

Development of Methods to Reduce Nitrogen Oxides from Stored Dairy Manure

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The agricultural activity is a source of almost 11% of global greenhouse gas emissions (GHG) (Rotz, 2017). The animal production sector releases large amounts of carbon dioxide, methane, ammonia and nitrous oxide to the environment. It would seem that the harmfulness of these gases is local. However, due to the scope and intensification of modern animal production, the amount of gases released and processes occurring during the storage of manure is of great importance for the environment on a global scale. The group of animals producing significant amounts of greenhouse gases includes dairy cattle. It is estimated that cattle all over the world produces 5.335 Mt of CO₂(CO₂e) equivalent, which accounts for 11% of the total anthropogenic emission (Smith et al., 2014). The fact that the source of GHG in cattle breeding are intestinal fermentation processes and biological-chemical changes occurring during the storage of manure is significant. To fully understand these processes and the possibilities of accurate gas emission estimation, a "Molly" model was designed to simulate the cow's digestion and metabolism processes. Based on this model, researchers from New Zealand created an accurate forecast of methane production from dairy cows kept in pasture (Gregorini et al., 2014). The inventory of greenhouse gases is carried out by a number of scientific institutions and governmental organisations. The unit responsible for calculating greenhouse gas emissions in Poland is the National Centre for Emissions Management (KOBiZE), which, according to IPCC recommendations, uses Tier 2 methodology to estimate GHG emissions. At the same time, in the presented methodological assumptions there are no data on the hitherto effect of GHG reduction in agriculture. That is why according to Walczak (2017), in the context of these activities, there arises a demand for the elaboration of methodology for estimating greenhouse gas reductions.

Manure arising from the production of animals is a potential source of greenhouse gases because it contains significant amounts of nitrogen (most in inorganic form), carbon and water - i.e. three important constituents of nitrogen dioxide and methane (Chadwick, 2011). The proper management of manure affects the amount of gas losses and the possibility of their reduction. Manure management is a continuous process and starts when animals produce waste, through manure storage, treatment to fertilising. Each of these stages, due to, inter alia, different conditions of the physicochemical environment, is characterised by its own reduction potential. In the place of livestock keeping, harmful gas admixtures are created, which together with the ventilated air are emitted to the external environment. The reduction of emissions of these gases from animal husbandry is possible due to the use of various technological, zoo-hygienic or nutritional treatments (Szewczyk and Pawłowska, 2017). In the case of fertilisation, one of the methods characterised by a relatively high reduction potential is a ground injection of slurry (Hansen et al., 2003, Rodhe et al., 2004). On the other hand, when manure is stored, the reduction of gas emissions is also possible through the use of traditional or modern reduction techniques (composting, heap roofing and acidification of manure) (Portejoie et al., 2003; Bicudo et al., 2004; Guarino et al., 2006).

The purpose of the conducted research was to determine the possibility of reducing the emission of nitrogen oxides from manure from high-yielding, low-yielding and dry dairy cows.

Materials and methods

The experimental material was manure in the amount of 5 t/heap, originating from 158 dairy cows of the czb breed (with a share of 70% hf breed). Dairy cows were divided on the basis of milk yield (dry, average yield - 7,000 kg of milk, high efficiency - 10,000 kg of milk). The manure, apart from the yields, also included sawdust and uncut wheat straw used as a litter in the farms, depending on the animal housing system used.

The animals were fed in accordance with the current IZ INRA (2009) standards, with unrestricted access to water. The manure of dairy cows was stored on a dung bed in 5 heaps - corresponding to a particular technological group - with dimensions of 3.0 x 2.0 x 1.5 m for a period of 3 months in the spring and summer period (from May to July).

The experiment was carried out in three repetitions, and the manure heaps were subjected to appropriate modifications. The first was a control group without modification, and the remaining 4 were covered with silage foil, wheat straw, oil film and subjected to liming (the experimental design presented below), respectively.

Experimental design

Item	Number of repetitions	Manure		
		cows (7,000 kg of milk)	Cows (10,000 kg of milk)	dry cows
Control	3	15 t	15 t	15 t
Silage wrap	3	15 t	15 t	15 t
Vegetable oil	3	15 t	15 t	15 t
Liming	3	15 t	15 t	15 t
Wheat straw	3	15 t	15 t	15 t

During the individual measurements, the heaps were covered with aerodynamic tunnels of own project, so-called *climatic tunnel*. The inlet of the tunnel was tightly connected to a low-speed ventilator of a diameter of 1.0 m and a flow rate of 1 m/s. The "fresh" air inflow and the removal of "discharged" air were fully controlled through a mechanical ventilation system. Owing to this, the detailed monitoring included both the composition of the inlet and outlet air. Detailed measurement data regarding the microclimate (external temperature, relative humidity and air movement) and internal temperature of the heaps were collected using the Testosterm electronic meter - Testo 9610 while the level of emission of nitrogen oxides into the air was determined by using a gas photo intensifier (MEXA-1170HCLD) made by Horiba. The emission of the mentioned oxides per unit of time per ton was determined, which was calculated from the volume of airflow and the concentration of gas present in it, divided by the number of manure tons.

The collected data was compiled statistically using the Statgraphics 6.0 computer package by means of a one-factor analysis of variance. The significance of differences between the averages was determined by the Duncan's test.

The results and their discussion

The average values of microclimatic parameters of the environment from the storage period of bovine manure in the spring and summer season are presented in Table 1. Proper storage of manure allows the reduction of gas emissions; in addition, there are many agro-technical measures that have a reduction potential. Our own research used modifications or additions, characterised by easy availability and a relatively low price. The data on the reduction of nitrogen oxides from storage places for the manure coming from dairy cows are presented in Table 2.

Table 1. Mean outdoor climate values during manure heaps storage

Temperature (°C)	Rate of air movement (m/s)	Outdoor humidity (%)
17,67	2,97	64,55

Table 2. Mean daily emission of nitrogen oxides from dairy cattle manure stored for a three-month period (kg/t)

Item	Technological group								
	cows (7,000 kg of milk)			cows (10,000 kg of milk)			dry cows		
	NO	NO ₂	NO _x	NO	NO ₂	NO _x	NO	NO ₂	NO _x
Control	0,0261 a	0,0152 Aa	0,0413 Aa	0,0227 a	0,0142 Aa	0,0369 Aa	0,0196	0,0079 Aa	0,0275 a
Silage wrap	0,0204 b	0,0058 Bb	0,0262 Bb	0,0195 b	0,0061 Bb	0,0256 Bb	0,0181	0,0052 Bb	0,0232 ab
Vegetable oil	0,0243 a	0,0046 Bc	0,0289 ABb	0,0231 a	0,0060 Bb	0,0291 BCbc	0,0184	0,0052 Bb	0,0236 ab
Liming	0,0260 a	0,0071 Cd	0,0331 ABab	0,0226 a	0,0067 Bb	0,0293 BCbc	0,0159	0,0055 BCbc	0,0214 bc
Wheat straw	0,0240 a	0,0080 Cd	0,0320 ABab	0,0225 a	0,0103 Cc	0,0328 ACac	0,0169	0,0041 Cc	0,0211 bc
SEM	0,002	0,0002	0,002	0,001	0,0002	0,001	0,001	0,0001	0,001

a, b – values in columns with different letters differ significantly ($P \leq 0.05$).

A, B – values in columns with different letters differ highly significantly ($P \leq 0.01$).

The coverage of manure heaps with silage foil resulted in a statistically significant reduction in NO emissions in all the technological groups with the exception of manure from dried cows, where NO reduction was the smallest and statistically insignificant. The use of silage film allowed the reduction of NO emissions from cow manure with the average yield by 22%, and with the high yield by 14%. The application of NO oxides modifications from bovine manure heaps was more efficient in the case of NO₂ emission. Silage film, vegetable oil, liming and wheat straw significantly reduced the emission of nitrogen dioxide from manure from all the technological groups of cattle.

The most effective method of reducing gas emissions in the case of medium and high-yield cow manure was covering the heaps with oil film layer, which reduced the emission by 70% and 58%, respectively ($P \leq 0.01$). The treatment significantly reduced the NO₂ emission ($P \leq 0.01$) also from the manure of dried cows while the highest reduction from manure of this technological group, reaching 48%, was found in the heaps covered with straw, which turned out to be a material with a lower potential of reducing nitrogen dioxide from medium yield cow manure, and the lowest level of reduction of this gas emission from high yield cow manure. In all the technological groups, the high reduction potential of NO₂, to a small extent yielding to vegetable oil, was characterised by silage film which in the case of dried cows manure reduced the NO₂ emission almost to the same extent as vegetable oil layer (34%).

On the basis of the values presented in Table 2 regarding the average emission of all the total nitrogen oxides (NO_x) from dairy cow manure, it can be concluded that the highest, statistically confirmed ($P \leq 0.01$) effectiveness of reduction of NO_x in the case of medium yield cow manure was characterised by covering the heap with silage foil (37%) and the layer of vegetable oil (30%), while the least effective operation was liming (20%). High-yield cow's manure covered by a layer of vegetable oil emitted 21%, and silage film 31% less NO_x while the effectiveness of reduction of this gas fraction in the case of foil and oil in the heaps of dried cow's manure was the lowest. The largest reduction of NO_x emissions in this technological group of cows was found for heaps covered with straw (24%).

The effectiveness of the applied additives or reduction measures depends on many factors, and in the case of manure cover, the effectiveness of this treatment depends on the physical and chemical properties of the used organic material, its permeability, degradation or porosity (FAO, 2013). Sawdust, expanded clay or straw used in the described experiment are characterised by semi-permeability, diversified porosity and slightly lower effectiveness of reducing the emission of harmful gas admixtures accompanying animal production compared to those used in research: silage film and vegetable oil, however, the highest straw efficiency in NO₂ and NO_x reduction should be emphasised from manure of dried cows. One of the limitations of using this organic material as the manure cover is its relatively short time of use - depending on the weather conditions it is several months whereas, for example, the silage foil can be used even for several years. Despite these limitations, as already mentioned, the straw used to cover manure is characterised by a favourable reduction potential. In the case of medium-yield cattle manure, straw had a higher reduction potential than vegetable oil. A similar dependence was found in the case of manure from dried cows for which limestone was used. Nielsen et al. (2010) incline towards the opinion that the use of semi-permeable materials for covering the heap creates optimal oxygen conditions on their surface for the nitrification processes, the by-product of which is nitrogen dioxide (NO₂), as confirmed by our own research and the lowest reduction of the gas fraction emission from the medium-yield (48%) and high yield cows (27%) while using straw cover. At the same time, the use of this technique has a positive effect on emissions of other harmful gases, i.e. ammonia and methane (VanderZaag et al. 2008). The comparison of results obtained by Guarino et al. (2006) also shows the effect of straw layer thickness on the reduction of ammonia from stored pig slurry. Based on the literature, it can be concluded that the use of 70 mm of the straw layer does not have a significant reduction potential, while the layer thickness of 140 mm reduces the gas by nearly 86%. Thus, the straw reduction potential and its efficiency depend not only on its type and properties but also on the thickness of the layer. The use of widely available fertiliser lime also favours the reduction of nitrogen oxides. According to Skowrońska and Filipek (2017), the application of soil fertiliser lime, by changing the activity of denitrators and nitrators, regulates the amount of produced N₂O. Therefore, on the basis of our own research, it can be assumed that liming the manure, by increasing its pH, reduces gas losses, which may contribute to the increased use of nitrogen from natural fertilisers. In the presented research, liming has contributed the most to the reduction of NO production from manure of dry cows (19%) and exceeded the effectiveness of limiting the emissions of this gas by the use of straw (14%), silage film (8%) and vegetable oil (6%) at P≤0.05. In turn, covering the cow manure with a layer of oil film to the largest extent reduced NO₂ emissions from the heaps of manure from medium and high yield cows, reducing this gas fraction by 70% and 58%, respectively. Literature sources indicate that the application of film layers from vegetable oil on manure heaps may have a reduction potential of 90% (Portejoie et al., 2003, Guarino et al., 2006). In the case of this liquid plant substance, attention is drawn to the fact that, despite the mentioned effectiveness, it is not practical due to the difficulties in its application and the related possibility of mixing with manure. Silage film proved to be the most effective material used in the described experiment to reduce nitrogen oxides from the tested manure. It has limited the NO and NO_x emission from medium yield cows and (respectively: 22% and 37%) and high yield cows manure (respectively: 14% and 31%). It is the most expensive material for the reduction of nitrogen oxides from cow manure, and the costs incurred with its purchase significantly exceeded the costs associated with the use of natural materials. At the same time, the film has high durability and resistance to external conditions due to the high reduction efficiency.

In the agricultural practice, the choice of storage method (securing) of manure depends mainly on its availability and economic conditions of the farm. The costs of using artificial, impervious cover materials far outweigh the costs of natural raw materials, and the initial financial outlays are a barrier to their universal use, although the use of artificial materials ensures their durability

Table 3. Mean temperature range inside cattle manure heaps over a three-month storage period (°C)

Item	Technological group		
	cows (7,000 kg of milk)	cows (10,000 kg of milk)	dry cows
Kontrola – Control	45,38 ABb	53,77 a	43,04 a
Folia kiszonkarska – Silage wrap	36,53 BCc	47,57 ab	48,23 ab
Olej roślinny – Vegetable oil	33,16 Cc	45,98 ab	56,56 b
Wapnowanie – Liming	57,77 Aa	44,96 b	48,31 ab
Słoma pszenna – Wheat straw	48,18 Bb	43,43 b	45,11 a
SEM	1,54	1,31	1,53

a, b – values in columns with different letters differ significantly ($P \leq 0.05$).

A, B – values in columns with different letters differ highly significantly ($P \leq 0.01$).

A factor significantly affecting the emission of nitrogen oxides in the spring-summer season (May-July) from the manure of cows of medium and high yields and dried ones, including by regulating the processes occurring in the stored manure is the internal temperature of the heap. The analysis of the average values of temperature inside the heap showed differences between additions within the groups (Tab. 3).

The largest variation in the level of average temperatures in heaps was noted in the case of manure from cows with the medium milk yield.

In the case of this technological group, the highest average temperature was characterised by a heap that was covered with lime. After applying this cover, it was found to have a statistically significant increase, at the level of of 57.8°C. On the other hand, in the case of heaps covered with silage foil and vegetable oil, a decrease in temperature was recorded. The average temperature value of these two heaps was at the level of 34.9°C. The applied experimental factors had a negative effect on the temperature inside the heaps in the technological group of cows with high milk yield. The average temperature of heaps in the groups with the reducing additives used was at the level of 45.5°C and was lower than in the control group by 20%. In the case of manure from dried cows the highest temperature inside the heap was found in manure covered with a film from vegetable oil and the lowest in the heaps of manure without a neutraliser. The differences in both cases were statistically significant. Research on the influence of the internal temperature of heaps on the rate of changes occurring in the manure of dairy cows as well as the amount of nitrogen oxides emission and the type of reduction methods used require continuation and additional experiments also in autumn and winter.

Based on the obtained results we can present the following generalisations regarding the effectiveness of the applied reduction methods. After comparing the values for the average emission of all total oxides, it should be stated that all applied coverage types/raw materials had a reduction potential.

The most effective method of reducing nitrogen oxides from the storage of bovine manure was in the case of cows with the average milk yield, by covering the heaps with silage foil and vegetable oil. In the case of manure from cows with high yield, the largest reduction of nitrogen oxides was also obtained using the silage foil. In turn, the emission of nitrogen oxides from manure from dried cows was the lowest after the addition of lime. The conducted research shows that differences in the effectiveness of the applied methods/raw materials in the reduction of nitrogen oxides depends on the manure origin and the selectivity of reduction is caused by the difference in nitrogen content in animal manure depending on the category of farm animals and their breeding technology.

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**DEVELOPMENT OF METHODS TO REDUCE NITROGEN OXIDES FROM
STORED DAIRY MANURE**

Summary

Given the current knowledge about greenhouses gas emission from agriculture, the aim of this study was to determine the reduction potential of nitrogen oxides from livestock manure storage. The study was aimed at evaluating the efficiency of four treatments in reducing nitrogen oxides from manure coming from various technological groups of dairy cattle. The coverings included: wheat straw, silage film, vegetable oil and liming. Gas emissions were measured according to the “climatic tunnel”, using the gas meter. All the treatments proved effective in reducing nitrogen oxides from dairy manure. Silage film, vegetable oil and liming were the most effective materials. It was observed that effectiveness of nitrogen oxides emission reduction treatments depends on technological group of dairy cattle.

Key words: cattle manure, nitrogen oxide, reduction of emissions