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Study of the Content of Essential Mineral Elements in the Feed of Dairy Cows Against the Background of Increased Concentrations of Toxic Metals Cd and Pb in Plants

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Abstract. Uncontrolled entry of pollutants – heavy metals into the environment creates obstacles to the production of environmentally safe, biologically complete cow's milk. The accumulation of pollutants in the soil reduces the supply of essential mineral elements to plants, which are necessary to ensure the full feeding of animals. In such environmental situations, it is important to analyse feed rations for the content of essential and non-essential mineral elements. Samples of feed included in the main diet were taken on four experimental farms specialising in the production of cow's milk, the agroecosystems of which were located around the industrial centre and near environmentally unfavourable objects – roads, enterprises for the extraction (processing) of gas condensate, etc. The samples were analysed for the content of mineral elements by atomic adsorption spectrophotometry. Statistical data processing – STATISTICA software suite version 10.0. The feed was found to exceed the permissible level for cadmium by an average of 2.1-3.2 times, lead – 2.4-5.7 times, copper – 1.4-2.3 times, zinc – 1.2-2.4 times. In cereal and legume hay, the concentration of cadmium and lead exceeded permissible levels by 3.2 and 5.7 times, respectively. Against this background, there is a deficiency of calcium in various types of diets of cows from 1.4% to 47.5%, phosphorus – from 1.5% to 62.3%, magnesium – from 2.7% to 64.4%, potassium – from 0.8 % to 37.9 %, sulphur – from 2.3% to 48.8%, among trace elements, iron – from 2.3 % to 48.8%, cobalt – from 5.0% to 80.0%, iodine – from 4.0% to 60.7%. The reason for the deficiency of vital mineral elements in plants (feed) is different, including changes in soil pH, but mainly antagonism between mobile forms of toxic elements and essential elements. For the production of high-quality milk, it is necessary to normalise toxic metals in the diets of cows with different types of feeding and eliminate the lack of minerals with the help of specially developed feed additives (mineral and vitamin premixes), which will prevent elementosis in cows, which is a pressing issue in many countries of the world. Future studies will be aimed at monitoring the concentration of mineral elements in animal feed kept in the forest-steppe and steppe zone and Donetsk oblast of Ukraine

Keywords: heavy metals, lead, trace elements, macronutrients, calcium, phosphorus



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INTRODUCTION

Contamination of agroecosystems with heavy metals, especially cadmium and lead, is a major concern in various countries around the world. Under various conditions of agricultural production, the influence of abiotic and biotic environmental factors, pollutants that have accumulated in the soil easily migrate through the root system of the plant, accumulating in it in quantities that often exceed the established permissible levels (Bigalke *et al.*, 2017; Borah *et al.*, 2018). Further, plants are added by specialists to animal diets and affect the physiological state, productivity, quality, and environmental safety of products. They get into the manure, and as an organic fertiliser, back into the soil. The high concentration of heavy metals in livestock manure is also a concern. Researchers from China (Xu *et al.*, 2021) prove that manure can pollute agricultural land when animals are fed large amounts of mineral feed additives. China recently issued new regulations restricting the use of high doses of mineral feed additives. To reduce environmental pollution and increase the competitiveness of industrial enterprises in the market, researchers highlight the importance of understanding the characteristics of heavy metals in animal feed, in this case, pigs, with an intent to develop some alternative and more efficient approaches in conducting technological processes. To do this, scientists analyse a large number of research papers over the past twenty years. They found that copper and zinc exceed the existing standards established for feed used in feeding pigs. Researchers suggest that organic and new inorganic mineral feed additives can effectively replace high doses of inorganic minerals, which, in turn, will reduce cases of diarrhoea in piglets, improve animal productivity, growth and development, and reduce pollution. The concentration of Zn and Cu in pig manure will decrease by 8.21×10^7 and 3.23×10^7 kg, respectively, per year. In addition, the quality and economic efficiency of production will improve, and the income of breeding enterprises will increase by USD 1.28×10^{10} per year (Xu *et al.*, 2021).

Researchers from Germany (Schöne *et al.*, 2017) also indicate that milk can be a source of iodine intake in the human body, but its value directly depends on the iodine content in cow feed. The researchers focused their attention on investigating the concentration of this essential mineral element in cow feed and milk in the German practice of animal feeding. The results obtained were compared with the results of previous monitoring of milk and experiments to investigate the dependence of the iodine content in the diet and its content in the milk of dairy cows. 73 samples of various feeds were analysed, including 41 samples of concentrated feed, 32 samples of silage made from green corn or grasses (haylage), 83 samples of vitamin and mineral premixes and feed additives for iodine content, the daily intake with the diet of animals of this trace element was determined. Grains of cereals and legumes had a low iodine content. In silage, the element content was slightly higher than in concentrated feed. In general, researchers report the need for the additional introduction of this mineral element into

the diets of cows in Germany, if there is a shortage of it in feed, which will support the health of animals and ensure the production of milk with iodine content, increase the intake of the essential element in the human body with the product. Studies of the mineral composition of feed were also conducted by researchers from England (Nicholson *et al.*, 1999). They analysed 183 samples of animal feed and 85 samples of animal manure from commercial farms in England and Wales. The concentration of zinc, copper, lead, nickel, cadmium, arsenic, chromium, mercury and other essential and non-essential elements was determined. Zinc and copper concentrations ranged from 150-2,920 mg Zn/kg dm (dry matter) and 18-217 mg Cu/kg dm in pig feeds, depending on the age of the pigs. In poultry feeds, concentrations ranged from 28-4,030 mg Zn/kg dm and 5-234 mg Cu/kg dm, with laying hen feeds generally having higher heavy metal contents than broiler feeds. Pig manures typically contained c.500 mg Zn/kg dm and c.360 mg Cu/kg dm, reflecting metal concentrations in the feeds. Typical concentrations in poultry manures were c.400 mg Zn/kg dm and c.80 mg Cu/kg dm, and in cattle manures c.180 mg Zn/kg dm and c.50 mg Cu/kg dm.

Thus, against the background of the problem of accumulation of heavy metals in plants (feed), including toxic ones, there is a problem of low content of essential mineral elements for the animal body, for example, iodine, etc. The reasons for the lack of mineral elements in feed can be any, not only caused by the content of an increased concentration of antagonist elements in the soil, which block the flow of iodine, calcium, and phosphorus through the root system. To ensure the normal physiological state of a dairy cow, seven mineral elements such as calcium, phosphorus, magnesium, sodium, potassium, chlorine, and sulphur must be present in the diet in very large amounts every day (Goff, 2018). R.J. Van Saun (2022) lists nine mineral elements: chromium, cobalt, copper, iodine, iron, manganese, selenium, and zinc, which play a significant biological and metabolic role in the body of dairy animals. Researchers (Séboussi *et al.*, 2016) in an experiment on dairy cows prove the positive role of diets with the addition of selenium. In the experimental groups of cows, the content of somatic cells in milk was significantly lower than in the control groups of animals. Another group of researchers also highlights the important role of calcium and phosphorus in the diet of lactating cows (Moreira *et al.*, 2009), because a lack of elements in the diet leads to hypocalcemia and hypophosphatemia. Absorption of elements in the intestine occurs mainly due to passive diffusion, when animals receive a diet with a sufficient amount of minerals. Calcium and phosphorus deficiency in the feed, and accordingly, in the diet, will lead to resorption of elements from the bones. This mechanism was studied at the southeastern research station of the agricultural centre of the University of Louisiana, located in Franklinton, Louisiana.

The nutritional value of feed included in the diet of productive animals depends on their physiological state, quality and environmental safety of the milk

produced. A lack or excess of any mineral element can negatively affect the homeostasis of the animal's body, its productivity.

Originality of the study. For the first time, the content of essential mineral elements in plants (fodder), included in different types of diets of dairy cows in farms located around the industrial centre, where agroecosystems have an increased anthropogenic load with heavy metals, was analysed.

The purpose of the study is to analyse the concentration of essential and non-essential mineral elements in various feeding rations of silage and root crops, silage and hay, silage and haylage, and silage-haylage-concentrate feeding types in agroecosystems located around the industrial centre of farms and near sources of anthropogenic pollution to assess new technological methods for the production of environmentally safe, pollutant-free cow's milk.

MATERIALS AND METHODS

Testing of new technological methods for the production of pollutant-free cow's milk using special antitoxic mineral and vitamin premixes requires a deep analysis of the nutritional value of animal feed, especially with respect to the content of essential and non-essential mineral elements. For this purpose, average samples of various feeds were selected, which were included in the diets of dairy cows in four experimental farms: the first – "Druzhba" specialised agricultural enterprise with silage and root crop type of feeding cows; the second – "Khoroshkivsky" agricultural production cooperative-silage and hay; the third – agricultural limited liability company "Svitanok" – silage and haylage; the fourth – agricultural limited liability company "Uday" – silage-haylage-concentrate feeding type. The rations included such feed as alfalfa hay and legumes, wheat straw, corn silage, alfalfa haylage, fodder beet, and various types of stock feed: barley, pea, and corn. Structure of diets of experimental cows in animals with silage-haylage-concentrate feeding type: hay and straw – 17.7%, silage and haylage – 53.5%, concentrates – 28.8%; with silage and hay type: hay and straw – 23%, silage and haylage – 44%, root crops – 17%, concentrates – 16%; with silage and root crops type: hay and straw – 19.8%, silage and haylage – 41%, root crops – 22.8%, concentrates – 16.4%; with silage and haylage type: hay and straw – 22%, silage and haylage – 60.8%, concentrates – 17.2%. Agroecosystems of farms are located around the industrial city, near the Kyiv – Kharkiv – Dovzhanskyi highway (Ukraine), where there is a high traffic intensity, as well as near natural gas production fields and gas condensate enterprises, asphalt concrete production enterprises, main oil and gas pipelines, etc. Feed analysis and economic experiments on animals to balance animal feeding with a special mineral and vitamin premix MP-A together with subcutaneous injection of the biologically active drug BP-9 of plant origin were conducted in Poltavaska oblast during 2000-2007. In the experiment, we were able to test new technological methods for feeding a specially developed mineral and vitamin premix MP-A in combination with

subcutaneous injection of the biologically active drug BP-9 for the production of pollutant-free milk. The role of premix was to introduce mineral elements of heavy metal antagonists into its composition to prevent the absorption of pollutants in the gastrointestinal tract, essential elements to restore their balance in the body, and vitamins, which are extremely important for an intoxicated body. A biological product is developed from an extract of 9 medicinal herbs. The role of herbal preparation is to enhance the elimination of toxic metals that have been absorbed into the blood and block their harmful effects at the cellular level, at the level of organs and systems of the body. The drug has a hepatoprotective function, increases the excretion of cadmium and lead through the kidneys in the urine, and has a rich mineral composition – partially contributes to the restoration of the deficiency of essential elements in the animal body caused by a lack of plant feed diets. For the experiment, three groups of animals were formed in each farm. First – control, second and third – experimental groups. In the second experimental group, premix MP-A was fed as part of the diet, and in the third – premix MP-A were fed along with the subcutaneous injection of the biologically active drug BP-9.

The analysis of selected feed samples for the content of mineral elements, including heavy metals, was carried out by atomic absorption spectrophotometry (AAS-30 spectrophotometer) (Praise, 1972). The deficiency of macro- and microelements in feed was established relative to the average nutritional value of feed, defined in detailed standards (Kalashnikov *et al.*, 1985), and considering the maximum permissible concentrations of heavy metals established by the mandatory list of raw materials, products of animal and plant origin, mixed feed raw materials, mixed feed, vitamin preparations, etc., which should be carried out in state laboratories of veterinary medicine and according to the results of which a veterinary certificate (F-2) is issued (Mandatory minimum list..., 1998).

Statistical data processing was performed in the STATISTICA software suite version 10.0 for the Windows 7 operating system.

RESULTS AND DISCUSSION

Content of mineral elements belonging to the category of heavy metals in the main diet

It is established that the permissible concentrations of mineral elements belonging to the category of heavy metals in the diet of cows are exceeded. In particular, the concentration of cadmium in the diet of animals of the first experimental farm exceeded the permissible levels by an average of 2.1-3.2 times, lead – 2.4-5.7 times, copper – 1.4-2.3 times, zinc – 1.2-2.4 times, respectively. Cereal and legume hay had the highest concentration of toxic metals – cadmium and lead, which exceeded permissible levels by 3.2 and 5.7 times, respectively. Copper is a heavy metal, which belongs to the category of essential mineral elements, the maximum accumulation was recorded in corn stock feed with an excess of the norm by 2.3 times. Wheat straw accumulated an

excess of zinc, which exceeded the permissible level by 2.4 times.

The influence of various environmental factors, including anthropogenic ones – various pollutants and different distances to the industrial centre, natural gas production sites, transport highway, gas condensate enterprise; the use of agrochemicals, in particular, mineral fertilisers – significantly affected the content of mobile forms of chemical elements in the soils where plants were grown, which went to feed farm animals, since the content of heavy metals in the feed of other experimental farms fluctuated. In the diet of cows of the second experimental farm, an excess of cadmium, lead, copper, and zinc in fodder beet was found by 2.5, 3.4, 3.8, 4.1 times, respectively. As it turned out, of all the feeds in the diet, fodder beets had the highest content of heavy metals, in particular, including toxic ones such as cadmium and lead.

The diet of animals of the third experimental farm exceeded the permissible concentration of cadmium, lead, copper, and zinc. In comparison with the analysis of feed from other farms, a high concentration of zinc was recorded in oats and peas, which on average exceeded permissible levels by 6.3-6.8 times. Pea stock feed was characterised by the highest accumulation of cadmium and lead, and cereal and legume hay accumulated the most copper, which exceeded the permissible level by 3.9 times.

The lead accumulation in the diet of dairy cows was highest at the fourth experimental farm. The content of the element exceeded permissible levels by 7.3 times, which is due to the location of agricultural land actually along the highway with heavy traffic Kyiv – Kharkiv – Dovzhanskyi. The concentration of zinc exceeded permissible levels by 7.8 times, copper – 4.1 times, respectively. At the same time, the feed of this farm had the lowest level of contamination with cadmium. Among the feed of the diet, hay and legumes had the highest content of Cd, Pb, Cu, and Zn. However, the last essential element accumulated the most in corn grain.

Among the studied mineral elements in feed, cadmium and lead are not essential, unlike copper and zinc. The ingress of cadmium and lead from the soil into plants – animal feed, and then into the body and milk – leads to the content of pollutants in products that are consumed by humans. Cadmium and lead can cause disruption of the body's enzymatic, hormonal, and other systems. Milk containing cadmium and lead is dangerous for humans. Copper and zinc are essential, vital mineral elements for the body, although they are heavy metals. In the appropriate normalised amount, they must necessarily enter the body of both animals and humans. To develop new technological methods for the production of environmentally safe cow's milk, it is necessary to investigate not only the content of such ecocidal mineral elements as cadmium and lead, but also the concentration of essential mineral elements in the main diet of animals, because such mineral elements as calcium, phosphorus, magnesium, potassium, iron, sulphur, cobalt, manganese, iodine, etc. have an antagonistic effect on the absorption of toxic metals in the gastrointestinal tract. The availability of detailed

information about the content of essential macro- and microelements in the diet will allow specialists to develop appropriate effective feed additives, premixes, etc. – to balance the diet to ensure intensive removal of harmful elements from the body and support its vital physiological functions against the background of intoxication.

Content of essential mineral elements in the animal feed

The lowest calcium content was found: in fodder beet (47.5%) and wheat straw (31.4%) – in the first experimental farm; in wheat straw (38.6%) and alfalfa hay (22.6%) – in the second farm; corn stock feed (36%) – in the fourth; pea stock feed (12.5%) – in the third experimental farm; the rest of the feed had an average calcium content of 1.4-31.4% lower than the average for nutritional value (Fig. 1).

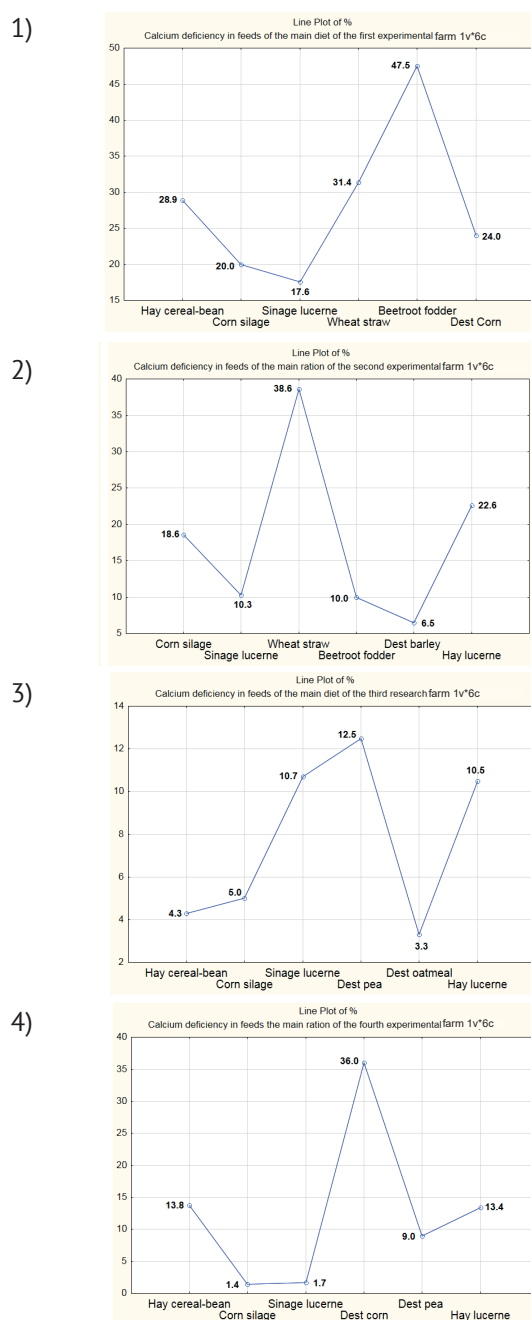


Figure 1. Calcium deficiency in the diet: 1 – first experimental farm; 2 – second experimental farm; 3 – third experimental farm; 4 – fourth experimental farm

The content of another mineral element phosphorus in the lowest concentration was found: in alfalfa hay 62.3% and oat stock feed (46.2%) – in the third farm; in alfalfa haylage (45%) – in the fourth and 31% – in the first experimental farm; in corn silage (42.5%) – in the second and (22.5%) – in the third farm; the rest of the feed had a phosphorus content of 1.5-22.3% lower than average (Fig. 2).

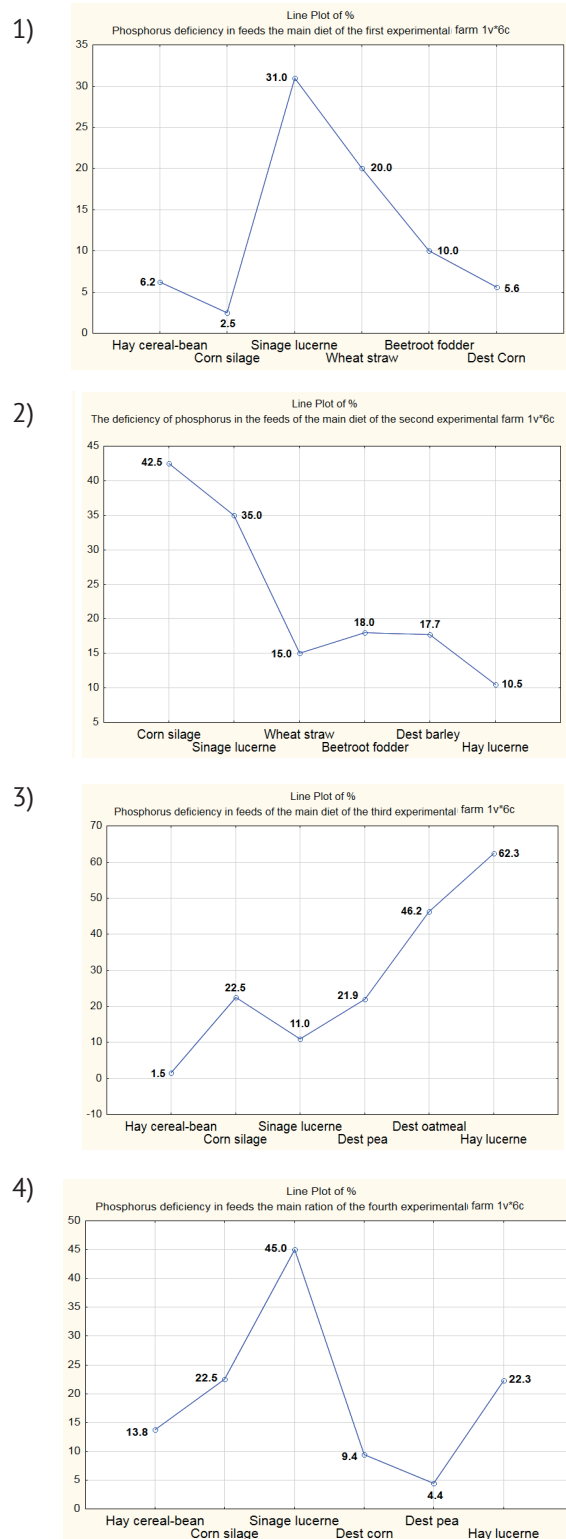


Figure 2. Phosphorus deficiency in the diet:

1 – first experimental farm; 2 – second experimental farm;
3 – third experimental farm; 4 – fourth experimental farm

Magnesium deficiency was observed in wheat straw (51.3%) in the first farm, the most scarce relative to this macronutrient was alfalfa haylage, which was in the diet of cows of all four experimental farms. In the second experimental farm, a significant magnesium deficiency was observed in barley stock feed – 34%, the rest of the feed had a magnesium deficiency on average from 2.7% to 27.1% (Fig. 3).

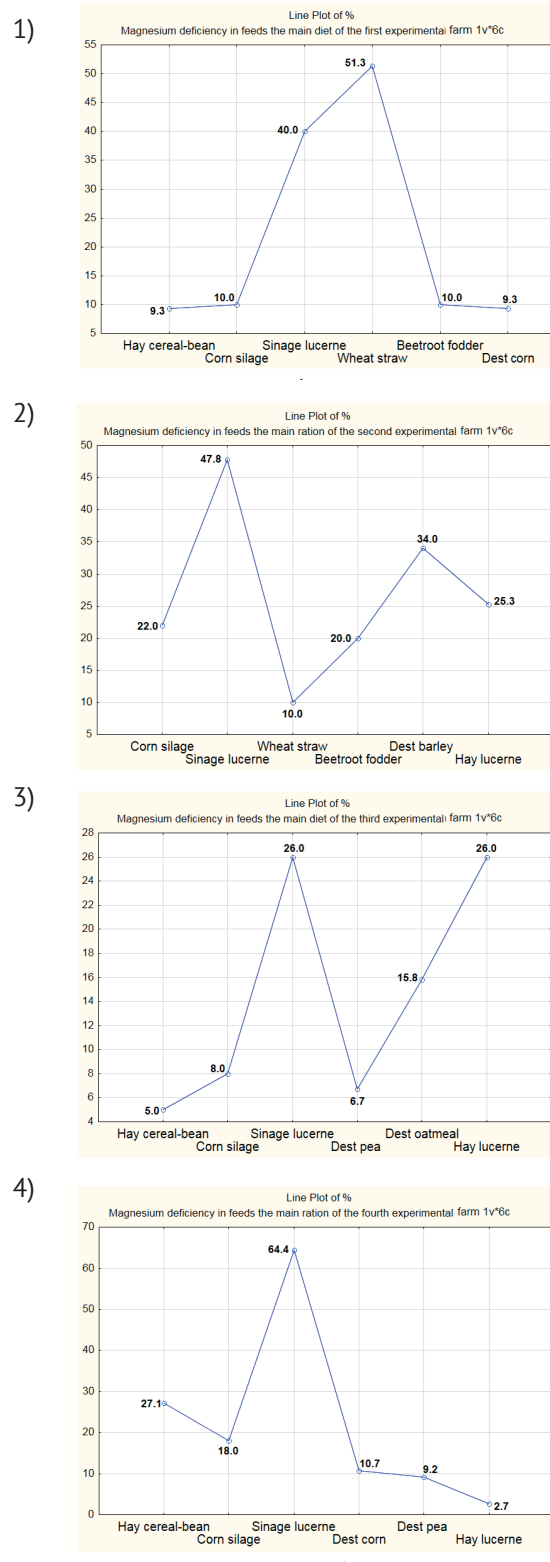


Figure 3. Magnesium deficiency in the diet:

1 – first experimental farm; 2 – second experimental farm;
3 – third experimental farm; 4 – fourth experimental farm

Potassium deficiency in the largest amount of 37.9% was found in wheat straw and 26.8% in fodder beet of the first farm; 33.5% in alfalfa haylage and 31.2% in alfalfa hay of the fourth experimental farm; 25% in alfalfa haylage in the second agricultural enterprise, other feeds had a potassium deficiency of 0.8-18.5% (Fig. 4).

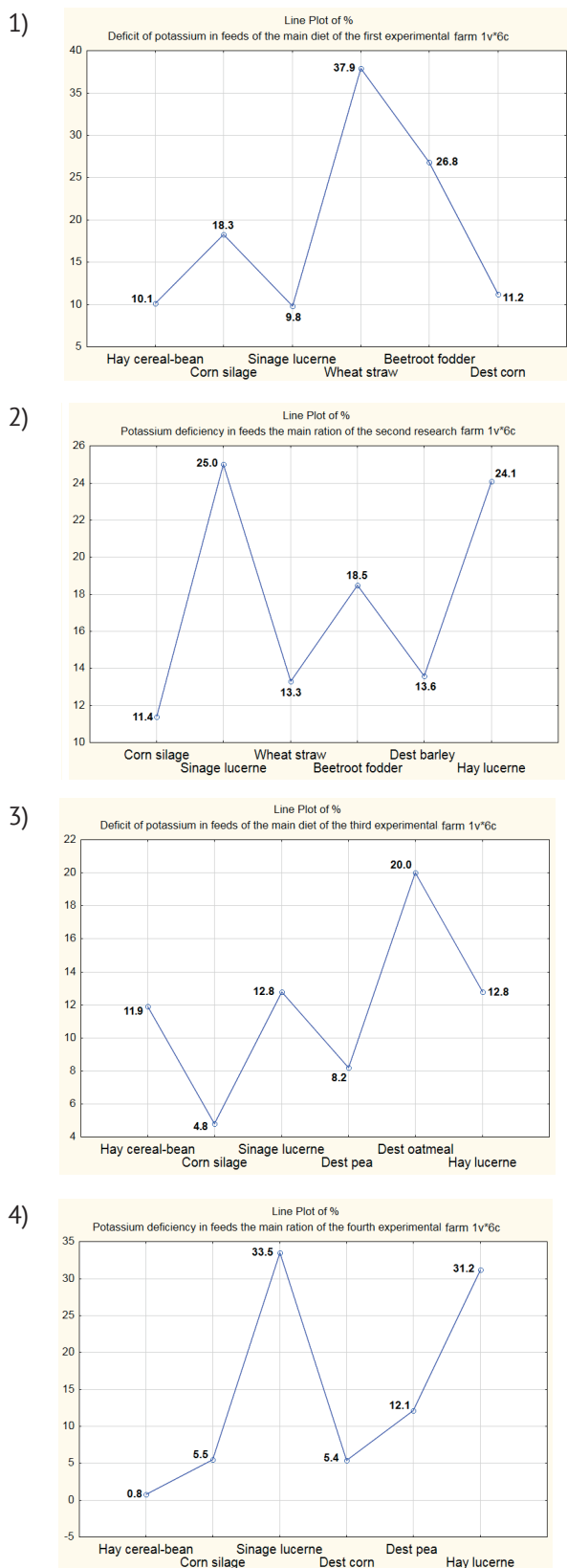


Figure 4. Potassium deficiency in the diet:

1 – first experimental farm; 2 – second experimental farm;
3 – third experimental farm; 4 – fourth experimental farm

Sulphur in the feed of all farms was also at a low level on average – from 2.3 to 48.8% (Fig. 5).

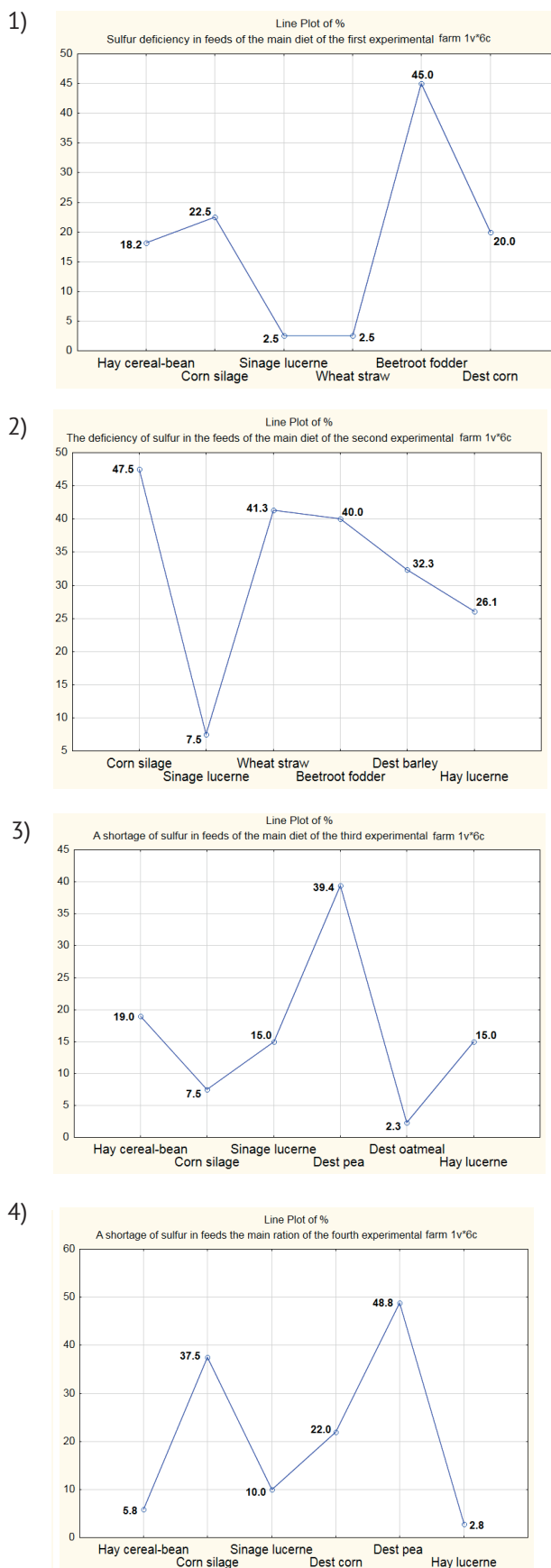


Figure 5. Sulphur deficiency in the diet:

1 – first experimental farm; 2 – second experimental farm;
3 – third experimental farm;
4 – fourth experimental farm

Sulphur is a fairly important trace element in case of intoxication of the body with heavy metals, especially cadmium and lead, as it is a part of sulphur-containing amino acids (methionine, cystine, cysteine) and sulphhydryl groups that form chelated compounds with toxicants. The content of sulphur in feed is very important, since its deficiency can lead to a deficiency of trace elements in the diet, which will be more dangerous for the health of cows

and all the more affect the quality and safety of milk.

The reason for the low iron content in animal feed, and especially in the plants from which it is made, is the antagonism between Fe and Mn, Fe and Cu in the soil. A significant role in this is played by the increased concentration of mobile forms of copper in the soils of farms. Iron deficiency in feed is observed, which averaged 2-29.2% (Fig. 6).

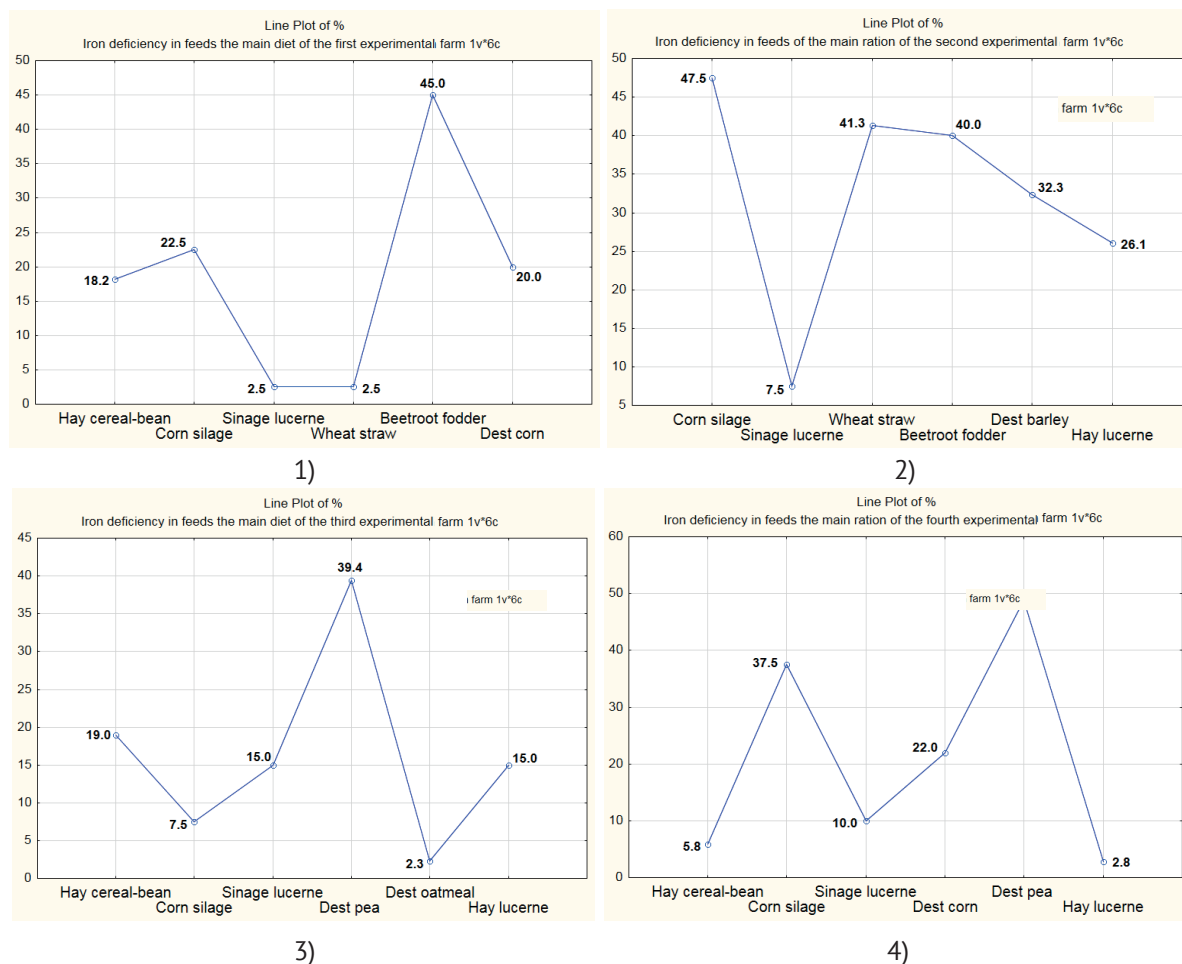


Figure 6. Iron deficiency in the diet:

1 – first experimental farm; 2 – second experimental farm; 3 – third experimental farm;
4 – fourth experimental farm

The absence of cobalt in feed may be conditioned by their cultivation in wetlands and the presence in the soil of a high concentration of cobalt antagonist elements, which include cadmium and lead. Applying phosphorous fertilisers to the soil can increase the supply of cobalt to plants. Cobalt deficiency can affect its deficiency not only in feed, but also in the diet, which will pose a danger of increased intoxication with cadmium and lead, and the death of the animal is also possible (the paradox is starvation with a sufficient amount of feed). The shortage of cobalt in feed is quite high (Fig. 7).

The lowest deficiency was found in cereal and legume hay (5%) – in the fourth experimental farm; in other feed – at least 11.5% in barley feed of the second farm, and beyond 15%, 20%, 40%, 50% and even 80% in alfalfa haylage in the first farm. In such a situation, a lack of cobalt in the diet and, as a result, in milk is very

likely. In the ruminant's body there is a struggle for cobalt between rumen micro-organisms and enzyme systems. This element is used for the synthesis of vitamin B₁₂ in the body. The presence of this vitamin in milk under such conditions is unlikely, which was confirmed by the study. Content of vitamin B₁₂ in the milk of cows of all control groups was at the level of "traces".

The manganese deficiency in feed was relatively insignificant and on average ranged from 2.2% to 11.7%, 22.5%, and 29%. But the greatest manganese deficiency was distinguished by corn stock feed in the first and fourth experimental farms, where it was 35.6% and 29%, respectively. Under certain pH conditions in the soil, manganese can show antagonism to cadmium, lead, cobalt, and iron. Excessive amounts of mobile forms of cadmium and lead in the soil affected a decrease in the absorption of manganese by the root system of plants (Fig. 8).

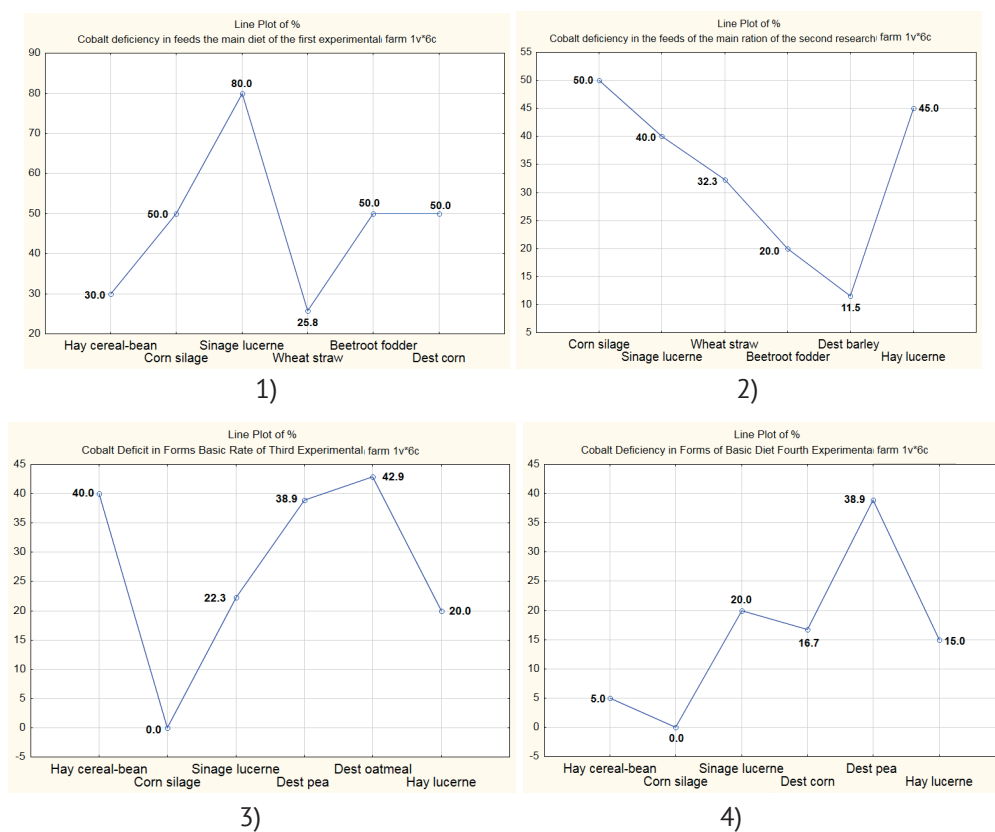


Figure 7. Cobalt deficiency in the diet

1 – first experimental farm; 2 – second experimental farm; 3 – third experimental farm;
4 – fourth experimental farm

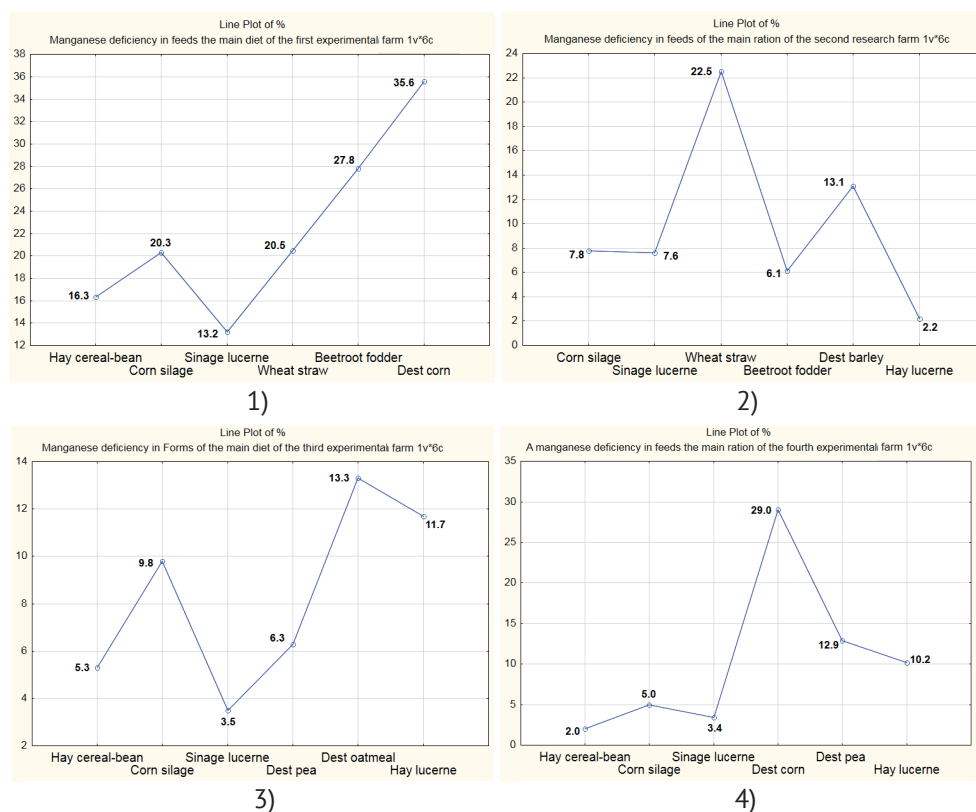


Figure 8. Manganese deficiency in the diet:

1 – first experimental farm; 2 – second experimental farm; 3 – third experimental farm;
4 – fourth experimental farm

Iodine deficiency in feed is caused by the presence of its antagonists in the soil – lead. Moreover, this element is part of the thyroid hormones, in particular, tetraiodothyronine (thyroxine) and triiodothyronine, which regulate the

main types of metabolism in the body, growth and development of the animal. Iodine deficiency in feed from 4% to 60.7% (Fig. 9) leads to a lack of it in the diet, and consequently, in milk. Milk without iodine is not the best raw milk.

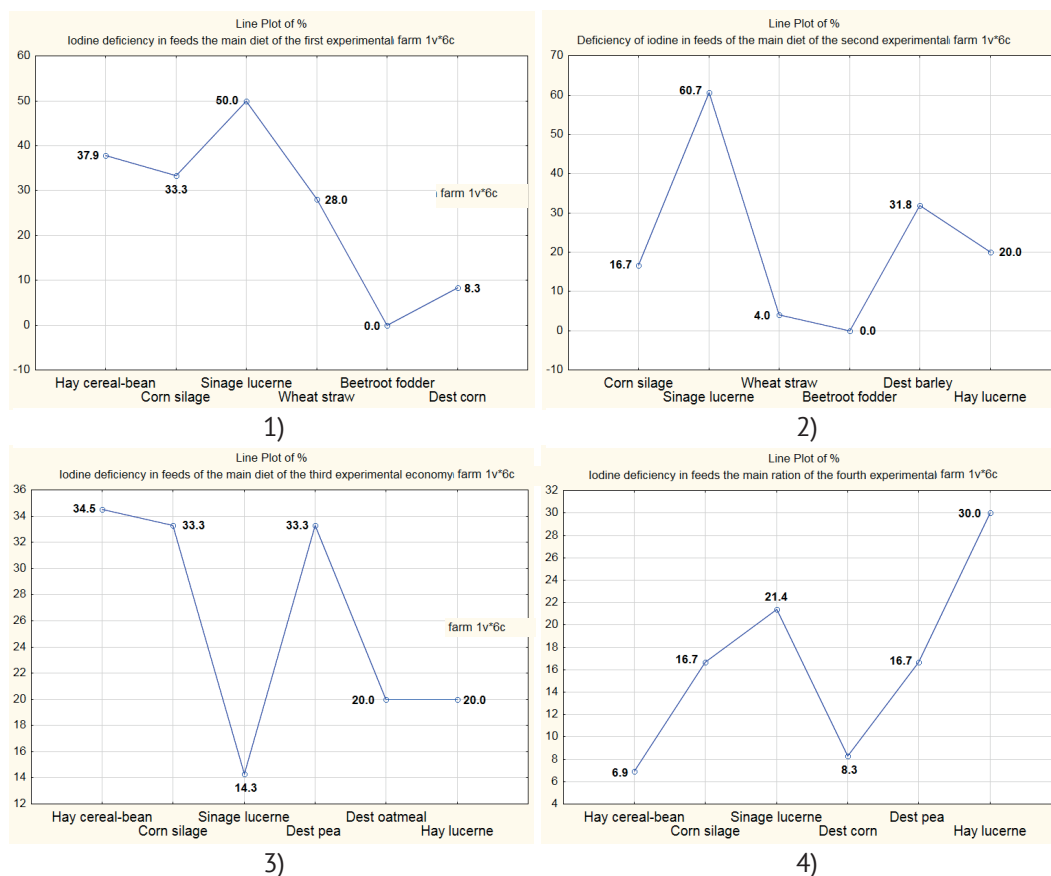


Figure 9. Iodine deficiency in the diet:

1 – first experimental farm; 2 – second experimental farm; 3 – third experimental farm;
4 – fourth experimental farm

The chemical analysis of feed showed not only an excess of heavy metals, but also a low content of essential macro- and microelements in plants – antagonists of cadmium, lead, copper, and zinc (Fig. 1-9). At the same time, there was a significant fluctuation in the content of macro- and microelements both in different feeds and in different experimental farms, which is natural. The problem is that the content of these elements did not correspond to the average nutritional values according to the detailed animal feeding standards. The results of laboratory analysis of feed from all experimental farms showed a characteristic low content of essential macro – and microelements against the background of an excess of dangerous heavy metals, especially cadmium and lead. In such circumstances, rationing and balancing rations becomes more difficult. There is a problem with the production of environmentally safe high-quality milk with the content of heavy metals within the permissible levels provided for by the standards, and with the content of essential elements important for the human body: calcium, phosphorus, potassium, magnesium, sulphur, iron, iodine, cobalt, etc., which bring dairy raw materials into the category of biologically complete and functional products.

Microelements are necessary for the plant in small amounts for normal development, unlike macronutrients (Castro *et al.*, 2018). They are not directly incorporated into the plant structure, but are involved in various enzymatic reactions, for example, as catalysts for chemical reactions in living systems. The concentration of iron in plants is insignificant and its physiological role in plant life is that it is a part of enzymes, participates in the synthesis of chlorophyll and metabolism. It plays an important role in the process of plant respiration, since it is an integral part of respiratory enzymes. Without iron, plant respiration is simply impossible. Since iron can pass from an oxidising form to a nitrous one and vice versa, it is involved in the redox processes that occur in plants. The problem of low iron content in plants may be related to pH problems. Iron is better absorbed at lower pH values of 5.5-6.0, and at higher pH levels, especially above 7.0, it is usually blocked. The introduction of mineral fertilisers into the soil, which reduce the pH, in farms should not have caused a deficiency of the element in plants – obviously, the antagonism between iron and other elements, including heavy metals, affected the iron intake in plants more. Excess copper in the soil can lead to iron deficiency in plants. During this study, there

was a slight excess of copper in the soil and during migration in plants, in particular, in corn, the excess of the norm was 2.3 times. Similarly, iron deficiency can cause problems with calcium and magnesium. Calcium deficiency in plants (feed) of the first experimental farm ranged from 17.6% to 47.5%, the second – from 6.5% to 38.6%, the third – from 3.3% to 12.5%, the fourth – from 1.4% to 36.0%, the situation was similar in terms of magnesium content – 9.3-51.3%, 10.0-47.8%, 5.0-26.0%, and 2.7-64.4%, respectively. No external visible signs of iron deficiency were observed on the plants. Bird droppings can increase the pH of the soil, but on farms, cattle manure is mainly used as organic fertiliser. Excess iron in plants is very rare, and the growth and development of the root system can stop. The leaves can die off and fall off without any visible changes.

Manganese activates more than 35 enzymes and participates in various reactions, including nitrogen metabolism. In this regard, plants that are deficient in the element have difficulty using nitrates as a source of nitrogen nutrition. Manganese is involved in the synthesis of vitamin C, regulates the water regime, increases resistance to adverse factors in the plant. Manganese, like iron, is better absorbed at lower temperatures with a pH of 5.5-6.0. If the pH level is very high in the soil, it can lead to a deficiency of the element in plants (Orynyk, *et al.*, 2020). For all the years of research, the pH of soils in all farms ranged from 6.0 to 6.7. Therefore, the reason for the low content of manganese in plants (feed) is obviously different and most likely conditioned by the excessive amount of mobile forms of manganese antagonist elements in the soil. Excess manganese can lead to interstitial chlorosis, signs similar to those with a significant lack of magnesium, but no visible signs of this were observed. In the plants (feed) under study, the manganese deficiency ranged from 13.2% to 35.6% on the first farm, 2.2-22.5% on the second, 3.5-13.3% on the third, and 2.0-29.0% on the fourth farm, respectively.

Low soil pH, emissions of pollutants, and the use of agrochemicals affected the accumulation of heavy metals copper and zinc in plants (feed), including toxic cadmium and lead. Cadmium can affect the redistribution of calcium in the structural elements of the plant (leaves, stem), which is important for forage harvesting, for example, hay, straw, silage or haylage, and grain feed. Other studies (Morina & Küpper, 2020) found that cadmium mainly accumulates in the veins and limits the distribution of iron and zinc in the plant, and the concentration of potassium increases throughout the leaves. Cadmium did not affect the distribution of calcium, but reduced its content in the leaves. This toxic element disrupted the processes of photosynthesis, in part, it may be the result of a selective violation of the homeostasis of leaf nutrients.

Researchers from China (Zhao *et al.*, 2020) point to the global problem of mineral element deficiency in plants, which can negatively affect human health. Scientists focused on maintaining the proper concentration of mineral elements in the corn grain. In 2017, a field survey of four main areas of China's corn production was

conducted. 980 pairs of soil and grain samples were taken from farm fields, and geospatial fluctuations in the concentration of zinc, iron, manganese, and copper in the grain were also investigated. Zinc and iron concentrations were 18-89% lower. Top dressing of the soil with nitrogen fertilisers increased the concentration of copper and zinc in the grain, and phosphorous fertilisers reduced the content of zinc and iron. A decrease in the pH of the soil and an increase in the content of organic substances, according to researchers, can lead to an increase in the accumulation of iron and manganese in the grain.

Another problem that affects the level of mineral elements in plants can be the pollination. Researchers from Brazil (Porto *et al.*, 2021) note that half of the nutrients in plants and, accordingly, in animal feed and human food depend on pollination. Concentrations of lipids, vitamin B₉, and potassium are higher in pollinated plants. Reducing the number of pollinators can lead to a loss of 7.9-29.5% of nutrients. The researchers investigated the relative differences in nutrient concentrations of 45 major crops grown in Brazil. Of the 45 crops, some were classified as pollinator-dependent; some, on the contrary, were independent. Researchers estimate that reducing the number of pollinators can lead to total nutrient losses of 4% to 18% for all macronutrients, 6.8-26.2% for all minerals, and 2.4-31.5% for all vitamins. Scientists emphasise the importance of maintaining the number of pollinators, ensuring sustainable agricultural development and food security of the country.

Excess of mobile forms of heavy metals in the soil Cd, Pb, Cu, Zn, which are antagonists of essential elements: Ca, P, Mg, K, S, Fe, Co, Mn, I, affects their transformation into forms inaccessible to assimilation by plants, which causes a lack of data on macro- and microelements in them, which was revealed by US during laboratory analysis of fodder.

A lack of essential elements in feed in the amount of more than 50% can lead to a loss not only of milk quality, but also to a decrease in cow productivity and deterioration of animal health (Roche & Satter, 2022). With a low intake of calcium and phosphorus in the animal's body, a disease develops – osteomalacia; a low intake of potassium – allotriophagia; cobalt – pining (anemia-acobaltosis), this element also participates in haematopoiesis, is part of vitamin B₁₂; copper – anemia; sulphur deficiency causes a violation of ether-sulphur compounds formed in the liver as a result of neutralisation of certain toxic substances contained in the blood and urine in the form of inorganic sulphates; magnesium activates many enzymatic systems including those that catalyse synthesis reactions associated with adenosine triphosphoric acid, which is important in intoxication of the body with heavy metals; iron – its most important physiological function is that it is part of haemoglobin and some respiratory enzymes, in the lungs easily combines with oxygen to form oxyhaemoglobin; manganese – takes part in tissue respiration affects the metabolism of carbohydrates when there is a lack in the body slows down the growth of the animal and worsens the skeletal development; iodine – lack of it significantly affects the function of the

thyroid gland, which produces the thyroxine hormone, which includes iodine, and this, in turn, affects the calcium and phosphorus metabolism in the body.

The low content of essential elements and an excess of heavy metals in the studied conditions could have been caused by a violation of the timing and types of mineral fertilisers applied. At all experimental farms, approximately 70-80% of mineral fertilisers are applied to the soil in the spring due to various production and economic reasons, instead of being applied with the main tillage. Nitrogen fertilisers were mainly applied. This creates not only organisational tension in spring field work, but also reduces the effectiveness of fertilisers to a certain extent. Studies (Vyrlyev, 1986) have established that the untimely application of fertilisers and their uneven distribution reduces the efficiency of nitrogen by 35-40%, phosphorus – by 20-25%, potassium – by 15-20%, complex fertilisers – by 30-35%.

Anthropogenic pollution of the natural environment around industrial centres leads to a violation of the cycle of substances, a decrease in the nutritional value of feed, which makes it almost impossible to produce high-quality environmentally safe milk and the raw materials for the production of dairy products, without the use of appropriate science-based technologies for the restoration of the balance of mineral elements both in the animal's body itself and in products. All the studied feeds were included in the main diets with different types of feeding of dairy cows.

CONCLUSIONS

In conditions of local contamination of agroecosystems with heavy metals, especially cadmium and lead, it is unacceptable to balance the main diets of dairy cows without considering the actual nutritional value of feed. The production of environmentally safe, high-quality cow's milk is much more complicated without rationing the content of heavy metals of cadmium, lead, copper, and zinc in the feed that exceeds the permissible level of pollutants and has a deficiency of essential mineral elements, such as calcium, phosphorus, magnesium, potassium, sulphur, and among the trace elements of iron, cobalt, manganese, iodine. The development of special mineral and vitamin premixes or other new feed additives specifically adapted to such diets will reduce the negative impact of toxic trace elements and compensate for the lack of biologically important elements in the body of highly productive animals, which will ensure the production of pollutant-free milk and dairy raw materials with a sufficient content of iodine, cobalt, iron. Such feed additives would help to improve the health of cows and prevent the occurrence of hypocalcemia, hypophosphatemia, and other diseases characteristic of lactating animals.

Further study will be aimed at environmental monitoring of the content of essential and non-essential mineral elements, including heavy metals, in plants (feed) of various farms of the forest-steppe, steppe regions of Ukraine and Donetsk oblast, where dairy cows are kept.

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Дослідження вмісту есенціальних мінеральних елементів у кормах раціонів дійних корів на фоні підвищеної концентрації в рослинах токсичних металів Cd та Pb

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Анотація. Неконтрольоване надходження у довкілля забруднюючих речовин — важких металів, створює перешкоди для виробництва екологічно безпечного, біологічно повноцінного коров'ячого молока. Акумуляція полутантів у ґрунті зменшує надходження в рослини есенціальних мінеральних елементів, необхідних для забезпечення повноцінної годівлі тварин. У таких екологічних ситуаціях важливе значення має аналіз кормів раціонів на вміст есенціальних і неесенціальних мінеральних елементів. У чотирьох дослідних господарствах, які спеціалізуються на виробництві коров'ячого молока, агроєкосистеми розміщені навколо промислового центру і поблизу екологічно несприятливих об'єктів — автошляхи, підприємства з видобутку (переробки) газоконденсату тощо, відібрано зразки кормів, що входили до основного раціону. Методом атомно-адсорбційної спектрофотометрії проведено аналіз їх на вміст мінеральних елементів. Статистична обробка даних — STATISTICA версії 10.0. У кормах встановлено перевищення допустимої норми по кадмію у середньому в 2,1–3,2 рази, свинцю — 2,4–5,7 рази, міді — 1,4–2,3 рази, цинку — 1,2–2,4 рази. У сіні злаково-бобовому концентрація кадмію, свинцю перевищувала норму у 3,2 і 5,7 рази відповідно. На цьому фоні встановлено дефіцит кальцію в кормах раціонів різних типів годівлі корів від 1,4 % до 47,5 %, фосфору — від 1,5 % до 62,3 %, магнію — від 2,7 % до 64,4 %, калію — від 0,8 % до 37,9 %, сірки — від 2,3 % до 48,8 %, серед мікроелементів, заліза — від 2,3 % до 48,8 %, кобальту — від 5,0 % до 80,0 %, йоду — від 4,0 % до 60,7 %. Причина дефіциту в рослинах (кормах) життєво важливих мінеральних елементів носить різний характер, що включає зміни рН ґрунту, але переважно — антагонізм між рухомими формами токсичних елементів та есенціальними елементами. Для виробництва високоякісного молока необхідно здійснювати нормування токсичних металів у раціонах корів з різними типами годівлі, ліквідувати дефіцит мінералів за допомогою спеціально розроблених кормових добавок (мінерально-вітамінних преміксів), що дозволить забезпечити профілактику елементозів корів, які є проблемними в різних країнах світу. Майбутні дослідження спрямовані на моніторинг концентрації мінеральних елементів в кормах тварин, які утримуються в Лісостеповій і Степовій зоні та Донецькому регіоні України

Ключові слова: важкі метали, свинець, мікроелементи, макроелементи, кальцій, фосфор