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INFLUENCE OF MANURE STORAGE AND PROCESSING TECHNOLOGIES ON THE CHEMICAL PARAMETERS OF WATER

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Studies to study the impact of various options for storing and processing manure on the content of chemical compounds in the catchment area of farms were carried out in two farms in the Kyiv region with loose housing of cows. At AIS LLC, animals are kept in an easy-to-collect room, and manure is stored in a room with a deep, long-changing straw litter separately from waste from the milking and dairy block. In Terezine ALC, cows are kept in an easily assembled room with boxes. At the same time, manure is stored and processed in a bioreactor-fermenter. Water sampling for analysis on farms, springs within a radius of 1 km from farms, and in the nearest natural reservoirs (Ros and Protoka rivers, Bila Tserkva district, Kyiv region) was carried out during the second decade of September 2021. With the option of storage and processing of manure in a bioreactor-fermenter, the concentration of chlorides was 16.36 mg/dm3 higher compared to the option of storage and processing of manure in a room with deep, long-lasting straw litter. The sulfate and phosphate content was also higher – by 11.97 and 0.01 mg/dm3 Under. The content of chlorides, phosphates, and sulfites in water samples taken within a radius of 1 km from farms was 17.22 higher than the option of storage and processing of manure in a bioreactor-fermenter; 0.02 and 11.27 mg/dm 3. The content of chlorides, phosphates, and sulfites in drinking water samples taken from drinking bowls for animals was also slightly higher for the option of storage and processing of manure in a bioreactor-fermenter by 17.22; 0.02 and 12.91 mg/dm 3. In samples of drinking water taken from drinking bowls for animals under the option of storage and processing of manure in a room with deep, long-changing straw litter, The ammonium content was slightly higher than the indicators obtained from the farm where manure processing takes place in a bioreactor-fermenter (by 0.05 mg/dm3). So, with the option of storing and processing manure in a room with a deep, long-lasting straw litter, wastewater after washing milking equipment does not get into organic waste but settles and is disposed of. With this technology, the concentration of chemical compounds in the drinking water of the farm and the springs used by the population within a radius of 1 km from the research object and in the nearest natural reservoirs with running water is lower than in the case when the water after washing the milking equipment enters the general storage of manure (bioreactor-fermenter).

Key words: dairy cows, water, deep litter, bioreactor-fermenter, chemical compounds.

ВПЛИВ ТЕХНОЛОГІЙ ЗБЕРІГАННЯ ТА ПЕРЕРОБКИ ГНОЮ НА ХІМІЧНІ ПОКАЗНИКИ ВОДИ

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Дослідження з вивчення впливу різних варіантів зберігання та переробки гною на показники вмісту хімічних сполук водозбірного басейну ферм проводили у двох господарствах Київської області з безприв'язним утриманням корів. У ТОВ «АІС» тварин утримують у легкозбірному приміщенні, а зберігання гною відбувається у приміщенні з глибокою довгонезмінюваною солом'яною підстилкою окремо від відходів з доїльно-молочного блоку. У ТДВ «Терезине» корів утримують у легкозбірному приміщенні з боксами, при цьому зберігання та переробка гною відбувається у біореакторі-ферментері. Відбір зразків води для аналізу у господарствах, джерелах у радіусі 1 км від ферм та у найближчих природних водоймах (річки Рось і Протока Білоцерківський район Київська область) здійснювали упродовж другої декади вересня 2021 року. За варіанту зберігання та переробки гною у біореакторі-ферментері концентрація хлоридів була на 16,36 мг/дм3 вищою порівняно з варіантом зберігання та переробки гною у приміщенні з глибокою довгонезмінюваною солом'яною підстилкою. Також вищими були й значення вмісту сульфатів та фосфатів – на 11,97 та 0,01 мг/дм3 відповідно. Вміст хлоридів, фосфатів і сульфітів у зразках води, відібраної в радіусі 1 км від ферм, був вищим за варіанту зберігання та переробки гною у біореакторі-ферментері на 17,22; 0,02 та 11,27 мг/дм3. Вміст хлоридів, фосфатів і сульфітів у зразках питної води, відібраних із напувалок для тварин, був дещо вищим також за варіанту зберігання і переробки гною у біореакторі-ферментері на 17,22; 0,02 та 12,91 мг/дм3. У зразках питної води, відібраних із напувалок для тварин за варіанту зберігання і переробки гною у приміщенні з глибокою довгонезмінюваною солом'яною підстилкою, вміст амонію дещо переважав показники, отримані із ферми, де переробка гною відбувається у біореакторі-ферментері (на 0,05 мг/дм3). Отже, за варіанту зберігання і переробки гною у приміщенні з глибокою довгонезмінюваною солом'яною підстилкою стічна вода після процедури промивання доїльного обладнання не потрапляє до органічних відходів, а відстоюється та утилізується. За такої технології концентрація хімічних сполук у питній воді ферми та джерелах, якими користується населення у радіусі 1 км від об'єкту дослідження та у найближчих природніх водоймах з проточною водою, нижча, ніж за варіанту, коли вода після промивання доїльного обладнання надходить до загального зберігання гною (біореактор-ферментер).

Ключові слова: молочні корови, вода, глибока підстилка, біореактор-ферментер, хімічні сполуки.

Entry. The problem of providing the population of Ukraine with high-quality and safe dairy products has become a priority at this time (Borshch et al., 2020; Ruban, et al., 2022). This is especially true in areas that have been and continue to be subjected to significant anthropogenic pressure. As a result of the accident at the Chornobyl nuclear power plant, a large part of Ukraine was subjected to radioactive contamination (Rozputnii et al., 2018). At the same time, almost 9% of agricultural land with different types of soils and their moisture level were polluted. These factors have affected the

health of the country's population and the agricultural sector, particularly animal husbandry (Krysinska & Klymenko, 2021).

In the current conditions of intensive development of industrial production, as a result of the activities of metallurgical, chemical, fuel and energy, processing, and other enterprises, the concentration of toxic substances dangerous to human health in soil, water, air, and food products is several times higher than the permissible norms (Hejna et al., 2018; Chirinos-Peinado & Castro-Bedriñana, 2020). One of the sources of environmental pollution is agriculture, particularly dairy cattle breeding (Zhao et al., 2019; Libisch et al., 2022; Lin et al., 2023). Traditionally, environmental issues associated with the dairy industry have been considered to relate to impacts on water quality in reservoirs and springs close to animal housing sites (Cortés, et al., 2020; Fusco et al., 2020). However, due to global warming trends, global scientists have recently argued that dairy cattle are one of the primary biological sources of greenhouse gas production (Kou et al., 2021).

During their life, cattle produce waste accumulated in feces, urine, steam, etc., which, under certain conditions, can cause significant harm to nature (Portiannyk & Mamenko, 2022). Modern technologies for the production of livestock products can significantly reduce the risks of environmental pollution. However, it is necessary to adapt these technologies to specific production conditions in the most rational way, depending on natural and climatic conditions (Ny et al., 2022). A dairy farm with 500 cows of average productivity emits more than 3 tons of carbon dioxide, almost 5 tons of water vapor, a significant amount of ammonia, and other gases into the atmosphere daily, producing about 20 tons of effluent and about 30 tons of excrement. Therefore, the acute problem of reducing environmental pollution by livestock waste makes it necessary to look for ways to more rationally utilize and efficiently use manure and effluents from dairy farms and complexes (Borshch et al., 2021).

Harmonization of the development of technology and nature is possible only due to scientifically based compromises between human economic activity and the problem of sustainability of environmental conditions (Borshch et al., 2020). To date, the only acceptable option for the progressive movement of humanity is the movement "according to the principles of sustainable development", which does not destroy the natural biotic mechanism of self-regulation of the natural environment. Therefore, when creating and implementing technological and technical systems in production, one should strive to minimize the artificial impact on the environment (Saber et al., 2022).

Technological processes of livestock production associated with the processing of natural and energy resources are accompanied by the emergence of a significant amount of waste. Hence, a cattle farm is a manufactured object that can significantly impact the environment, being a source of air, soil, and water pollution (Cortés, et al., 2020). The chemical composition of drinking and river water, along with agricultural sources of pollution, Heavy industry enterprises, infrastructure facilities, and the location of cities or settlements along rivers, also have a significant impact (Esterhuizen et al., 2012).

The research aimed to study the effect of different options for storing and processing Manure on the indicators of the chemical compounds content in the farms' catchment area.

Materials and methods. The study was carried out in two farms in the Kyiv region with loose housing of cows but with different options for storing and processing Manure. The object of the study was the chemical parameters of water on farms with different technologies for the storage and processing of Manure. At AIS LLC, animals are kept in an easy-to-collect room with deep, long-lasting straw bedding. Manure is

removed from the premises twice a year. In Terezine ALC, animals are kept in an easily assembled room in boxes. At the same time, storage and processing of Manure, together with waste from washing and disinfection of milking and dairy equipment, takes place in a bioreactor-fermenter (Fig. 1). Manure is removed from the room using a delta scraper with a frequency of 12 times a day. The application of Manure to the fields in the studied farms takes place in August-October and March-April. Under the option of storing and processing Manure in a room with deep, long-term unchanging straw litter (AIS LLC), in contrast to Terezin ALC, waste from washing milking and dairy equipment enters a separate container and is disposed of without getting into the soil.

Rice. 1. **Manure storage and processing options: a) deep straw bedding; b) bioreactor-fermenter**

The location of the nearest natural reservoirs and agricultural lands from farms with various options for storing and processing manure, where the research was carried out, is shown in Table. 1 and in Fig. 2.

Table 1

The location of the nearest natural reservoirs and agricultural lands in relation to farms with different options for storing and processing manure

Indicator	Manure storage and processing option	
	deep, long-lasting litter	Bioreactor-fermenter
Name of the reservoir	Ros River	Protoka River
Reservoir basin area, m2	12 575	580
Distance from the reservoir to the farm, km	2,3	5,5
Distance from the reservoir to the agricultural land in which organic fertilizers were applied, km	0,080	0,150

Water sampling for analysis on farms, springs within a radius of 1 km from the farm, and in the nearest natural reservoirs (Ros and Protoka rivers, Bila Tserkva district, Kyiv region) was carried out at an average daily ambient air temperature of +15.2 °C (second decade of September 2021). Eight samples were taken at each of the three locations (the nearest natural reservoir from the farm, spring water within a radius of 1 km from the farm, and water from the farm). Determination of water quality indicators was carried out in the State Institution "Bila Tserkva City Sanitary and Epidemiological Station" of the Ministry of Health of Ukraine. The volume of water samples for analysis was 5 liters. Bottles were plastic, cleanly washed, and rinsed with distilled water.

a) b)

Rice. 2. **Location of farms about water bodies and agricultural lands: a) with storage and processing of manure in a room with deep, long-lasting straw bedding; b) with the storage and processing of manure in a bioreactor-fermenter**

Water samples from rivers were taken above the potential source of pollution (agricultural land), against it, and downstream. Water sampling from open reservoirs of rivers was carried out following DSTU ISO 5667-1-2003. Water was taken at a depth of 0.5–1 m from the reservoir's surface at a distance of 1–2 m from the shore. Water samples from open reservoirs (wells) were taken at a depth of at least 1 m from the surface – in the morning when water had not yet been taken from it. The content of chlorides and sulfates the values of total hardness, nitrates, and nitrites in water were determined according to generally accepted methods (Malina et al., 2014). The permanganate oxidation and alkalinity of the studied water samples were detected according to the Kubel method and titrimetric study, respectively. The content of phenols in water was estimated by the photocolorimetric method.

The research materials were processed by the method of variational statistics based on the calculation of the arithmetic mean (M), the standard error (m), and the significance of the difference between the compared indicators (P). To show the probability in the tables, the symbols $P \geq 0.95$; $R \geq 0.99$; and $P \geq 0.999$, are respectively marked with asterisks (*;**;***).

Research results. Natural water contains significant impurities, ranging from dissolved metals and their salts to mechanical inclusions like rust, sand, and clay. The chemical composition of impurities is significant and affects water's total amount of chlorides, sulfates, and phosphates (Rozputnii et al., 2018).

The relationship between the variant of storage and processing of manure and the content of chemical compounds in river water samples has been established. In particular, the content of chlorides, which in high concentrations cause respiratory and skin diseases in animals (Malina et al., 2014), in the water of the studied rivers was the lowest than in the case of storage and processing of manure in a room with deep long-lasting straw litter by 36.25 mg/dm3 (Table 2).

As for the content of sulfates (salts of sulfuric acid), which, when exceeding the permissible norms in the body of both humans and animals, can cause allergic reactions and gastrointestinal disorders (Krysinska & Klymenko, 2021), their slightly higher concentration in river water was observed with the option of processing and storing manure in a bioreactor-fermenter – 52.31 mg/dm3, which is 11.97 mg/dm3 more than in a room with deep, long-lasting straw litter. The content of phosphates, which, at high concentrations, cause eutrophication (enrichment of water bodies with nutrients, accompanied by a decrease in their productivity) in natural objects and cause a nerve

agent in the body (Zhovnir & Grebin, 2018), was the lowest for the option of storage and processing of manure in a room with deep long-changing straw litter and amounted to 0.03 mg/dm3, which is 0.01 mg/dm3 lower than the values obtained in the fermenter bioreactor. In general, the concentration of the three main chemical compounds in the water samples of the zone of the studied farms was within the maximum permissible norm.

Table 2

Water quality indicators in the nearest natural reservoir from the farm depending on the option of manure storage and processing, mg/dm3, (M±m)

Indicator	Maximum permissible norm (not more than) mg/dm3	Manure storage and processing option	
		deep, long-lasting litter	Bioreactor-fermenter
Chlorides	350	36,25±1,032	52,61±0,680***
Sulphates	250	40,34±1,188	52,31±1,282***
Phosphates	3,5	0,03±0,001	0,04±0,002***

*Note. *** P≥0.999 – compared to the option of storing and processing manure on deep long-changing litter.*

Similar research results were observed in drinking water samples taken within a radius of 1 km from the location of the farms. The content of chlorides and phosphates was higher in the bioreactor-fermenter by 17.22 and 0.02 mg/dm3. A higher concentration of sulfites in the studied water samples was also found with this variant of manure storage and processing – 43.46 mg/dm3, which is 11.27 mg/dm3 more than with the option of processing and storage of manure in a room with deep long-changing straw litter (Table 3).

Table 3

Indicators of drinking water quality within a radius of 1 km from farms depending on the options for storage and processing of manure, mg/dm3, (M±m)

Indicator	Maximum permissible norm (not more than) mg/dm3	Manure storage and processing option	
		Deep long-immutable Litter	Bioreactor-fermenter
Chlorides	350	26,05±0,235	43,27±0,142***
Sulphates	250	32,19±0,531	43,46±0,810***
Phosphates	3,5	0,01±0,001	0,03±0,001***

*Note. *** P≥0.999 – compared to the option of storing and processing manure in a room with deep, long-lasting straw litter.*

The goal was to study the content of those indicators that directly depend on the activities of agricultural enterprises to determine the quality indicators of drinking tap water from drinking bowls on farms. Concerning the content of chemical compounds in samples taken from animal drinkers, there was a general trend towards the highest values for the content of chlorides and phosphates for the option of storing and processing manure in a bioreactor-fermenter, and slightly lower - in a room with deep, long-lasting straw bedding. However, in terms of the ammonium content, which at high concentrations affects the increase in blood pressure and respiratory rate and leads to

disorders in the liver and kidneys (UNESCO, 2019), the highest value was registered for the option of storage and processing of manure in a room with deep long-changing straw litter – 0.08 mg/dm3, which exceeded similar values for storage and processing of manure in a bioreactor-fermenter – by 0.05 mg/dm3 (Table 4).

Table 4

Indicators of the quality of drinking water on the territory of the farm depending on the option of storage and processing of manure, (M±m)

Indicator	Maximum permissible norm (no more)	Manure storage and processing option	
		deep, long-lasting litter	Bioreactor-fermenter
Chlorides, mg/dm^3	350	28,33±0,172	45,55±0,203***
Sulfates, mg/dm^3	250	32,54±0,773	45,45±0,927***
Phosphates, mg/dm^3	3,5	0,02±0,001	0,04±0,001***
Ammonium, mg/dm^3	0,5	0,08±0,0005	0,03±0,0001***
Nitrites, mg/dm^3	0,002-0,003	0,006±0,002	0,016±0,004*
Nitrates, mg/dm^3	45	0,88±0,09	7,19±2,04***
Permanganate oxidation, mg/dm^3	2,0	0,67±0,03	0,72±0,09
Phenols, mg/dm^3	0,001	0,0001±0,00001	0,0002±0,00001
Alkalinity, mmol/dm^3	6,5–8,5	7,09±0,08	7,95±0,05
Total hardness, mEq/l	1,5-7,0	8,10±0,22	9,40±0,34**

*Notes: * – P≥0.95; ** – R≥0.99; ¯ P≥0.001 – compared to the option of storing and processing manure in a room with deep, long-lasting straw bedding.*

In terms of the content of nitrites in water, which are capable of destroying red cells in the blood of mammals (Damania et al., 2019), the highest concentration was observed with the option of storage and processing of manure in a bioreactor-fermenter of 0.016 mg/dm3, which was 0.010 mg/dm3 higher than the content in water samples obtained from a farm with deep litter. High nitrate content in water increases the risk of chronic stomach upset, causes endocrinological disruption to the human body and can lead to abortion and stillbirth in farm animals (Malina et al., 2014). According to this indicator, the highest value was noted for the variant of storage and processing of manure in a bioreactor-fermenter of 7.19 mg/dm3, which is 8.17 times more than the indicators obtained in water from a farm with storage and processing of manure in a room with deep long-changing straw bedding. Permanganate oxidation determines the content of organic and mineral substances in water (Barnwal et al., 2017). It makes it possible to establish a specific indicator for water pollution in general. The smaller the permanganate oxidation, the more likely water will be used not only for operational needs. A high index of permanganate oxidation indicates the presence of a significant proportion of bacteria among organic matter. As a rule, an indicator higher than 2.0 mgO 2/dm3 negatively affects the body's reproductive function, liver, and kidneys (UNESCO, 2019). A slightly higher value of the permanganate oxidation of water among the studied farms was recorded during the storage and processing of manure in a bioreactor-fermenter of 0.72 mg/dm3, which by 0.05 mg/dm3 exceeded the value of indicators from samples obtained from a room with deep long-changing straw litter. Phenols are organic aromatic compounds used in the production of various aldehyde resins, polyamides, epoxy resins, antioxidants, etc.; when ingested by humans or animals, they can cause devastating effects on the kidneys and brain (Boyle et

al., 2010). Compared to the bioreactor-fermenter, a slight decrease in the phenol content was found in the variant of storage and processing of manure on deep litter (by 0.0001 mg/dm3). The alkalinity of water is a measure of the ability of a water solution to neutralize strongly, that is, those that completely dissociate into their ions when mixed with water acids. When they come into contact with mucous membranes or on the skin, highly mineralized alkaline waters cause them to dry out excessively (Keiser & Shapiro, 2019). In the studied farms, the total alkalinity of drinking water on the farm was within the permissible norm. It amounted to 7.09-7.95 mmol/dm3 with a slight advantage (less by 0.86 mmol/dm3) in the option of storing and processing manure in a room with deep long-changing straw litter, compared to a bioreactor-fermenter.

The total hardness of the water depends on the amount of soluble minerals, particularly calcium and magnesium. Hard water does not pose a danger to human and animal health. At the same time, hard drinking water in drinking bowls of farm animals can cause mold on the walls (Malina et al., 2014). The highest value of the total hardness of drinking water was stated for the option of storage and processing of manure in a bioreactor-fermenter – 9.40 mEq/l, which is 1.30 mEq/l higher than in a room with deep long-changing straw litter. At the same time, the total hardness of water in both farms where the study was carried out exceeded the maximum permissible norm by 1.1–2.4 mEq/l.

Discussion. In their life, cattle produce waste, which, under certain conditions, can cause significant harm to nature. Modern technologies for the production of livestock products can significantly reduce the risks of environmental pollution. However, it is necessary to adapt them most rationally, depending on natural and climatic conditions.

Hamill K. D. & McBride G. B. (2003), in studies conducted on the South Island of New Zealand in a subtropical climate, examined the phosphate content of six small rivers located near farmland or dairy farms. They established a relationship between the phosphate content in river water and the location of dairy farms. In water samples from rivers adjacent to farmland, phosphate concentration was lower than in water samples from rivers near dairy farms. Similar data are provided by another group of New Zealand researchers, who found an increased sulfate content in river water samples during organic fertilizer application to the fields (Wilcock et al., 1999).

The data obtained coincide with the data of Indonesian scientists who studied the content of chlorides, sulfates, and phosphates in the water of the Solo River (Java Island, equatorial climate), as well as in the drinking water of settlements located in its basin, where dairy farms were located (Widiastuti et al., 2015). They established an increased content of chlorides, sulfates, and phosphates in rivers and drinking water. At the same time, waste from washing milking equipment and washing the pre-milking area on the farms under study fell into the soil and water bodies. Scientists from the Republic of South Africa (subtropical climate zone) reported increased chlorides, sulfates, and phosphates in drinking spring water in settlements near the farm (Esterhuizen et al., 2012).

A decrease in the concentration of phosphates in water from Lake Champlain (Vermont, USA, continental climate) after constructing a sedimentation system on a nearby farm is reported in the work of American scientists (Kominami & Lovell, 2012).

Conclusions. The dependence of the indicators of the content of chemical compounds chlorides, sulfates, and phosphates in water from the nearest natural water bodies on storing and processing manure on the farm has been established. With the option of storing and processing manure in the room for keeping animals on deep, long-changing bedding and regulated disposal twice a year, wastewater after washing

milking equipment does not get into organic waste and is settled and disposed of separately. With this technology, the concentration of chemical compounds in the drinking water of the farm, the sources of which are used by the population within a radius of 1 km from the farm and in the nearest natural reservoirs with running water, is lower than in the case when the water after washing the milking equipment enters the general manure storage (bioreactor-fermenter).

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