UDC 504

MONITORING OF THE CONTENT AND MIGRATION OF HEAVY METALS IN THE SOILS-MELLIFEROUS PLANTS-BEES-BEEKEEPING PRODUCTS SYSTEM IN BIOCENOSES OF THE COMBAT AREAS

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Aim. To process the methodological approaches to the monitoring of the content and migration of heavy metals in the soils-melliferous plants-bees-beekeeping products system in 2022–2023 for the ecological assessment of biocenoses in the territories which were affected by military operations. **Methods.** The first stage of the study was to measure the content of zinc and lead in melliferous plants (inflorescences of buckwheat, sunflower, and various herbs), and honey from three territories in the Cherkasy region. The second stage of the study covered the following apiaries: NSC P.I. Prokopovych Institute of Beekeeping (located in the village of Yaryshiv, Mohyliv-Podilsky district, Vinnytsia region; the apiaries, located in the de-occupied territories: Kharkiv region, Chuhuiv district, Shestakove village, and Chernihiv region, Novhorod-Siverskyi district; the apiaries located in the territories near the range of military operations in Mykolaiv region, Bashtanka district, Novooleksandrivka village, and Sumy region, Lebedyn. The selection of matrices to determine the content of volatile forms of heavy metals (HM) (soil, plants, pollen, bees, and honey) was carried out three times in 5 apiaries in 2022–2023 (May, July, and August). Thirty soil samples were taken along with 30 plant samples, 90 samples of pollen, bees, and honey each. Soil samples were taken using the envelope method from a depth of 0–20 cm. In melliferous plants (a mixed sample of various herbs), the aerial part was taken for the study of volatile forms of the HM content. Live bees were selected from three hives of each apiary, from entrances (30–35 bees from each) to jars. Prior to the analysis, the bees were stored in a freezer at a temperature of –20 °C (Gutiérrez et al, 2015). Pollen collection in the studied apiaries was carried out with the help of a hinged pollen catcher. Honey samples were taken from the frames; the honey was separated by filtration through gauze. We conducted a quantitative analysis of the content and accumulation of volatile forms of HM (Fe, Cd, Cu, Ni, Pb, Zn) in soil, melliferous plants, bees, bee pollen, and honey. Sample preparation was carried out by dry mineralization. The content of volatile forms of heavy metals (iron, cadmium, copper, nickel, lead, and zinc) was determined by atomic adsorption spectrophotometry. **Results.** In the first stage of the study, we determined the content of volatile forms of heavy metals (Pb, Zn) in plants and honey on the territory of Cherkasy region (Right-Bank Forest-Steppe). Using the data, obtained by chemical studies and the correlation and regression analysis, we developed statistical models for predicting the content of heavy metals in plants, depending on their content in honey. In the second stage of the study, we determined the content of volatile forms of heavy metals (Fe, Cd, Cu, Ni, Pb, Zn) in soil, melliferous plants, bees, pollen, and honey in the biocenoses of the zones which had been affected by the military operations. **Conclusions.** In soils of all the investigated territories (Kharkiv, Mykolayiv, Sumy, and Chernihiv regions), we determined an increased level of heavy metals Fe, Cd, Cu, Ni, Pb, Zn, as compared to the control (Vinnytsia region). For instance, the concentration of cadmium in the territory of Chernihiv region (1.13 ± 0.28 mg/kg) exceeded MAC (1.0 mg/kg). The concentration of lead in all the investigated territories did not exceed MAC (55.0 mg/kg). The exceedance in MAC of the total form of lead (30 mg/kg) was registered in soil samples in Sumy region – 37.88 ± 6.21 mg/kg. The content of lead in Mykolayiv region exceeded that in the control 2.7 times. The content of iron in melliferous plants increased in all plant samples as compared to the control, 1–1.3 times respectively (p > 0.05). The highest values for cadmium content were found in Kharkiv region – 0.6 ± 0.034 mg/kg, Mykolayiv region – 0.5 ± 0.034 mg/kg, Chernihiv region – 0.5 ± 0.067 mg/kg, which exceeded the control values 1.7–2 times. High values were determined for a share of copper in plants as compared to the control in Kharkiv region – 5 ± 0.23 mg/kg and Mykolayiv region – 5.5 ± 0.21 mg/kg. Also, in Kharkiv region, the concentration of lead in the samples of entomophilous plants, collected on the territories near the apiary, exceeded the control indices 1.7 times. The data, obtained in five investigated territories of Ukraine, reflect the increased level of concentration of heavy metals in the bodies of bees as compared to the control. The highest concentration values of cadmium were registered in bee samples, collected from the apiary in the Sumy region (1.83 ± 0.03 mg/kg), and in the control – 0.50 ± 0.17 mg/kg. The content of lead was high in the samples from Kharkiv (10.77 ± 1.08 mg/kg) and Sumy (14.45 ± 0.89 mg/kg) regions; in the control, the lead content was 4.94 ± 0.54 mg/kg. The study of the accumulation of heavy metals in the bee pollen demonstrated the highest concentrations of heavy metals in the territories of Kharkiv and Mykolayiv regions (iron, copper, nickel, zinc), Sumy region (cadmium) as compared to the control. The highest copper content was found in the pollen samples from Mykolayiv region 9.22 ± 1.07 mg/kg (control – 0.79 ± 0.36 mg/kg). The increased level of zinc content as compared to the control (5.47 ± 0.003 mg/kg) was registered in Kharkiv region (16.13 ± 4.41 mg/kg) and Mykolayiv region (17.69 ± 1.96 mg/kg). The analysis of the concentrations of volatile forms of HM in honey samples demonstrated that in Kharkiv region there was an exceedance of MAC (1.0 mg/kg) for lead – 1.13 ± 0.12 mg/kg. The exceedance of MAC for copper in honey samples (0.5 mg/kg) was noted for all the investigated territories except for the control (0.11 ± 0.05 mg/kg). The exceedance of MAC for zinc in honey samples (5.0 mg/kg) was registered in Mykolayiv region (9.25 ± 2.10 mg/kg), Sumy region (6.75 ± 1.10 mg/kg), and Chernihiv region (6.60 ± 0.90 mg/kg). Taking into account the differences in ecologic and climatic conditions and the possible impact of numerous factors on the content and migration of HM in the soils–melliferous plants–bees–beekeeping products, it would be reasonable to have actual parameters of the HM content in the samples for each investigated territory and to take the relevant management conclusions based on them.

Key words: heavy metals; biomonitoring; Apis mellifera, bioindicators; products of beekeeping.

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INTRODUCTION

Environmental pollution is reaching dangerous scales due to excessive man-induced load on the agroecosystems. It leads to the impairment of the ecological equilibrium and natural balance in biogeocenoses. A considerable impact in this process is made by the excessive flux of contaminants of chemical origin into the biosphere, which tend to bioaccumulate in the food chain, thus posing a threat to human health and reflecting an ecologic situation, notable for many countries, including Ukraine (Shanker et al, 2005).

Some of the most dangerous pollutants of the biosphere are heavy metals (Demura et al, 2013). These chemical toxicants can penetrate the organism of animals via trophic chains, cause the impairment of metabolism processes, inhibit their growth and development, and may become a reason for the drop in the safety and biological value of animal products, and, as a result, for food poisoning in people.

Global anthropogenesis leads to changes in the qualitative and quantitative redistribution of chemical elements in the biosphere and their migration (Johnson, 2015).

Due to the full-scale military invasion of Ukraine's territory, many toxicants, ammunition combustion products, residues of destroyed civil and military equipment, infrastructure objects as well as fuel and lubricant materials from the movement of heavy machinery enter the environment; these pollutants penetrate the environment and remain therein for a long time (Denisov et al, 2017). In addition, mobile forms of microelements can migrate via the food chains of biological organisms, posing an immediate threat to the population's health due to their toxicity, carcinogenicity, and mutagenicity (Denisov et al, 2017). And polluted air has no limits.

Forager bees and beekeeping products can be used to detect chemical pollution of their environment while studying different variants of impact that result in mortality (if highly hazardous pesticides are used); physiological, biochemical, or behavioral changes; reaction of the population to the sublethal toxicity of the pollutant (Dolores, 2018). It is known that the content of polluting elements in the bodies of bees is impacted by different factors, including the area of apiary and its ecological state, reproduction ways of bee families, age of working bees, physiological state, and health of individual bees and bee communities in general. Scientists also specify that the concentration of heavy metals in the bodies of bees is also impacted by the territory of sample selection (Di Fiore, Nuzzo, 2022). An especially relevant aspect of the study lies in the fact that the primary source of heavy metals is anthropogenic activity (i.e. metallurgy, vehicles, road works, agriculture, and consequences of a full-scale military invasion) (Briffa et al, 2020). Therefore, the issues of determining the content of heavy metals and controlling their content in the soils-plants-bees-beekeeping products (honey) system are urgent for obtaining ecologically safe animal products and the creation of the relevant monitoring system (Zhukorskyi, Atarshchykova, 2023). We use the soils-plants-bees-beekeeping products system for the purposes of bioindication of the actual pollution with mobile forms of heavy metals to search for ways of predicting the pollution of territories, including those close to the zone of active combat.

The aim of the study is to process the methodological approaches to the monitoring of the content and migration of heavy metals in the soils-plants-honey plants-bees-beekeeping products system in 2022–2023 for the ecological assessment of biocenoses in the areas affected by military operations.

MATERIALS AND METHODS

The first stage of the study was to measure the content of heavy metals in honey plants and honey from three territories in the Cherkasy region: the village of Novoselytsia, Katerynopil district, the village of Chervone, Talne district, the village of Stebne, Zvenyhorodka district. While investigating the territory of Cherkasy region, we selected the inflorescence of buckwheat, sunflower, and various herbs. Using the data obtained by chemical studies and the correlation and regression analysis, we developed mathematical models for predicting the content of heavy metals in plants, depending on their content in honey (Boltyk, 2014).

The second experimental stage, with the consideration of the load on ecosystems in current conditions, was conducted in the following apiaries: NSC P.I. Prokopovych Institute of Beekeeping, located in the village of Yaryshiv, Mohyliv-Podilsky district, Vinnytsia region; the apiaries, situated in the de-occupied territories: Kharkiv region, Chuhuiv district, Shestakove village, and Chernihiv region, Novhorod-Siversky district; the apiaries located in the territory near the range of military operations in Mykolaiv region, Bashtanka district, Novooleksandrivka village, and Sumy region, Lebedyn, in 2022–2023.

The apiaries were set far from large industrial centers, in the distance of 25–45 km, but in the immediate vicinity of highways with heavy traffic (at a distance of not more than 4 km). The apiary, located in Vinnytsia region (Mohyliv-Podilsky district) at a distance of over 5 km from the highways, was accepted as a control for the second stage of the study. This district was notable for the relatively low intensity of anthropogenic load. The conditions of apiary maintenance and the technology of obtaining beekeeping products were identical in all apiaries. The apiaries with the Ukrainian steppe species of bees were chosen for the study (Grechka, 2013).

The selection of matrices to determine the content of heavy metals (HM) (soil, plants, pollen, bees, and honey) was carried out three times in 5 apiaries in 2022–2023 (May, July, and August). Five territories and five apiaries were studied for two years. 30 soil samples were taken along with 30 plant samples, 90 samples of pollen, bees, and honey each. Soil samples were taken using the envelope method from a depth of 0–20 cm. The scheme of sample selection was the same for all the territories. The total probe was well mixed, then the soil was spread in a 1-cm-deep layer on the cardboard, and the average probe was taken. To prepare for the chemical analysis, the samples of the average probe of soil were placed in a thin layer on a clean spreadsheet and dried at ambient temperature to the frail state. The division of the air-dried material was conducted to the degree when soil could pass through the sieve with 1-mm-wide holes. The weight of the average soil probe was 200 g. While collecting the weights, the probe was thoroughly mixed once again to rule out the possibility of particle fractionation by size and mass. In melliferous plants (a mixed sample of various herbs), the aerial part was taken for the study of the HM content. The plants were dried in the shadow until the permanent weight was achieved. Live bees were selected from three hives of each apiary, from entrances (30–35 bees from each) to jars covered with gauze. Before the analysis, the bees were stored in a freezer at a temperature of –20 °C (Gutiérrez et al, 2015). Pollen collection in the studied apiaries was carried out with the help of a hinged pollen catcher. The force of the family was considered while setting hinged pollen catchers. Then the collected pollen was put into trays of about 1–1.5 cm and dried in the cabinet drier at 38–41 °C. Honey samples were taken from the frames. A 5 × 5 cm piece of a honeycomb was cut out in the upper part of the frame; the honey was separated by filtration through gauze. For the analysis, honey was kept in tightly closed glass jars at +5 °C.

We conducted a quantitative analysis of the content and accumulation of HM (Fe, Cd, Cu, Ni, Pb, Zn) in soil, melliferous plants, bees, and beekeeping products via atomic adsorption spectrophotometry. In our studies, in particular in the territories close to the active combat zone, we paid special attention to such HM as cadmium, lead, and copper, because these HM penetrate natural objects due to military operations (Sploditel et al, 2023).

Samples were prepared by dry mineralization. The amount of heavy metals (iron, cadmium, copper, nickel, lead, and zinc) was determined by atomic adsorption spectrophotometry on Saturn-3 device (Alemasova et al, 2008).

The digital data were processed using a standard package of statistical programs Microsoft EXCEL (Mulyk et al, 2023).

RESULTS OF INVESTIGATIONS

The first part of the study on the qualitative composition of the components in the plant-beekeeping products (honey) system was to analyze the data of three apiaries in Cherkasy region. The results of the analysis demonstrated that the content of the investigated elements – lead and zinc (Pb, Zn) in plants and honey was registered in small amounts (**Table 1**).

Using the correlation and regression analysis, we developed mathematical models for the prediction of HM content in plants, depending on their content in honey (**Fig. 1**).

Based on the calculated regression equations, the content of HM in plants can be evaluated by the formulas: for lead $Y = -0.0365 + 3.2561 \cdot X$; for zinc $Y = 3.6857 + 12.3726 \cdot X$, where Y – HM content in melliferous plants, mg/kg, X – HM content in honey, mg/kg, the coefficients were obtained after statistical processing of the results of chemical studies. The correlation coefficients (for Pb $r = 0.9914$, Zn $r = 0.9031$) demonstrate a high degree of closeness between the above-mentioned values. The determination coefficients (for lead $r^2 = 0.9829$, zinc $r^2 = 0.8156$) explain 98.29 %, 81.56 % of the impact of the independent variable (Y – HM content in honey plants) on the dependent

Table 1. The content of heavy metals in honey plants, apiaries, Cherkasy region

Place of sampling location	Species of melliferous plants	Content of HM in honey plants, mg/kg		Coefficient of data variation, %	Content of HM in honey, mg/kg
		Calculated	Actual		
Pb					
Novoselytsia	Buckwheat	0.22	0.22 ± 0.01	0.28	0.08 ± 0.02
Novoselytsia	Various herbs	0.19	0.21 ± 0.01	1.31	0.07 ± 0.02
Novoselytsia	Sunflower	0.25	0.25 ± 0.02	0.46	0.09 ± 0.004
Chervone	Buckwheat	0.28	0.27 ± 0.04	1.35	0.1 ± 0.01
Chervone	Various herbs	0.54	0.59 ± 0.04	2.86	0.18 ± 0.02
Chervone	Sunflower	0.15	0.16 ± 0.01	0.08	0.06 ± 0.005
Stebne	Buckwheat	0.32	0.29 ± 0.02	2.24	0.11 ± 0.04
Stebne	Various herbs	0.64	0.63 ± 0.03	1.22	0.21 ± 0.002
Stebne	Sunflower	0.19	0.21 ± 0.01	1.31	0.07 ± 0.004
Average coefficient of data variation				1.24	
Zn					
Novoselytsia	Buckwheat	39.44	41.17 ± 3.58	1.22	2.56 ± 0.07
Novoselytsia	Various herbs	39.44	45.87 ± 2.79	4.54	3.54 ± 0.14
Novoselytsia	Sunflower	54.90	55.42 ± 4.92	0.36	4.14 ± 0.2
Chervone	Buckwheat	35.35	32.08 ± 0.9	2.32	2.56 ± 0.07
Chervone	Various herbs	39.44	40.21 ± 3.89	0.54	2.89 ± 0.22
Chervone	Sunflower	42.90	42.29 ± 3.9	0.44	3.17 ± 0.17
Stebne	Buckwheat	33.00	32.79 ± 3.6	0.15	2.37 ± 0.44
Stebne	Various herbs	40.80	38.75 ± 0.81	1.45	3.0 ± 0.4
Stebne	Sunflower	44.88	41.62 ± 2.24	2.31	3.33 ± 0.02
Average coefficient of data variation				1.48	

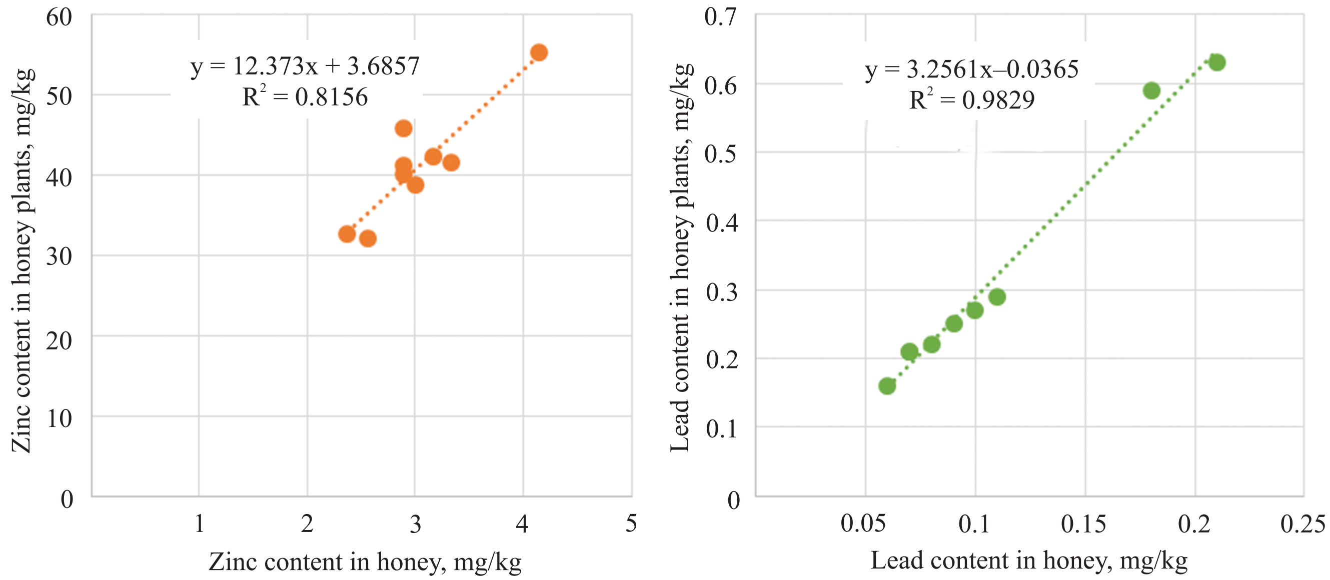

Fig. 1. The correlation relations and the equations of regression between the content of heavy metals in honey plants and honey

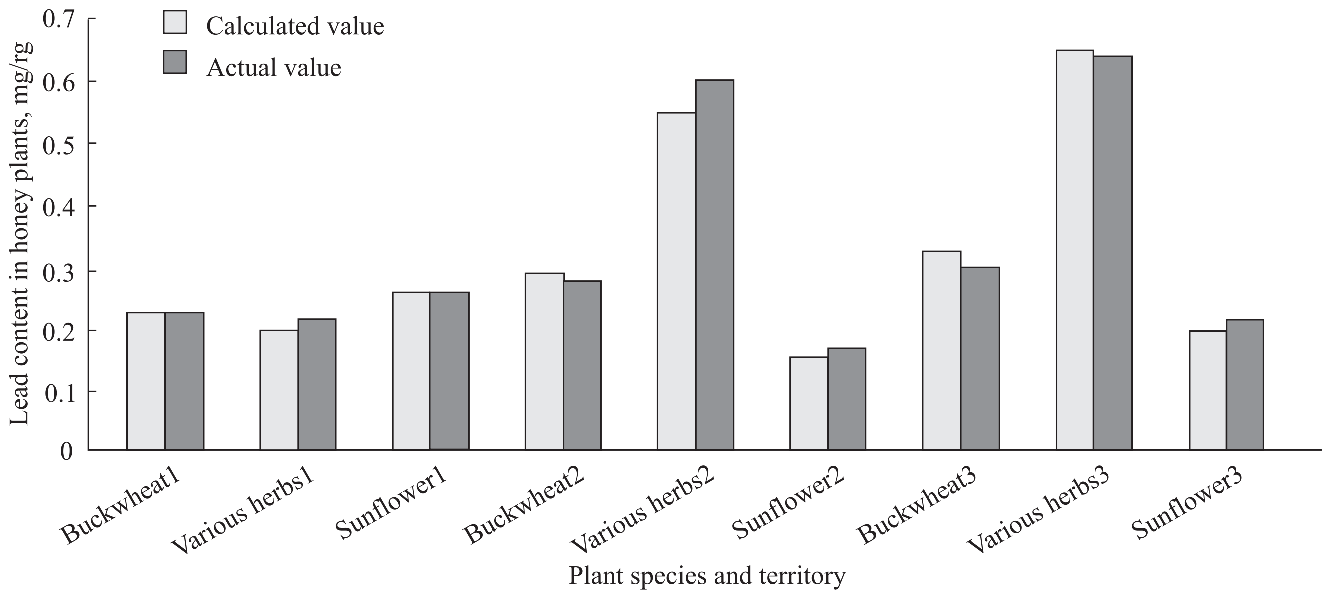

Fig. 2. The difference between the actual and estimated content of lead in melliferous plants, mg/kg (where indicator 1 – Novoselytsia, 2 – Chervone, 3 – Stebne)

variable (X – HM content in honey), respectively. All the coefficients in the equation have a high degree of reliability, since the possibility of the zero-hypothesis $p < 0.05$.

A low and unreliable correlation was noted in the "honey-melliferous plant" chain for cadmium r = = 0.2726, for nickel r = 0.626, for copper r = 0.6207, for cobalt r = 0.2706, for chromium r = 0.1591.

Using the estimated regression equations, we evaluated the content of lead and zinc in melliferous plants and compared them against the actual HM content (**Fig. 2, 3**).

The suggested histograms (Fig. 2, 3) can be used to evaluate the content of heavy metals (lead and zinc) in the "melliferous plants-honey" system. The comparison of the estimated and actual HM content in melliferous plants using the correlation coefficient gives grounds for the assumption that the abovementioned indices do not differ much, which demonstrates the high efficiency of the elaborated statistical models in determining the content of lead and zinc in melliferous plants as compared to their known concentrations in honey.

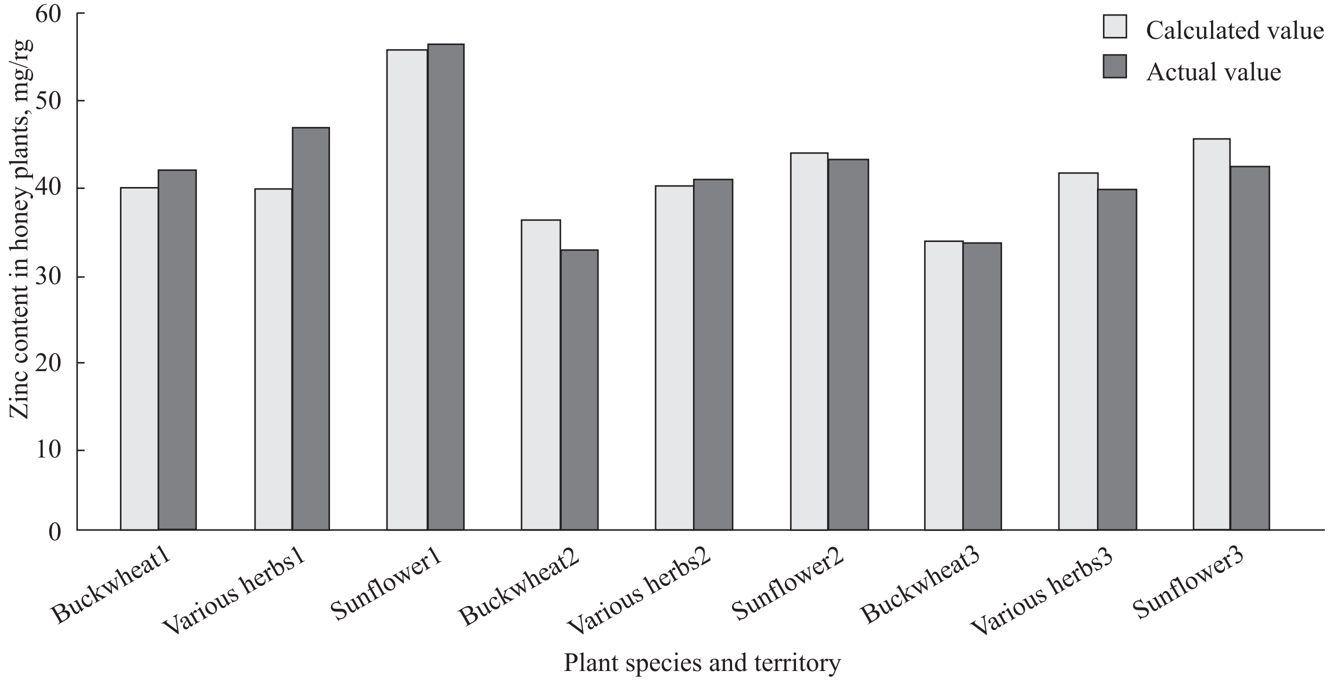

Fig. 3. The difference between the actual and estimated content of zinc in melliferous plants, mg/kg (where indicator 1 – Novoselytsia, 2 – Chervone, 3 – Stebne)

Having the data about the content of heavy metals (Pb, Zn) in honey, we can compare their content in melliferous plants on the territories where military operations took place in 2022–2023.

The second stage of the study on the quantitative composition of the components of the soils-plants-bees-beekeeping products (honey, pollen) was conducted in 2022–2023. The results of the studies demonstrated that the content of the investigated elements (iron, cadmium, copper, nickel, lead, and zinc) was mainly within the maximally allowable values (Dovhopola, 2016). The exception was found in the value of lead content in the samples of soil and melliferous plants (**Table 2**) in territory No. 4 (Sumy region).

Table 2. The average content of heavy metals in the samples of soil and melliferous plants in 2022-2023 (mg/kg) in some territories of Ukraine (M ± s)

No of territory	Fe	Cd	Cu	Ni	Pb	Zn
Soil						
1	1246.76 ± 132.60	0.69 ± 0.11	3.85 ± 0.15	12.52 ± 0.66	13.56 ± 2.49	23.34 ± 1.29
2	1996.62 ± 154.97 *	0.87 ± 0.03	8.58 ± 2.90	35.78 ± 2.42 *	22.53 ± 1.99 *	29.2 ± 5.83
3	1701.72 ± 127.30	0.81 ± 0.06	10.33 ± 2.24 *	14.54 ± 2.30	25.26 ± 2.66 *	82.33 ± 39.6
4	1966.71 ± 75.90 *	0.87 ± 0.03	9.87 ± 3.69	26.73 ± 8.22	37.88 ± 6.21 *	23.01 ± 5.83
5	1459.90 ± 38.20	1.13 ± 0.28	5.92 ± 2.64	22.48 ± 8.50	17.15 ± 1.69	36.66 ± 7.53
MAC	–	1.0	55.0	85.0	30.0	115.0
Melliferous plants						
1	602.68 ± 27.78	0.29 ± 0.09	2.59 ± 0.41	4.28 ± 0.26	5.35 ± 0.24	10.24 ± 0.78
2	767.02 ± 72.53	0.56 ± 0.03 *	5.02 ± 0.23 *	9.31 ± 1.67 *	8.97 ± 0.68 *	17.75 ± 1.26 *
3	686.03 ± 53.38	0.48 ± 0.03 *	5.51 ± 0.21 *	7.27 ± 0.96 *	7.33 ± 0.85	19.54 ± 0.88 *
4	698.68 ± 36.80	0.28 ± 0.11	4.54 ± 0.55 *	7,31 ± 0,38 **	7.05 ± 0.40 *	15.87 ± 1.03 *
5	749.33 ± 78.48	0.47 ± 0.07 *	4.23 ± 1.21	7.77 ± 2.57	6.06 ± 0.23	13.87 ± 0.41 *

Note. $^*p < 0.05$, $^{**}p < 0.01$; 1 – Vinnytsia (control), 2 – Kharkiv, 3 – Mykolayiv, 4 – Sumy, 5 – Chernihiv regions.

The analysis of the HM concentration in soil demonstrated that in the investigated territories 2 and 4, there was a statistically significant difference in the data as compared to the same indices in the control. The lowest indices of iron content were notable for the soils of territory 1. The concentration of cadmium content in soil fluctuated, its highest parameters were notable for territory 5 (1.13 ± 0.28 mg/kg) ($p > 0.05$), which demonstrated the 1.6-fold exceedance of Cd concentration as compared to the control. High values of copper concentration in soil were registered in territory 3 – 10.3 ± 2.24 mg/kg ($p < 0.05$). The minimal concentration of copper as compared to the control was found in soil samples, taken from territory 1 (Vinnytsia region, control).

The exceedance of MAC of the total form of lead (30 mg/kg) was registered in soil samples from territory 4 – 37.88 ± 6.21 mg/kg ($p < 0.05$). The content of lead in territory 3 exceeded that in the control 2.7 times. Thus, the data obtained demonstrate the increased content in soil for such pollutants as iron, cadmium, copper, nickel, and lead as compared to the control and manifest different degrees of soil pollution in the investigated territories.

While evaluating the accumulation of heavy metals in soil, one should consider the concentration of these elements in other investigated objects of the ecosystem. The analysis of the data about melliferous plants, presented in Table 2, yields a conclusion that the content of iron increased 1–1.3 times in all the plant samples as compared to the control, respectively ($p > 0.05$). The highest values for cadmium were found in territory 2 – 0.6 ± 0.034 mg/kg ($p < 0.01$), territory 3 – 0.5 ± 0.034 mg/kg ($p < 0.05$), territory 5 – 0.5 ± 0.067 mg/kg ($p < 0.05$) which exceeded the control values 1.7–2 times.

High values, as compared to the control, were noted for copper content in plants in territory 2 – 5 ± 0.23 mg/kg ($p < 0.01$) and territory 3 – 5.5 ± 0.21 mg/kg ($p<0.01$). Also in the investigated region 2, the concentration of lead in the samples of entomophilous plants, collected on the territories near the apiary, exceeded the control indices 1.7 times ($p \leq 0.01$). The study on the character of the accumulation of heavy metals by plants demonstrated the highest concentrations for such elements as zinc, lead, nickel, and copper.

The data, obtained in five investigated territories of Ukraine, reflect the increased level of concentration of heavy metals in the bodies of bees as compared to the control. The highest concentration values of cadmium were registered in bee samples, collected from the apiaries in territory 2 (Kharkiv region). The level of lead remained high in the samples from Kharkiv and Mykolayiv regions.

The results of the quantitative analysis of metals in the bodies of bees and beekeeping products are presented in **Table 3.**

The results of the studies demonstrated that the highest values of cadmium in the organism of bees were also found in the samples from territory 3 (1.83 ± 0.03 mg/kg), territory 4 (1.63 ± 0.19 mg/kg) and territory 2 (1.62 ± 0.1 mg/kg) which exceeded the control values 3.2–3.6 times ($p < 0.01$). In the samples of bees from territories 2 (12.23 ± 5.86 mg/kg) and 3 (8.89 ± ± 1.58 mg/kg), high copper indices were registered, exceeding the control values 4–5 times ($p < 0.05$).

High values of lead were noted in bee samples from territory 4 – 14.45 ± 0.89 mg/kg, territory 2 – 10.77 ± ± 1.08 mg/kg ($p < 0.01$), where its share was 2.7–3 times higher than in the control (4.94 ± 0.54 mg/kg).

The study of the pollution in bee pollen demonstrated the highest concentrations of heavy metals in territories 2 and 3 (iron, copper, nickel, zinc), and territory 4 (cadmium) as compared to the control. There was a statistically significant increase in the copper content in the pollen samples on territory 3 ($p < 0.01$) and 5 ($p < 0.05$). The increased level of zinc content was noted on the investigated territories 2, 3, 4, and 5.

High concentrations of heavy metals in bees and bee pollen are likely to be impacted by man-made factors, including the explosions of artillery shells, movement of heavy military machinery, and the use of firearms near the investigated apiaries in Kharkiv and Mykolayiv regions.

The analysis of HM concentrations in honey (Table 3) demonstrated that their content in honey samples depended on the district and place of sampling i.e. on the investigated de-occupied territories and the territories near the combat zones (Kharkiv, Mykolayiv, Sumy, and Chernihiv regions) there were higher concentrations of HM as compared to the control. We assume that the pollutants are transferred with dust, and thus get accumulated in soils, melliferous plants, and pollen. High indices of HM content were noted in territories 2, 3, 4. In the honey sample from territory 3, the concentration of iron was 21.1 % higher compared to the control, but Fe indices of territory 3 were minimal among all the samples. It was determined that copper content in honey samples from all

Table 3. The average content of heavy metals in the samples of bees, pollen, and honey (mg/kg) in some territories of Ukraine (M ± s)

No of territory	Fe	Cd	Cu	Ni	Pb	Zn
Bees						
1	840.76 ± 10.69	0.50 ± 0.17	2.40 ± 1.40	0.59 ± 0.20	4.94 ± 0.54	9.21 ± 0.10
2	965.05 ± 55.77	1.63 ± 0.19 **	12.23 ± 5.86	5.69 ± 2.55	10.77 ± 1.08 **	131.69 ± 6.50 **
3	1239.70 ± 126.75 *	1.62 ± 0.10 **	8.89 ± 1.58 *	0.84 ± 0.00	8.27 ± 1.59	94.68 ± 56.55
4	880.04 ± 46.29	1.83 ± 0.03 **	7.37 ± 0.83 *	7.77 ± 0.64 **	14.45 ± 0.89 **	63.01 ± 9.11 **
5	994.74 ± 38.74	0.91 ± 0.16	5.17 ± 0.53	0.78 ± 0.06	9.37 ± 3.02	63.63 ± 13.26 *
Pollen						
1	56.13 ± 5.63	0.07 ± 0.027	0.79 ± 0.36	0.36 ± 0.14	1.39 ± 0.07	5.47 ± 0.003
2	87.54 ± 17.60	0.37 ± 0.003	8.07 ± 2.80	0.73 ± 0.16	1.54 ± 0.04	16.13 ± 4.41 *
3	97.82 ± 7.66 *	0.37 ± 0.003	9.22 ± 1.07 **	0.75 ± 0.06 *	1.55 ± 0.06	17.69 ± 1.96 **
4	72.34 ± 14.90	0.38 ± 0.007	6.89 ± 2.31	0.61 ± 0.034	1.45 ± 0.13	10.99 ± 0.39 **
5	61.54 ± 1.78	0.37 ± 0.003	5.78 ± 1.20 *	0.57 ± 0.02	1.45 ± 0.06	6.09 ± 0.91 **
Honey						
1	6.95 ± 0.74	0.001 ± 0.00	0.11 ± 0.05	0.56 ± 0.28	0.12 ± 0.11	2.36 ± 0.03
2	10.91 ± 1.51	0.01 ± 0.01	1.21 ± 0.51	2.77 ± 1.25	1.13 ± 0.12 **	4.99 ± 0.06 **
3	5.48 ± 0.50	0.01 ± 0.01	1.27 ± 0.03 **	1.74 ± 1.08	0.59 ± 0.04 *	9.25 ± 2.10 *
4	11.76 ± 1.96	0.01 ± 0.01	1.43 ± 0.15 **	1.40 ± 0.10 *	0.77 ± 0.029 *	6.75 ± 1.10 *
5	8.16 ± 0.72	0.02 ± 0.01	0.71 ± 0.30	0.27 ± 0.04	0.20 ± 0.10 **	6.60 ± 0.90 **

Note. * $p < 0.05$, ** $p < 0.01$; 1 – Vinnytsia (*control*), 2 – Kharkiv, 3 – Mykolayiv, 4 – Sumy, 5 – Chernihiv regions.

the investigated territories, except for the control, exceeded the set norm of MAC (0.5 mg/kg) for polyflora honey (Dubin, Vasylenko, 2017). The content of zinc demonstrated high levels as compared to the control in the samples from territories 3 (6.75 ± ± 1.10 mg/kg), and 4 (9.25 ± 2.10 mg/kg).

We assume that while nectar is being processed into honey, due to the physiological specificity of the walls of the honey sac, there is partial filtration of heavy metals, which are transported into the hemolymph and deposited in different anatomic sites of bees because the concentrations of lead, copper, iron, and cadmium in honey are much lower than the concentrations of these metals, determined in bee pollen and bodies.

After the comparison of the calculated and actual content of lead in melliferous plants using the elaborated statistical models of predicting the content of heavy metals in plants depending on their content in honey in the first stage of the studies, we can conclude that this mathematical model is not accurate regarding such metals as lead and zinc.

DISCUSSION

The organism of bees is a leading link in the soils-plants-animals-food products system, which is penetrated by different organic substances and chemical elements, including heavy metals, with pollen, nectar, and water (Tsekhmistrenko et al, 2023). For instance, according to Monchanin et al, 2021, terrestrial invertebrates are especially vulnerable to arsenic, cadmium, lead, and mercury, and most current global standards for the level of these HM are not sufficient to decrease their harmful impact on invertebrates, including honey bees. Having obtained the data about HM content (in soils, plants, bees, honey, and bee pollen) on the investigated territories, we can state that the highest concentrations were notable for such elements as zinc, lead, nickel, and copper. Mobile forms of HM can be transferred to the hive with the polluted dust, settled on the soil, pollen, or directly with bee fibers on the bee body (Gillanders, Ross, 2021) or absorbed when bees consume nectar and water. When analyzing the main output of HM due to the military man-made load (in the air-soil-water system) (**Table 4**), we can note that such

Table 4. Heavy metals, entering the environment due to the military technogenic load (in the air-soil-water system) in terms of types and kinds of applied armament systems (Sploditel et al, 2023)

Types and kinds of applied armament systems	Penetration of heavy metals		
	Air	Water	Soil
Firearms (handguns sniper guns submachine guns light machine guns company machine guns)	Cu, Mn, Al, Mg, Fe C, Pb	Cu, Fe, Al, Mn, Zn, Pb, Sn, Mg	Cu, Fe, Al, Fe, Mn, Zn, Pb, Sn, Mg, Al
Grenade launcher firearms hand grenades automatic (under-barrel) hand-held mounted anti-tank	Cu, Mn, Al, Mg, Fe, Pb	Cu, Fe, Al, Pb, Zn, Hg, Cd, Cr	Cu, Fe, Al, Fe, Mn, Zn, Pb; Sn, Mg, Al, Hg, Cd, Cr
MICV (APC) armament: firearms hand grenades 14.5 mm HMG 73 mm P 30 mm P 14.5 AP	Cu, Mn, Al, Mg, Fe, Pb	Cu, Fe, Al, Pb, Zn, Hg, Cd, Cr	Cu, Fe, Al, Mn, Sn, Mg, Pb, Zn, Hg, Cd, Cr
MICV, APC armament, hand grenades	Cu, Mn, Al, Mg, Fe C, Pb	Cu, Fe, Al, Mn, Sn, Mg, Pb, Zn, Hg, Cd, Cr	Cu, Fe, Al, Mn, Sn, Mg, Pb, Zn, Hg, Cd, Cr
MICV, APC armament, anti-tank missile systems (with simulated electronic launches) hand grenades	Cu, Mn, Al, Mg, Fe C, Pb	–	Cu, Fe, Al, Mn, Sn, Mg, Pb, Hg, Zn, Cd, Cr
Tank armament, SPG armament firearms hand grenades 23 mm VYa 115 mm HMG 125 mm HMG	Cu, Mn, Al, Mg, Fe, Pb	Cu, Fe, Al, Mn, Sn, Mg, Zn, Hg, Pb, Cd, Cr	Cu, Fe, Mn, Sn, Mg, Pb, Zn, Hg, Cd, Cr
Tank armament anti-aircraft machine gun hand grenades	Cu, Mn, Al, Mg, Fe, Pb	–	Cu, Fe, Al, Mn, Sn, Mg, Hg, Pb, Zn, Cd, Cr
Cannon artillery, artillery mortars 76 mm P ZiS-3; 85 mm P D-44; 100 mm ATM MT-12; 122 mm GD-30; 152 mm PG D-20; 152 mm SG 2S5; 152 mm SG 2CS19; 203.2 mm P 2S7 82 mm BM-38, 2B9; 120 mm PM; 120 mm M 2S9, 2S12; 240 mm M2S4	Cu, Mn, Al, Mg, Fe, Pb	Cu, Fe, Al, Mn, Sn, Mg, Zn, Hg, Pb, Cd, Cr	Cu, Fe, Al, Mn, Sn, Mg, Pb, Zn, Hg, Cd, Cr
Cannon artillery anti-tank missile systems, anti-tank artillery, battle firing of field artillery –//–, 9K111 9K113 9K149	Cu, Mn, Al, Mg, Fe, Pb	Cu, Fe, Al, Mn, Sn, Mg, Pb, Hg, Zn, Cd, Cr	Cu, Fe, Al, Mn, Sn, Mg, Pb, Hg, Zn, Cd, Cr
Shooting artillery rounds	Cu, Mn, Al, Mg, Fe, Pb		Cu, Fe, Al, Cd, Pb, Zn, Cr, Mn, Mg, Hg
Movement of self-propelled artillery weapons and anti-aircraft mounts, MICV, wheeled, tracked APC	–	Pb	Pb
Movement of engineering machinery and vehicles	Pb	–	Pb
Movement of vehicles, tracked towing vehicles and crawler-transporters	Pb	Pb	Pb

HM as lead and copper penetrate the environment in the highest amounts when all the armament systems, presented in the Table, are used. We conducted the studies in the territories, impacted by active combat (Kharkiv, Sumy, Mykolayiv, and Chernihiv regions). The increased level of HM (lead, cadmium, and copper) on these territories as compared to the control (Vinnytsia region) is caused by the transfer and accumulation of toxicants in natural objects.

The prediction of the migration of pollutants in the soil cover is complicated because the soil is a complex colloid-disperse system with the accumulation of pollutants and their redistribution under the impact of military and technogenic factors with further migration along trophic chains (soil – plant – bee – beekeeping product – human) (Kumar, 2022). After combustible substances and heavy metals penetrate the soil, their transmission by food chains is impacted by both abiotic and biotic factors. Some publications demonstrate the accumulation of potentially toxic levels of Pb, Cu, and Ni in forage crops, growing on the territories of former shooting ranges in Switzerland (Robinson, 2008).

According to the research of Roman, 2010, the content of macro- and microelements in the organism of bees varied within a wide range and depended on several factors, including types of soils and nectar-bearing plants, methods of beekeeping and the physiological state and health condition of bees (Roman, 2010). We assume that the statistical model of predicting the HM content in plants, depending on their content in honey, presented by us, was found ineffective due to different ecologic and climatic conditions of the investigated territories. According to Lambert et al (2012), weather conditions impact the content of metals in the organisms of bees and beekeeping products, dry weather and higher temperatures cause an increase in the accumulation of heavy metals. Our study was conducted in 2022–2023 when drought weather conditions and higher temperatures were noted, especially in summer period of active honey collection (https://ecoaction.org.ua/).

A close correlation between the accumulation of metals in soil and plants and the HM content in the samples of honey bees and beekeeping products was observed in the study of Adeoye in 2021. The author did not present any mathematical model but highlighted that honey bees and honey were good potential bioindicators of environmental pollution with heavy metals. The study also showed a common source of HM (air, soil, plants, or water) in the environment (Adeoye, 2021).

The prediction models for HM transformation (cadmium, lead, zinc, and copper) in the organism of animals and into animal products (milk) were elaborated by Boltyk N.P. in 2014 for the study on the qualitative composition of food chain components: soil – water – plant – animal – animal product (milk). According to the author's opinion, the elaborated monitoring models ensure reliable prediction of the amount of HM in fodder and animal products based on the indices of HM content in soil (Boltyk, 2014). We did not find the mathematical models for the soil-plants-bees-beekeeping products system in the scientific literature, which we studied, the scientists mainly estimated the transition coefficients and the concentration coefficients for the elements (Postoienko, Halenko, 2007; Adeoye et al, 2021). In the study of Postoienko, Halenko 2007, the estimation of transition coefficients (C_t) for HM in the consecutive chain of "soil-melliferous plant-honey" was conducted in several stages: stage 1 – "soil–melliferous plant" system; stage 2 – "melliferous plants–honey" system; stage 3 – "soil–honey" system. The transition coefficient in the "soil-plant" system is a share of the HM content in plants in the amount of HM in soils, etc. (Postoienko, Halenko, 2007). The authors concluded that the indices of C_t of HM can be used to predict the limits of pollution with the toxicants of a specific area, reliably within the distance of 7 sq.km. that can be covered by a bee during honey collection (Brovarskyi et al, 2017). If the HM concentration in honey samples from the investigated territory does not exceed MAC, it may be assumed that the content of toxicants in this territory is within limits, not exceeding the normative indices of the concentration of toxicants. Therefore, the use of the estimated coefficients ensures the prediction of the pollution by toxicants in a specific area and provides for preliminary prediction of the state of territories in terms of HM pollution, for instance, for the safe location of apiaries (Postoienko, Halenko, 2007).

The coefficient of metal concentration is a share (similar to the transition coefficient), transformed into a percentage value (Adeoye et al, 2021). According to the data of Auxiliadora Soriano and Fereres (2003), the coefficient of metal concentration for Cd and Zn in plants and soils was considerably higher and depended on the type of soil and pH.

Taking into account the differences in ecologic and climatic conditions and the possible impact of numerous factors on the content and migration of HM in the soils–melliferous plants–bees–beekeeping products, it would be reasonable to have actual parameters of the HM content in the samples for each investigated territory and to take the relevant management conclusions based on them.

It would be reasonable for further studies to pay attention to the synergic impact of HM in the soils-melliferous plants-bees-beekeeping products system and the organism of bees, and to conduct detailed investigations on the immunological response of bees to sublethal doses because, in the opinion of Jensen and Trumble 2003, the simultaneous uptake of several HM may have the additive or synergic effect (Jensen, Trumble, 2003). It could be especially urgent to study the synergic effect of pesticides and HM on the organism of bees and the transfer of pollution into beekeeping products (Desneux et al, 2007; Alaux et al, 2010; Klein et al, 2017).

CONCLUSIONS

In soils of all the investigated territories (Kharkiv, Mykolayiv, Sumy, and Chernihiv regions), there was an increased level of heavy metals Fe, Cd, Cu, Ni, Pb, Zn, as compared to the control (Vinnytsia region). For instance, the concentration of cadmium in the territory of Chernihiv region (1.13 ± 0.28 mg/kg) exceeded MAC (1.0 mg/kg). The concentration of lead in all the investigated territories did not exceed MAC (55.0 mg/kg). The exceedance in MAC of the total form of lead (30 mg/kg) was registered in soil samples in Sumy region – 37.88 ± 6.21 mg/kg. The content of lead in Mykolayiv region exceeded that in the control 2.7 times.

The content of iron in melliferous plants increased in all plant samples as compared to the control, 1–1.3 times respectively ($p > 0.05$). The highest values for cadmium content were found in Kharkiv region – 0.6 ± ± 0.034 mg/kg, Mykolayiv region – 0.5 ± 0.034 mg/kg, Chernihiv region – 0.5 ± 0.067 mg/kg, which exceeded the control values 1.7–2 times. High values were determined for a share of copper in plants as compared to the control in Kharkiv region – 5 ± 0.23 mg/kg and Mykolayiv region – 5.5 ± 0.21 mg/kg. Also, in Kharkiv region, the concentration of lead in the samples of entomophilous plants, collected in the territories near the apiary, exceeded the control indices 1.7 times.

The data, obtained in five investigated territories of Ukraine, reflect the increased level of concentration of heavy metals in the bodies of bees as compared to the control. The highest concentration values of cadmium were registered in bee samples, collected from the apiary in the Sumy region (1.83 ± 0.03 mg/kg), and in the control – 0.50 ± 0.17 mg/kg. The content of lead was high in the samples from Kharkiv (10.77 ± 1.08 mg/kg) and Sumy (14.45 ± 0.89 mg/kg) regions; in the control the lead content was 4.94 ± 0.54 mg/kg.

The study of the bee pollen pollution demonstrated the highest concentrations of heavy metals in the territories of Kharkiv and Mykolayiv regions (iron, copper, nickel, zinc), Sumy region (cadmium) as compared to the control. The highest copper content was found in the pollen samples from Mykolayiv region 9.22 ± ± 1.07 mg/kg (control – 0.79 ± 0.36 mg/kg). The increased level of zinc content as compared to the control (5.47 ± 0.003 mg/kg) was registered in Kharkiv region (16.13 ± 4.41 mg/kg) and Mykolayiv region (17.69 ± ± 1.96 mg/kg).

The analysis of HM concentrations in honey samples demonstrated that in Kharkiv region there was an exceedance of MAC (1.0 mg/kg) of lead – 1.13 ± ± 0.12 mg/kg. The exceedance of MAC for copper in honey samples (0.5 mg/kg) was noted for all the investigated territories except for the control (0.11 ± ± 0.05 mg/kg). The exceedance of MAC for zinc in honey samples (5.0 mg/kg) was registered in Mykolayiv region (9.25 ± 2.10 mg/kg), Sumy region (6.75 ± ± 1.10 mg/kg) and Chernihiv region (6.60 ± 0.90 mg/kg).

Adherence to ethical principles. All the experimental results, presented in this article, were obtained without the use of any animals.

Conflict of interests. The authors declare the absence of any conflicts of interests.

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Моніторинг вмісту та міграції важких металів у системі грунти–рослини-медоноси–бджоли–продукти бджільництва у біоценозах зон бойових дій

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Мета. Опрацювати методичні підходи щодо моніторингу вмісту та міграції важких металів у системі ґрунти–рослини-медоноси–бджоли–продукти бджільництва в 2022–2023 рр. задля екологічної оцінки біоценозів територій, що зазнали впливу бойових дій. **Методи.** Перший етап досліджень полягав у встановленні вмісту цинку та свинцю у рослинах-медоносах (суцвіття гречки, соняшнику та різнотрав’я) та медах з трьох територій у Черкаській області. Другий етап досліджень охоплював пасіки: ННЦ “Інститут бджільництва імені П. І. Прокоповича” (розташовані в с. Яришів, Могилів-Подільського р-ну, Вінницької обл.); пасіках, розташованих на деокупованих територіях: Харківська обл., Чугуївський р-н, с. Шестакове та Чернігівська обл., Новгород-Сіверський р-н; пасіках, що розташовані на територіях, поблизу проведення бойових дій Миколаївська обл., Баштанський р-н, с. Новоолександрівка та Сумська обл., м. Лебедин. Відбір матриць на визначення рухомих форм вмісту важких металів (ВМ) (ґрунт, рослини, обніжжя, бджоли та мед) проводився на 5 пасіках протягом 2022–2023 рр. триразово (травень, липень і серпень). Відібрано 30 зразків ґрунту, 30 проб рослин, по 90 проб пилку, бджіл та меду. Проби ґрунту відбирали методом конверту з глибини 0–20 см. У медоносних рослин (змішаний зразок різнотрав'я) на дослідження рухомих форм вмісту ВМ відбиралася надземна частина. Живі бджоли відбиралися з трьох вуликів кожної пасіки з льотків (по 30–35 бджіл з кожного) у банки. До аналізу бджоли зберігалися у морозильній камері при температурі – 20 °C (Gutiérrez et al, 2015). Збір квіткового пилку на досліджуваних пасіках здійснювався за допомогою навісного пилковловлювача. Проби меду відбиралися із рамок, мед відокремлювався фільтруванням через марлю. Нами було проведено кількісний аналіз вмісту та накопичення рухомих форм ВМ (Fe, Cd, Cu, Ni, Pb, Zn) у ґрунті, рослинах-медоносах, бджолах, бджолиному обніжжі та меді. Підготовка проб виконувалася методом сухої мінералізації. Вміст рухомих форм важких металів (заліза, кадмію, міді, нікелю, свинцю та цинку) визначали методом атомно адсорбційної спектрофотометрії. **Результати.** На першому етапі дослідження визначено вміст рухомих форм важких металів (Pb, Zn) у рослинах та медах для території Черкаської області (Правобережного Лісостепу). На основі отриманих даних хімічних досліджень з використанням методу кореляційно-регресійного аналізу розроблено статистичні моделі прогнозування вмісту важких металів у рослинах, залежно від їх вмісту в меді. На другому етапі дослідження визначено вміст рухомих форм важких металів (Fe, Cd, Cu, Ni, Pb, Zn) у ґрунті, рослинах-медоносах, бджолах, бджолиному обніжжі та медах у біоценозах зони, що зазнали впливу бойових дій. **Висновки.** У ґрунтах усіх досліджуваних територій (Харківська, Миколаївська, Сумська та Чернігівська області) встановлено підвищений рівень важких металів Fe, Cd, Cu, Ni, Pb, Zn, щодо контролю (Вінницька обл.). Зокрема концентрація кадмію на території Чернігівської обл. (1,13 ± 0,28 мг/кг) перевищувала ГДК (1,0 мг/кг). Концентрація свинцю на всіх досліджуваних територіях не перевищувала ГДК (55,0 мг/кг). Перевищення ГДК рухомої форми свинцю (30 мг/кг) зафіксовано у пробах ґрунту Сумської обл. – 37,88 ± ± 6,21 мг/кг. Вміст свинцю у Миколаївській обл. у 2,7 раз перевищувала вміст свинцю щодо контролю. Вміст заліза у медоносних рослинах зростав у всіх пробах рослин щодо контролю, відповідно в 1–1,3 рази ($p > 0,05$). Найбільші значення вмісту кадмію виявлено у Харківській обл. – 0,6 ± 0,034 мг/кг, Миколаївській обл. – 0,5 ± 0,034 мг/кг, Чернігівській обл. – 0,5 ± 0,067 мг/кг, що у 1,7–2 рази перевищували контрольні показники. Високих значень досягає вміст міді в рослинах щодо контролю у Харківській обл. – 5 ± 0,23 мг/кг та Миколаївській обл. – 5,5 ± 0,21 мг/кг. Також, у Харківській досліджуваній області концентрація свинцю в зразках ентомофільних рослин, зібраних на територіях біля пасіки в 1,7 раз перевищила контрольні показники. Отримані дані щодо п'яти досліджуваних територій України відображають підвищений рівень концентрації важких металів у тілах бджіл порівняно з контролем. Найбільш високі значення досягала концентрація кадмію у зразках бджіл, узятих з пасіки Сумської області (1,83 ± 0,03 мг/кг), у контролі – 0,50 ± 0,17мг/кг. Вміст свинцю був високим у пробах з Харківської (10,77 ± 1,08 мг/кг) та Сумської (14,45 ± 0,89 мг/кг) областей, на контролі вміст свинцю становив 4,94 ± 0,54 мг/кг. Дослідження накопичення важких металів у обніжжі бджолиному показало, що найбільші концентрації важких металів – на територіях Харківській та Миколаївській обл. (залізо, мідь, нікель, цинк), Сумській обл. (кадмій) щодо контролю. Найвищим був вміст міді у зразках обніжжя Миколаївської обл. 9,22 ± 1,07 мг/кг (контроль 0,79 ± 0,36 мг/кг). Підвищений рівень вмісту цинку щодо контролю (5,47 ± 0,003 мг/кг) фіксували у Харківській обл. (16,13 ± 4,41 мг/кг) та Миколаївській обл. (17,69 ± 1,96 мг/кг). Аналіз концентрацій рухомих форм важких металів в медах показує, що для Харківської обл. спостерігається перевищення ГДК (1,0 мг/кг) свинцю 1,13 ± 0,12 мг/кг. Перевищення ГДК для міді в медах (0,5 мг/кг) відмічено для всіх досліджуваних територій, окрім контролю (0,11 ± ± 0,05 мг/кг). Перевищення ГДК для цинку в медах (5,0 мг/кг) відмічено у Миколаївській обл. (9,25 ± ± 2,10 мг/кг), Сумській обл. (6,75 ± 1,10 мг/кг) та Чернігівській обл. (6,60 ± 0,90 мг/кг). Зважаючи на відмінність еколого-кліматичних умов і можливий вплив багатьох факторів на вміст та міграцію важких металів у системі ґрунти–рослини-медоноси–бджоли–продукти бджільництва, для кожної досліджуваної території необхідно мати фактичні параметри вмісту важких металів у зразках та робити з цього управлінські висновки.

Ключові слова: важкі метали; біомоніторинг; Apis mellifera; біоіндикатори; продукти бджільництва.

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