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Hydrogen sulfide emissions from cattle manure: experimental study

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Abstract. Animal waste products, manure, in particular, are the sources of gases harmful to human and animal health. Hydrogen sulfide (H_2S), which is produced from the breakdown of organic matter in animal faeces, is one of them. Its concentration in the cow barn air should not exceed 5 mg m^{-3}. A special laboratory setup was designed and the level of hydrogen sulfide emissions from the cow manure was determined depending on the time and manure temperature and moisture content. The most intensive emission of hydrogen sulfide from manure was in the first 24 hours – the increment of H_2S concentration was 0.168 mg m^{-3} per hour average. During the next 24 hours, it was 0.021 mg m^{-3} per hour. When the manure temperature increased, H_2S concentration increased also; when the temperature manure decreased, H_2S concentration decreased also. In 48 hours, the hydrogen sulfide concentration was 1.1 mg m^{-3} at the manure temperature of +3.0 °C. At the manure temperature of +23.4 °C and 21.3 °C, H_2S concentration was 6.53 mg m^{-3} and 4.97 mg m^{-3}, respectively. The higher was the manure moisture content, the lower was the emission of hydrogen sulfide into the environment. After 24 hours under the manure moisture content of 88.5% and 92.5% and its temperature of 21 °C ± 0.3 °C, the difference in the hydrogen sulfide concentration was 1.18 times depending on the manure moisture content. The selected regression equations described the dependence of the hydrogen sulfide concentration on the considered factors. The determination coefficients and Student's criteria proved the reliability of the results obtained at the significance level $P \leq 0.05$.

Key words: hydrogen sulphide, emission, manure, cattle, farm.

INTRODUCTION

During its lifetime the cattle produces both the products required by human beings and the co-products, which can be applied as organic fertilisers essential for crop growing or, if used inefficiently, become a waste and cause significant damage to the environment. Manure (slurry) have an adverse effect on the livestock house air quality that, in turn, negatively affects the physiological condition and animal welfare in general. In the unfavourable environment their productivity drops – the deviations of the cowbarn climate parameters from the rated values lead to 10–20% lower milk yield, 20–33% lower live weight increment and up to 5–40% higher young animals' mortality (Mishurov & Kuzmina, 2004).

The basic factors, which have the major impact on the barn air quality, are the temperature, relative humidity and air flow rate as well as the content of carbon dioxide, ammonia, and hydrogen sulphide. The emission intensity of the latter elements varies depending on the nutrient supply, animal productivity and physiological condition, and climate factors.

Livestock farms have a negative impact on the environment, increasing the anthropogenic pressure. Annually, they emit 39 billion m^3 of carbon dioxide, 1.8 billion m^3 of ammonia, and 700 thousand m^3 of hydrogen sulfide (Jerebcov, 2017).

Hydrogen sulfide (H_2S) is a colourless, flammable gas with a characteristic smell of rotten eggs. It is highly soluble in water. H_2S low concentrations negatively affect the respiratory organs and eyes, reduce the oxygen absorption, and cause the appetite loss. Exceeded permissible H_2S concentrations may cause paralysis or mortality in humans or animals (Yurkov, 1985; WHO, 2003).

Hydrogen sulfide is formed continuously as a result of breakdown of sulphur-containing proteins in manure, bedding and feed residues. It is also emitted with intestinal gas. It penetrates the human and animal body through the skin and mucous membrane of the respiratory tract.

A dairy farm produces a large quantity of manure (slurry), which includes animal excrement (faeces and urine), bedding, uneaten feed, process water and others. Depending on the cows' productivity and weight, the output of excrement with the average relative moisture content of 88.4% ranges from 50.7 to 107.4 kg per day that can amount to 40 tons per head per year together with bedding (Tekuchev & Chernovol, 2017). This is the main source of hydrogen sulfide in the cow barn. Long-term storage of manure in the cow barns with the poor air exchange contributes to accumulation of hydrogen sulfide in the animal house air in excess of the maximum normalised concentrations (Shi et al., 2019).

Improved manure removal and utilisation technologies may reduce the hydrogen sulfide emissions from manure. Installation of biological filters with 65–96% cleaning efficiency may reduce the anthropogenic pressure on the environment when removing the polluted air from the barn (Krivolapov et al., 2016).

Another promising method in this respect is to use the gases from the barn, hydrogen sulfide included, for plant nutrition in greenhouses adjacent to the cow barns (Gordeev & Gordeeva, 2011; Gordeev & Mironov, 2014). Such application must, however, take into account that hydrogen sulfide is useful for plants only at very low concentrations – it improves their status and the stress factor resistance. At elevated concentrations, the hydrogen sulfide has a suppressing effect on plants (Dooley et al., 2013).

The study was aimed to assess the level of hydrogen sulfide emissions from the cattle manure (slurry) depending on the manure temperature and its storage time. The study findings will be used to justify the environmentally sound technological processes of cattle manure removal, storage and utilisation.

MATERIALS AND METHODS

A laboratory setup was designed for the study as shown in Figs 1–2.

The main part of the laboratory setup was an airtight chamber with a stainless steel trough and a frame above it. The frame had a mounted air temperature and humidity sensor DVT-0.3.TE with the limit of effective range from +20 °C to +50 °C and a manure temperature sensor T.p/p-420-DIN with the limit of effective range from 0 to 100 °C with a measurement resolution of ± 1 °C (both manufactured by NPK 'RELSIB', Russia). Hydrogen sulfide concentration was measured by ADT53-1197 sensor of MSR-Electronic GmbH, Germany, with the measurement range from 0 to 100 ppm and a measurement resolution of ± 0.2 ppm. Under the trough, there was a heating element – a 0.08 kW thermoelectric flexible cable, and a cooling element – a thermoelectric module (Peltier unit) or cool-packs. The real-time analogue signal coming from the sensors was recorded in the memory of the electronic recorder PARAGRAPH PL2 ('Avtomatika', Russia) with the measurement error of 25% installed in the data recording unit and then transferred to Excel tables on the computer for further analysis (Lantsova et al., 2015).

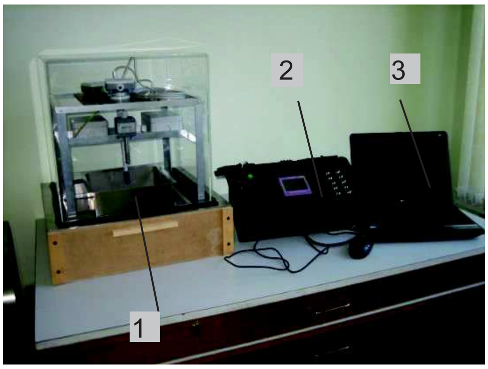

Figure 1. General view of the laboratory setup.

Figure 2. Trough with the tested manure sample.

1 – airtight chamber with the sensors of manure temperature and H_2S concentration; 2 – data recorder; 3 – computer; 4 – trough with manure (slurry).

Fresh manure from a dairy farm was used in the study. This was the semi-liquid manure (slurry) with 85–87% moisture content, the solid bedding (peat) manure with 78% moisture content and the liquid manure with up to 92.5% moisture content. According to the valid classification in Russia, the manure with the relative moisture content below 85% is solid manure, 85–92% moisture content – semi-liquid manure (slurry), 92–97% moisture content – liquid manure, above 97% – manure-bearing wastewater (Khazanov et al., 2008). The mass of each sample was 1 kg. The samples were weighed on SW-1 scales of CAS Corporation, South Korea, with the weighing capacity range from 40 to 5,000 g and 2 g readability.

The experiment duration was 24 or 48 hours. The hydrogen sulfide emission degree was determined by the gas concentration in the airtight chamber. The manure moisture content was determined before placing the sample in the trough using an MX-50 weight hygrometer (A&D Co. LTD, Japan) with a measurement accuracy of 0.02% min^{-1} and a display resolution of 0.01%.

The experiments ran as follows. The studied material was placed into the trough 4, which was installed in the chamber of the laboratory setup 1. The chamber was hermetically sealed and additionally thermally insulated from the external environment. Then, the temperature of manure was brought to the specified parameters by either heating or cooling and the specified time interval was maintained. At the same time, the specified parameters were measured and the sensor readings were recorded in the data recorded 2 with their further processing on computer 3. The recording interval was 10 minutes.

The experimental data were analysed using *Excel* and *Mathcad* software packages; the mathematical expectation and variance of random variables were estimated; the regression models were created, the reliability of which was estimated by the multiple correlation and determination coefficients, and Student's criterion (Valge, 2013; Papez & Kic, 2015).

RESULTS AND DISCUSSION

The animals excrete waste products throughout 24 hours. These products mix with the bedding material producing manure, accumulate in the animal house and are transported to the long-term storage or processing sites following the adopted technology. The method and conditions of manure accumulation inside the barn affect the degree of the negative impact on animals and personnel (Herbut & Angrecka, 2014).

The microclimate in the premises depends on the type and location of the cow barn, climatic conditions, the cattle housing and tending practices, and manure handling techniques (Angrecka & Herbut, 2014). The permissible concentration of hydrogen sulfide in the livestock farms in Russia is 5 mg m^{-3} (Volkov et al., 1986; Management Directive for Agro-Industrial Complex, 2018). When the sufficient air exchange is in place in the barn, the permissible concentration of hydrogen sulfide is not exceeded. Under the poor ventilation and unfavourable climatic conditions, a dangerous increase in the harmful gases content, including the hydrogen sulphide, is possible (Herbut, 2010; Herbut et al., 2013).

The intensity of hydrogen sulfide emission under various internal and external conditions can differ significantly (Maasikmets et al., 2015). According to Shi et al. (2019), the concentration of H_2S in the cow barn is in the range from 0.024 to 0.151 mg m^{-3}, with the average value being 0.092 mg m^{-3}, and reliably correlates with the sulfur content in feed and manure ($P \leq 0.05$), as well as with the inside temperature ($P \leq 0.05$).

In this regard, it is important to forecast the state of the microclimate in the livestock house for a certain period. Changes in the production technology and weather conditions and the technological equipment failures can result in the above-level maximum permissible concentrations of hydrogen sulfide and lower animals' productivity.

The control models are required to prevent the emergences and to ensure a favorable climate inside the barn. To create such models, the patterns of hydrogen sulfide emission from manure under various conditions must be known. The focus of the study was to identify these patterns.

In the study, the intensity of hydrogen sulfide emission from the cattle manure (slurry) was found to depend on the manure temperature, its moisture content and time.

Fig. 3 shows the time dependence of H_2S concentration during 48 hours under the relatively stable temperature of 23 ± 0.6 °C, the sample mass of 1 kg and 86.7% moisture content.

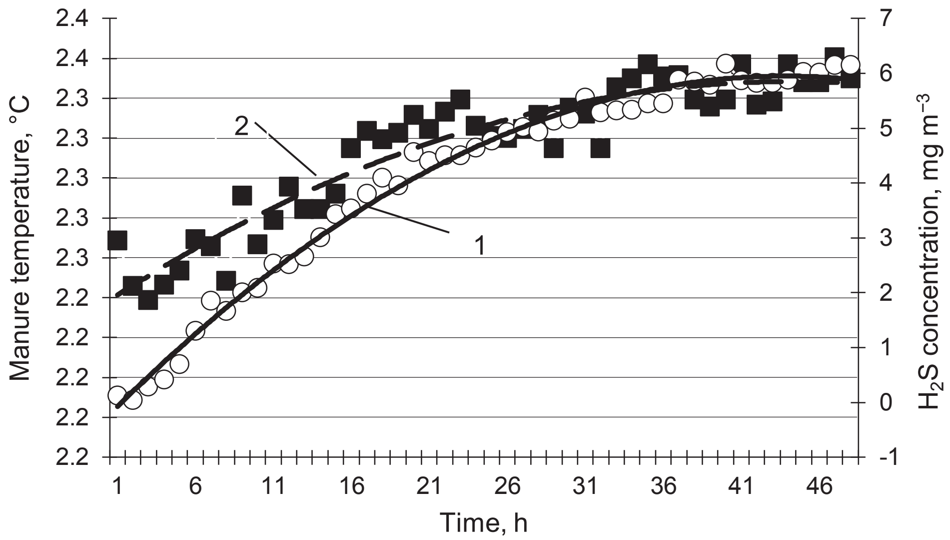

Figure 3. Time dependence of H_2S concentration: 1 – H_2S concentration, mg m^{-3}; 2 – manure temperature, °C.

According to the experimental data exploring, the most intensive hydrogen sulfide emission of from manure was in the first 24 hours. The increment of H_2S concentration was 0.168 mg m^{-3} per hour average; during the next 24 hours it was 0.021 mg m^{-3} per hour.

$$K_s = -0.003 \times T_{\exp}^2 + 0.288 \times T_{\exp} - 0.364,\ R^2 = 0.991 \qquad (1)$$

where K_s – the hydrogen sulfide concentration, mg m^{-3}; $T_{\exp}$ – the experiment duration, hour.

The selected regression equation (1) describes the dependence of hydrogen sulfide concentration K_s on the experiment duration $T_{\exp}$ under a slight increase in the manure temperature associated with the course of biochemical processes. The hydrogen sulfide concentration during this period increased from 0.03 to 6 mg m^{-3}. The determination coefficient $R^2 = 0.991$ showed a significant relationship between the dependent and independent variables, and the Student's *t-test* indicated the results reliability at a significance level of ($P \leq 0.05$).

Fig. 4 shows the dependence of H_2S concentration on time under the low manure temperature in the range from 3.0 °C to 9.7 °C. The bedding manure moisture content was 78%.

The hydrogen sulfide concentration varied from 0.91 mg m^{-3} to 2.11 mg m^{-3} versus the manure temperature. Under the manure temperature rise, the H_2S concentration increased; under the decreasing temperature, it also decreased. This is possibly due to a change in the hydrogen sulfide solubility in the water contained in the manure. It is known that the lower is the water temperature, the higher is the hydrogen sulfide solubility (Frog & Levchenko, 1996).

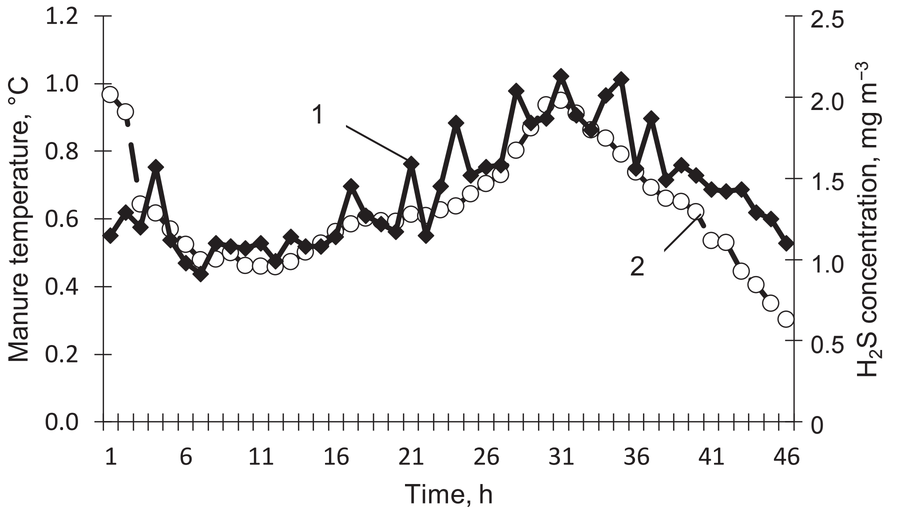

Figure 4. Dependence of H_2S concentration on time and manure temperature: 1 – H_2S concentration, mg m^{-3}; 2 – manure temperature, °C.

Fig. 5 presents the experimental data on the dependence of H_2S concentration on time and the manure temperature. The graphs demonstrate a distinct tendency of the hydrogen sulfide emission intensity to rise with an increase in the manure temperature. The difference in the dependences in Fig. 5 and in Fig. 4 is in the manure temperature and moisture content.

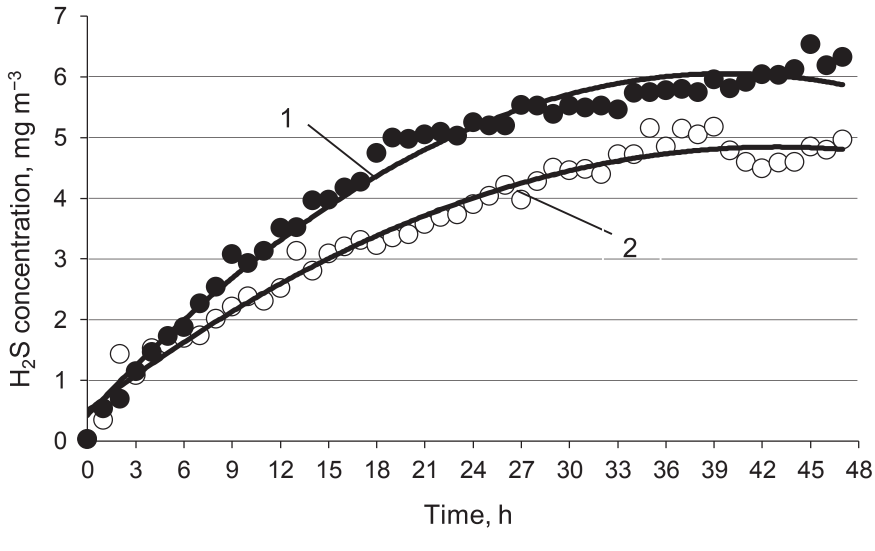

Figure 5. Dependence of H_2S concentration on time and manure temperature: 1 – manure temperature of +23.4 °C; 2 – manure temperature of +21.3 °C.

After 48 hours, the hydrogen sulfide concentration was 1.1 mg m^{-3} at the manure temperature +3.0 °C (Fig. 4) and 6.53 mg m^{-3} and 4.97 mg m^{-3} at the manure temperature of +23.4 °C and 21.3 °C, respectively (Fig. 5), with the manure moisture content being 85.6%.

$$K_{s1}=-0.003\times T_{\mathrm{exp}}^2 + 0.283 \times T_{\mathrm{exp}} + 0.423,\ R_1^2 = 0.981 \quad (2)$$

where K_{s1} – the hydrogen sulfide concentration, mg m^{-3}, under the manure temperature of +23.4 °C; T_{exp} – the experiment duration, hour.

$$K_{s1}=-0.003\times T_{\mathrm{exp}}^2 + 0.283 \times T_{\mathrm{exp}} + 0.423,\ R_2^2 = 0.975 \quad (3)$$

where K_{s2} – the hydrogen sulfide concentration, mg m^{-3}, under the manure temperature of +21.3 °C; T_{exp} – the experiment duration, hour.

The selected regression equations (2–3) describe the dependence of the hydrogen sulfide concentration K_{s1}, K_{s2} on the experiment duration T_{exp} at the manure temperatures of +23.4 °C and +21.3 °C. After 48 hours, the difference in the hydrogen sulfide concentration depending on the manure temperature was 1.31 times. The determination coefficients $R_1^2 = 0.981$ and $R_2^2 = 0.975$ showed a significant relationship between the dependent and independent variables, and the Student's *t-test* indicated the results reliability at a significance level of $P \leq 0.05$.

Fig. 6 presents the experimental data on the dependence of H_2S concentration on the experiment duration and the manure moisture content. The graphs show the dependence of the increase in H_2S concentration in the setup chamber air with the decrease in the manure moisture content. In this case, the presence of free water in the manure contributed to the dissolution of a larger volume of gas and affected the emission intensity. The manure temperature was 21 ± 0.3 °C. The experiment duration was 24 hours.

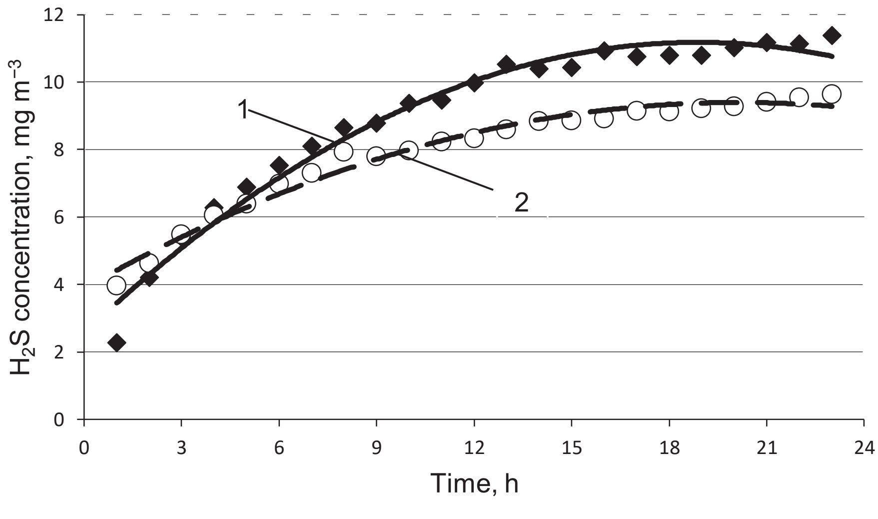

Figure 6. Dependence of H_2S concentration on time and manure moisture content: 1 – manure moisture content of 88.5%; 2 – manure moisture content of 92.5%.

$$K_{s1}=-0.024 \times T_{\exp}^2 + 0.912 \times T_{\exp} + 2.558,\ R_1^2 = 0.975 \quad (4)$$

where K_{s1} – the hydrogen sulfide concentration, mg m^{-3}, under the manure moisture content of 88.5%; $T_{\exp}$ – the experiment duration, hour.

$$K_{s2}=-0.013 \times T_{\exp}^2 + 0.576 \times T_{\exp} + 3.884,\ R_2^2 = 0.979 \quad (5)$$

where K_{s2} – the hydrogen sulfide concentration, mg m^{-3}, under the manure moisture content of 92.5%; $T_{\exp}$ – the experiment duration, hour.

The selected regression equations (4–5) describe the dependence of H_2S concentration K_{s1}, K_{s2} on the experiment duration $T_{\exp}$ under the manure moisture content of 88.5% and 92.5%. After 24 hours, the difference in H_2S concentration depending on manure moisture content was 1.18 times. The determination coefficients $R_1^2 = 0.975$ and $R_2^2 = 0.979$ showed a significant relationship between the dependent and independent variables, and the Student's *t-test* indicated the results reliability at a significance level of $P \leq 0.05$.

CONCLUSIONS

Hydrogen sulfide has a depressing effect on the vital functions of animals and the tending personnel. Its main source in cattle barns is faeces and urine, excreted by animals, mixed with the bedding material and diluted with the process water producing manure (slurry). The amount of hydrogen sulfide released and the air quality in the cow barn depends on the manure accumulation time in the livestock premises and its temperature.

The laboratory study revealed the most intensive emission of hydrogen sulfide from manure to take place in the first 24 hours. Then the process was significantly slowed down. The emission rate was influenced by the manure temperature – the hydrogen sulfide release was more active with the increasing temperature. The relative moisture content of manure also had a certain effect on the hydrogen sulfide emission. The higher was the manure moisture content, the lower was the hydrogen sulfide release into the environment.

The selected regression equations described the dependence of the hydrogen sulfide concentration on the considered factors with a high degree of reliability. They will be subsequently used to simulate the processes of microclimate formation in the cow barns.

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