Agronomy Research **22**(1), 157–167, 2024
https://doi.org/10.15159/AR.24.049

Effectiveness of reducing ammonia emissions from solid manure by using bio-covers

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Received: January 31st, 2024; Accepted: May 7th, 2024; Published: May 23rd, 2024

Abstract. According to the European Environment Agency, in 2021, 93 percent of ammonia was released into the environment due to agricultural activities. Almost half of the pollutants were released from cowsheds. The next significant source of pollution is liquid and/or solid manure storage facilities. Many dairy farms use liquid manure systems, but inevitably there is some solid manure produced in every cattle farm. Ammonia emissions increase when air penetrates the top layer of the manure pile. This is the reason why it is recommended to reduce the surface area of the manure piles that contact with open air. Straw, peat, sawdust, or other materials can be used as bio-covers. The purpose of this study is to determine the efficiency of bio-covers while covering solid manure. Experimental studies were carried out in field conditions, covering solid cattle manure with a > 10 cm thick layer of chopped straw. As the results show, chopped straw reduced ammonia emissions by up to 44.49 percent, but the emission declination rate is 1.85 times higher during the period when NH_3 volatilization is the most intensive.

Key words: air pollution, ammonia, bio-covers, cattle manure, emissions.

INTRODUCTION

Researches conducted by many scientists have provided a perception of how ammonia (NH_3) emissions alter natural structures and function of ecosystems. Ammonia can easily form new compounds with water vapor in the atmosphere, develop into acid rain, and acidify oceans, forests, freshwaters, and other ecological communities (Pereira et al., 2010; Kitidis et al., 2011; Driscoll & Wang, 2019). According to the European Environmental Agency (2023), in 2021, 93 percent of ammonia gas was released due to agricultural activities. Medėkšaitė & Čingienė (2014) established that 49 percent of these harmful gases volatilize from cattle sheds. Another significant source of ammonia gas is manure heaps, slurry pits, composting systems, and heaps of manure in the field (Hassouna et al., 2016; Kavanagh et al., 2019).

The type of manure is determined by the amount of dry matter (DM) found in the substance. The content of DM in solid cattle manure reaches 20 percent or more (Skurdenienė et al., 2007; Bagdonienė et al., 2011). In Lithuania, if there are not more than 50 livestock units kept on the farm, solid manure can be stored in manure stacks near barns or in fields that will be fertilized with manure. In all cases, it is desirable to use measures that reduce emitting odors and gas emissions into the environment. Manure should be covered with flexible, waterproof artificial coatings or a layer of bio-coatings (peat, soil, chopped or unchopped straw, sawdust) no thinner than 10 cm (Inventory of Environmental Requirements…, 2005).

NH_3 volatilization into the environment is a complex process influenced by various biological, chemical, and physical factors. Besides air humidity and temperature, air velocity, protein content in manure, and pH of the manure, DM content, concentration of ammonia at the surface of the manure, and the area of manure exposed to the air are the most common contributors affecting the intensity of ammonia emission (Freney et al., 1981; Philippe et al., 2011; van der Weerden et al., 2023). The phenomenon of NH_3 volatilization occurs when the ammonium-N present in the manure or slurry is converted to dissolved ammonia gas in the manure (Meisinger & Jokela, 2000). The higher the pH and ambient temperature of the manure, and the higher the NH_4-N concentration, the more active this process is (Holly et al., 2017). This results in a high amount of dissolved ammonia gas in the manure. Then liquid ammonia turns into gaseous form and evaporates from the manure due to convective mass exchange (Meisinger & Jokela, 2000; Grzyb et al., 2021).

In solid manure, the emission of ammonia is induced by the air that penetrates the outer layer of the manure stack. Therefore, the area exposed to the air needs to be reduced as much as possible (Karlsson & Tersmeden, 2001; Ye et al., 2011; McCollough et al., 2022). This can be done by forming higher manure heaps or covering the surface of manure with various materials (Guarino et al., 2006; Zhu et al., 2014). Most of the research is focused on liquid manure (Zhu et al., 2014). However many small and medium-sized farms still use livestock housing systems where solid manure is produced.

For small and medium-sized farms in many cases, it is uneconomical to install manure pits. Furthermore, even commercial farms have facilities in which solid manure is formed, such as calf barns, calving pens, etc. The Environmental Requirements For Manure And Slurry Management in Lithuania allow the storage of thick manure in heaps near barns or in crop fields. But recently, discussions were going on that manure heaps should be prohibited. This research was conducted to scientifically prove the advantage of using recommendations mentioned in The Environmental Requirements For Manure And Slurry Management under realistic field conditions, found in farms in Lithuania. Therefore, the experiment shows the scientifically investigated efficiency of bio-based manure covers and also demonstrates that it is possible to store manure in piles, posing a lower threat to environmental pollution by ammonia gas.

MATERIALS AND METHODS

Cattle housing system and diets

Fresh solid cattle manure used for the research was collected from the Vytautas Magnus University Agriculture Academy (VMU-AA) Training farm. Approximately 160 Holstein cows are kept on this farm. Cows are divided into two groups: dry cows and lactating cows. The group of dry cows consists of ~40 cows all year round. The rest of the cows form a lactating cow group which includes various lactation-stage cows: early, mid, and late.

All cows were fed with a feed mixture that included wheat, barley, or other kinds of crop straw, corn silage, grass silage, hay, water, essential mineral compounds, additional nutrients, and trace elements. The feed mixture for lactating cows is enriched with rapeseed oilcake, soy groats, minced wheat, barley, and oat blend to meet their feed intake needs.

To ensure animal welfare, the cowshed was designed relying on loose housing system parameters. However, beds for cows were built by combining two major types of loose systems: cubicle system and straw yard system. Cubicles and straw yard are cleaned every day by using farm machinery and bedded with fresh good quality chopped straw. In summer time, 5–6 bales of straw, weighing approx. 200 kg each, are used for bedding. During cold season, the number of bales used for bedding increases up to 8 each day.

Manure samples

Experimental studies in field conditions were carried out in the VMU-AA Training farm crop field. Manure pile (MP) (Fig. 1. a) and manure stack (MS) (Fig. 1, b) were formed in crop field which later was fertilized with manure used for the experimental study.

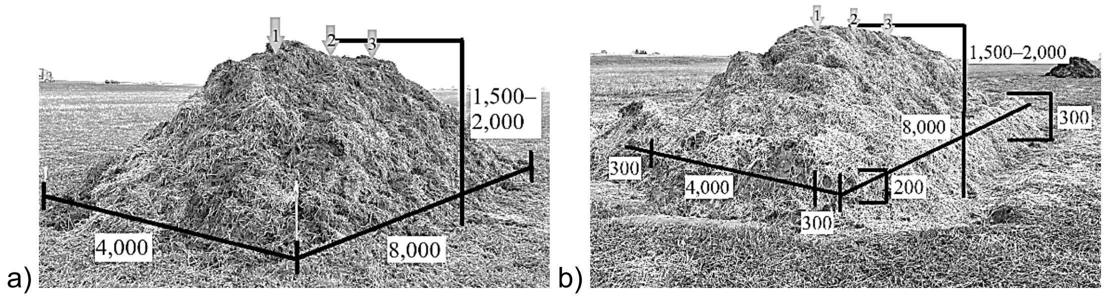

Figure 1. Measurements of manure pile and manure stack used for the experiment.

Both, the manure stack, and manure pile were 8 m long, 4 m wide, and 1.5–2 m high. Each pile consisted of 35 t (or 48 m^3) of fresh solid cattle manure. The difference between the MP and MS is:

– Manure Pile (MP) was formed simply by piling layers of manure straight on the surface of the ground. It also didn’t have any kind of bio-based cover and the surface of the manure was in contact with open air;

– Manure Stack (MS) was formed according to Environmental Requirements for Manure and Slurry Management in Lithuania. MS was formed on top of an 8.6 m long, 4.6 wide (clarification: underlayer has to be 0.3 m wider than the manure stack on all sides), and 0.2 m thick underlayer made of compressed chopped straw. Additionally, the manure stack was covered in a >10 cm thick layer of chopper straw. Furthermore, a 0.3 m high embankment encircled the same manure stack.

The amount of dry matter in manure samples varied from 21.01% to 28.76%. The total amount of nitrogen content at the beginning of the experiment was 0.52–0.67%. Elemental composition studies were carried out in the Lithuanian Research Centre for Agriculture and Forestry, Institute of Agriculture, Chemical Research Laboratory.

Instrumentation

A portable air monitor 'Aeroqual Series 500' (range: 0–1,000 ppm; accuracy: < ± 0.5 ppm + 10%) was used for measuring ammonia (NH_3) concentration (ppm) during experimental studies in field conditions. At least 3 measurements were taken at the top of the manure stack and manure pile. Measuring sites are marked with arrows and numbered as '1', '2', and '3' (Fig. 1, a & b).

Methods

Direct measurement of the NH_3 emission fluxes at the manure-air interface was measured using the method of Static Chamber. During sampling, the cylindrical plastic chamber (H = 37 cm; Ø = 32 cm; V = 30 L) was deployed above the surface of the manure. Ammonia concentration readings were recorded at the 3-minute mark from when the air monitor was covered with the chamber (Fig. 2). At least 3 measurements were taken at different areas of the same stack. All measurements were done at the top of the heap.

The waiting duration (3 minutes) was chosen experimentally. The intensity of ammonia volatilization is bound to a concentration gradient. When a static chamber is used, NH_3 gasses accumulate under the hood, the diffusion coefficient declines until equilibrium is reached and the evaporation process to the air hardly occurs. Numerous attempts showed that a duration of 3 minutes is enough to reach an equilibrium of gas concentrations between the surface of the manure and the air inside the chamber.

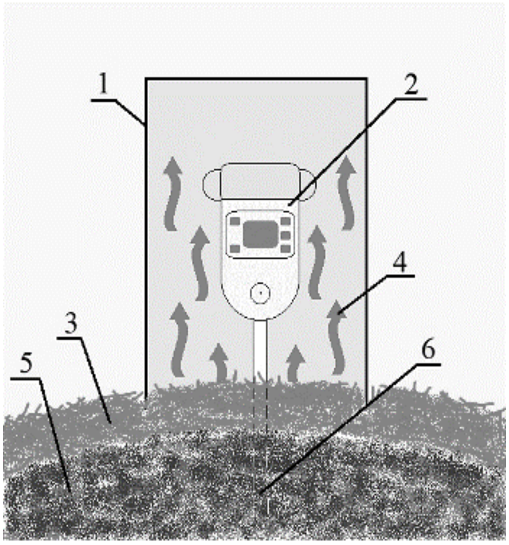

Figure 2. Schematic image of measuring ammonia gas concentration at the manure-air interface using static chamber: 1 – static chamber with a volume of 30 L; 2 – NH3 gas concentration monitor; 3 – manure cover (straw); 4 – NH_3 evaporation flux; 5 – manure; 6 – monitor mounting rod.

Ammonia concentration measurements in ppm then are used to determine the intensity of gas emission into the environment in mg $m^{-2}h^{-1}$. The calculations are done using the equation written below:

$$E = \frac{\Delta C}{\Delta \tau} \cdot \frac{V_k}{F_k} \quad (1)$$

where ΔC – the difference of ammonia concentration at the beginning and end of measurement, mg $m^{-2}h^{-1}$; $\Delta\tau$ – time difference ($\tau_{beginning} - \tau_{end}$), h; V_k – the capacity of the static chamber, m^3; F_k – floor area of the static chamber, m^2.

The research data were statistically evaluated by calculating the arithmetic averages of the indicators and their confidence intervals. Statistical reliability was assessed according to the methodology of Student's *t-test* and Tukey *HSD test*. The level of statistical significance is $p < 0.05$. Thus, the results were presented using descriptive statistics.

The results of this research are valid only for the case under consideration. This case study represents the actual approach to forming manure piles in crop fields and does not provide ideal conditions such as homogenization of the manure before storing. Therefore, the study results can be related to fundamental knowledge of what processes occur while storing manure in piles and how they progress but do not represent situations in other farms than VMU-AA Training farm.

RESULTS AND DISCUSSION

Experimental field research was conducted from November to March. This period coincides with the period in which it is prohibited to fertilize the fields with manure. Therefore, the study conditions correspond to real conditions when farmers store manure in stacks in crop fields until they are allowed to use manure as a fertilizer again.

To ensure the reliability of results, ammonia concentration rates were measured after 2 weeks since manure heaps were formed. The 2 weeks were designated to ensure that biological and thermodynamical processes in manure had stabilized. The results of experimental studies in field conditions are shown in Table 1.

Table 1. Statistical evaluation of calculated ammonia emission rates in mg m^{-2} h^{-1}, according to the data results of experimental studies in field conditions (MS – manure stack, covered with straw; MP – manure pile, uncovered)

Date (day of the experiment)		Emission, mg m^{-2} h^{-1}					
		$\bar{y}$[1]	S[2]	n[3]	s[4]	$t_{n\text{-}1,\,P}$[5]	$\pm\Delta y_{n\text{-}1,\,P}$[6]
11–11 (22)	MS	**713.20**	28.89	3	16.68	4.30	71.77
	MP	**611.03**	13.72	3	7.92	4.30	34.08
11–28 (28)	MS	**168.94**	18.85	4	9.42	3.18	29.99
	MP	**359.00**	60.63	4	30.32	3.18	96.48
12–02 (43)	MS	**36.28**	3.88	3	2.24	4.30	9.63
	MP	**71.99**	6.54	3	3.77	4.30	16.24
01–16 (88)	MS	**11.90**	0.50	3	0.29	4.30	1.25
	MP	**15.38**	0.50	3	0.29	4.30	1.25
02–03 (106)	MS	**9.58**	0.00	3	0.00	4.30	0.00
	MP	**7.26**	1.33	3	0.77	4.30	3.30
03–02 (133)	MS	**9.58**	0.87	3	0.50	4.30	2.16
	MP	**7.84**	1.74	3	1.01	4.30	4.33
03–24 (155)	MS	**12.48**	0.5	3	0.29	4.30	1.25
	MP	**10.74**	1.33	3	0.77	4.30	3.30

[1] Average; [2] Standard deviation; [3] Number of samples; [4] Standard error of the mean; [5] *t* value; [6] Confidence interval.

During the experiment, average air temperature was 1.15 ± 0.79 °C in the range from lowest at -10.30 °C in December and the highest at 12.90 °C in March. The meteorological data was gathered from Kaunas' meteorological station which the Lithuanian Hydrometeorological Service operates under the Ministry of the Environment.

According to the data in Table 1, ammonia volatilization into the atmosphere during the first 30 days is the most intense. The same tendencies are described by Zhuang et al. (2020) in their study. Based on other authors' research, this occurrence corresponds to the temperature of manure. When solid cattle manure is stored in heaps, the process of composting develops due to bacterial activity (Flynn & Wood, 1996; Petric & Selimbašić, 2008; Chen et al., 2011). During the first 30 days, the temperature of the manure reached 74–76 °C in both heaps, 0.1 m – 1.2 m deep. After day 30 of the experiment, the temperature started to subside until it reached the maturation stage temperature of 18.48 ± 0.52 °C on average. The only exception was a 0.1 m deep manure layer in an uncovered manure pile (MP) with an average temperature of 8.17 ± 0.47 °C which was close to the air temperature at the same period (88–155 days of the experiment).

The highest emission rate from MS was 713.20 ± 71.77 mg m^{-2} h^{-1} on the 22nd day of the experiment. The highest NH_3 emission rate from MS was also established on the 22nd day of the research (611.03 ± 34.08 mg m^{-2} h^{-1}). Although at the beginning of the research, it is acknowledged that the ammonia flux rate from the covered manure stack is more intense, on the 28th day of the research a radical change can be noted (Fig. 3).

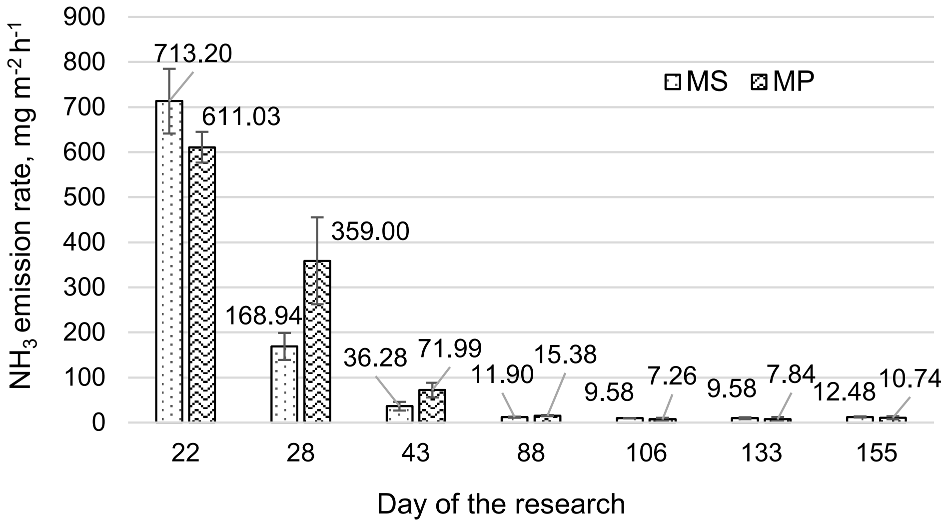

Figure 3. Tendencies in the change of ammonia volatilization from solid manure during field experiment (MS – manure stack, covered with straw; MP – manure pile, uncovered).

On the 22nd day of the research, the NH_3 volatilization flux rate from the manure stack covered in straw was 14.32 percent higher than from the uncovered manure pile. However, according to Student's *t-test* and Tukey *HSD test* the difference is not significant. A completely different situation was acknowledged on the 28th day of research. A significant difference of 52.94 percent between MS and MP was recorded. During the rest of the research, no significant differences were observed.

As results show, when manure is not covered with a layer of straw or another substance, the highest rate of ammonia emission declination can be seen until day 88 of the research (Fig. 4). Due to natural causes, between day 22 and 28, NH_3 volatilization decreased by 41.25 percent. The data implies that the lesion of ammonia emission is 6.88 percent a day on average. However, NH_3 emission rate abatement drops to 3.13 percent a day on average, between days 28 and 43. The declination rate lessens to 0.21 percent a day on average during the 43rd–88th day period. A decrease in ammonia emission lux rate can be observed until day 106 of the research. On this day, the lowest emission rate (7.26 ± 3.30 mg m^{-2} h^{-1}) was observed. But from this point of the research, NH_3 volatilization started to increase until the end of the experiment.

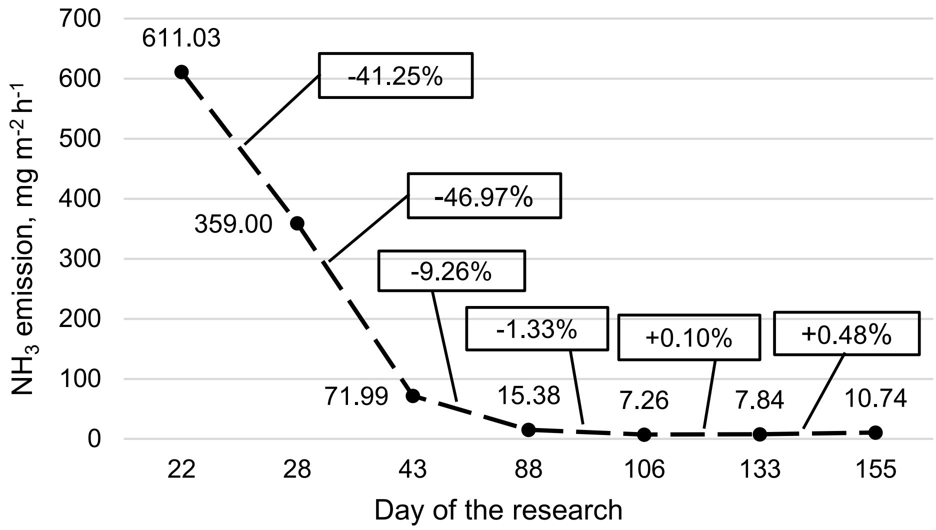

Figure 4. NH_3 emission flux rate declination from manure pile (MP) without cover.

According to data gathered during the research in field conditions, when manure is covered with chopped straw, the NH_3 volatilization flux rate declines much faster (Fig. 5).

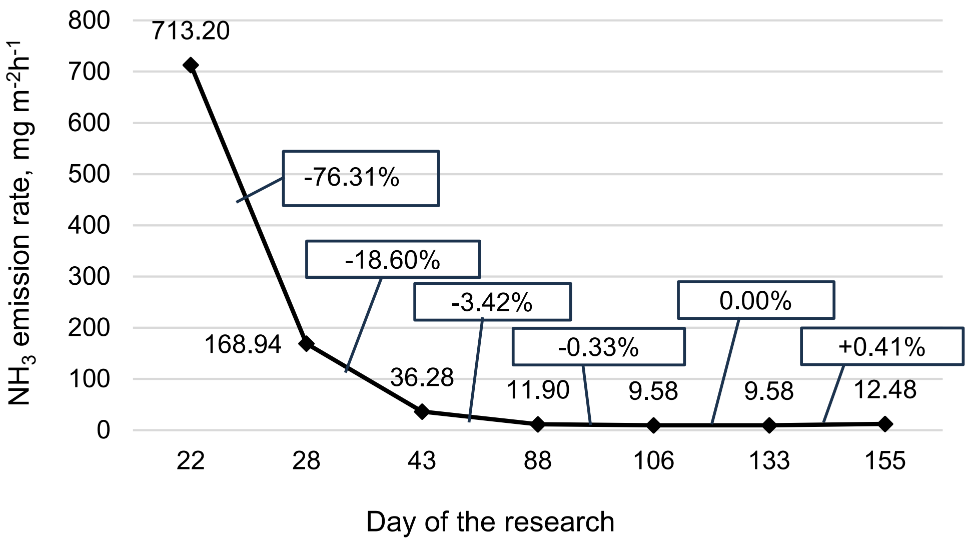

Figure 5. NH_3 emission flux rate declination from manure stack (MS) covered in chopped straw.

Between days 22 and 28 of the study NH_3 emission rate decreased by 76.31 percent. Results suggest that ammonia emission from manure stacks covered in straw diminishes by 12.72 percent a day on average. The decline rate between days 28 and 43 lowers to 1.24 percent a day on average. The ammonia volatilization rate continued decreasing until day 133 of the research and declined to the lowest rate of 9.58 ± 2.16 mg m^{-2} h^{-1}. At the very end of the research, between days 133 and 155, a slight increase in ammonia emission was observed. Compared to previous results, the emission rate increased by 0.41 percent and reached 12.48 ± 1.25 mg m^{-2} h^{-1} but this change was not statistically significant.

The biggest amount of NH_3 volatilizes into the atmosphere in the first 30 days from the formation of manure stack or pile. The most intense ammonia vaporization occurs at 10–14 days of manure storage. Some researchers found that evaporation of NH_3 from an uncovered manure pile is the most intense in the first 7 days (VanderZaag et al., 2015). Whereas, the formation of the natural crust begins after 10 to 20 days and stabilizes after 40 to 60 days (Nielsen et al., 2010; Aguerre et al., 2012). This tendency implies that measures and tools to reduce air pollution with ammonia gas are the most necessary in the first month after stacking manure. >10 cm thick layer of straw helps reduce NH_3 emissions 1.85 times faster.

This occurrence can be explained by processes happening in the manure during the storage period. The composting process naturally occurs in manure due to bacterial activity. In the first and second composting stages (active phase), bacterial activity is very high, therefore the temperature of manure increases (Chen et al., 2011; Nozhevnikova et al., 2019). Temperature is one of the factors that amplifies NH_3 emissions from manure. Hence, ammonia volatilization depends on bacterial activity. Bacteria found in solid manure are aerobic, which means they require oxygen to digest compounds found in manure. When manure has an open surface, air with oxygen keeps penetrating manure, and bacteria are continuously provided with the vital gas. While covered manure does not have an open surface and air access to the manure surface is restricted. Bacteria experience a lack of oxygen much sooner and cannot continue aerobic digestion, thus ammonia emission is reduced.

According to previously conducted laboratory research, chopped straw lowers the NH_3 emission flux rate up to 73.42 percent. However, experimental studies in field conditions indicate that a > 10 cm thick layer of chopped straw lessens the vaporization of ammonia gas only by 44.49 percent. This is thought to be due to the porosity of the straw layer.

CONCLUSIONS

1. The highest NH_3 emission rates were acknowledged on day 22 of the trial and were as high as 713.20 ± 71.77 mg m^{-2} h^{-1} from manure stack (MS) and 611.03 ± 34.08 mg m^{-2} h^{-1} from manure pile (MP).

2. During experimental studies in field conditions, it was found that ammonia evaporates into the environment most intensively in the first 30 days after the manure is piled up. During this period, ammonia emission reduction measures are needed the most.

3. Due to natural causes, ammonia emission lowers on itself, but it takes ~1.85 times longer. When chopped straw is used as a bio-cover, the NH_3 emission reduction rate can reach up to 12.72 percent a day between days 22 and 28 of research. Meanwhile, ammonia emissions declined only by 6.88 percent a day at the same time from the uncovered manure pile.

4. The effectiveness of > 10 cm thick chopped straw layer on field conditions can reach up to 44.49 percent. The porosity of the substance could be the cause of such results. To confirm or deny this hypothesis, it is suggested to complement research results with material porosity studies.

5. In both, the manure stack and manure pile, high ammonia emission rates were noticed at the beginning of the trial. It is believed that the activity of aerobic bacteria caused this. Therefore, on day 28 a significant decline in NH_3 volatilization was observed which supposedly could be caused by a lack of oxygen in the covered manure stack. To confirm or deny this hypothesis, it is suggested to complement the results of the research with oxygen level data during the composting process.

6. The experimental research scientifically proves the positive effect of methods mentioned in the Inventory of Environmental Requirements for Manure and Slurry Management reducing air pollution with ammonia gasses from thick cattle manure stored in heaps in the case under consideration.

7. Reduced ammonia emissions are related to lessened loss of nitrogen from the manure. Therefore, manure remains more beneficial as a fertilizer. Hence, using such manure as fertilizer, fewer inorganic fertilizers are needed which is economically beneficial.

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