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RESEARCH ARTICLE

Reducing the risks of contamination of agricultural land with toxic heavy metals during the application of organic fertilizers

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The risk of environmental pollution with organic livestock waste, especially cattle manure, which contains toxic heavy metals, is relevant for various countries of the world, including the United States of America, the countries of the European Union and Ukraine. Manure containing pollutants such as Cd, Pb, Cu, Zn, etc. is a much greater threat to agrobiogeocenoses and, in particular, to the soil. In the forest-steppe zone of Ukraine, an experiment was conducted on dairy cows for the production of ecologically safe milk. In the experimental groups, the animals were fed a special premix and injected with an antitoxic biopreparation, which increased the removal of heavy metals with excrement. The experiment was conducted in four farms with different herds of cows. At the end of the experiment, 10 samples of manure mass were taken from each farm (total of 40 samples), chemical analysis of the concentration of Cd, Pb, Cu and Zn was carried out by the method of Atomic Absorption Spectrophotometry (AAS-30 spectrophotometer). The content of feed in animal rations with exceeding the maximum allowable concentrations of heavy metals leads to their transition from the gastrointestinal tract into feces and urine and into manure, which, after disinfection in the manure storage, is introduced into the soil as an organic fertilizer for plants. The average concentration of Cd was 0.07-0.11 mg/kg, Pb 5.48-8.25 mg/kg, Cu 37.71-47.42 mg/kg, Zn 66.55-81.49 mg/kg. In order to prevent the ecological risk of soil contamination with heavy metals, it is necessary to establish the expediency of applying organic fertilizers to vegetable and fodder crops in each specific case, especially those that are fed to dairy cows. Farmers have difficulties in purchasing a sufficient amount of expensive mineral fertilizers, so they increase the use of available organic fertilizers, if their quantity is sufficient in the farm. At the same time, the introduction into the soil should be controlled, standardized taking into account the concentration of pollutants in the manure mass and the soil of agricultural land with simultaneous improvement of grinding and uniformity of distribution over the field. The use of modern equipment for crushing and spreading manure and scientifically based methods of its composting, growing vermiculture, synanthropic fly larvae or biogas production will contribute to the introduction of manure into the soil as an ecologically safe organic fertilizer, will have a positive effect on its mechanical and physico-chemical properties, will provide a good economic effective yield of crops, cows with ecologically safe feed, will reduce environmental risks of pollution of agroecosystems.

Keywords: Organic waste, Pollutants, Environmental safety, Cattle.

Introduction

The use of organic fertilizers, applied to the soil, usually has a positive effect on agrobiogeocenoses. Their use is important during alternative organic and biological farming. When traditional mineral fertilizers have a low price and are available to farmers, they, unfortunately, rarely pay much attention to organic fertilizers. The destruction as a result of hostilities of chemical industry enterprises that produced mineral fertilizers and the termination of trade relations with the aggressor will prompt agricultural producers to pay more and more attention to compensating for the loss of soil nutrients by increased application of organic fertilizers; especially in those regions of Ukraine where it was possible to preserve the livestock of agricultural animals, including cattle. The task of the nearest perspective will be the preservation of the existing animal population, their productivity and the yield of agricultural crops.

Manure, as an organic fertilizer, is very valuable - a natural source of macronutrients nitrogen, phosphorus, potassium, as well as a large number of micronutrients, including magnesium, sulfur, chlorine, silicon, etc., which are necessary for plants. Manure can also contain toxic heavy metals dangerous for agro-ecosystems, which also belong to mineral elements, but are pollutants of xenobiotic origin, such as lead, cadmium, arsenic, mercury, etc., which enter the body of farm animals, including cattle, dairy cows, are excreted with feces and urine. The application of organic fertilizers containing toxic metals to the soil can lead to an increase in the ecological risks of pollution, which will cause undesirable ecological consequences in agro-ecosystems where plants are grown, which are used as feed, especially for dairy cows, or even risks of harmful effects on human health due to direct consumption. Conducting organic and biological agriculture will require taking into account new technological approaches.

Scientifically based ecologically safe application of organic fertilizers improves the physical and chemical properties of the soil, reduces its acidification, migration of heavy metals from the soil to plants, against this background, also decreases. Organic fertilizers are an important source of humus in the soil, which accordingly increases its sorption capacity. Organic substances, especially humic acids, are a good binding agent for small soil particles.

The ecological problem of the content of heavy metals in animal feed and livestock waste and its solution is relevant in various countries of the world, not only in Ukraine. Moreover, attention is paid to the content of toxic metals in the mass of manure when it is not traditionally applied to the soil as an organic fertilizer, but undergoes anaerobic fermentation and composting. At the same time, toxic metals can be contained in both biogas and compost (Zheng X., et al., 2022). Scientists from Great Britain (Nicholson, FA., et al., 1999) considering the soil as a long-term absorber and holder of heavy metals, where pollutants can remain for hundreds or even thousands of years, de-pending on the element of its properties, potentially a long time of negative impact on fertility, taking into account legislation of the European Union, regarding the concentration of cadmium and lead in food raw materials, considerable attention is paid to the quantitative determination of the entry of toxic metals into agricultural soils with the possibility of assessing which soils are most vulnerable to pollution by pollutants. Only then will it be possible to predict and manage potential risks to reduce the negative impact on agroecosystems. Scientists took 183 samples of animal feed, 85 samples of manure from various commercial farms in England and Wales and examined the concentration of zinc, copper, nickel, lead, cadmium, arsenic, chromium and mercury in them (Nicholson, FA., et al., 1999). Other scientists from China (Wang H., et al., 2013) analyzed 360 feed and manure samples collected from 150 livestock farms in Jiangsu Province, an area of intensive live-stock farming and analyzed for the content of heavy metals and various mineral elements.

The transformation of heavy metals in the process of composting manure with the help of vermiculture also attracts the attention of scientists (Lv B., et al., 2016). Unlike other organic compounds, heavy metals are not decomposed by earthworms and aerobic microorganisms. Biohumus and earthworms can accumulate toxic metals. Based on this, scientists (Lv B., et al., 2016) recom-mend studying the changes and transformations of heavy metals during vermicomposting of ma-nure, this rather ecologically safe non-traditional method of processing and disposal of livestock waste. Scientists from China (Song X., et al., 2014) prove that the vermicomposting process can improve the nutrient quality of biohumus and reduce the risk of soil contamination by heavy metals

that accumulate in agricultural organic waste. Therefore, the ecological feasibility of ver-micomposting in the disposal of waste containing heavy metals is beyond doubt.

The purpose of the research is to assess the ecological risk of contamination of agrobiogeocenoses in the area of activity of agricultural enterprises producing milk and to ensure the ecological safety of the use of organic fertilizers.

Materials and Methods

Scientific and economic research on the production of ecologically safe milk and monitoring of the state of agrobiogeocenoses was carried out in the farms of the forest-steppe zone of Ukraine, where a large herd of cattle is kept even after the full-scale war. When conducting a scientific experiment with dairy cows of the black and red-speckled dairy breed, during the selection of average samples of feed and milk, the methods generally accepted in zootechnical practice were followed the method of ecological monitoring of ecosystems has been ongoing since 2000 until today. Biochemical analysis of samples of plant origin (feed), milk, excrement for the content of macro- and microelements, toxic metals, etc. carried out by the method of atomic absorption spectrophotometry (spectrophotometer AAS-30) (Praice, W. 1972).

For the experiment, 36 cows were selected with silage-root type of feeding (farm No. 1), 195 cows with silage-hay (farm No. 2), 63 with silage-hay (farm No. 3) and 126 cows with silage-hay-concentrate type feeding (farm No. 4), respectively. The experimental herd was divided into three groups: the first control and the second and third experimental groups. Animals of all groups were fed feed containing heavy metals cadmium, lead, copper and zinc above the maximum permissible concentrations. The cows of the second experimental group additionally received a special anti-toxic Mineral-vitamin Premix "MP-A" and the third - a premix and a subcutaneous injection of the Biopreparation "BP-9", which contains an extract of nine medicinal plants. Antidotes premix "MP-A" and drug "BP-9" were used to enhance elimination with excrement of toxic metals. The average live weight of cows is 500-545 kg. The cows were selected by the method of analogues in terms of live weight and productivity and were kept in the same conditions of feeding and keeping. Sampling of litter manure samples was carried out from the on-farm manure storage at the end of the experiment. The experimental period lasted 120 days. The agricultural lands of the experimental farms are located around the industrial city and near ecologically harmful anthropogenic objects of impact on agroecosystems - highway with increased traffic Kyiv - Kharkiv - Dovzhanskyi, natural gas production fields and gas condensate enterprises, main oil and gas pipelines, enterprises with production of asphalt concrete, etc.

Statistical data processing was carried out in the STATISTICA software package version 10.0 for the Windows 7 operating system..

Results

Cattle manure of dairy cows is formed from excrement, bedding material, remains of uneaten fod-der, etc. Determining the concentration of heavy metals in the manure mass from the manure storage is important for ensuring the ecological safety of agrobiogeocenoses when manure is applied to the soil on agricultural land as an organic fertilizer. After the complex application of antidotes in the experiment to enhance the removal of toxic metals from the body of productive animals, pollutants in greater quantities fall into the manure with excrement, further into the soil, continuing to migrate in the trophic chain and various components of the biosphere. The concentration of the studied toxic heavy metals is shown in Table 1. The main indicators of descriptive statistics for Cd and Pb, includ-ing the median (Table 2 and Fig.1).

Cows produce approximately 50-60 kg of excrement per day. The annual yield of manure from each cow is 15-20 m^3, or on average (per stall period) it is approximately 7 tons. Based on this, 252 t of manure fell into the agricultural lands of the first research farm as organic fertilizer (36 heads × 7 t), the second ¬ (195 heads × 7 t) 1365 t, the third ¬ (63 heads × 7 t) 441 t and the fourth ¬ (126 heads × 7 tons) 882 tons of manure. The concentration of heavy metals in this amount of organic fertilizer is 0.018 kg of cadmium, 1.69 kg of lead, 10.63 kg of copper and 18.89 kg of zinc in the first farm; to the arc ¬ respectively 0.123 kg, 9.99 kg, 54.5 kg and 104.63 kg; the third ¬ 0.035 kg, 3.64 kg, 20.91 kg and 29.35 kg; the fourth ¬ respectively 0.097 kg, 4.83 kg, 33.26 kg and 71.87 kg. Such an influx of heavy metals into the soil of agro-ecosystems together with man-made pollution requires the

controlled, standardized and rational use of manure as an organic fertilizer to reduce ecological risk, ensure the ecological safety of agricultural lands, where plants are grown that feed dairy cows and other farm animals or are sold on market as plant products.

Table 1. Concentration of heavy metals in manure of dairy cows of experimental farms, mg/kg (M ± SD).

Heavy Metal	MPC of Gross Forms in the Soil	Manure from Manure Storages of Experimental Farms, n=10			
		No. 1	No. 2	No. 3	No. 4
Cadmium	3	0.07 ± 0.035	0.09 ± 0.07	0.08 ± 0.037	0.11 ± 0.057
Lead	32	6.73 ± 2.29	7.32 ± 1.69	8.25 ± 1.24	5.48 ± 1.18
Copper	55	42.18 ± 5.36	39.93 ± 6.72	47.42 ± 4.78	37.71 ± 4.91
Zinc	100	74.95 ± 5.70	76.65 ± 5.34	66.55 ± 4.28	81.49 ± 3.34

Table 2. The main indicators of descriptive statistics for Cd and Pb.

Farms	Variable	Valid N	Mean	Median	Minimum	Maximum	Std. Dev
No. 1	Cd (Spreadsheet 2)	10	0.070	0.075	0.010	0.120	0.34641
	Pb (Spreadsheet 28)		6.734	6.765	3.020	9.970	2.295528
No. 2	Cd (Spreadsheet 2)	10	0.094	0.075	0.010	0.220	0.070427
	Pb (Spreadsheet 28)		7.317	7.890	4.010	9.370	1.692966
No. 3	Cd (Spreadsheet 2)	10	0.082	0.070	0.030	0.140	0.037357
	Pb (Spreadsheet 28)		8.252	8.455	5.850	9.910	1.243381
No. 4	Cd (Spreadsheet 2)	10	0.112	0.090	0.040	0.190	0.057310
	Pb (Spreadsheet 28)		5.479	5.230	3.920	7.320	1.184112

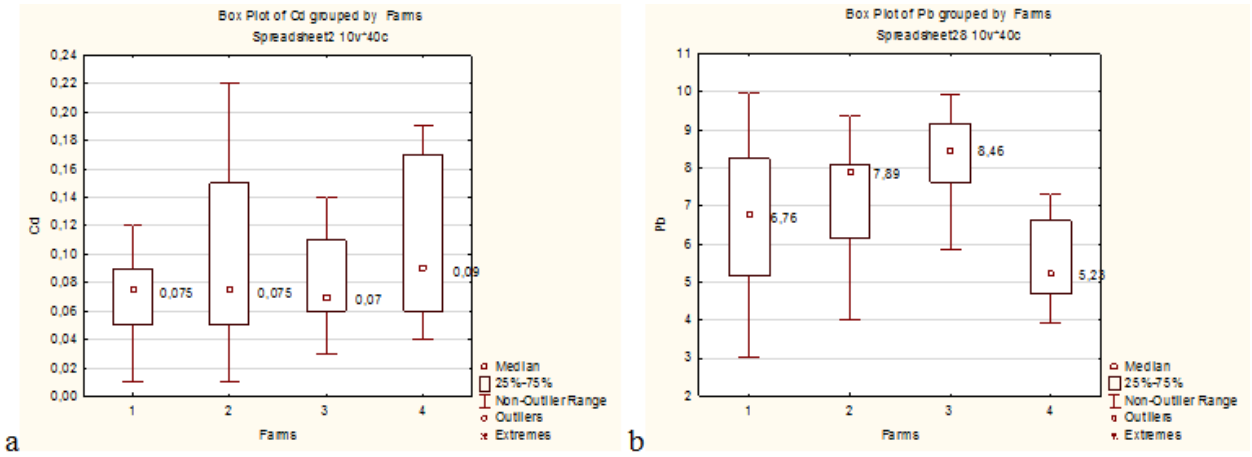

Fig. 1. Quartile diagram of the median content of Cd (a) and Pb (b) in the manure of dairy cows (mg/kg) in 4 experimental farms.

The concentration of cadmium in the fodder of the first farm, included in the diet of dairy cows, exceeded the established permissible standards by an average of 2.1-3.2 times, lead – 2.4-5.7 times, copper – 1.4-2.3 and zinc – 1.2-2.4 times, respectively. The greatest excess of the norm for Cd and Pb was found in cereal and leguminous hay (3.2 and 5.7 times), for Cu in corn cob (2.3 times) and for Zn in wheat straw (2.4 times).

The concentration of heavy metals in the fodder of other experimental farms fluctuated, which was due to the different content of mobile forms of toxicants in the soil and the location of agricultural lands where plants were grown, depending on the distance to the industrial center, highways, natu-ral gas extraction sites, gas-condensate enterprises, etc. . In the fodder of the second farm, the content of Cd, Pb, Cu, Zn exceeding the permissible norm was found in fodder beets, respectively, at 2.5; 3.4; 3.8; and 4.1 times. Plants accumulate heavy metals to a greater extent in the root system, i.e. in the part that is in the soil and a few less pollutants enter the vegetative system, therefore, of all fodder, it was fodder beet that had the highest level of pollution for all the studied elements in comparison with other fodder.

In fodder grown on the agricultural lands of the third farm, in addition to exceeding the norm in the content of Cd, Pb, Cu, Zn, in comparison with other farms, a high zinc content in fodder and in particular in oat and pea grains was recorded, on average 6.3-6.8 times. The highest content of cadmium and lead among the rest of the fodder was distinguished by pea grit and copper by cereal and leguminous hay (3.9 times). Among all four farms, the fodder of the fourth farm had the highest lead contamination by 7.3 times, zinc by 7.8 times and copper by 4.1 times. In terms of feed contamination with cadmium, the farm ranks last along with the second farm. Cereal-legume hay had the highest content of cadmium, lead and copper among the forages in the diet and corn grain accumulated the most zinc.

According to the level of contamination, farm fodder can be arranged as follows (in descending or-der): Cd No. 1 → No. 3 → No. 2 → No. 4; Pb No. 4 → No. 1 → No. 3 → No. 2; Cu No. 4 → No. 3 → No. 2 → No. 1; Zn No. 4 → No. 3 → No. 2 → No. 1. Copper and zinc are essential elements involved in various biochemical processes vital for the animal body: hormonal, enzymatic, etc. They must enter the animal's body in a certain amount. Their role is also important for growing plants, so it is necessary to prevent oversaturation of the soil with Cu and Zn. Taking into account the concentration of copper and zinc, as well as other more dangerous toxic heavy metals such as cadmium and lead in the manure mass, gross and mobile forms of pollutants in the soil, it is necessary to monitor compliance with the norm of applying organic fertilizer per 1 hectare of agricultural land. The scientifically based rate of application of organic fertilizers obtained from cattle manure to prevent the accumulation of nitrates in the soil is 50-70 tons per hectare. Non-traditional manure processing technologies using manure composting, vermiculture or biogas production are also practiced in different countries of the world to improve the ecological situation and avoid the risks of soil contamination of agrobiogeocenoses in the respective region and the country as a whole, which is also important for Ukraine.

Discussion

Cattle litter is one of the most common types of organic fertilizer. Organic fertilizers play a significant role in the accumulation of humus reserves, the level of which decreases with the constant use of chemical mineral fertilizers. It is humus that is the energy base of biological processes occurring in the soil and a source of plant-available macro- and microelements, including heavy metals, physiologically active substances, as well as a sorbent for various pollutants, toxic metals, pesticides, etc. The background content of the studied heavy metals in the soils of all the experimental farms was within the limits of the maximum permissible concentrations, while an excess of the permissible norm of mobile forms was found on average for cadmium by 4.3-8.3 times, lead by 4.9-8.8 times, copper by ¬ 3.3-4.5 and of zinc by 1.8-2 times, respectively, in the first economy. In the second and fourth experimental farms, a similar situation of exceeding the MPC of mobile forms of pollutants in the soil of both farms was observed on average: for Cd - by 3.9-9 and 3.6-7.3 times, for Pb - by 4.8-9 and 4.7-8.2 times, Cu – 3.2-5 and 1.9-4 times, Zn – 1.8-2 and 1.7-1.9 times, respectively, for the third economy 3-8.6 times for cadmium, 4-9 times for lead, 2.6-4.7 times for copper and 1.7- 2.1 times zinc. In the experiment, it is difficult to establish what proportion of heavy metals that got into the soil came with organic fertilizers, which came with agrochemicals and which came with man-made emissions. It is obvious that when mineral fertilizers are available at a price and farmers use them in large quantities, they acidify the soil and thus increase the increase in mobile forms of pollutants in the soil and cause the migration of heavy metals into plants. Organic fertilizers have the opposite effect. Therefore, an increase in the application of organic fertilizers against the background of a significant decrease in the application of mineral fertilizers in this aspect will give a favorable result. Moreover, cattle manure is the main and most ecologically safe organic fertilizer. The content of nutrients in it directly depends on the degree of its decomposition. Litter manure is a good organic fertilizer. The average content of nitrogen in high-quality bedding manure is 5 kg/t, phosphorus 2.5-3 kg/t, potassium up to 6 kg/t. This content of nutrients is achieved with proper storage of manure in the manure storage. Violation of manure storage rules leads to a 50% loss of nitrogen and carbon, up to 20-30% of phosphorus and potassium are washed out. The effectiveness of litter manure depends on the soil and climatic conditions and increases from the south to the north of Ukraine and in its central forest-steppe zone, where a large herd of cattle is concentrated, the intensity of application of organic fertilizers in the fields becomes extremely important, including from the point of view of the development of organic biological agriculture.

Scientists from China (Wang H., et al., 2013) analyzed a large number of feed and manure samples for the content of heavy metals, which were not collected in four farms, as in our case, but in 150 livestock farms in Jiangsu Province (Jiangsu Province, China). Concentrations of Zn and Cu in an-imal feed were approximately 15.9-2041.8 and 392.1 mg/kg, respectively, while Hg, As, Pb, Cd and Cr in all feeds were below 10 mg/kg. The concentrations of Cu, Zn and Cr in animal manure were 8.4-1726, 39.5-11379 and 1.0-1602 mg/kg, respectively and As, Cd, Hg and Pb were < 10 mg/kg. The concentration of Cu, Zn, As and Cr in animal feed and manure had a positive correlation ($P<0.001$), but Cd, Hg and Pb were not statistically correlated between the content in feed and the content in manure. Concentrations of Cu, Zn were the highest in feed for pigs and manure, followed by poultry and dairy animals.

During 1990-2008, the content of Cu, Zn, As, Cr, Cd increased by 771%, 410%, 420%, 220% and 63% in pig manure, by 212%, 95%, 200%, 791% and – 63% in the manure of dairy animals and 181%, 197%, 1500%, 261 and 196% in bird droppings. According to the scientists, the most significant increase occurred from 2002 to 2008, indicating the widespread use of feed additives after 2002. In contrast, Pb and Hg levels in manure decreased continuously from 1990 to 2008. Research results indicate that the content of heavy metals in animal manure has increased significantly for more than 18 years, which will accordingly increase their entry into the soil. (Xu, Y., et al., 2019) also note that livestock manure in China has a significant potential for contamination with heavy metals, as excessive addition of mineral elements that are heavy metals, in particular copper and zinc, to feed is common in the country. In order to reduce the morbidity of animals, feed is treated with various trace element additives and copper and zinc are their main el-ements. Undigested large amounts of heavy metals end up in manure. The excess of copper and zinc in cattle manure in different regions of China fluctuated in a wide range.

Scientists from different countries and continents of the planet are interested in researching the con-tent of heavy metals in fodder and manure. Scientists (Nicholson, FA., et al., 1999) from England studied 183 samples of livestock feed and 85 samples of animal manure collected from commercial farms in England, including Wales. We examined 40 samples of manure ¬ 10 samples from each commercial farm. British scientists determined the content of zinc, copper, nickel, lead, cadmium, arsenic, chromium and mercury. Our research was focused on the most dangerous heavy metals of cadmium, lead, copper and zinc, the pollution of which is typical for this region according to environmental monitoring data. Scientists (Nicholson, FA., et al., 1999) established concentrations of zinc and copper in feed for pigs, which ranged from 150-2920 mg/kg of dry matter for zinc and 18-217 mg/kg for copper, depending on the age of the pigs. In poultry feed, concentrations ranged from 28-4030 mg/kg for zinc and 5-234 mg/kg for copper, with laying hen feed generally having higher heavy metal content than broiler feed. Concentrations of Zn and Cu in dairy and meat cattle feed were significantly lower than in pig and poultry feed. Pig manure usually contained about 500 mg/kg of zinc and about 360 mg/kg of copper, indicating the concentration of the metal in the feed. Typical concentrations in bird droppings were 400 mg/kg zinc and 80 mg/kg copper and in cattle manure 180 mg/kg zinc and 50 mg/kg copper. We recorded significantly lower concentrations, which averaged 66.55-81.49 mg/kg for zinc and 37.71-47.42 mg/kg for copper, respectively, which is due to significantly less contamination of feed. The dry matter content of cattle and pig wastes was a useful indicator of the concentration of heavy metals in natural matter.

Cattle manure is used by plants not only in direct action - its effectiveness is also monitored in the after-effect, 2 and 3 years after application. It is most expedient to apply litter manure in the fertilization system under sugar and fodder beets, corn for grain and silage, sunflower, rapeseed and soy-beans. Of course, the introduction of manure under fodder beet, corn for silage and other fodder crops, especially those that are fed to dairy cows for the production of ecologically safe milk, re-quires taking into account the norm of organic fertilizer application per 1 ha of agricultural land, based on the concentrations of toxic heavy metals such as cadmium, lead in manure and soil. Under grain crops (winter wheat, barley, rye) manure is not recommended, as it is not agronomically and economically expedient. It is necessary to be careful with high doses of organic fertilizer application at the level of 40-60 t/ha, because there will be a lodging of crops due to an excess of nitrogen, the resistance of plants to fungal diseases decreases. Cereal crops use the after-effect of cattle manure.

Optimal doses of bedding manure application depend on the soil and climate zone of Ukraine, which is associated with different percentages of humus in the soil and its physico-chemical and mechanical properties (flowability, moisture content, etc.). The recommended optimal norms for corn for grain and silage are 30-40 t/ha, fodder beet 50 t/ha, they must be followed and approached differently, taking into account the concentration of pollutants in manure and soil of the correspond-ing crop rotation. To calculate the rates of organic matter, it is necessary to conduct a soil study and study the composition of the organic fertilizer itself. It is also worth knowing the type of culture and its planned yield. Depending on the amount of mineral nutrients, including heavy metals, in soils, organic fertilizers and plants, the total amount of nutrients necessary for the application of minerals is formed and the maximum intake of toxic metals is established. For the most accurate calculation, of course, it is necessary to take into account the effect of organic fertilizer for 3-5 years. The max-imum permissible rates of application of organic fertilizers are stipulated in the state standard of Ukraine 7925:2015. For example, if the content of nitrogen in the litter of cattle manure is 5 kg/t, the maximum allowable rate of introduction into the soil is no more than 34 t/ha.

The main requirement when applying litter manure is the degree of its grinding and the uniformity of distribution over the soil surface in the established norm. Unfortunately, many farmers still use outdated equipment (spreaders). Its huge drawback is the lack of high-quality crushing of manure and a small spreading width (up to 3 meters). Evenness of distribution is low and practically absent, namely grinding and uniform distribution over the field surface increases the assimilation of manure nutrients by plants and the yield increases by 20-40%. Any agricultural enterprise today will count the costs of spreading manure, because the cost of fuel is high. New modern technology is much more effective in solving this problem.

Cattle manure is best applied to the surface of the soil in the fall under deep plowing, as well as in the spring under spring plowing, worse ¬ under disking or cultivation, since a significant part of the fertilizers remains on the surface of the field. Unevenness of grinding and application of manure leads to a decrease in the efficiency of the use of organic matter by the root system of plants, reduces the productivity of the entire field, leads to a loss of yield, causes variegation of crops and in-creased accumulation of heavy metals. Manure must be plowed into the soil on the same day after the manure spreader has passed, because every day of delay in manure plowing leads to a loss of ammonium nitrogen of up to 50%. If the scattered manure is plowed after a day, the positive effect on the yield of crops decreases by 10-15%, after four days by 30%. Moreover, untimely plowing of manure leads to high ecological risks of surface and underground water pollution. Contamination of drinking water with nitrates and heavy metals will pose a threat to human life and health.

Very often, on large farms, manure accumulates in large quantities and can threaten the environ-ment. Pollution damage and related environmental biohazard risks are exacerbated if industrial farms are located near populated areas or water resources. There are cases when farmers, due to the overflow of manure storages, take manure directly to the fields in violation of any established state standards of Ukraine 7925:2015 maximum permissible norms, violate methods of application, which will definitely lead to pollution of ecosystems with nitrates, phosphates, sulfates, chlorides, including heavy metals such as cadmium, lead, copper and zinc, which is confirmed by the results of our studies and research (Kuzurziak, KV. 2017). In China, as well as in Ukraine, there is a standard for maximum permissible rates of organic fertilizer application (Yang X., et al., 2017). Moreover, a nationwide survey of animal manure composts was conducted in the country. The samples were analyzed for the content of 9 heavy metals. Concentrations of toxic metals vary widely: Zn 11.8-3692 mg/kg, Cu 3.6-916, Cr 0.7-6603, Ni 0.7-73, Pb 0.05-189, As 0.4-72, Co 0.1-94, Cd 0.01-8.7 and Hg 0.01-1.9 mg/kg, respectively. There were significant correlations between the concentrations of zinc, copper and arsenic, which indicated the joint contamination of composts with these elements. Repeated application of compost with an increased concentration of heavy metals significantly increases the concentration of zinc, copper, cadmium and mercury in the soil compared to the background concentrations. Research by scientists (Yang X., et al., 2017) emphasizes the need to minimize the concentration of Zn, Cu, Cd, Hg and As in animal manure to ensure the ecological safety of agricultural land.

Some producers of agricultural products use unbalanced rations and fodder of questionable, often low quality, including those containing heavy metals, to increase the intensity of animal productivity. Studies of the mineral composition of animal feed are often

not conducted for various reasons. Diets with fodder containing heavy metals will lead to their transition into manure mass, which we established during the research (Tables 1 and 2, Fig. 1). Manure contains a large amount of dissolved salts, including heavy metals, which after evaporation of moisture remain in the soil, in particular in the form of chlorides and sulfates, which causes soil salinization and contamination with toxic metals.

In the Netherlands, as well as in the north-west of Germany, animal husbandry is developing intensively. Due to the high content of nutrients in manure, it is used as a valuable organic fertilizer, which saves farmers from the need to buy expensive mineral fertilizers. However, in the small Netherlands, there is not enough space for huge amounts of manure and manure has simply become waste. Dutch farmers pay 18 to 25 euros per cubic meter to remove excess manure. It is cheaper for farmers to deliver manure to Germany. In 2016, more than 2.2 million tons of animal manure were exported. Germany is the largest buyer of manure from Holland, although it is reasonably available in Germany itself. The formation of a huge amount of manure creates a problem for Germany as well. Nitrate nitrogen and phosphates worsen the condition of rivers, lakes and coastal areas. The legally permissible concentration of nitrates for the countries of the European Union is 50 mg/l in accordance with Directive 91/676/EU of December 21, 1991 on the protection of waters against pollution caused by nitrates from agricultural sources. Nitrate content in more than 27% of under-ground waters in Germany already exceeds the established norm. Too high a concentration of nitrates in water poses a risk to human health. Research indicates the need to transport manure from some critical regions of China to others, taking into account the model of spatial distribution of nutrients in manure and the need for agricultural land to maintain the ecological well-being of the territories (Zhi B., et al., 2022).

Effective and ecologically safe use of manure in farms, as an organic fertilizer, is possible only with a clear organization of work on its storage, application to the fields, which includes all operations of removal, grinding and uniform distribution on the soil surface. The result of combining the application of organic fertilizers together with mineral fertilizers will be positive, if it is possible to purchase them in farms with traditional farming practices. A similar effect from the combined use of organic and mineral fertilizers can be achieved by doubling the rate of application of organic fertilizers and thereby completely abandoning the use of mineral fertilizers - a purely organic fertilization system. The results obtained in the Kyiv region (Bobyk S. 2015), also in the forest-steppe zone, at the experimental enterprise showed that when doubling the dose of cattle manure, if there is a sufficient amount of it in the farm, the replacement of mineral fertilizers with manure increases the humus content in the gray forest soil to 1.88%, while when applying organic-mineral fertilizers up to 1.77%. At the same time, financial costs for mineral fertilizers are significantly reduced. Applying more than the normalized amount of manure to the soil causes not only its pollution, but also the insensitivity of fertilizers in the future, the accumulation of an excess of nutrients and heavy metals can cause the opposite effect - a decrease in soil fertility and deterioration of its properties due to the suppression of biogeocenotic processes, which disrupts the processes of self-cleaning of the soil.

Scientists (Song X., et al., 2014) conducted a 4-month experiment to study the reaction of heavy metals and nutrients in manure in the process of its composting with the addition of mush-room residues with and without earthworms. The results showed that earthworms accelerate the mineralization of organic matter (for example, the C/N ratio decreases, the total concentration of N, P, K increases) and humification. Despite the fact that composting increased the total concentration of heavy metals (As, Pb, Cu, Zn) regardless of earthworm, the availability of heavy metals was significantly reduced ($P<0.05$) especially when treated with earthworms. The transition from accessible to unavailable heavy metal fractions was either due to earthworm bioaccumulation, as indicated by total heavy metal concentrations that were higher in earthworm tissues, or due to the formation of stable metal-humus complexes, indicating the promotion of humification. Thus, studies (Song X., et al., 2014) prove that the vermicomposting process can improve the quality of nutrients and reduce the risk of heavy metals in agricultural organic wastes entering the soil.

The effectiveness of composting pig manure containing heavy metals is indicated by research (Wang C., et al., 2023) (Fig. 2). Manure containing heavy metals was composted under the action of nitrogen-fixing microorganisms. Compared to the control, the experimental compost showed significantly lower extractable Cd (23.10%), Cu (48.15%), Cr (82.79%), Pb (4.49%) and Zn

(29.15%) (P<0.05). Scientists conclude that the method of manure composting is effective for ensuring the biosafety of organic fertilizers. Research on the quality and environmental safety of manure com-posting was also conducted by Korean scientists (Ko HJ., et al., 2008). An experiment of com-posting manure with sawdust was carried out. At different stages of composting, the concentrations of Zn, Cu and Pb varied significantly, which made it possible to propose appropriate parameters for the maturation of the compost mass, which ensured the maximum environmental friendliness of its use as organic fertilizer.

Pyrolysis of manure waste biomass into biochar for soil restoration (reclamation) belongs to some rather rare, but such, which are being studied by scientists (Tan S., et al., 2023). The positive role of scientists is burdened by the fact that traditional manure processing technologies are quite slow and not always effective. In order to improve carbon management and reduce greenhouse gas emissions, this method of manure processing may also be interesting in the future and will stimulate the development of the biochar industry. Due to pyrolysis, heavy metals from manure are fixed in biochar, thus minimizing soil pollution both through leaching and absorption of toxicants by agricultural crops. Pyrolysis biochar can potentially be used for soil reclamation, agronomic and eco-logical expediency. American scientists (Shea K., et al., 2022) are investigating the use of remote sensing to determine manure application in eastern North Carolina, where farms have a large live-stock population. A significant amount of manure is concentrated in a small area. Satellite radar was used to determine the place and time of manure application on agricultural land to avoid oversaturation of the soil with substances. Such studies by scientists only prove the importance of the mandatory solution to the issue of ecologically safe use of organic fertilizers in livestock farms.

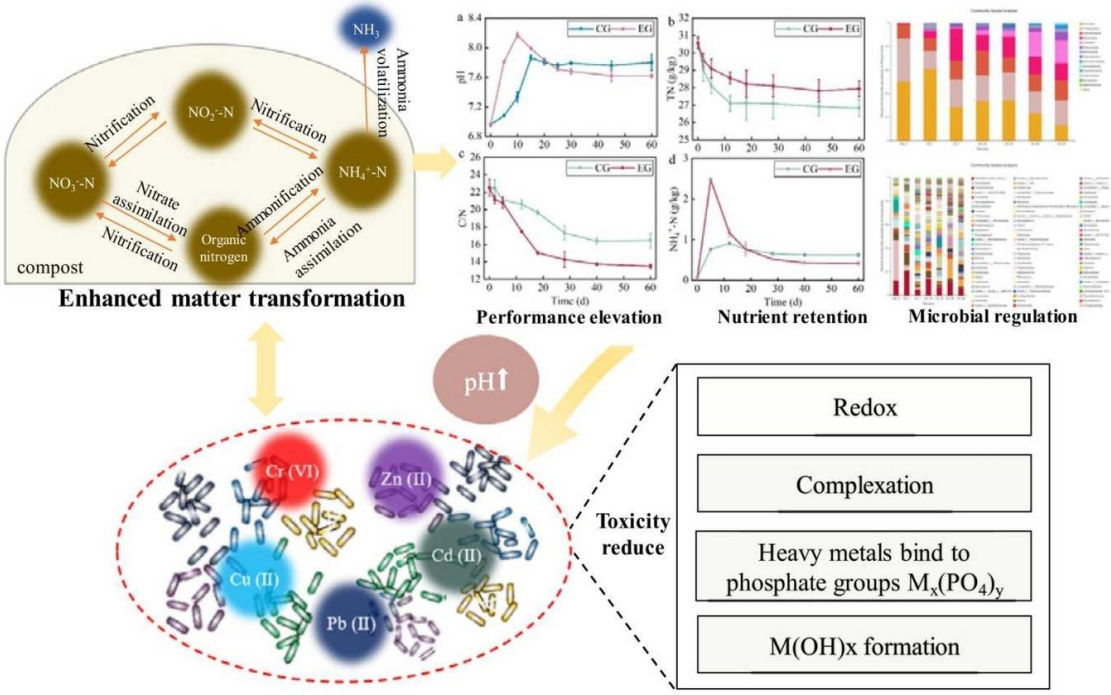

Fig. 2. Heavy metal influenced manure composting with NRMA augmentation.

Thus, toxic heavy metals such as cadmium, lead, copper and zinc, as well as many other mineral elements, enter the body of animals with feed, easily pass through the gastrointestinal tract of dairy cows, part of them accumulates in internal organs and tissues, a certain amount is excreted from milk and excrement, which is confirmed by the chemical analysis of animal dung and is consistent with the research of other scientists. The greater the excess of the maximum allowable concentration of heavy metals in feed, as a result, the greater their entry into the body of animals with daily rations, the greater the entry of pollutants with excrement in manure. Therefore, it is important to examine both the manure itself for the content of nutrients and harmful substances, heavy metals and the soil before applying organic fertilizer, in order to avoid the risks of negative environmental consequences that may arise as a result of its overtime application. In global practice, various technological methods are used to reduce the negative impact of manure on ecosystems, which include the regulation of the application of organic fertilizers, manure composting, the cultivation of vermiculture or larvae of the black soldier (synanthropic) fly (Liu T., et al., 2022), the production of

biogas (Chozhavendhan S., et al. al., 2023), the development of ecologically safe organic and biological agriculture, etc. and the concentration of heavy metals in manure must be controlled before ap-plying it to the fields as an organic fertilizer (Dong R., et al., 2022).

Conclusion

Modern conditions of agribusiness, high prices for mineral fertilizers and many other factors have led farmers to the question of more intensive use of manure as a high-quality and ecologically safe organic fertilizer. Manure in farms where dairy herds are kept accumulates in large quantities and acts as the final link in the concentration of heavy metals cadmium, lead, copper, zinc, which after metabolism turn into excrement and manure. Feeding a mineral-vitamin premix and injection of a biopreparation enhance the elimination of toxic metals from the body and increase their concentration in manure. When preparing ecologically safe fodder for dairy cows and producing high-quality ecologically safe milk, it is necessary to follow scientifically based methods of applying organic fertilizers, taking into account the concentration of toxic heavy metals in manure and soil, especially Cd and Pb, in order to reduce the environmental risks of contamination of agrobiogeocenoses. Manure formed during the feeding of fodder with heavy metals should be applied as an organic fertilizer, having previously determined the rate of its application taking into account the content of pollu-tants in the soil, applying differentiated application and in this way reducing the load of toxicants both on the unit area of agricultural land and on the plants themselves, especially when the concentration of pollutants in feed exceeds the maximum permissible concentration by 10 or more times. Use equipment that allows you to efficiently remove, grind and evenly spread organic matter over the field. Applying manure as an organic fertilizer requires systematic monitoring of the dynamics of migration of heavy metals in the soils of agricultural lands of pastoral farms for the maintenance of dairy cows in the forest-steppe and other agricultural zones. Take into account the complex anthropogenic impact on agro-ecosystems of sources of environmental pollution, more widely apply non-traditional methods of processing manure using composting, growing vermiculture, synanthropic fly larvae or biogas production. Manure formed when eating feed with an excess of the maximum allowable concentration of heavy metals by 20 or more times should be applied to tech-nical crops, limit the rate to vegetable and fodder crops. If the maximum permissible concentration of heavy metals in the mass of manure exceeds 100 times, the method of pyrolysis and biochar production will be more effective. Composting manure by mixing it with peat, earth, straw and saw-dust with materials safer in terms of the content of heavy metals will also reduce the concentration of toxicants in 1 kg of manure.

Further research is aimed at correlational, regression analysis of the content of heavy metals in animal feed and manure and monitoring of agroecosystems in the forest-steppe zone, where a large herd of cattle is kept.

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Conflict of Interest

The authors declare no conflict of interest.

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