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Migration of heavy metal mobile forms into the plant vegetative mass under anthropogenic load

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In the conditions of the strengthened technogenic loading on the environment, one of the priority and actual directions is the research of the maintenance of heavy metals in the soil are the plants are grown in separate biogeocenoses.
The research aimed to study the migration of mobile forms of heavy metals (Cadmium, Plumbum, Mercury, and Zinc) in the trophic chain system: soil-plant under local human-made load. Also, to explore the peculiarities of their accumulation in the ground, entry into the vegetative part of plants, and develop measures to prevent the migration.
The experiment was conducted at Zubra LLC. Agricultural lands are directly adjacent to the Mykolayiv Cement and Mining Plant territory, which is a powerful source of emissions of toxic chemical elements, the content of which exceeds the MAL (the maximum allowable level) for all investigated ingredients. In scientific and economic research. We studied heavy metals' migration in the soil-plant (feed) system. Therefore, our research object was soil samples, forage crops, which determined heavy metals' content. In some micro field experiments, soil contamination with heavy metals was modeled, reflecting the range of real loads in the study area. Ameliorants of organic and inorganic nature were applied to the soil contaminated with heavy metals to mitigate pollutants' adverse effects.
A high level of heavy metals was registered in the soils of Zubra LLC surveyed by us. It should be noted that the content of toxic metals in the studied ground samples decreases with increasing distance from the source of human-made pollution, i.e., the migration of heavy metals following the laws of their distribution in the horizontal direction. The study of acid-base conditions (pH) of soils indicates a violation of acid-base balance. Our research shows that the highest level of mobile forms of heavy metals is registered in conditions of low winds, high humidity, and fog. The decrease in the level of mobile forms of heavy metals in the soil is directly related to the vegetative period of plant development, during which heavy metals migrate intensively into the vegetative part of plants. The coefficient of biological absorption of heavy metals by plants often exceeds one. In micro field experiments, ground contamination with Cadmium, Lead, and Zinc ions at concentrations of 2 and 3 MAL were simulated. It is established that antagonistic and synergistic interactions of toxicants largely determine the accumulation of heavy metals in plants' vegetative part.
To mitigate the adverse effects of pollutants, we applied ameliorants of inorganic and organic nature. Among the used ameliorants, the most effective was the zeolite of the Sokyrnytsia deposit. The introduction of which into the soil leads to a significant reduction in plants' accumulation of heavy metals. Under the influence of zeolite, the concentration of Lead and Zinc's mobile forms in the green mass of corn was within.
Promising further research is developing measures for the preliminary transfer of essential metals in the food chain: soil-plant – feed – animal – products – humans, testing, experimental verification of the effectiveness of measures to attract environmentally friendly products produced and grown in local processing facilities.
Keywords: monitoring, trophic chains, soil samples, pollutants, adsorbents, ameliorants of organic and inorganic nature, accumulation coefficient of heavy metals.

Introduction

The current state of agricultural production is in conditions of increasing human-made load. Anthropogenic activity is accompanied by the dispersion of many chemical elements involved in the migration process. A unique role among them belongs to heavy metals, which are highly toxic and can affect living organisms even in small concentrations, which is a valid reason for classifying them as priority pollutants in the industrial and environmental. This problem is quite acute in industrialized regions, where large industrial enterprises are located, numerous vehicles are concentrated. In such areas, biogeochemical provinces are formed with a high content of heavy metals in soil, water, and plants, which reduces the biological value of plant products and leads to heavy metals in the food chain (Martyshuk et al., 2016; Gutyj et al., 2016; 2017; 2019; Rudenko et al., 2019; Vishchur et al., 2019; Boiko et al., 2020).

In the conditions of the strengthened technogenic loading on the environment, one of the priority directions in monitoring heavy metals in a trophic chain: soil – a plant – a forage – an animal – production – the person. The development of scientific and practical foundations of the crop industry in human-made pollution is one of the current agricultural science problems (Slivinska et al., 2019; 2020; Piven et al., 2020; Sobolev et al., 2020).

In this regard, scientific and practical relevance is studying heavy metals in soil and plants are grown in individual biogeocenoses. Such studies' expediency is due to the need to correct the cycle of heavy metals in the environment and reduce environmental stress in certain parts of the food chain to obtain environmentally friendly plant products for the livestock industry and human nutrition.

Environmentally friendly, relatively low, previously considered safe levels of heavy metals in soil, water, feed, and food cause many metabolic disorders that contribute to developing chronic diseases in animals and humans. The influence of environmental factors on animals and humans' health is now one of the current scientific and practical problems (Tanker, 2000). After all, each inhabitant of Ukraine has about 150 kg of toxic substances that pollute the air, almost 100 m^3 of wastewater entering the reservoirs, and 500 tons of accumulated solid waste.

Due to uncontrolled emissions from industrial enterprises, the Chernobyl accident, and other human-made violations, the environmental situation in Ukraine has led to a growing threat to animal and human health. Extensive industrial facilities can pollute the environment for tens of kilometers. This primarily applies to mining complexes and alumina plants. Industrial emissions of the latter, in some cases, can lead to the creation of artificial, local geochemical provinces, which occupy reasonably large areas. They are characterized by a high content of heavy metals in water, soil, plants. According to forecasts and estimates, in the future heavy metals may become more hazardous than nuclear power plant waste and come out on top or share it with pesticides (Andreyuk et al., 2001).

Pollution of heavy metals by the environment has increased by 2.5-3.0 times in recent years, and it is projected to increase (Andreyuk et al., 2001). Anthropogenic pollution has led to the involvement in planetary biogeochemical cycles of a large number of foreign substances. Biogeochemical cycles annually receive $3 \cdot 10^5$ tons of Lead, $2 \cdot 10^3$ tons of Cadmium. As a result of the work of metallurgical enterprises and concentrators alone, at least 154,650 tons of copper fall to the surface of the earth every year; 121500 – Zinc; 765 – Cobalt; 30.5 tons of mercury; with road emissions on the earth's surface gets 260,000 tons of Lead per year; combustion of coal and oil causes the arrival of 1600 tons of mercury on the earth's surface; 3600 – Lead; 2100 – Copper; 7000 – Zinc; 3700 tons of Nickel. Ukraine outperforms the United States and developed European countries in human-made chemical loads.

When migrating in the environment, heavy metals are concentrated in the soil, water, and vegetative part of plants, without noticeable external manifestations that can cause contamination of animals and humans. According to internationally accepted estimates, heavy metals' stress index for biological systems is 60, which means that they are second only to pesticides in ecotoxicity.

Carrying out ecological monitoring provides an opportunity to obtain detailed information on the actual state of natural ecosystems, assess and predict their changes under the influence of anthropogenic pressure. As part of ecological monitoring, the study of accumulation, migration, and distribution of toxic elements, including heavy metals, in biocenoses will assess the negative trends associated with local or regional environmental pollution. Recently, ecologists' attention to the initial links of chemical elements' migration process, such as soil and flora (Fedoruk et al., 2002).

Material and methods

The study was conducted in the production conditions in the fields and the Zubra Peasant Limited Liability Company and homesteads in the villages of Rozvadiv, Ustya, and Drohovyzh, Mykolayiv district, Lviv region, where fodder crops were grown for animal nutrition and human nutrition. Agricultural lands are directly adjacent to the Mykolayiv Cement and Mining Plant territory, which is a powerful source of emissions of toxic chemical elements, the content of which exceeds the MAL for all investigated ingredients, the radius of pollution exceeding the MPC, more than 15 km. The maximum air pollution values by cement and clinker dust range from 1.68 to 3.10 mg/m^3.

The control was the land of Zorya LLC of Kamyansko-Buzka district of Lviv region. This farm belongs to a relatively environmentally friendly area; it is located 45 km from the primary sources of human-made pollution.

In scientific and economic research, we studied the migration of heavy metals in the soil - plant (feed) system to investigate the patterns of accumulation of pollutants by plants and the possibility of preventing their migration through the introduction of agronomic measures. Therefore, our research object was soil samples, forage crops, which determined the content of heavy metals: Cd^{2+}, Pb^{2+}, Hg^{2+}, and Zn^{2+} by atomic absorption spectrophotometry, using the adsorption mode in an air-acetylene flame on a spectrophotometer AAS-30 (Price, 1972).

Average soil samples were taken according to the method (Vishkulov et al., 2002), from the surface of the unploughed layer of soil (0-10 cm) on the tested grid (scale 1: 50000) at a distance between the sampling points mainly 0.5 km, as well as following the requirements for selected samples in case of general and local pollution. As a rule, soil contamination with heavy metals was assessed by their repulsive content. However, the level of metals may not always characterize the degree of safety of soil contamination. The latter can bind metal compounds, making them unsuitable for assimilation by plants.

It is better to determine their mobile forms to characterize polluting metals' migration from the ground to plants objectively. Extraction of mobile forms of Cadmium, Lead, mercury, and Zinc was performed with a 1 M solution of HNO_3 (Methodical guidelines..., 1991). For this purpose, soil samples of 5 g, weighed to the nearest 0.1 g, were placed in a conical flask of 250 cm^3, 50 cm^3 of 1 M HNO_3 (1:10) was added here. The flasks with the samples were shaken on a rotator (1 h), infused (1 day), and filtered through an ashless filter pre-soaked in 1 M HNO_3.

Feed samples were taken following the methodological developments of CINAO (Methodical guidelines..., 1991) and GOST 13.586.3-83. Mineralization of the selected samples was considered complete when the ash was white, without charred particles following GOST 26929-86. The hydrogen index (pH) of the soil was determined by the unified method described in the "Guidelines for agrochemical inspection of agricultural land" and the method of Arinushkin: 10 g of air-dry soil was sieved through a sieve with a diameter of 1 mm, placed in a flask with a capacity of 50-100 ml distilled water. The flask was tightly closed, shaken for 5 min, and then the suspension's pH was determined by the potentiometric method.

In some micro field experiments, soil contamination with heavy metal salts was modeled, which reflected the range of real anthropogenic loads in local zones of technogenic loading. Aerial contamination of plants was simulated by systematic (twice a week) spraying with solutions of a mixture of salts of heavy metals ($CdSO_4$, $PbCl_2$, and $ZnSO_4$) in quantities equal to soil contamination of 1, 2, and 3 MAC, respectively. Simultaneously, at the rate of 1 MAL, the samples were $CdSO_4$ – 5.56 mg/kg, $PbCl_2$ – 26.8 mg/kg, and $ZnSO_4 \times 7H_2O$ 101.12 mg/kg.

The effect of heavy metal ions on seed germination of fodder crops was studied by the generally accepted germination test, germination, and seed growth (Ivasivka, 2001). Petri dishes were filled with 100 g of soil, which was brought to full moisture content. A mixture of heavy metals and ameliorant (white zeolite) was added, covered with a lid, and kept for 45 days at room temperature (approximately 18–20 °C). The aged soil was sown with seeds of different crops (10 seeds from other crops) and incubated for 15 days at a temperature of +23 °C. The obtained sprouts were washed, examined for germination, and performed a comparative measurement of stem and root length.

Ameliorants of organic and inorganic nature were added to the soil contaminated with heavy metals to mitigate pollutants' adverse effects. For this purpose, five experimental plots (0.2 ha each), one control plot, and four experimental plots were allocated to the area where corn was grown for fodder. Ameliorants were added to the experimental plots' soil: white zeolite, bio humus, limestone, and green manures at 20 t/ha; 20 t/ha; 20 t/ha, and 20 t/ha, respectively. To study the optimal dose of natural ameliorant – zeolite, we conducted a similar experiment. The soil's experimental areas by uniform scattering under the fallow plowing made zeolite in the amount of 10; 15; 20; 25, and 30 t/ha.

According to generally accepted variation statistics, the obtained data were processed mathematically (Kokunin, 1975). The probability of differences between the experimental and control groups' indicators was assessed using Student's t-test.

Results and Discussion

The most significant and informative changes due to human-made pollution occur in the composition of soil microbiocenoses. Soil is a necessary component of any ecosystem and habitat for a variety of living things. Heavy metals by active transport penetrate the membranes of microorganisms. Violation of cell membranes' integrity and heterogeneity is the primary way to implement xenobiotics' toxic effects. Selective permeability for various substances is one of the essential functions of biological membranes, ensuring compartmentalization and integrity of metabolic processes in the cell and under the influence of heavy metals, the stability of biomembranes changes, negatively affecting the distribution of crucial metabolites at the tissue, cellular, and other levels (Osipov et al., 2001).

In small concentrations, metals as trace elements are necessary for the normal functioning of soil biota. In high concentrations, heavy metals adversely affect the structure and function of natural ecosystems, which leads to the formation of local biogeochemical provinces of anthropogenic origin. Man-caused impact on the soil changes the soil biocenosis, which supports soil fertility and leads to the degradation of the entire natural complex, disrupting the biological mechanisms of ecosystem self-renewal. Under the influence of heavy metals, there is a disturbance in microorganisms' systems – plants, their physiological activity is suppressed, and many enzymatic transformations are inhibited (Skopetska, 2001).

Soil microorganisms can adapt to the increased content of heavy metals. Under selective pressure from heavy metals, stable strains of bacteria are formed that can grow under conditions of increased pollution. The presence of virulent antigens is directly related to the ecological state of the environment. Numerous scientific data have shown various adverse effects (acute, chronic, and remote) that occur due to the spread of anthropogenic pollutants in soil, terrestrial, and aquatic ecosystems. This leads to the development of the problem of the impact of harmful chemicals in the environment on living organisms and their populations.

Due to the decrease in the diversity and number of microorganisms in the local areas of human-made pollution, the destruction of organic matter and the cycle of nutrients decreases. It should be noted that heavy metals are one of the most dangerous factors of environmental pollution. Once in the soil, they accumulate in it in large quantities. There are violations of mineralization processes under such conditions by reducing soil self-cleaning physiological activity (Samokhvalova et al., 2001).

Different concentrations of heavy metals in food and feed in some regions are closely linked to sanitation and environmental conditions. In some industrialized areas, soils can become entirely unsuitable for agricultural production or require detoxification measures due to their excessive content of heavy metals. With their buffering ability to bind excess harmful ingredients, soils smooth out the adverse effects of toxicants. However, different chemicals bind soils to different intensities. Thus, peat soils form the following series in terms of binding power: Cu> Mn> Zn> Cd> Sr. Most toxic metals are concentrated in the topsoil.

It was found that 57-74% of Lead and Mercury under anthropogenic pollution conditions are fixed in a layer of 0-10 cm, and only 3-8% migrate to a depth of 30-40 cm. Nitrification processes are best carried out in soils with pH-7. The increased amount of metals in the soil inhibits the growth and development of microorganisms, which leads to a slowdown in the processes of humification, nitrification, and nitrogen fixation. This, in turn, slows down the formation of humus in the soil, which undoubtedly harms plant growth and development. Heavy metals contribute to soil acidification, with Calcium and magnesium leaching from the ground and their replacement by toxic metals (Kravtsiv & Butsyak, 2002).

Cadmium salts inhibit the nitrification process by 75%, Zinc – 30%, and Lead – 14%. On soils with high organic content, the risk of accumulation of excess heavy metals in plants is less than on low-yielding and soils where mineral fertilizers are used, which, firstly, acidify the soil, promoting better splitting and migration of heavy metals, and secondly, together with mineral fertilizers are applied a significant amount of heavy metals. Comparing the gross metal content of mineral fertilizers showed that potentially dangerous fertilizers are: Phosphate in terms of Pb; Phosphate and Potassium – Cd and Ni; organic and Phosphate – Cu. From contaminated soils, heavy metals are transferred to plants, animals, and food. Under the influence of anthropogenic pollution, several toxic metals accumulate in the ground at the same time. Emissions of Lead, Mercury, Cadmium, Strontium, oxides of Nitrogen, and Sulfur are some of the environmental factors that have a dominant impact on farm animal veterinary health indicators and productivity, and quality of products (Korshun, 2002). Many of these compounds with atmospheric moisture form acids, which, together with rain, fall on plants, soils, and water.

Toxic elements can be stored in the soil for years, and with their additional annual input and accumulation, the risk of transformation of chemical ingredients in other environmental objects increases. Unlike organic compounds, heavy metals are not destroyed in soil and water but accumulate and migrate in trophic chains to animals and humans, posing a real threat to their health. Soil's current state needs close attention, as they are contaminated with chemical plant protection products, fertilizer residues, and human-made waste – heavy metals. The danger lies in soil's ability to accumulate anthropogenic pollution to a greater extent than the atmosphere or hydrosphere.

According to the land fund structure, 2/3 of the territory of Ukraine is occupied by agricultural lands, but their ecological condition is of concern. They are subject to significant anthropogenic impact, the undesirable consequence of soil fertility loss. Soils in Ukraine are well studied, but this has not prevented the intensive development of degradation processes. The latter's main reasons are underestimating the real threat, which is the degradation of soils for current and future generations. To assess the level of danger of soil contamination with heavy metals, it is necessary to conduct sanitary and hygienic, and soil and ecological examinations. A simple comparison with the existing maximum allowable concentrations (MACs) does not provide the required information for a realistic assessment of the degree of danger and consequences of pollution, rational land use, and justification of detoxification measures.

In Western Europe, the MAC developed by A. Kloke became widespread. In recent years, German authors had proven the need to clarify the maximum concentration limit for A. Kloke both upwards and downwards depending on specific soil conditions. Thus, even in Germany, with its relatively small variety of soils, a differential approach to the maximum allowable concentration of the same metal is recommended depending on the soil environment, which primarily considers the amount of humus and fine minerals, as well as soil reactions. The flexibility of foreign approaches to the rationing of heavy metals is manifested in the fact that for low-buffer soils, in which the humus content is insignificant, it is recommended, on the contrary, to reduce the norms of MAC.

The maximum permissible level (MAL) of heavy metals in the soil is considered the full amount (expressed in mg per 1 kg of dry soil), which guarantees the absence of adverse direct or indirect effects on animal and human health sanitary living conditions. Assessment of the safety of harmful substances must be carried out without exceeding the limits of the organism's adaptive capacity and the soil self-cleaning ability, i.e., the threshold of safe action. Under the point of safe chemicals, chemicals are understood as their number, which does not cause destructive body changes. Still, the excess leads to negative functional and biological consequences (Korshun, 2002).

One of the dangerous manifestations of heavy metal's negative impact on soil biota is its ability to influence the cell's mutational processes. The genetic danger of contamination is due to the action of heavy metals and the products of their transformation. Therefore, in environmental monitoring to assess soil conditions, it is necessary to determine their mutagenic background and toxicity level.

It is impossible to overestimate the importance of soil for the proper functioning of the agroecosystem. This object study is critical because it is the initial link in the natural food chain, which receives chemical compounds, including heavy metals, animals, and humans (Kravtsiv & Butsyak, 2002). Transformation of various forms of toxic elements is due primarily to soil properties: the number and shapes of organic compounds, the ability to form with heavy metal cations different degrees of mobility and solubility of compounds, adsorption processes on the surface of the solid phase, soil type and condition, and biological features plants.

The mobility of heavy metals in the soil is significantly affected by acid-base conditions (pH). Neutral and alkaline conditions limit the mobility of heavy metals in the ground, as most of them bind and precipitate carbonates, while in acidic soils, on the other hand, toxic elements actively migrate. Studies of soils contaminated with Cadmium, Lead, Mercury, and Zinc have shown that with increasing pH, the content of mobile forms of toxicants decreases. Simultaneously, the availability of metals for plants declines (Eskov et al., 2001).

Thus, there are mechanisms of accumulation of metals in the soil, binding in passive, and inaccessible to living organisms forms. There are also opposite mechanisms for the transition of bound states into moving ones. For example, soil pH changes from alkaline to acidic increase the mobile forms of heavy metals, more accessible to plants. The total (gross) content of heavy metals in the soil reflects the total amount of metal in all its forms.

There is a positive correlation between the gross content of metals and their mobile forms. Yu. Mazhaisky and co-authors believe that for the depreciation of the availability of heavy metal ions, it is necessary to maintain the pH in the soil to about 6.5. M. Ovcharenko and co-authors note that liming of acid soils to pH - 6.5–6.8 reduces the flow of heavy metals (Cadmium,

Lead, and Zinc) in plants by 5-8 times. Only in carbonate soils with a high content of humic acids, increasing the pH can contribute to the leaching of Cadmium. In acidic humus soils (especially forest litter), even acid rain cannot wash it away because humic acids (and their complexes with Cadmium) are insoluble in an acidic environment (Eskov et al., 2001).
A significant part of soil pollutants accumulates in the upper humus-containing layer. In the soil, heavy metals undergo various reactions: redox, complexing, cleavage. Due to these processes, heavy metals in the soil are bound or converted into an exchangeable (mobile, water-soluble) form. All this affects the level of their toxicity to soil organisms and plants (Vishkulov et al., 2002). Moving through the food chains, some substances dissipate; others migrate in the food chains. Therefore, a relatively small concentration of these substances in the soil can be dangerous to animals and humans.
In the local areas adjacent to the robust processing plants and plants, a potential source of chemical compounds' emissions into the environment, a human-made press on the area's ecosystem. Excessive amounts of heavy metals negatively affect ecosystems structure and functions, changing the soil biocenosis, supporting soil fertility. Anthropogenic impact on the soil leads to the degradation of the biocenosis natural complex critical biological processes. It disrupts the ecosystem self-restoration, which creates a precondition for significant migration of heavy metal ions by trophic chains.
A high level of heavy metals was registered in the soils of Zubra LLC surveyed by us and in the homesteads of the settlements of Rozvadiv, Ustya, and Drohovyzh of Mykolaiv district, the lands of which directly border the mining and cement plant. The concentration of the studied mobile forms of heavy metals (Zinc, Lead, Cadmium, and mercury) significantly exceeded the maximum allowable concentration (MAC) (Table 1).

Table 1. The content of heavy metals in the studied soils depending on the distance of the source of contamination (mg/kg of dry soil, M±m, n=6)

Distance to the source of pollution	Zn	Pb	Cd	Hg
Up to 2 km	45.67±1.76	17.18±1.99	0.66±0.08	5.91±0.62
Up to 4 km	31.22±2.04	15.70±1.31	0.66±0.11	6.23±0.40
Up to 6 km	35.34±2.55	13.40±0.94	0.58±0.02	5.77±0.58
Up to 8 km	29.84±1.54	13.6±1.35	0.42±0,02	4.55±0.36
Up to 10 km	25.04±1.22	8.75±1.23	0.31±0.05	3.31±0.38
MAC *	23.0	6.0	0.1	2.1

MAC - according to J. Berdi, V. Jegerey, A. Kidasyuk and others (1999).

It should be noted that the content of toxic metals in the studied soil samples decreases with increasing distance from the source of human-made pollution, i.e., the migration of heavy metals following the laws of their distribution in the horizontal direction. Among the technogenic geochemical processes in our research area, the acidification of soils and the associated accumulation of mobile forms of heavy metals are of negative importance. The acidity of the studied soil extracts (Table 2) increases in the distance from the human-made load source. With increasing soil pH, mobile forms of heavy metals decrease sharply (Kravtsiv et al., 2005). Raising the pH mainly promotes heavy metals' fixation, preventing their entry into groundwater and assimilation by plants.

Table 2. The average pH value of the studied soils depending on the distance to the Nikolaev Mining and Cement Plant

Distance to the source of pollution	Up to 2 km	Up to 4 km	Up to 6 km	Up to 8 km	Up to 10 km
pH of the soil extract	5.78±0.1	5.82±0.1	6.02±0.08	5.96±0.06	6.12±0.1

The study of acid-base conditions (pH) of soils indicates a violation of acid-base balance. As the acidity increases, the mobile forms of heavy metal ions available to plants increase. Accordingly, their migration to the vegetative part of fodder crops used for feeding farm animals increases. Under such conditions of contamination, when the studied ingredients' content exceeds the MAC, there is a violation of mineralization processes by reducing soil self-cleaning's physiological activity.
The peculiarity of the region's soils is their loaminess; it also contributes to the accumulation of toxic chemical elements, which creates a precondition for significant migration of heavy metal ions by trophic chains (soil – plant – animal – animal products – man). All this contributes to a substantial increase in mobile forms of heavy metals in the soil, their accumulation by plants, and migration through the trophic chain.
The concentration of Zinc in all soil samples exceeded the MAC; the maximum concentration was recorded in the soils of the 2-kilometer zone, which exceeded the MAC by 1.98 times. The fluctuations of mobile forms of Lead in the experimental grounds were in the range of 8.75–17.8 mg/kg, which were 1.45 and 2.96 times higher than the MAC. Characteristically, with increasing distance from the source of pollution, its level decreases. The content of mobile forms of Cadmium in the experimental soils exceeds the MAC by 3–6 times. Simultaneously, a significant accumulation of this toxic element is observed in all experimental soil samples (Fig. 1).

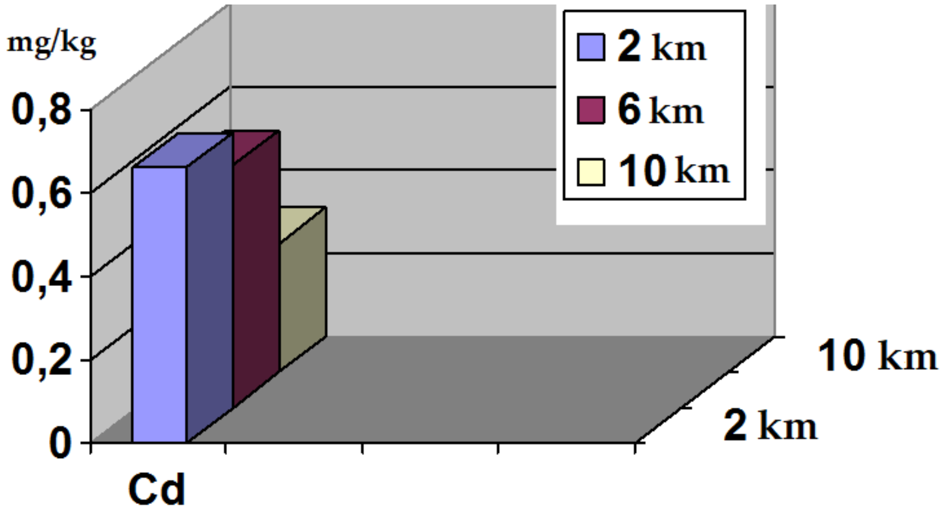

Fig. 1. The level of Cadmium in the soil depending on the distance to the mining and cement plant.

Mobile forms of mercury in all soils were higher than the MAC, although, with increasing distance from the source of pollution, its content decreases from 5.91 to 3.31 mg/kg. Given that the level of mobile forms of heavy metals (Pb^{2+}, Cd^{2+}, Hg^{2+}, Zn^{2+}) decreases in the horizontal direction from the source of human-made pollution, we can assume that under the influence of the Nikolaev Mining and Cement Plant formed a biogeochemical province with high heavy metals. Elevated levels of heavy metals in the soils of the local area of anthropogenic pollution indicate an unfavorable environmental situation, negatively affecting the soil biota, plants, and human and farm health. These data, which characterize the background content of certain toxic elements in the soil, show that the average concentrations of heavy metals (Cadmium, Lead, Mercury, and Zinc) are higher than the MAC and range from Cd – 0.31–0.66, Pb – 8.75–17.18, Hg – 3.31–5.91 and Zn – 25.04–45.67.
Our research shows that the highest level of mobile forms of heavy metals is registered in conditions of low winds, high humidity, and fog. As the wind increases and the humidity decreases, the content of pollutants decreases significantly. In the cold season, the degree of pollution is higher than in the warm. In samples of snow and water, which were studied in early spring, there was an increase in heavy metals' salts (Cadmium, Lead, Mercury, and Zinc). This confirms the assumptions about the patterns associated with winter inversion, increased humidity, increased rainfall, and lower temperatures, which leads to accelerated condensation of aerosol particles of toxic metals. The highest concentrations of toxic metals in the soil samples were in winter, and the lowest – in summer (Table 3).

Table 3. Seasonal dynamics of heavy metals content in the studied soils (μ/kg of dry soil, M ± m, n = 6)

Month	Zinc	Lead	Cadmium	Mercury
April	57,08±4,12	15,94±0,78	0,62±0,03	5,09±0,05
July	46,42±3,38	14,23±1,57	0,47±0,03	4,26±0,02
October	50,20±2,3	16,41±0,67	0,63±0,04	4,98±0,07
January	61,10±1,76	19,34±1,08	0,70±0,01	5,76±0,05
MAC *	23,0	6,0	0,1	2,1

*- according to J. Berdiy, V. Dzhegerey, A. Kidasyuk, and others. (1999).

In spring and autumn, the concentrations of mobile forms of Lead, Cadmium, and Mercury were close, but their levels are higher than the maximum allowable. If the concentration of the studied heavy metals in winter is taken as 100%, then their content in autumn, summer and spring, respectively, will be zinc: 82.0; 75.9; 43.4%; for lead: 84.8; 73.5; 82.3%; for cadmium: 90.0; 67.1; 88.5% and for mercury: 86.4; 73.9; 88.3%.
It was contaminated by agricultural plants, based on the feed component of heavy metals, mainly through the soil. Accumulation of essential metals in the vegetative part of fodder crops without noticeable external manifestations of suppression can cause contamination of livestock products. The increased amount of essential metals in plants leads to the transformation of the physiological tolerance level, which causes destructive changes in plant growth.
In recent years, there have been reports of some plants accumulating heavy metals in the air, with the degree of accumulation depending on air pollution. Lower and higher plants can be successfully used as indicators of environmental pollution. There is a direct correlation between zinc and lead levels in the environment and their accumulation in plant leaves. Heavy metals are released through plants' green parts as part of volatile compounds captured by the wind or washed away by rain. An area of 1 m^2 of vegetation during the year can emit up to 5 g of Lead.
The main organ of the accumulation of heavy metals in plants is the roots. High concentrations of Lead in the soil prevent the entry of vital elements (phosphorus and potassium) into various plant organs. It should be noted that the properties of K^+ ions to maintain the most favorable for the functioning of the cytoplasm physicochemical properties (elasticity, viscosity, dispersion, hydration) is essential for the formation of plant resistance to adverse environmental conditions (Stepanok, 2000). Trace elements, including heavy metals, are present in background amounts in all objects of the environment.

The decrease in the level of mobile forms of heavy metals in the soil is directly related to the vegetative period of plant development, during which heavy metals migrate intensively into the vegetative part of plants. The study of heavy metals' migration in the soil-plant system depending on the year's season is given in table. 4.

Table 4. Accumulation of heavy metals by the vegetative part of plants depending on the season of the year (mg/kg,M±m, n=6)

Components of the diet of animals	Month	Pb	Cd	Hg
Hay	April	-	-	-
	July	5.65±0.31	0.50±0.03	0.14±0.01
Straw	April	-	-	-
	July	6.46±0.30	0.52±0.03	0.24±0.01
Corn	April	4.47±0.27	0.29±0.01	0.09±0.01
	July	12.9±0.91	0.59±0.03	0.25±0.01
Green alfalfa mass	April	3.40±0.27	0.26±0.01	0.09±0.009
	July	3.59±0.03	0.30±0.02	0.11±0.02
Green pasture mass	April	3.41±0.09	0.25±0.01	0.1±0.008
	July	5.16±0.18	0.53±0.03	0.21±0.02
Sugar beet tops	April	-	-	-
	July	14.1±0.92	0.74±0.09	0.46±0.03
Green clover mass	April	4.96±0.02	0.81±0.01	0.15±0.01
	July	5.81±0.20	0.89±0.01	0.14±0.008
MAC		5.0	0.3	0.1

MAC – according to G. Talanov, B. Khmelevsky, 1991

It is established that contaminated soils with heavy metals in concentrations above the MAC cause a significant accumulation of the latter in plants' biomass. Feed crops belonging to different species and families are characterized by different tolerance to the increased level of mobile forms of heavy metals in the soil. They have the ability to absorb or be resistant to pollutants selectively. Tolerances are concentrations that exceed their average level in the system but do not lead to plant death. Due to plants' specific characteristics, there is a different sensitivity of the latter to chemical agents' action.

The green mass of clover and sugar beet buds accumulates the most Cadmium; corn – Lead; cereals – Zinc; wheat straw and sugar beet stalks – Mercury. Accumulated heavy metals cause toxic effects in both the plants themselves and the animals that consume them. There is a natural increase in the accumulation of heavy metals in plants' vegetative part in summer compared to spring, primarily due to the marketing season's duration.

The accumulation of toxic metals by corn stalks in summer exceeded the accumulation of Lead, Cadmium, Mercury, and Zinc by 2.8, respectively; 2.0; 2.7, and 1.4 times compared to spring, which is probably due to the intensive growth of vegetation (this area is quite green), because of actively accumulates heavy metals not only from the soil, but can also fix them directly from the air. The intensification of production in this region is an influential factor influencing the current biological cycle of chemical elements that exhibit aggressive properties, circulating in the environment among animals and humans.

At present, special attention should be paid to the plant world as a biogeochemical barrier that concentrates air and soil migrants, including heavy metals, facilitating their migration in the trophic parts of the ecosystem. This issue is especially acute in local areas of anthropogenic pollution, located near powerful enterprises of metallurgical, machine-building, coal, and chemical industries, near major highways, in agricultural fields with intensive use of mineral fertilizers, and more. High, unbalanced doses of mineral fertilizers lead to significant soil contamination. Besides, in the studied mass of alfalfa of the first and third slopes, there is also a slight increase in heavy metals in summer, namely the concentration of the studied heavy metal ions (Cadmium, Lead, Mercury, and Zinc) was higher by 5.5, respectively; 15.3; 22.2 and 17.4%. Studies of the green mass of clover on the first and third slopes showed that Lead and Cadmium accumulation in summer (July) was slightly higher – 3.0 and 9.8%, and mercury and Zinc contrary, lower by 7.1 and 1.1%.

In the conditions of our experimental research, the toxic substances accumulated in the root system of agricultural fodder crops migrate more intensively to the vegetative part of plants in the summer than in spring. The green mass of clover in the spring in terms of Lead was within the MAL, and in terms of Cadmium, Mercury, Zinc and Lead (in summer) exceeded 2.7–2.9; 1.4–1.5; 1.3–1.4 and 1.1 times. Coarse fodder (hay and straw) and sugar beet tops for all studied toxic metals exceeded the maximum allowable levels.

The concentration of heavy metals in the green mass of pasture at the beginning of grazing (April) was within the MAC, but the zinc content was higher by 23.7%. In mid-summer (July), all investigated heavy metals exceeded the MAC. This may be due to the longer growing season, the additional influx of heavy metals with precipitation and air, and the increase in their number due to the excrement of animals grazing on pastures. Coefficients of accumulation of heavy metals by the vegetative part of plants under local anthropogenic load conditions are given in table 5. The coefficient of biological absorption of heavy metals by plants and, in particular, by agricultural fodder crops often exceeds one. It is known that some plants can accumulate heavy metals even in higher concentrations than their content in the soil. The accumulation of heavy metals by plants depends on the concentration of metals, pH, range of organic matter in the ground, the type and age of plants, the concentration of antagonist metals, and other factors. Thus, the coefficient of biological absorption of Lead (the concentration of which in the soil is 14.23

mg/kg in July, Table 5), was highest in the beet sugar beet (0.98) and samples of green mass of corn for silage (0.90). In roughage, it was 0.45 and 0.39, respectively.

Table 5. Coefficient of accumulation of heavy metals by plants and fodder used in animal feed

Object of study	Metals			
	Cadmium	Lead	Mercury	Zinc
Hay	1.06	0.39	0.33	1.51
Straw	1.01	0.45	0.36	1.55
Silage corn	1.25	0.90	0.45	1.12
Alfalfa grass	0.63	0.25	0.13	1.30
Grass pastures	1.89	0.36	0.23	1.48
Clover grass	1.12	0.35	0.43	1.81
Sugar beet topsoil	1.57	0.98	0.50	1.13

As for the green masses of alfalfa, clover, and pasture, their accumulation was lower. Cadmium in all studied feed samples, except for alfalfa's green mass, was accumulated with a coefficient of accumulation greater than one. The coefficient of Zinc accumulation in all studied plants exceeded one. The zinc content in legumes (green mass of alfalfa and clover) was on average 13.4–17.9% lower than in cereals, which may be due to the significant content of phytic compounds in legumes which can inhibit zinc absorption.
The soils of the studied local zone of anthropogenic load in terms of concentrations of mobile forms of Lead, Cadmium, mercury, and Zinc significantly exceed the MPC. Still, the intensity of the accumulation of toxic metals in feed crops is different (Fig. 2).

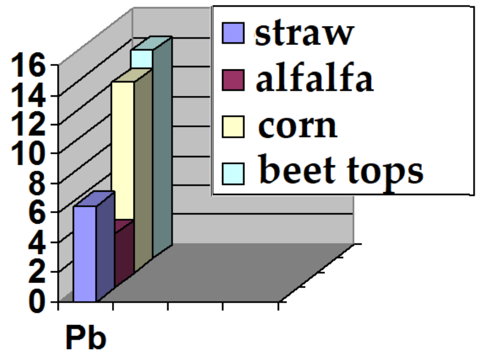

Fig. 2. Tolerance of forage crops to elevated levels of lead ions in the soil, mg/kg

Among all the studied crops (Table 6), the green mass of alfalfa and cereals for green fodder accumulates the least toxic metals. They are the most resistant to the accumulation of heavy metals in the vegetative part. Therefore, in this farm, in the structure of sown areas, more attention should be paid to these crops, which under human-made load show the least tolerance to heavy metals.

Table 6. The concentration of heavy metals in feed samples (mg/kg of natural feed, M±m, n=5)

Indexes	Zn	Pb	Cd	Hg
1. Hay	67.2±5.31	5.10±0.18	0.44±0.05	0.14±0.03
2. Wheat straw	69.48±5.9	6.03±0.20	0.52±0.06	0.26±0.02
3. Green mass of corn	51.36±3.9	12.06±2.78	0.51±0.04	0.22±0.03
4. Green alfalfa mass	59.34±3.7	3.29±0.05	0.28±0.02	0.11±0.02
5. Green mass of cereals	76.42±4.7	3.34±0.28	0.31±0.02	0.10±0.01
6. Green table clover	68.3±2.62	4.82±0.05	0.80±0.04	0.16±0.02
7. Sugar beet tops	52.90±2.9	14.06±3.00	0.74±0.09	0.46±0.03
8. Silage	56.0±2.37	9.28±1.20	0.40±0.02	0.16±0.02
9. Compound feed	63.4±2.88	3.82±0.29	0.30±0.02	0.19±0.03
10. MAC	50.0	5.0	0.3	0.1

MAC - according to G. Talanov, B. Khmelevsky, 1991

Toxic manifestations in animals accompany excessive intake of heavy metal ions in the body. Under such conditions, human-made pollution causes negative pressure on the agroecosystem, has a direct and long-term effect on animals and humans. Toxic substances often cause diseases that lead to changes in the functional state of organs and systems, their physiological and biochemical status, directly related to quantitative and qualitative indicators of farm animals' productivity.
Monitoring heavy metals in the conditions of man-caused pollution of the atmosphere plays the role of primary identifying indicators of agricultural products' quality. Under certain soil conditions (low pH, low cationic absorption capacity, soft organic

matter, and phosphate content), heavy metals that are inaccessible to plants can enter them in significant quantities. Green mass as the main feed in summer is one of the main links in the natural food chain: water – soil-plant – feed – animal – animal products – man and under certain conditions can and does affect the clinical condition of animals and, consequently, the quality of livestock products and human health.

Heavy metal contamination of plants is directly related to soil and climatic conditions and factors that determine the area's nature. In the conditions of technogenic pollution of the environment, heavy metals in the harvest of agricultural fodder crops play one of the leading indicators of product quality. Besides, contamination of the body with heavy metals by 75–87% is due to plant origin feed.

Most industrial emissions are a mixture of toxic substances that simultaneously accumulate in the soil and act independently of each other (additive action) and enter into different interactions, affecting the degree of accumulation and toxicity of individual elements (Kravtsiv et al., 2007). The real threat of their simultaneous loading on a biological object makes the study of their joint action especially relevant. The latter, according to the analysis of the scientific literature, the latter is a complex process that depends on many factors: routes of entry into the body, doses and their ratios, toxicokinetics of substances that are part of the mixture, the interaction of metals, their effects on metabolic processes. In this case, depending on the combinations' qualitative composition, the dose level is observed as the summation of the impact and their antagonism or potentiation (Butsyak, 2002).

In general, the mechanism of the combined action of pollutants has not been definitively disclosed to date. However, the principal, most universal provisions based on ideas about xenobiotic metabolism pathways have been definitively defined. The difficulty of predicting the nature of the combined action in each case, especially in complex multi-component combinations at the threshold and subthreshold doses, is due to many reasons, including the peculiarity of exogenous biotransformation chemicals by plants.

Under such conditions, it is vital to study the features, mechanisms, and patterns of combined action of common toxicants, contaminants of agricultural land – risk factors for many environmentally dependent multifactorial diseases. Depending on the available causes, the combined action manifests itself in the form of antagonism, heteroadditivity, potentiation, sensitization, desensitization, and independent action (Butsyak, 2002). The problem of the combined effort of toxic agents of different nature and modification with other environmental factors remains the ever-increasing human-made pressure on animals and humans and the environment as a whole.

Experimental data conducted in micro field experiments, which simulated soil contamination with Lead, Cadmium, and Zinc salts in the ratios 1, 2, and 3 MAC (Butsyak, 2002), showed that heavy metals' interaction is mainly synergistic. As a result, the vegetative part of corn, which was grown for silage, received more toxic elements. Pb^{2+} ions increase the accumulation of mobile forms of Cadmium in the vegetative part of corn, and Zn^{2+} ions, on the contrary, inhibit it. There is a synergistic interaction between Zn^{2+} ions in lower organisms – an essential nutrient and Cd^{2+} ions, which is due to the similarity of their chemical properties. Cadmium can be considered a chemical analog of Zinc, and, probably, it can replace zinc ions in molecules of various enzymes, which leads to enzymatic imbalance. For example, it reduces Copper-Zinc-dependent superoxide dismutase activity, leading to spontaneous dismutation of the superoxide anion with the formation of hydrogen peroxide and singlet oxygen.

There is an opinion about the biological competition of cadmium ions with Zinc, which determines the nature of many changes in the body and Zinc's protective effect in Cadmium intoxication. The antagonism of Zn – Cd has been studied in many living organisms. This interaction can be explained by the competition of these elements for the same link. The reduction of the accumulation of mobile forms of Cadmium is also observed under the influence of the use of a combination of three heavy metals (Pb_2^{+}, Cd^{2+} and Zn^{2+}). This interaction is accompanied by the antagonism between Zn^{2+} ions and Cd^{2+} + Pb^{2+} ions, manifested in a decrease in the accumulation of cadmium ions in the green mass corn by 11.2%. In our studies, Zinc and Cadmium's action reduces synergistic and increased antagonistic effects.

Application of heavy metal salts (Cd, Pb, Zn, Cu) in the soil in various combinations inhibit the growth of roots and stems of sprouts in the range of 28.4 – 52.6%. In all studied samples, the most pronounced inhibition of winter wheat seed germination was observed in experimentally contaminated soils with Cd^{2+} + Pb^{2+} and Cd^{2+} ions at pH 5.0 (44.2 – 52.6%) in the concentration of heavy 3 MAC salts (Table 7). Increasing the acid-base soil conditions (pH) from 5.0 to 7.0 significantly reduces the toxic effects of heavy metal salts on sprouts' growth activity, which ranged from 28.4 to 32.7% and was 15.8 to 22.1% higher compared to the samples of the studied soil at pH 5.0. Thus, the mobility of heavy metals in the soil is significantly affected by acid-base conditions (pH). Neutral soils limit the mobility of heavy metals, as most of them bind, and in acidic soils, on the other hand, toxic elements actively migrate.

Table 7. Inhibition of growth activity of wheat seedlings depending on the combined effect of heavy metal salts and pH (%)

pH	A mixture of heavy metal salts: $CdCl_2$; $(CH_3COO)_2Pb$; $ZnSO_4$ x $7H_2O$; $CuCl_2$ in terms of metal cations 1,17, 3,14, 425, and 5,30 mg, respectively, at a concentration of 3 MAC				
	Cd	Cd+Pb	Cd+Pb+Zn	Cd+Pb+Cu	Cd+Pb+Zn+Cu
5.0	49.2	52.6	48.1	48.9	44.2
6.0	42.4	48.6	42.2	38.1	36.4
7.0	30.5	32.7	29.2	30.2	28.4

Under such conditions, the mineralization processes are disrupted by reducing soil self-cleaning physiological activity and their buffering ability to bind pollutants. All this creates the preconditions for a significant accumulation of mobile forms of heavy

metals in the soil, their accumulation by plants, and migration by trophic chains. Expansion of mobile forms of heavy metals is due primarily to soil properties: the number and forms of organic compounds, the ability to form with metal cations different degrees of mobility and solubility of compounds, adsorption processes on the solid surface, and biotic features of plants.
Micro field experiments simulated soil contamination with Cadmium, Lead, and Zinc ions at concentrations of 2 and 3 MAC (reflecting the total human-made load in biogeochemical provinces), and simulated contamination by systematic (twice a week) spraying of the metal ($CdSO_4$, $PbCl_2$, and $ZnSO_4$) (Table 8).

Table 8. Accumulation of Cadmium by the vegetative part of corn depending on the combined action of metals (mg/kg, M ± m, n = 5)

Elements	2MAL	Accumulation coefficient	3MAL	Accumulation coefficient
Cd	0.47±0.03	0.78	0.73±0.04	0.81
Cd+Pb	0.54±0.03	0.90	0.83±0.06	0.92
Cd+Zn	0.37±0.02	0.61	0.59±0.02	0.66
Cd+Pb+Zn	0.48±0.04	0.80	0.74±0.04	0.82

It is established that antagonistic and synergistic interactions of toxicants largely determine the accumulation of heavy metals in plants' vegetative part. Studies of Cadmium's background content in experimentally contaminated soil showed that the largest amount of this toxicant was found in experimental samples of green mass of corn grown on soils contaminated with ions of Cd^{2+} and Pb^{2+}. The concentration of Cadmium's mobile forms was equal to 0.54 mg/kg with a transformation coefficient of 0.90 (2 MAC) and – 0.83 mg/kg with a transformation coefficient of 0.92 (3 MAC). Under the influence of lead ions, Cadmium concentration in the vegetative part increased by 14.8% (2 MAC) and 13.6% (3 MAC). This interaction of heavy metals is mainly synergistic.
In our studies, Zinc and Cadmium's collective action's combined action leads to decreased synergistic and increased antagonistic effects. In the vegetative part of maize grown in fields artificially contaminated with Cd^{2+} and Zn^{2+} salts, the concentration of mobile forms of Cd^{2+} ions was lower by 21.3% (2 MAC) and 19.2% (3 MAC) relative to contaminated soil only with Cadmium salts. The combined effect of three heavy metals (Pb^{2+}, Cd^{2+}, and Zn^{2+}), which artificially contaminated the ground where the green mass of corn was grown for silage, is manifested in a decrease in the accumulation of Cd^{2+} ions by green mass of corn by 11.2% (2 MAC) and 10.9% (3 MAC) compared with the experimental field, which was contaminated with Cd^{2+} + Pb^{2+} ions.
As a result of experimental studies, data were obtained on the interaction of heavy metals on their accumulation processes by the vegetative part of plants; it was shown that there are not only pairs but also interactions between three heavy metals. It is established that in the case of poly element soil contamination, the phytotoxicity and inflow of heavy metals to plants are primarily determined by antagonistic and synergistic interactions of elements (Fig. 3).
The interaction efficiency analysis showed the existence of both general and specific interactions of these metals, which can be explained by the similarity of properties and their role in metabolism in plants. Considering all the studied combinations of heavy metals, it is possible to form many toxic interactions. In this series, the placement of heavy metals reflects a decrease in their synergistic and increased antagonistic properties: $Cd^{2+} + Pb^{2+} > Cd^{2+} + Pb^{2+} + Zn^{2+} > Cd^{2+} + Zn^{2+}$. The combined action of lead and Cadmium ions enhances the accumulation of the latter, and Zinc ions, on the contrary, inhibit it.

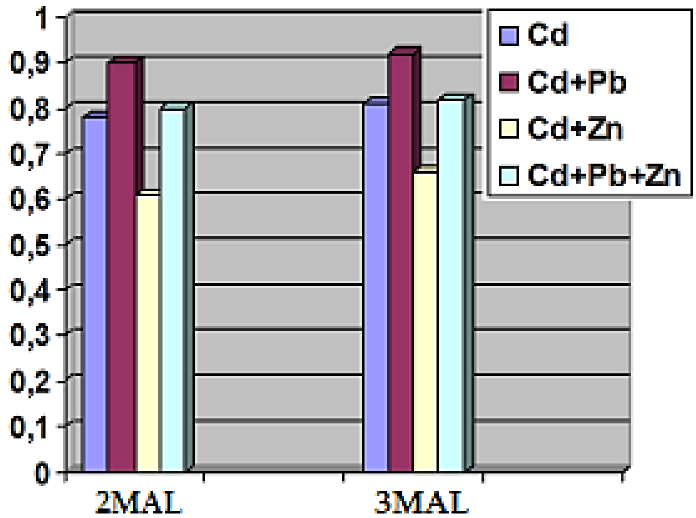

Fig. 3. The combined effect of Pb^{2+}, Zn^{2+} ions on the accumulation of Cd^{2+} ions in the vegetative part of the corn

Besides, the antagonism between Zn^{2+} and Pb^{2+} is also known. Thus, oral administration of zinc salts promotes the mobilization of previously deposited Lead in bone tissue, which leads to an accelerated process of its excretion, and acute cadmium poisoning, in contrast, reduces the level of Pb^{2+} in the blood. Thus, the soil's complex contamination with Pb^{2+} and Cd^{2+} ions increases their toxicity. Firstly, this is due to the summation of adverse physiological effects, and secondly, due to the elements' synergistic interaction. Thus, complexes of heavy metals under conditions of poly element pollution act differently from individual components. Therefore, plants' final impact depends on their sensitivity (general and poly element), soil conditions, forms of heavy metal compounds, and their ratio.

Lead in the body can affect oxidative processes by reacting directly with thiol groups of proteins or by activating other links of oxidative stress, for example, by reproducing the action of Calcium. It is known from the literature that the mechanism of development of lead intoxication is closely related to disorders of Calcium homeostasis. Insufficient Calcium in the diet can increase the level of lead adsorption. When the Calcium level in the blood decreases, homeostatic systems mobilize it and lead, which is deposited in the bones. "Molecular mimicry" is essential in the mechanism of membrane-tropic action of Lead, as a result of which the body recognizes Lead as Calcium, and transmembrane transfer of Lead is activated due to depletion of calcium reserves.

In soils whose pollution by human-made waste exceeds the MAC, it is necessary to take extraordinary measures to restore their condition suitable for use. Such actions are called soil remediation or rehabilitation, rehabilitation. Thus, studying and implementing such measures would not cause radical changes in traditional crop production technologies, ensure the preservation and increase of fertility, improve quality, and reduce crop products' pollution with heavy metals. According to available scientific data, an effective measure to reduce heavy metals' toxic effects is the use of compounds that limit toxic ions' mobility, converting them into bound, inaccessible to plants forms (Butsyak, 2002). Crops have a significant accumulative capacity, even in conditions of the low density of soil contamination by pollutants. Therefore, for the "rehabilitation" of soils contaminated with human-made waste more than the MAC, it is necessary to take extraordinary measures to rehabilitate them. This issue is especially acute in industrialized regions. Biogeochemical provinces are formed with high heavy metals content in the soil, water, and vegetative part of forage crops. It is necessary to implement reclamation measures to ensure the preservation and increase soil fertility and reduce plant pollution.

To mitigate the negative impact of pollutants, as well as to minimize the accumulation of their plants in soil contaminated with heavy metals, we applied reclamation inorganic and organic nature (zeolite 20 t/ha, compost 20 t/ha, limestone 20 t/ha and green manure 20 t/ha) (Table 9). A study of the effectiveness of measures to reduce the negative impact of anthropogenic pollution by heavy metals showed that the ameliorants used to limit the mobility of heavy metal ions, converting them into bound and less accessible to plants forms, significantly reduce the accumulation of toxicants in vegetative crops (Butsyak, 2002).

Table 9. Coefficient (C) of accumulation of heavy metals by green mass of corn against the background of ameliorants (mg/kg of dry fodder, M±m, n= 5)

Indexes	Meliorants				
	Control	Zeolite	Biohumus	Limestone	Siderates
Cd^{2+}	0.68	0,38±0,01	0,41±0,03	0,46±0,03	0,51±0.03
K	0.79	0,56	0,60	0,68	0,75
Pb^{2+}	7.81	4,63±0,16	6,17±0,51	6,90±0,53	6,28±0,18
K	0.86	0,51	0,68	0,76	0,69
Zn^{2+}	41.6	27,5±1,51	24,6±1,3	32,1±1,4	36,4±1,4
K	0.83	0,54	0,49	0,64	0,72

With the background level of man-caused soil contamination by mobile forms of Cd^{2+} ions (0.68 mg/kg); Pb^{2+} (7.81 mg/kg), and Zn^{2+} (41.60 mg/kg), which exceeded the maximum allowable norms by 1.5–2.0 times, all applied ameliorants - zeolite, biohumus, limestone, and green manures shaved the concentration of toxicants: Cd^{2+} (25.0–44.1%); Pb^{2+} (by 11.7–40.8%) and Zn^{2+} (by 12.5–41.0%) compared to their amount in the green mass of corn grown on soils without the introduction of ameliorants.

A comprehensive assessment of the studied ameliorants showed that in the conditions of local anthropogenic soil contamination with heavy metals in doses of 1.5 – 2.0 MAC, the most promising is zeolite, the use of which reduces the concentration of mobile metals compared to control: Cd^{2+} – by 44.1%; Pb^{2+} – by 40.8%; Zn^{2+} – by 34.1%.

The least effective in our conditions were green manures, which reduced the concentration of mobile forms of Cadmium, Lead, and Zinc ions, respectively, by 25.0, 19.6, and 12.5%. Besides, it should be noted that greens are 7.9% more likely to prevent the accumulation of lead ions in the vegetative part of corn compared to plants grown on soils where limestone was used as an ameliorant. Biohumus and limestone occupied an intermediate place between zeolite and green manures, the use of which reduced the accumulation of toxic Cadmium, Lead, and Zinc ions in corn stalks by 39.7 and 30.0%, respectively; 21.0 and 11.7%; 41.0 and 22.9%.

In the conditions of local technogenic soil contamination, the content of heavy metals in fodder crops can be one of the primary identification indicators of product quality. Used ameliorants prevent the entry of toxicants into food and feed raw materials. Some of them provide optimal plant nutrition (compost, green manure), improving soil structure, which increases the buffering capacity of soils to bind toxic elements. Others, due to their unique adsorption and ion exchange (zeolites) and metal protective (limestone) properties, deoxidize soils and prevent heavy metals' entry into plants by reducing heavy metals' competitiveness in ion-exchange adsorption on the root system.

Under the influence of zeolite flour during the first year of the experiment, soils' active and potential activity is completely neutralized. The use of crushed limestone in the first year of the investigation does not give the desired effect. Accelerated reclamation effect of zeolite is achieved due to ion exchange reactions between cations of alkali and alkaline earth metals and acid equivalents of soil solution, which can take place on the ion principle exchanger in the soil-zeolite system.

Among the used ameliorants, the most effective is the zeolite of the Sokyrnytsia deposit. The introduction of which into the soil leads to a significant reduction in the accumulation of heavy metals. Under the influence of zeolite, the concentration of Lead and Zinc's mobile forms in the green mass of corn was within the MAL. However, the concentration of cadmium ions, under this experiment's conditions, exceeded the MDR by 26%, respectively. In experimental studies conducted in other conditions, it was proved that the zeolite flour introduced into the soil in the amount of 3 – 5% (N. Chelishchev, R. Chelishcheva, 1982) significantly increases the yield of forage crops, prevent the accumulation of heavy metals in feed, increase the functioning of bioorganomineral complex and enhances the nutrient regime of the soil.

The study of the dynamics of mobile ions of heavy metals in sod-podzolic soil under conditions of experimental contamination simulated by salts of Cadmium, Lead, and Zinc in concentrations of 1 MAC, 2 MAC, and 3 MAC against the background of zeolite is given in the table. 10. In the conditions of simulated pollution of 1 MAC, the introduced zeolite helped to reduce the number of mobile forms of metals: Cd^{2+} – by 5%, Pb^{2+} – by 19%, and Zn^{2+} – by 7.9%. The increase of soil contamination to the concentration of 2 MAC and 3 MAC differently affected zeolite properties concerning the adsorption of mobile forms of Cd^{2+}, Pb^{2+}, Zn^{2+} ions. The reduction of mobile forms of heavy metals was equal for Cadmium – 6.7 and 6.2%, for lead 20.0 and 18.9%, and zinc 10.3 and 11.4%, under the experiment's conditions.

Table 10. The content of mobile forms of heavy metals in the soil on the 60th day of the experiment (mg/kg of dry soil, M±m, n=5)

A variant of the experiment	Cd	Pb	Zn
MAC (control)	0.3	6.0	23.0
MAC + zeolite	0.285±0.001	4.86±0.11	21.2±0.69
2 MAC (control)	0.6	12.0	46.0
2 MAC + zeolite	0.56±0.03	9.6±0.57	41.3±0.72
3 MAC (control)	0.9	18.0	69.0
3 MAC + zeolite	0.845±0.04	14.6±0.51	61.2±0.60

Thus, under conditions of increased pollution (2 and 3 MAC), the zeolite more actively adsorbed Pb^{2+} and Zn^{2+} ions, and the adsorption of Cd^{2+} ions remained at the level of 1 MAC contamination. Thus, zeolite flour as an ameliorant helps reduce the concentration of mobile forms of heavy metals in soil samples, increasing the ability of soils to natural self-healing. In all experimentally contaminated soils, Pb^{2+} ions' adsorption was the highest in all experimentally contaminated soils. In experimental studies, the toxic effect of heavy metals on plant growth intensity in the system: soil-plant, we studied the above mixtures of salts. Cadmium, lead, and zinc salts (1 MAC) inhibit root and stem growth in sprouts in the range of 38.42–42.56% according to the control (standard deviation for such experiments is 20%). The germination of all plants was in the field of 90-100%. The mixture of salts (2 and 3 MAC) showed a further increase in the toxic effects of heavy metals on plant sprouts' growth. The range of plant growth inhibition ranged from 43.48–44.20% (2 MAC) and 46.80–52.40% (3 MAC).

The applied zeolite, as an ameliorant, increases the activity of root and stem growth in all contaminated soil samples, respectively: 18.16–21.30% (1 MAC); 24.60–28.10% (2 MAC) and 25.15–29.40% (3 MAC. With the increase in soil contamination with heavy metal salts at a dose of 3 MAC, the restoration of root and stem growth activity under zeolite was to the level of 2 MAC.

Thus, in artificial soil contamination conditions, an effective means of reducing the toxic effects of heavy metals is inorganic sorbent – zeolite, which is accompanied by an increase in the buffering capacity's natural ability of soils self-clean. Zeolite limits the accumulation of mobile toxic ions, converting them into bound, inaccessible to plants forms and restoring the growth activity of roots and stems of plants by 18-30%. Under local anthropogenic pollution conditions, soils acquire aggressive properties, manifested in the intensive accumulation of toxicants by plants' vegetative part. To prevent heavy metals' migration and limit their accumulation by plants, we recommend using zeolites as an ameliorant, which can adsorb and bind heavy metals. The dynamics of mobile forms of heavy metals (Cadmium, Lead, Mercury, and Zinc) and the optimal amount of zeolite introduced into the soil as an ameliorant are given in table.11. The use of zeolite leads to a significant reduction in the accumulation of mobile forms of Cadmium, Lead, mercury, and zinc ions in plants' vegetative part. Most significantly, the accumulation of all toxic ingredients is reduced when using zeolite in 20 tons or more per hectare. Increasing the application of white zeolite to the soil to 25–30 t/ha does not significantly affect the prevention of accumulation of heavy metals by plants. The level of Cadmium, Mercury, and Zinc in the vegetative part of corn remained up to the level of zeolite used in the amount of 20 t/ha, and the level of Lead in corn stalks collected from the area where 30 t/ha of zeolite was applied increased by 3.0%.

Table 11. The content of heavy metals in the green mass of corn on the background of the action of different amounts of ameliorant (M±m, n=5)

Experimental variant	Cd	Pb	Hg	Zn
Control soil (C)	0.68±0.02	7.94±0.25	0.22±0.01	51.38±2.35
C + zeolite, 10 t/ha	0.48±0.02	6.12±0.40	0.20±0.02	52.40±1.18
C + zeolite, 15 t/ha	0.46±0.02	5.10±0.58	0.20±0.02	51.20±3.12
C + zeolite, 20 t/ha	0.38±0.02	4.93±0.14	0.17±0.02	46.04±1.41
C + zeolite, 25 t/ha	0.39±0.02	4.93±0.59	0.17±0.01	48.20±2.58
C + zeolite, 30 t/ha	0.38±0.02	5.08±0.41	0.17±0.01	46.10±0.62

The yield of green mass of corn in the experimental plots was on average 12.4–26.8% higher than the yield of the control plot (table 12). Given that the use of zeolite by uniform scattering under fallow plowing at a dose of 20 t/ha most prevents the accumulation of heavy metals by forage plants, as well as its use in this dose contributes to the highest yield of green corn for silage, we recommend using zeolite as ameliorant dose of 20 t/ha.

Table 12. The effect of different doses of zeolite (z) on the yield of green mass of corn (t/ha, M±m, n=5)

Indexes	Yield
Control field	196.5±10.2
Introduced zeolite at a dose of 10 t/ha	220.8±10.6
Introduced zeolite at a dose of 15 t/ha	235.7±11.2
Introduced zeolite at a dose of 20 t/ha	249.2±10.8
Introduced zeolite at a dose of 25 t/ha	242.7±11.9
Introduced zeolite at a dose of 30 t/ha	246.1±12.1

The background level of mobile forms of heavy metals (Cadmium, Lead, Mercury, and Zinc) was significantly higher than the MAC. Under such conditions, the soil acquires aggressive properties, manifested in the intensive accumulation of toxic metals by plants' vegetative part (Table 13).
Thus, in the experimental farm, the green mass of corn accumulates the most lead ions (7.94 mg/kg) with an accumulation coefficient of 0.84, the least zinc ions (51.38 mg/kg) an accumulation coefficient of 0.70. Cadmium (0.52 mg/kg) and Mercury (0.22 mg/kg) ions occupy an intermediate position with an accumulation factor of 0.80 and 0.87, respectively. The use of zeolite as an ameliorant contributes to a significant reduction in the accumulation of the studied toxic ingredients. Most significantly, the transformation of Pb^{2+} ions, the concentration of which (4.93 mg/kg) does not exceed the MAC, decreases by 31.95%. The concentration of Cd^{2+} (0.38 mg/kg) and Hg^{2+} (0.17 mg/kg) ions under the influence of zeolite decreased by 26.03 and 22.73%, respectively, but they exceed the MAL. The content of Zn^{2+} ions (62.52 mg/kg) in the studied soil samples decreased by 10.4%, and its amount did not exceed the maximum allowable concentration.

Table 13. Accumulation of heavy metals by plants against the background of zeolite (mg/kg of dry food, M ± m, n = 4)

Object of study	Metals			
	Lead	Cadmium	Mercury	Zinc
Control field				
Soil	9.42±0.42	0.64±0.02	0.28±0.01	73.6±2.1
Plants	7.94±0.25	0.52±0.02	0.22±0.01	51.38±2.3
% accumulation	84.28	80.10	87.57	69.77
Research field				
Plants	4.93±0.14	0.38±0.02	0.17±0.01	46.04±1.4
% accumulation	52.33	59.37	60.71	62.52
± to control	- 31.95	- 20.73	- 26.8	- 7.25
MAC *	5.0	0.3	0.1	50.0

*- according to G. Talanov, B. Khmelevsky, 1991.

These measures create the preconditions for a significant reduction in the accumulation of mobile forms of heavy metals in the feed ration, making it possible to reduce the migration of toxic elements by trophic chains. The research results have shown that using different ameliorants does not equally affect heavy metals' transformation by the green mass of corn (Butsyak, 2002). Fixation and transition of heavy metals into forms that are inaccessible to plants are often the result of their interaction with the soil's organic substance. The high content of humus in the soil binds heavy metals with the formation of organometallic complexes. The accumulation of heavy metals in the soil can result from their interaction with inorganic compounds, such as carbonate and phosphate ions, effectively reducing the migration, leaching, and bioavailability of heavy metal ions.
However, in our research, zeolite as an inorganic ameliorant gives the most positive results. Natural zeolites are hydroalumino-silicates of the frame structure, which have cavities and channels of molecular size. They are active adsorbents of toxic substances, and at the same time, sources of nutrients, which improve the physical properties of soils. The introduction of zeolite into the experimental ground is accompanied by a significant reduction (by 34–44%) in the accumulation of a green mass of Zinc, Lead, and Cadmium in corn, higher (by 8–29%) compared to the use of other ameliorants.
The use of zeolite in the amount of 20 t/ha for fallow plowing, by uniform scattering, provides more effective prevention of accumulation of heavy metal salts (Cd, Pb, Hg, and Zn) by green mass of corn compared to the applied ameliorant in doses of 10, 15, 25 and 30 t / Ha. The applied ameliorant performs a protective but, in our case, a stimulating effect in the formation and functioning of the symbiosis between the microbiota and the plant. Furthermore, as a result, the yield of green mass of corn in this experimental area (where it was used as an ameliorant – zeolite at a dose of 20 t/ha under conditions of local human-made soil pollution) on average exceeds by 12.4 – 26.8% the yield of other experimental sites (Butsyak, 2002). Ameliorant enhances mineralization processes by increasing the physiological activity of soil self-cleaning and their buffering ability to bind toxicants, which allows expanding the gross yield of green mass of corn, with the content of heavy metals not exceeding the maximum allowable concentrations in the biogeochemical province forms of heavy metal ions in the soil. In the conditions of

experimentally contaminated soil with salts of Lead, Cadmium, and Zinc (1, 2, 3 MAC), the adsorption by zeolite of mobile forms of Lead was the highest. It averaged 19% compared to the control. Besides, zeolites limit the accumulation by plants of mobile states of pollutants, which helps restore the growth activity of roots and stems of plants by 18–30% (Vishkulov et al., 2002).

The use of zeolite as an ameliorant reduces the intensity of plant accumulation of mobile ions of Lead by 37.1%, Cadmium – by 26.3%, Mercury and Zinc by 22.4 and 10.4%, respectively. Simultaneously, the concentration of Cadmium and mercury ions in the experimental conditions remains higher than the MACThe use of this ameliorant on agricultural land, which is located in the zone of active human-made pollution by the Mykolayiv Mining and Cement Plant in combination with manure and at the same time limiting the use of mineral fertilizers, will promote the consolidation of heavy metals in the soil. Soil fertility improves the quality and significantly prevents heavy metals' entry into the vegetative part of plants.

The possibility of immobilization of Cadmium by zeolites has been proved, the use of which reduces the cadmium content in lettuce plants by 85% and in oat grains by 40%. This ameliorant's positive role in reducing the pressure of heavy metals and restoring the soil's nitrogen-fixing ability was confirmed in field experiments with contamination of gray podzolic soil with a mixture of salts Cadmium, Copper, Lead, and Zinc in doses from 1 to 20 MAC. The use of zeolite optimizes plant nutrition, which increases yields and prevents the accumulation of toxic substances in feed, grain, fruit, and eliminates their migration to human food.

In the Ukrainian Research Institute of Agriculture Scientific Development, it is established that the zeolites of the Sokyrnytsia deposit are good ameliorants on sod-podzolic, sandy, and loamy soils. Application of zeolite in the amount of 15–37 t/ha increases the bioorganic-mineral complex functions and improves soil nutrition regulation. Based on some authors' experimental data and research results, it is established that zeolite as an ameliorant is one of the effective means of reducing the content of mobile forms of toxic elements in the food chain: soil-plant-feed-animal-livestock-man. The distribution of chemical elements and their ratio in natural ecosystems' main components is an important environmental quality assessment. As part of environmental monitoring, the study of accumulation, migration, and distribution of heavy metals in soil and plants will assess the negative trends associated with local environmental pollution. Crops have a significant accumulative capacity, even under conditions of low levels of soil contamination by pollutants.

There are specific and general toxic effects of heavy metals. The first effect is manifested in a selective impact on plants' functional systems, general toxic – in the deterioration of the plant organism as a whole. A. Kovalevsky distinguishes between the barrier and barrier-free types of absorption. In the first, upon reaching a certain level of toxic elements, mechanisms begin to act that block further absorption; in the second, toxic metals in plants can increase without certain limits. Thus, the accumulation of toxicants at first stimulates plants' vital activity and productivity, further depresses, and finally leads to death.

Conclusions

The level of heavy metal ions (Cd; Pb; Hg; Zn) in soils within a radius of more than 15 km from the Mykolayiv Mining and Cement Plant exceeds the MAL. The highest concentration of investigated heavy metals in the ground was registered in low air velocity conditions and high humidity. With increasing wind and decreasing humidity, the content of heavy metals reduces significantly. In the cold season, the degree of pollution is higher than in the warm season. As soil acidity increases, the level of metal ions available to plants increases, contributing to plants' significant accumulation. The accumulative capacity of plants depends on their specific characteristics. Green clover mass and sugar beet buds accumulate the most Cadmium; corn – Lead; cereal fodder crops – Zinc; wheat straw – Mercury. In the structure of sown areas, more attention should be paid to crops of alfalfa and cereals for green fodder, which under conditions of anthropogenic load are more resistant to the accumulation of heavy metals.

With experimentally simulated co-contamination of the soil with salts of Cadmium, Lead, and Zinc (2 and 3 MPC), the inflow of heavy metals into the vegetative part of plants is largely determined by antagonistic and synergistic interactions between individual heavy metals, which directly affects the toxic manifestations of the latter. The combined effect of Pb^{2+} and Cd^{2+} ions increases the latter's accumulation by the vegetative part of corn by 14.8%, and Zn^{2+} ions, on the contrary, inhibit it by 21.3%.

The application of various ameliorants of organic and inorganic nature prevents heavy metals' entry to plants grown on contaminated soils under local anthropogenic pressure. The most promising in terms of experiments are ameliorants of inorganic nature – zeolites with unique adsorbent properties. To prevent heavy metals' entry into the vegetative part of fodder crops, it is advisable to use zeolite at a dose of 20 tons per hectare by uniform scattering under fallow plowing, which does not change traditional fodder cultivation technologies, improves plant quality, and preserves soil fertility.

References

Andreyuk, K.I., Iutinskaya, G.O., & Antipchuk, A.F. (2001). Functioning of microbial coenoses of soil in the conditions of anthropogenic loading. Kyiv: Oberehy.

Boiko, O.V., Honchar, O.F., Lesyk, Y.V., Kovalchuk, I.I., & Gutyj, B.V. (2020). Effect of zinc nanoaquacitrate on the biochemical and productive parameters of the organism of rabbits. Regulatory Mechanisms in Biosystems, 11(2), 243–248. doi:10.15421/022036

Butsyak, V.I. (2002). Accumulation of heavy metals by fodder crops in local zones of anthropogenic pollution. Scientific herald of LSAVM named after S.Z. Gzycki, 4 (2), 21-26.

Butsyak, V.I. (2002). Influence of ameliorants of organic and inorganic nature on the transformation of heavy metals by plants. Collection of scientific works of USAA, 55, 19-25.

Butsyak, V.I. (2002). Investigation of the combinatorial influence of heavy metals on the processes of cadmium ion transformation. Scientific herald of the LSAVM named after S.Z. Gzycki, 4(2), 3-6.

Butsyak, V.I. (2002). Migration of mobile forms of heavy metals into the vegetative mass of plants against the background of zeolite. Bulletin of the Poltava State Agrarian Academy, 2-3, 29-30.

Eskov, E.K., Eskov, K.E., Kolbina, L.M. et al. (2001). Content of heavy metals in soil, bees, and their products. Beekeeping, 4, 14-15.

Fedoruk, R.S., Kolisnyk, G.V., & Tsap, O.F. (2002). Man-caused impact on environmental pollution and quality of agricultural products. Scientific Bulletin of LSAVM. SZ Gzhytsky, 4(2), 62-64.

GOST 26929-86. Raw materials and products. Sample preparation. Mineralization for the determination of toxic elements.

Gutyj, B., Grymak, Y., Drach, M., Bilyk, O., Matsjuk, O., Magrelo, N., Zmiya, M., & Katsaraba, O. (2017). The impact of endogenous intoxication on biochemical indicators of blood of pregnant cows. Regulatory Mechanisms in Biosystems, 8(3), 438–443. doi: 10.15421/021768

Gutyj, B., Martyshchuk, T., Bushueva, I., Semeniv, B., Parchenko, V., Kaplaushenko, A., Magrelo, N., Hirkovyy, A., Musiy, L., & Murska, S. (2017). Morphological and biochemical indicators of blood of rats poisoned by carbon tetrachloride and subject to action of liposomal preparation. Regulatory Mechanisms in Biosystems, 8(2), 304–309. doi:10.15421/021748

Gutyj, B., Ostapiuk, A., Kachmar, N., Stadnytska, O., Sobolev, O., Binkevych, V., Petryshak, R., Petryshak, O., Kulyaba, O., Naumyuk, A., Nedashkivsky, V., Nedashkivska, N., Magrelo, N., Golodyuk, I., Nazaruk, N., & Binkevych, O. (2019). The effect of cadmium loading on protein synthesis function and functional state of laying hens' liver. Ukrainian Journal of Ecology, 9(3), 222-226

Gutyj, B., Stybel, V., Darmohray, L., Lavryshyn, Y., Turko, I., Hachak, Y., Shcherbatyy, A., Bushueva, I., Parchenko, V., Kaplaushenko, A., & Krushelnytska, O. (2017). Prooxidant-antioxidant balance in the organism of bulls (young cattle) after using cadmium load. Ukrainian Journal of Ecology, 7(4), 589–596.

Gutyj, B.V., Murs'ka, S.D., Gufrij, D.F., Hariv, I.I., Levkivs'ka, N.D., Nazaruk, N.V., Gajdjuk, M.B., Pryjma, O.B., Bilyk, O.Ja., & Guta, Z.A. (2016). Vplyv kadmijevogo navantazhennja na systemu antyoksydantnogo zahystu organizmu bugajciv. Visnyk Dnipropetrovs'kogo universytetu. Biologija, ekologija, 24(1), 96–102. doi:10.15421/011611.

Gutyj, B.V., Ostapyuk, A.Y., Sobolev, O.I., Vishchur, V.J., Gubash, O.P., Kurtyak, B.M, Kovalskyi, Y.V., Darmohray, L.M., Hunchak, A.V., Tsisaryk, O.Y., Shcherbatyy, A.R., Farionik, T.V., Savchuk, L.B., Palyadichuk, O.R., & Hrymak, K. (2019). Cadmium burden impact on morphological and biochemical blood indicators of poultry. Ukrainian Journal of Ecology, 9(1), 236-239.

Ivasivka, A.S. (2001). Influence of mixtures of copper, cadmium, and sulfur compounds on seed germination. Bulletin of Agrarian Science, 1, 83-85.

Kokunin, V.A. (1975). Statistical data processing with a small number of experiments. Ukr. biohim. Jorn, 47(6), 776-791.

Korshun, M.M. (2002). The problem of combinatorial action on the body of priority chemical soil pollutants. Environment and Health, 4(23), 51-56.

Kravtsiv, R.Y., & Butsyak, V.I. (2002). Influence of anthropogenic factor on the content of heavy metals in different fodder crops. Animal Biology, 4(1-2), 189-192.

Kravtsiv, R.Y., & Butsyak, V.I. (2002). Transformation of heavy metals by soils under man-made load conditions. Farmer, 1-2, 5-7.

Kravtsiv, R.Y., Butsyak, V.I., & Butsyak, G.A. (2005). Influence of physicochemical factors on toxic activity of heavy metals. Scientific Bulletin of Lviv National Academy of Veterinary Medicine named after S.Z. Gzhytsky, 7, 4(27), 51-56.

Kravtsiv, R.Y., Butsyak, V.I., & Butsyak, G.A. (2007). Toxic effect of the combined action of salts of heavy metals on the body of rats. Bulletin of Agrarian Science, 1, 33-36.

Martyshuk, T.V., Gutyj, B.V., & Vishchur, O.I. (2016). Riven produktiv perekysnoho okysnennia lipidiv u krovi shchuriv za umov oksydatsiinoho stresu ta za dii liposomalnoho preparatu "Butaselmevit" [Level of lipid peroxidation products in the blood of rats under the influence of oxidative stress and under the action of liposomal preparation of "Butaselmevit"]. Biological Bulletin of Bogdan Chmelnitskiy Melitopol State Pedagogical University, 6(2), 22–27. doi: 10.15421/201631(in Ukrainian).

Methodical guidelines for the determination of heavy metals in agricultural soils and crop production (1991). M.: TsINAO.

Osipov, A.N., Ryazanov, I.A., & Sypin, V.D. (2001). Changes in the structural and functional parameters of the cells of the blood system of mice under prolonged exposure to lead and cadmium. Toxicological Bulletin, 5, 2-5.

Piven, O.T., Khimych, M.S., Salata, V.Z., Gutyj, B.V., Naidich, O.V., Skrypka, H.A., Koreneva, Z.B., Dvylyuk, I.V., Gorobey, O.M., & Rud, V.O. (2020). Contamination of heavy metals and radionuclides in the honey with different production origin. Ukrainian Journal of Ecology, 10(2), 405-409.

Price, W.Y. (1972). Analytical atomic-absorption spectrometry. London, New York. Phein, 259-275.

Rudenko, O.P., Paranjak, R.P., Kovalchuk, N.A., Kit, L.P., Hradovych, N.I., Gutyj, B.V., Kalyn, B.M., Sukhorska, O.P., Butsiak, A.A., Kropyvka, S.I., Petruniv, V.V., & Kovalska, L.M. (2019). Influence of seasonal factors on carp fish immune reactivity. Ukrainian Journal of Ecology, 2019, 9(3), 168-173.

Samokhvalova, V.L., Miroshnichenko, M.M., & Fateev, A.I. (2001). Thresholds for the level of toxicity of metals important for agricultural crops. Bulletin of Agrarian Science, 10, 61-65.

Slivinska, L.G., Shcherbatyy, A.R., Lukashchuk, B.O., & Gutyj, B.V. (2020). The state of antioxidant protection system in cows under the influence of heavy metals. Regulatory Mechanisms in Biosystems, 11(2), 237–242. doi:10.15421/022035

Slivinska, L.G., Shcherbatyy, A.R., Lukashchuk, B.O., Zinko, H.O., Gutyj, B.V., Lychuk, M.G., Chernushkin, B.O., Leno, M.I., Prystupa, O.I., Leskiv, K.Y., Slepokura, O.I., Sobolev, O.I., Shkromada, O.I., Kysterna, O.S., & Musiienko, O.V. (2019). Correction of indicators of erythrocytopoesis and microelement blood levels in cows under conditions of technogenic pollution. Ukrainian Journal of Ecology, 9(2), 127-135.

Sobolev, O.I., Gutyj, B.V., Sobolieva, S.V., Borshch, O.O., Kushnir, I.M., Petryshak, R.A., Naumyuk, O.S., Kushnir, V.I., Petryshak, O.Y., Zhelavskyi, M.M., Todoriuk, V.B., Sus, H.V., Levkivska, N.D., Vysotskij, A.O., & Magrelo, N.V. (2020). Review of germanium environmental distribution, migration and accumulation. Ukrainian Journal of Ecology, 10(2), 200-208. doi: 10.15421/2020_86

Stepanok, V.V. (2000). Influence of a combination of heavy metal compounds on the yield of agricultural crops and the entry of heavy metals into plants. Agrochemistry, 1, 74-80.

Tanker, I.D. (2000). On the problem of establishing safe levels of toxic substances in the environment. Modern problems of toxicology, 2, 49-53.

Vishchur, V.Y., Gutyj, B.V., Nischemenko, N.P., Kushnir, I.M., Salata, V.Z., Tarasenko, L.O., Khimych, M.S., Kushnir, V.I., Kalyn, B.M., Magrelo, N.V., Boiko, P.K., Kolotnytskyy, V.A., Velesyk, T., Pundyak, T.O., & Gubash, O.P. (2019). Effect of industry on the content of fatty acids in the tissues of the honey-bee head. Ukrainian Journal of Ecology, 9(3), 174-179.

Vishkulov, N.P., Palgov, V.I., & Spector, D.R. (2002). Establishment of levels of heavy metals in soils of Ukraine. Environment and health, 6, 44-46.

Vishkulov, N.P., Palgov, V.I., & Spector, D.R. (2002). Establishment of heavy metals levels in the soils of Ukraine. Environment and Health, 6, 44-46.

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Butsiak, H.A., Butsiak, V.I., Gutyj, B.V., Kalyn, B.M., Muzyka, L.I., Stadnytska, O.I., Luchyn, I.S., Rozputnii, O.I., Kachan, L.M., Melnichenko, Yu.O., Sliusarenko, S.V., Bilkevich, V.V., Leskiv, K.Y. (2021). Migration of mobile forms of heavy metals into the vegetative mass of plants under local human-caused load. *Ukrainian Journal of Ecology, 11* (1), 239-343.

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