for pig, but increased for cattle manure. The differences in TKN and TAN content between the untreated manure and manure+additive, were slight.

Ammonia emission. Under the same storage conditions, untreated manure and manure+additive showed similar tendencies regarding ammonia emission rate (Fig. 2).

The emission rate of ammonia from untreated pig manure was highest at the beginning of the storage at 5°C . While at 15°C , the emission peaked after 8–11 d. of storage. At 25°C the emission was highest at the beginning and at the end of the storage period. Under all storage conditions the emission rate of NH_3 from cattle manure peaked after 4–8 d. of storage. Average NH_3 emission rate for untreated pig manure ranged from 21.16 to $172.33 \text{ mg m}^{-2} \text{ h}^{-1}$ and for untreated cattle manure emission was lower – from 14.25 to $77.24 \text{ mg m}^{-2} \text{ h}^{-1}$ (Table 2).

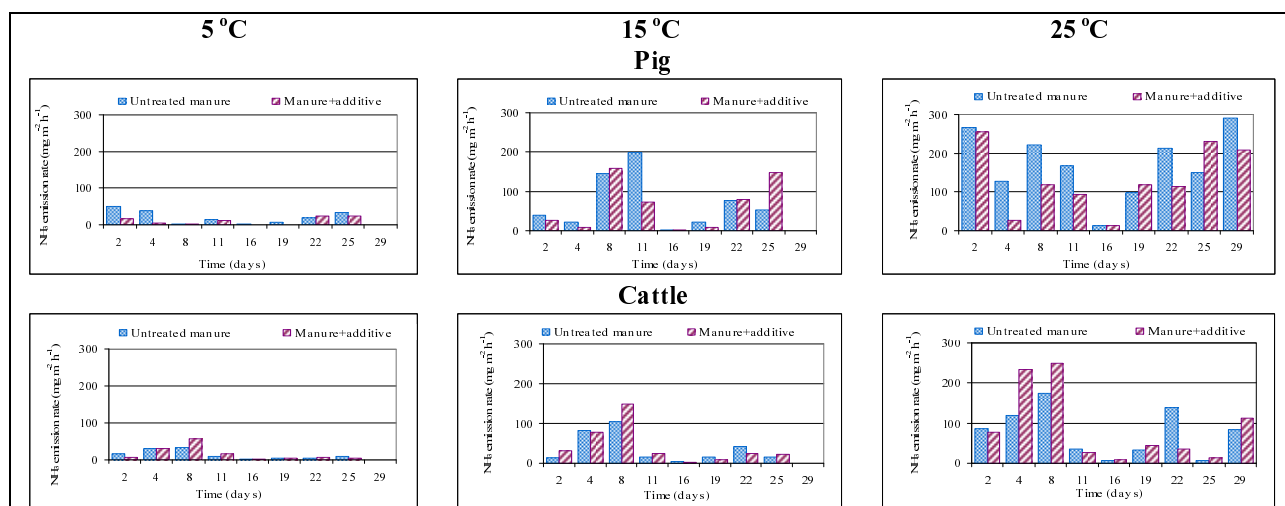
Fig. 2. Ammonia (NH₃) emission rate

Table 2. Average gas emission rates from manure

Storage temperature (°C):		5		15		25	
Type of manure:		Untreated manure	Manure+ additive	Untreated manure	Manure+ additive	Untreated manure	Manure+ additive
Type of animal:		Pig					
Average gas emission rates (mg m ⁻² h ⁻¹):	NH ₃	21.16	10.38	69.87	63.30	172.33	130.95
	CH ₄	27.95	97.41	788.51	880.70	1217.15	1692.92
	H ₂ S	1.58	6.40	55.60	54.94	114.83	113.98
	CO ₂	718.24	727.33	3653.97	3873.35	6611.20	5715.31
	CO	0.29	0.34	2.04	4.32	12.62	15.73
	NO	0.51	1.16	6.33	6.30	14.06	14.45
Type of animal:		Cattle					
Average gas emission rates (mg m ⁻² h ⁻¹):	NH ₃	14.25	16.32	34.33	42.52	77.24	89.16
	CH ₄	13.92	20.96	440.32	433.05	2038.17	2396.36
	H ₂ S	1.39	3.32	11.87	19.23	7.52	11.78
	CO ₂	817.46	442.97	1257.24	806.75	3882.81	3662.98
	CO	0.78	0.93	1.27	1.22	1.92	2.55
	NO	0.72	0.99	1.61	2.48	1.15	1.59

Table 3. Cumulative loss of NH₃, CH₄, H₂S, CO₂, CO and NO from the manure

Storage temperature (°C):		5		15		25	
Type of manure:		Untreated manure	Manure+ additive	Untreated manure	Manure+ additive	Untreated manure	Manure+ additive
Type of animal:		Pig					
Cumulative loss of gases over 29 days (mg 0.02 m ⁻² l ⁻¹):	NH ₃	329.94	161.88	1089.33	986.93	2686.66	2041.63
	CH ₄	435.82	1518.63	12293.24	13730.46	18975.86	26393.29
	H ₂ S	24.59	99.74	866.77	856.47	1790.23	1777.06
	CO ₂	11197.63	11339.37	56966.79	60387.09	103071.20	89104.01
	CO	4.57	5.31	31.73	67.30	196.71	245.18
	NO	7.99	18.07	98.75	98.28	219.22	225.21
Type of animal:		Cattle					
Cumulative loss of gases over 29 days (mg 0.02 m ⁻² l ⁻¹):	NH ₃	222.21	254.50	535.27	662.84	1204.24	1390.08
	CH ₄	217.08	326.83	6864.70	6751.38	31775.92	37360.14
	H ₂ S	21.73	51.79	184.99	299.83	117.31	183.59
	CO ₂	12744.58	6906.09	19600.91	12577.57	60534.51	57107.27
	CO	12.18	14.48	19.81	19.03	29.91	39.82
	NO	11.21	15.50	25.04	38.63	17.85	24.72

The cumulative losses of gases from the manure over 29 days of storage are given in Table 3. For pig manure, the addition of microbial-based additive tended to reduce ammonia losses, when compared with the storage of untreated pig manure. The average emission rate and cumulative loss of NH_3 from pig manure+additive was lower from 9.4 % to 50.9 % (depending on storage temperature) in relation to the untreated manure. However, for cattle manure, the NH_3 losses measured from the storage of manure+additive were from 12.69 % to 19.25 % higher than those measured from the untreated cattle manure stored at 5 and 15 °C, respectively. However, the differences between the NH_3 emission from the untreated manure and from manure+additive were not significant ($P>0.05$) for both pig and cattle, and showed

only a tendency.

The emission of ammonia increased with an increase in the storing temperature ($P<0.05$). The average NH_3 emission from untreated pig manure stored at 15 °C and 25 °C was 3.3 and 8.1 times higher respectively, than at 5 °C. While for the untreated cattle manure an increase of emission was 2.4 and 5.4 times, respectively.

During manure storage, the predominant loss of initial nitrogen (TKN) was as NH_3 (Table 4). In the following way, total losses of TKN ranged from 1.82 % to 32.96 %. For pig manure, the total NH_3 losses measured from the storage of untreated manure and manure+additive were significantly higher by 52 % and 28 % ($P<0.05$) in comparison with those measured from cattle manure.

Table 4 Mean losses of the initial nitrogen and carbon content occurring in the form of gas volatilization at the end of the experiment

Storage temperature (°C):		5		15		25	
Type of manure:		Untreated manure	Manure+additive	Untreated manure	Manure+additive	Untreated manure	Manure+additive
Type of animal:		Pig					
Loss of the initial nitrogen content (% TKN):	NH_3	3.70	1.82	12.22	11.07	30.15	22.91
	NO	0.05	0.12	0.63	0.63	1.40	1.43
Loss of the initial carbon content (% VS):	CH_4	0.26	0.91	7.37	8.24	11.38	15.83
	CO_2	2.45	2.48	12.45	13.20	22.53	19.47
	CO	0.00	0.00	0.01	0.02	0.07	0.08
Type of animal:		Cattle					
Loss of the initial nitrogen content (% TKN):	NH_3	5.27	6.04	12.69	15.72	28.56	32.96
	NO	0.15	0.21	0.34	0.52	0.24	0.33
Loss of the initial carbon content (% VS):	CH_4	0.18	0.26	5.56	5.47	25.74	30.27
	CO_2	3.76	2.04	5.79	3.71	17.87	16.86
	CO	0.01	0.01	0.01	0.01	0.01	0.02

Methane emission. Under storage at 5 °C, methane emission was negligible for both – cattle and pig manure. But at 15 °C and 25 °C the emission rate of methane was higher significantly and peaked two times – after 8-11 d. and after 25-29 d. of storage (Fig. 3). The average CH_4 emission rate for the untreated pig manure ranged from 27.95 to 1217.15 $\text{mg m}^{-2} \text{h}^{-1}$ and for the untreated cattle manure – from 13.92 to 2038.17 $\text{mg m}^{-2} \text{h}^{-1}$ (Table 2).

The use of microbial-based additive tended to increase the methane emission from manure. CH_4 emission from the untreated pig manure stored at 5 °C, 15 °C and 25 °C was 3.5, 1.1 and 1.4 times lower respectively, than that from the manure+additive (Table 2; Table 3). CH_4 emission from the untreated cattle manure stored at 5 °C and 25 °C was 1.5 and 1.2 times lower respectively, than that from the manure+additive. At 15 °C the difference was negligible. However, the differences between CH_4 emission from the untreated manure and from manure+additive were not significant ($P>0.05$) for both pigs and cattle, and showed only a tendency.

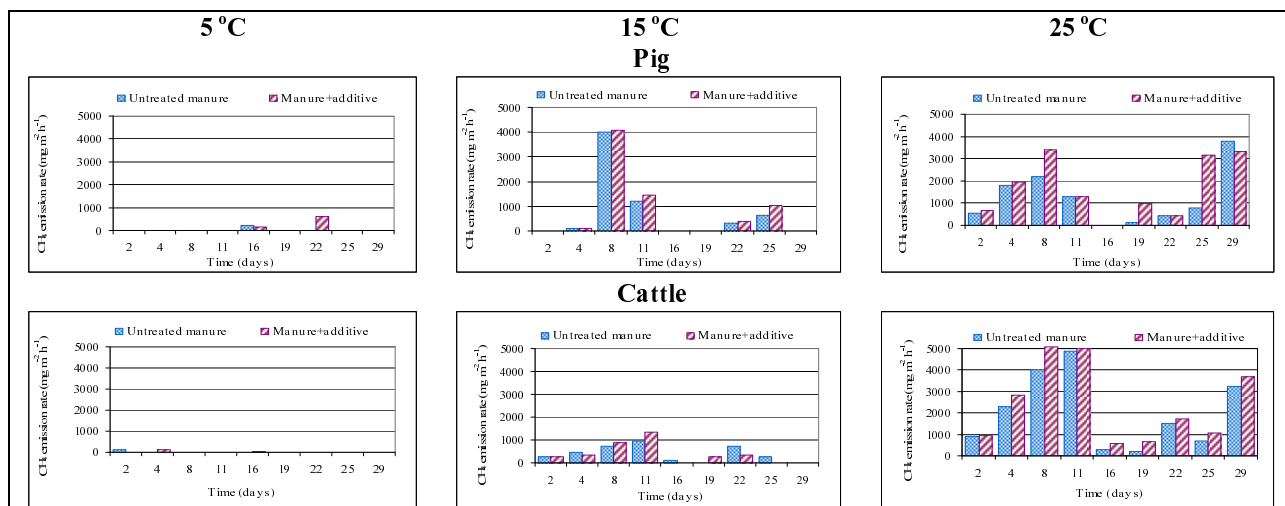
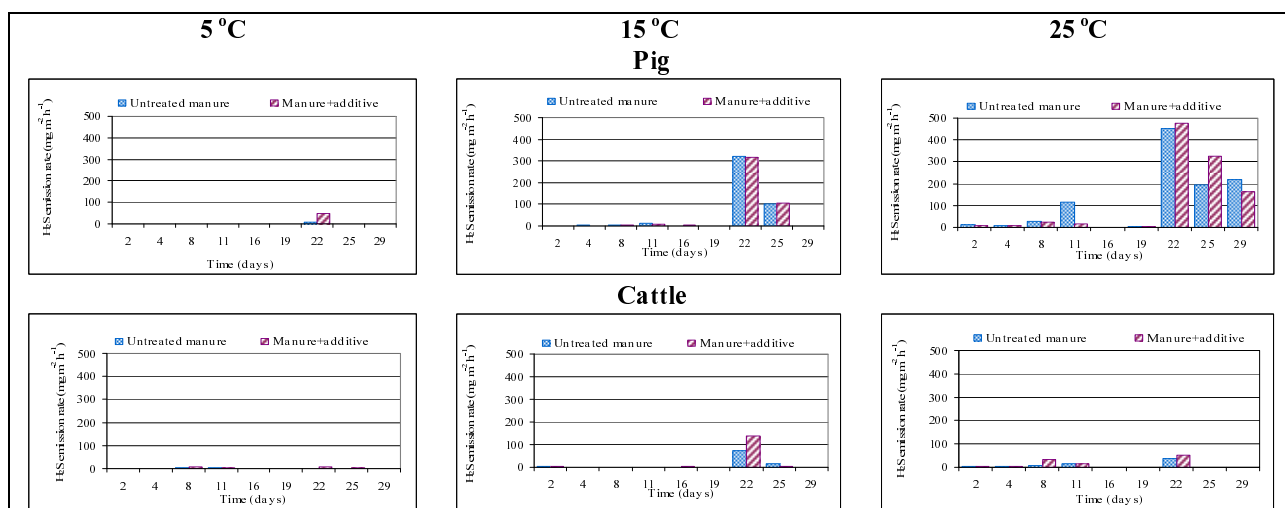
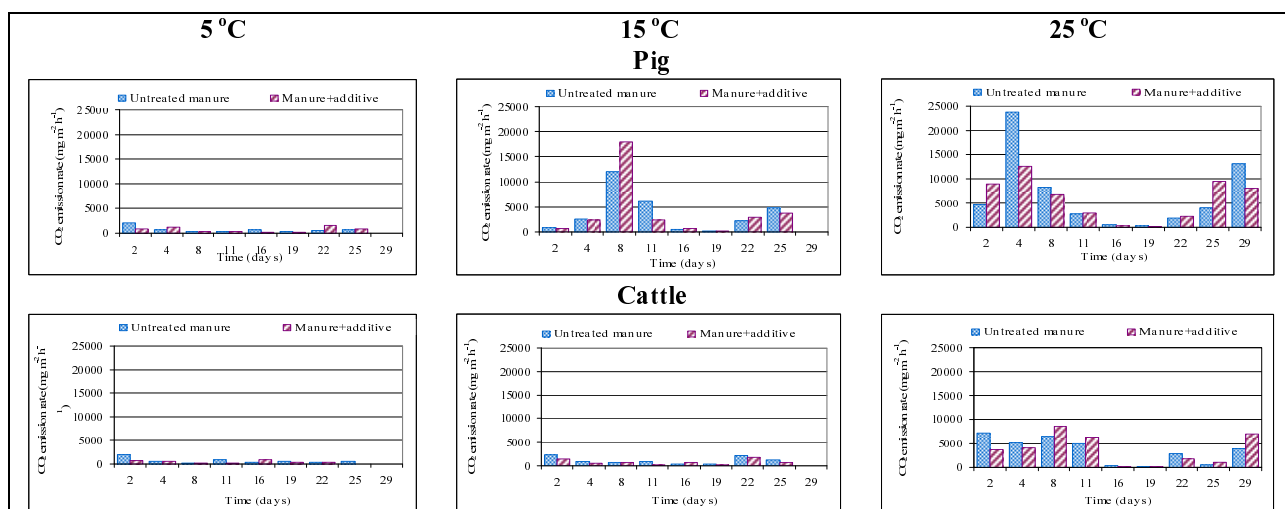
The emission of methane increased with an increase in the storing temperature ($P<0.05$). CH_4 emission from the untreated pig manure stored at 15 °C and 25 °C was 28.2 and 43.5 times higher respectively, than at 5 °C. From CH_4 emission viewpoint, cattle manure was more sensitive for changes in temperature. CH_4 emission from

the untreated cattle manure stored at 15 °C and 25 °C was 31.6 and 146.4 times higher, respectively, than at 5 °C.

The total losses of methane ranged from 0.18 % to 30.27 % of the initial carbon content, depending on the type of manure and storing temperature. The losses were higher for pig manure than for cattle only at 5 °C and 15 °C, while at 25 °C the losses were higher for cattle than for pig manure (Table 4).

Hydrogen sulphide emission. Hydrogen sulphide emission was negligible for both – cattle and pig manure under storage at 5 °C. At 15 °C and 25 °C the emission rate of H_2S peaked after 22 d. of storage for both – cattle and pig manure (Fig. 4). The average H_2S emission rate for the untreated pig manure ranged from 1.58 to 114.83 $\text{mg m}^{-2} \text{h}^{-1}$ and for the untreated cattle manure – from 1.39 to 7.52 $\text{mg m}^{-2} \text{h}^{-1}$ (Table 2).

H_2S emission from the untreated pig manure stored at 5 °C was 4.1 times lower than from manure+additive (Table 2; Table 3). At 15 °C and 25 °C the differences were negligible. H_2S emission from the untreated cattle manure stored at 5 °C, 15 °C and 25 °C was 2.4, 1.6 and 1.6 times lower respectively, than that from manure+additive. Unfortunately, the differences between H_2S emission from the untreated manure and from the manure+additive were not significant ($P>0.05$) for both pigs and cattle.

Fig. 3. Methane (CH₄) emission rateFig. 4. Hydrogen sulfide (H₂S) emission rateFig. 5. Carbon dioxide (CO₂) emission rate

The emission of H₂S was higher for pig manure than for cattle (P<0.05). Also, the emission tended to increase with an increase in the storing temperature. H₂S emission from the untreated pig manure stored at 15 °C and 25 °C

was 35.2 and 72.7 times higher respectively, than at 5 °C. For the untreated cattle manure an increase of emission was not significant ($P>0.05$).

Carbon dioxide emission. Under the same storage conditions, untreated manure and manure+additive showed similar tendencies on carbon dioxide emission rate (Fig. 5).

The emission rate of carbon dioxide from the untreated pig manure remained stable under the storage at 5 °C during all the experiment. While at 15 °C and at 25 °C the emission peaked after 8 d and 4 d of storage respectively. The emission of CO₂ from the untreated cattle manure remained stable under the storage at 5 °C and 15 °C during all the experiment. While at 25 °C the emission was highest at the beginning of the storage period. The average CO₂ emission rate for the untreated pig manure ranged from 718.24 to 6611.20 mg m⁻² h⁻¹ and for the untreated cattle manure – from 817.46 to 3882.81 mg m⁻² h⁻¹ (Table 2).

CO₂ emission from the untreated pig manure stored at 5 °C was equal to that from the manure+additive (Table 2; Table 3). The emission from the untreated pig manure stored at 15 °C was 1.1 times lower than from manure+additive. In contrast, CO₂ emission from the untreated pig manure stored at 25 °C was 1.2 times higher than from the manure+additive. The carbon dioxide emission from the untreated cattle manure stored at 5 °C, 15 °C and 25 °C was 1.8, 1.6 and 1.1 times higher respectively, than that from the manure+additive. However, the differences between CO₂ emission rate from the untreated manure and from the manure+additive were not significant ($P>0.05$), for both pigs and cattle, it showed only a tendency.

The emission of carbon dioxide increased with an increase in the storing temperature ($P<0.05$). CO₂ emission from the untreated pig manure stored at 15 °C and 25 °C was 5.1 and 9.2 times higher respectively, than at 5 °C. Whereas for the untreated cattle manure an increase of emission was lower, i.e. – 1.5 and 4.7 times, respectively.

Under all storage temperatures, the total losses of CO₂ were nearly twice higher from the pig than from cattle manure. Also, for pig manure, the main loss of carbon was in CO₂ form as opposed to CH₄ and CO (Table 4). In the following way, the total loss of carbon ranged from 2.04 % to 22.53 % depending on the type of manure and storage temperature.

Carbon monoxide emission. Under storage at 5 °C, carbon monoxide emission was negligible for both – cattle and pig manure. At the beginning of the experiment, at 15 °C and 25 °C the emission of CO was low, but a peak of CO emission has been observed at the second half of the experiment (Fig. 6). The average CO emission rate for the untreated pig manure ranged from 0.29 to 12.62 mg m⁻² h⁻¹ and for the untreated cattle manure – from 0.78 to 1.92 mg m⁻² h⁻¹ (Table 2).

The use of the microbial based additive tended to increase carbon monoxide emission from manure. CO emission from untreated pig manure stored at 5 °C, 15 °C and 25 °C was 1.2, 2.1 and 1.2 times lower respectively,

than that from manure+additive (Table 2; Table 3). CO emission from the untreated cattle manure stored at 5 °C and 25 °C was 1.2 and 1.3 times lower respectively, than that from manure+additive. At 15 °C the difference was negligible. However, the differences between CO emission from the untreated manure and from manure+additive were not significant ($P>0.05$) for both pigs and cattle.

The emission of carbon monoxide tended to increase with an increase in the storing temperature. Furthermore, under all storage temperatures, total CO losses were higher from pig than from cattle manure. CO emission from the untreated pig manure stored at 15 °C and 25 °C was 7.0 and 43.5 times higher respectively, than at 5 °C. While for the untreated cattle manure an increase of emission was only 1.6 and 2.5 times, respectively.

During pig and cattle manure storage, the least loss of carbon was as CO (Table 4). The total losses of CO, ranged from 0.00 % to 0.08 % of the initial carbon content.

Nitric oxide emission. Under storage at 5 °C, nitric oxide emission was negligible for both – cattle and pig manure. At the beginning of the experiment, at 15 °C and 25 °C the emission rate of NO was low, but a peak of NO emission rate has been observed at the second half of the storage period (Fig. 7). The average NO emission rate for the untreated pig manure ranged from 0.51 to 14.06 mg m⁻² h⁻¹ and for the untreated cattle manure – from 0.72 to 1.15 mg m⁻² h⁻¹ (Table 2).

NO emission from the untreated pig manure stored at 5 °C was 2.3 times lower than from the manure+additive (Table 2; Table 3). At 15 °C and 25 °C the differences were negligible. NO emission from the untreated cattle manure stored at 5 °C, 15 °C and 25 °C was 1.4, 1.5 and 1.4 times lower respectively, than that from the manure+additive. However, the differences between NO emission from the untreated manure and from the manure+additive were not significant ($P>0.05$) for both pigs and cattle, it showed only a tendency.

NO emission was higher by 6.0 times ($P<0.05$) from the untreated pig manure, compared with the untreated cattle manure. Also the emission was related with temperature. NO emission from the untreated pig manure stored at 15 °C and 25 °C was 12.4 and 27.6 times higher than that at 5 °C respectively. Meanwhile the increase of emission from the untreated cattle manure was not significant ($P>0.05$).

The total losses of NO, expressed as a percentage of the initial TKN, ranged from 0.05 % to 1.43 % depending on type of manure and storage temperature (Table 4).

Discussion

The results of this study confirm a positive relationship between some gas emission from manure and temperature found by other studies (Wang et al., 2010; You et al., 2008; Blunden, Aneja; Dinuccio et al., 2008; Van der Stelt et al., 2007; Aarnink, Elzing, 1998). However, no significant relationship between temperature and H₂S or NO gas emission was found in the case of cattle manure. This could be related with the differences in the composition of pig and cattle manure. Also after a

while, more intensive changes of manure composition including evaporation of water and formation of natural crust at 25 °C storage temperature, could have impact on changes of dominant microorganisms in manure (for example more active methanogen population developed – this can be seen from high methane emission rates from

cattle manure stored at 25 °C) and adequately changed the formation of H₂S and NO gases at the second half of the experiment. It was reported that natural crust that often develops on dairy manure storages can help to decrease H₂S emission by 10–90 % (Bicudo et al., 2004).

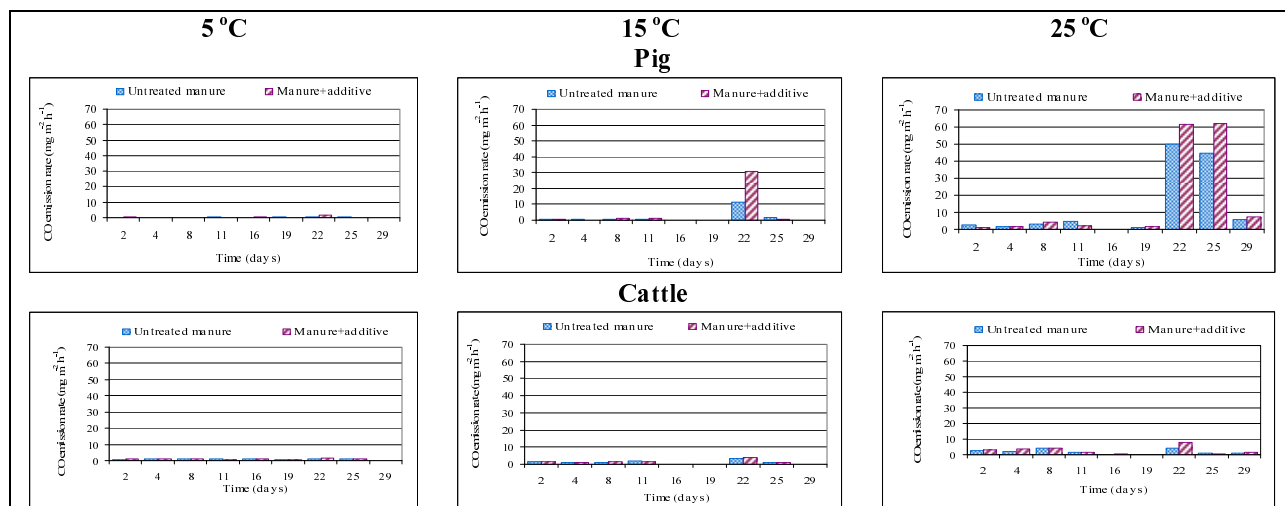


Fig. 6. Carbon monoxide (CO) emission rate

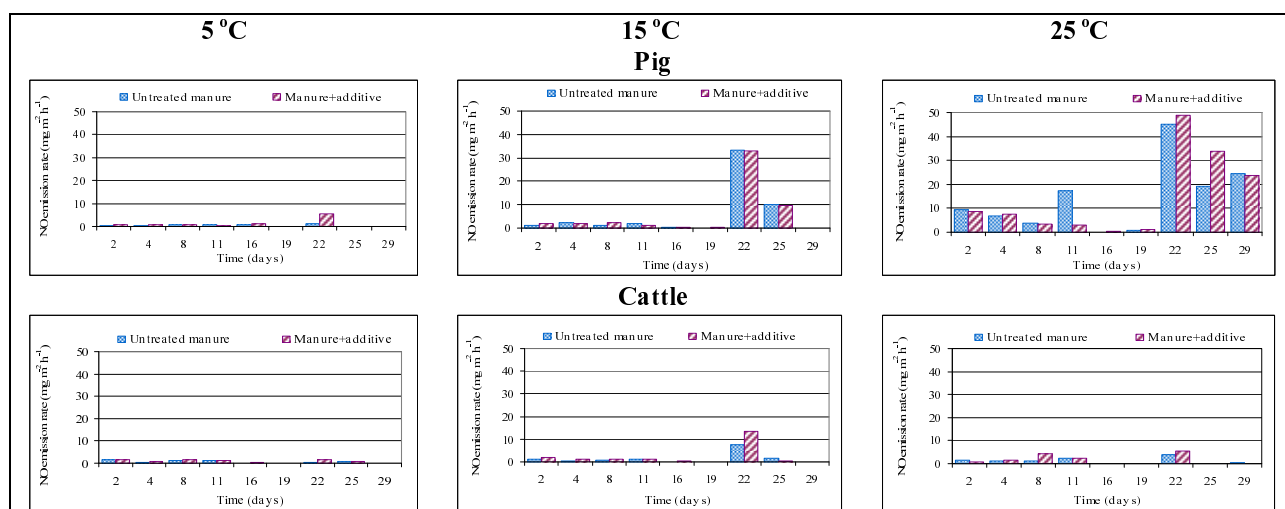


Fig. 7. Nitric oxide (NO) emission rate

In all samples of pig manure the dynamic of nitric oxide emission rates from manure were similar to as hydrogen sulphide and carbon monoxide. At the beginning of the experiment the emissions of those gases were low, but at the second half of the storage period the emission increased. It could be related with the consumption of dissolved oxygen in the liquid manure, when reduced conditions appeared and specific microorganisms could have developed that produce H₂S, CO and NO gases.

In our experiment the use of the additive did not change the manure characteristics strongly. This is confirmed by the results of Van der Stelt et al. (2007). However, in our study, pH was slightly lower in all samples of manure+additive. It could have resulted due to

acidic consistency of the additive and/or activity of microorganisms (formation of acetic and other organic acids during biodegradation of organic matter of manure). As it was shown in other studies (Berg et al., 2006; Kai et al., 2008; McCrory, Hobbs, 2001) low pH of manure is favourable for the reduction of NH₃ emission, and it could have had impact on the results of our experiment too. Our study showed that the addition of the microbial-based additive had a tendency to reduce ammonia emission from the pig manure. This is confirmed by the results of other studies, where microbial-based additives were used (e.g. Wang et al., 2009; Amon et al., 2005). But we did not find any reduction of NH₃ emission after the addition of the microbial-based additive to cattle manure. Probably, it could be related with different compositions of manures

and the interaction between microorganisms of the additive and different species of natural, better adapted bacteria.

In our study, the addition of the microbial-based additive had a tendency to increase CH₄ losses from pig and cattle manures. This is confirmed by the results of Amon et al. (2005). As mentioned before, the high methane losses from cattle manure stored at 25 °C (estimated in our study) can be explained by the formation of natural crust and high temperature. The cattle manure has higher viscosity than pig manure, and natural crust can form. Crust creates anaerobic conditions which generally promote methane production (Wang et al., 2010).

Wang et al. (2009) reported that supplementation of diets with a microbial-based additive had no effects on fecal hydrogen sulphide (H₂S) emission. In our study no clear tendency of the impact of the microbial-based additive on H₂S emission was found too. However, cumulative loss of H₂S from cattle manure+additive was higher at all storage temperatures, contrary to pig manure. Probably, it could be related with the different compositions of pig and cattle manures.

Conclusions

In this study, the use of the microbial-based additive did not change the manure characteristics and did not result in significant differences between measured gas (ammonia, methane, hydrogen sulphide, carbon dioxide, carbon monoxide and nitric oxide) emissions from the untreated manure and from the manure+additive, for both pigs and cattle. The differences between the gas emission rates also cumulative loss of gases from the untreated manure and from manure+additive shows only a tendency. Thus, to confirm these results, more studies are needed. Nevertheless, the use of the microbial-based additive showed a tendency to reduce the ammonia emission from pig manure, contrariwise it has the potential to increase emissions of CH₄, CO and NO of pig and cattle manures.

The study showed that during the experimental period, the temperature and the type of manure were the main factors related to emission rates of the investigated gases. It was observed that the rise of temperature increased the emission of all investigated gases from both types of manure – pig and cattle. Furthermore, gas emissions from pig manure were significantly higher than those from cattle (except CH₄). In this experiment, the predominant loss of the initial nitrogen content was as NH₃. The majority of the initial carbon content was emitted in CO₂ and CH₄ forms.

References

1. Aarnink A. J. A., Elzing A. Dynamic model for ammonia volatilization in housing with partially slatted floors, for fattening pig. *Livestock Production Science*. 1998. 53. P. 153–169.
2. Amon B., Kryvoruchko V., Fröhlich M., Amon T. Ammonia, Nitrous Oxide, Methane, and VOC Emissions During Storage of Pig Slurry and Pig Farmyard Manure and Influence of the Additive

“Effective Microorganisms (EM)”: Final Report. University of Natural Resources and Applied Life Sciences, Department of Sustainable Agricultural Systems, Division of Agricultural Engineering (ILT). 2005. 28 p.

3. Berg W., Brunsch R., Pazsiczki I. Greenhouse gas emissions from covered slurry compared with uncovered during storage. *Agriculture, Ecosystems and Environment*, 2006. 112. P. 129–134.

4. Bicudo J. R., Schmidt D. R., Jacobson L. D. Using Covers to Minimize Odour and Gas Emissions from Manure Storages. UK Cooperative extension service university of Kentucky –college of agriculture. AEN-84, 2004. 5 p.

5. Blunden J., Aneja V. P. Characterizing ammonia and hydrogen sulfide emissions from a swine waste treatment lagoon in North Carolina. *Atmospheric Environment*, 2008. 42. P. 3277–3290.

6. Dinuccio E., Berg W., Balsari P. Gaseous emissions from the storage of untreated slurries and the fractions obtained after mechanical separation. *Atmospheric Environment*, 2008. 42. P. 2448–2459.

7. EMEP/EEA air pollutant emission inventory guidebook 2009: Technical guidance to prepare national emission inventories. EEA Technical report, No 9. Lead authors: Hutchings N., Amon B., Dämmgen U., Webb J. EMEP/EEA, 2009. 73 p.

8. Kai P., Pedersen P., Jensen J. E., Hansen M. N., Sommer S. G. A whole-farm assessment of the efficacy of slurry acidification in reducing ammonia emissions. *European Journal of Agronomy*, 2008. 28. P. 148–154.

9. McCrory D. F., Hobbs P. J. Additives to Reduce Ammonia and Odor Emissions from Livestock Wastes: A Review. *Journal of Environmental Quality*, 2001. 30. P. 345–355.

10. Park J., Lee S.-R., Han J. K., Nam K. Mitigation of Ammonia and Hydrogen Sulfide Emissions by Stable Aqueous Foam-Microbial Media. *Environmental Science & Technology*, 2006. 40(9). P. 3030–3035.

11. Peters J. (ed.), Combs S. M., Hoskins B., Jarman J., Kovar J. L., Watson M. E., Wolf A. M., Wolf N. Recommended methods of manure analysis. United States: Cooperative Extension Publishing. 2003. 58 p.

12. Sasaki H., Kitazume O., Nonaka J., Hikosaka K., Otawa K., Itoh K., Nakai Y. Effect of a commercial microbiological additive on beef manure compost in the composting process. *Animal Science Journal*. 2006. 77. P. 545–548.

13. Sommer S. G. Emission of greenhouse gases from animal manure. *Plantekongres*. 2006. 93(2): P. 443–445.

14. Van der Stelt B., Temminghoff E. J. M., Van Vliet P. C. J., Van Riemsdijk W. H. Volatilization of

ammonia from manure as affected by manure additives, temperature and mixing. *Bioresource Technology*. 2007. 98. P. 3449–3455.

15. Wang J., Duan C., Ji Y., Sun Y. Methane emissions during storage of different treatments from cattle manure in Tianjin. *Journal of Environmental Sciences*. 2010. 22(10). P. 1564–1569.

16. Wang Y., Cho J. H., Chen Y. J., Yoo J. S., Huang Y., Kim H. J., Kim I. H. The effect of probiotic BioPlus 2B® on growth performance, dry matter and nitrogen digestibility and slurry noxious gas emission in growing pig. *Livestock Science*. 2009. 120. P. 35–42.

17. You Y. B., Dong H. M., Zhu Z. P., Tao X. P., Chen Y. X. Experiments on influencing factors of methane emissions from beef cattle manure stack. *Transactions of the CSAE*, 2008. 24(12). P. 168–172.

Received 18 September 2012

Accepted 2 October 2013