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LEAD AND CADMIUM TRANSITION IN SOIL – PLANT – HONEY SYSTEM

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Abstract. The quality of honey selected from apiaries located in the Vinnytsia region of the central part of Ukraine was assessed by the concentration of lead and cadmium. The study was conducted in different ecological zones. To determine the parameters of the transition of cadmium and lead into honey, samples of soil, plant generative organs and honey were taken. It was found that the content of heavy metals in honey depended on the floristic composition and flowering period of honey plants from which bees collected nectar, the location of honeybees and the concentration of heavy metals in the soil. The content of lead and cadmium was much lower than the maximum permissible concentrations. In spring honey plants, there is less accumulation of lead than in summer plants. The level of lead transfer from soil to honey plants was 2.2-2.6%, and from plants to honey – 3.7-7.4%. The transition of cadmium from soil to plants – 60-84.6%, and from plants to honey – from 2.6 to 8.8% is revealed. The content of lead and cadmium in honey reduced to a straight line distance from the source of increased environmental load. The level of concentration of lead and cadmium in the studied samples of honey does not exceed the permissible safety standards.

Key words: Bee plants; Soil; Lead; Cadmium; Translocation; Honey.

INTRODUCTION

The modern beekeeping is an important sector of agriculture. Ukraine is among the five countries that are the largest producers and exporters of honey (Skoromna, O., Razanova, O. 2019).

The honeybees have become an important element in maintaining multilateral relations in the animal and plant world and increases the value of bees as a living indicator of the environment (Kyrianova, L., Ulanova, T. 2001).

Today, the priority of quality in evaluating food products is their environmental friendliness (Razanova, O. 2018; Razanov, S. et al. 2019; Podolian, J. 2017; Xun, E. et al. 2018). In many countries around the world, an increasing attention is paid to the production of environmentally friendly products, including bee products.

It is possible to achieve high indicators in the production of beekeeping only because of peculiarities of the biology and ecology of bees. The environmental pollution implies the possibility of its impact on bees and beekeeping products, which leads to the need to study their toxic elements. It is known that environmental pollution with heavy metals leads to pose a serious threat to ecosystems and human health. Particularly dangerous are heavy metals that exhibit high toxicity in small quantities, including lead and cadmium. These substances, which are part of the emissions of industrial enterprises and road transport, fall into the nest of bees when they collect nectar. The entry of various types of anthropogenic pollution into the atmospheric air creates a high probability of toxic elements entering bee products during the active period of bee life (Paraniak, R. et al. 2007; Mudrak, O. et al. 2018; Razanov, S. et al. 2018). The bees are part of biogeocenosis, so they are influenced by a set of environmental factors. One of the factors of anthropogenic contamination of bee products is the heavy metals input from the environment. The plants growing in heavy-metal-rich soils can accumulate metals into their nectar (Xun, E. et al. 2018).

When producing organic beekeeping products, it is extremely important to place apiaries correctly. Quite often, apiaries are located near highways, despite the active contamination of vegetation with heavy metals that enter the bee products through the trophic chain. The requirements for organic beekeeping include not only compliance with environmental standards of product purity, but also issues of regulatory assessment and environmental protection according to established standards. The honeybees and the quality of their products are bioindicators of the ecological state of the environment and the results of the analysis can provide a wide range of ecological characteristics of its state (Burmystrova, L. et al. 2008; Kyrianova, L., Ulanova, T. 2001).

The beekeeping holds a special place among food products as well as medicines. Particularly valuable is that beekeeping products are natural means of combating diseases that have virtually no side, adverse effects on human health (Kutsak, R. 2015). Therefore, the bee products should not contain harmful impurities.

The quality of bee products depends on many conditions, including the environmental status of the environment. The contamination of fodder by heavy metals leads to the accumulation of these substances in bee products. The migration of harmful substances occurs along with the chain soil – plant – bee products – man (Herrero-Latorre, C. et al. 2017; Butt, A. et al. 2018; Xun, E. et al. 2018). The heavy metals enter the soil with precipitation, mineral fertilizers and toxic chemicals, with emissions from industrial enterprises, exhaust gases of road transport, waste from livestock farms (Bahlei, O. 2013).

With long-term cadmium and lead intake and their slow removal from the soil, the concentration of these heavy metals can be very high over time. From the soil, plants are nourished with the help of minerals, which contain heavy metals. On the surface of the plants, they can accumulate from the air, settling on leaves and flowers. Bees collect nectar from such plants and thus increase the concentration of heavy metals in honey (Bahlei, O. 2013). As a result of increasing the intensity of heavy metals accumulation in the trophic chains, the risk of their entry into the organism of the bee and, consequently, to their products is increased.

The content of heavy metals in the vegetative organs of plants differs depending on the region and place of cultivation, the time of year, and in beekeeping products – the floristic composition of melliferous vegetation, the age of the honeycomb (Brovarskyi, V. et al. 2016; Kovalchuk, I., Fedoruk, R. 2013).

The purpose of this study was to conduct apoindication of different regions of Vinnytsia region central Ukraine by assessing the quality of honey for lead and cadmium content.

MATERIALS AND METHODS

The objects of study were the territories of three apiaries located in the Vinnytsia region and samples soil, generative organs of plants, honey that were selected from these apiaries. The study was conducted in the spring-summer period 2019 year with the placement of apiaries in the agro-ecological conditions of Vinnytsia region central Ukraine with the different anthropogenic load on the environment. The research was conducted in different ecological zones of Vinnytsia region. The control was ecologically clean territory, in which moderate traffic was observed and there were no industrial enterprises. The researchers investigated the ecologically polluted areas of the apiary, which were located at a distance of 1 km (2-experimental) and 40 km (3-experimental) from the industrial center, as a zone of intensive technogenic pollution.

The environmental conditions and honey conditions in them are different. The apiary of the 2-experimental group is located in the botanical garden of Vinnytsia National Agrarian University near a high-traffic road. Honey collection in this apiary is weak, in spring, there is an increased release of nectar by plants. The main honey plants are willows of different species, medicinal dandelion, creeping clover, acacia and linden.

Apiary company»Agroetalon» i the village of Vasylivka, Tyvriv district (3-experimental) is on the edge of the array of garden plots. There are no industrial facilities in the apiary. The motorway is nearby. The most important honey plants are various garden trees, clover creeping, dandelion, sunflower. Private apiary (1-control) is located on the edge of Vasylivka village. There is no industrial production near the apiary, there is no traffic. The main collection of honey will arrive in May-June. The most important way to get honey from honey plants is white acacia, lime, sunflower. The area where this apiary is located has the largest honey harvest compared to the other two experimental apiaries.

Honey sampling was carried out according to the requirements of DSTU 4497: 2005. Sampling of honey was carried out during honey collection (May-October). A spot sample was taken from each container of honey by immersing a tubular sampler with a diameter of 10-12 mm along the vertical axis along the entire length of the working volume. The combined sample was grouped from spot samples, mixed well and then isolated an average sample weighing at least 500 g. The latter was divided into two parts weighing at least 200 g, placed in two clean dry glass jars, tightly closed and sealed. One jar was transferred to the laboratory for analysis, the other - stored until the end of acceptance in case of re-analysis. Average honey samples were taken in proportion to the amount of pumped honey from light shop honeycombs. Sampling of honey was performed in three repetitions. The content of lead and cadmium in the experimental samples was evaluated by atomic absorption spectrophotometry on the atomic absorption spectrophotometer.

A sampling of soil was carried out by the method of the average sample to the depth of the root layer of soil (up to 25 cm) (Marchuk, I., Savchuk, A. 2008). Plant samples of generative organs were taken from an average sample in the flowering phase (Brovarskyi, V. et al. 2017).

RESULTS AND DISCUSSION

Since for many consumers an important criterion for choosing products is quality and safety, the state standards for any raw materials in the production of food and finished products specify criteria for compliance with various parameters. Bee honey is distinguished by its organoleptic and physico-chemical qualities. Council Directive 2001/110/EC as regards honey lays down the basic provisions for the requirements to be met by honey within the EU internal market. As for the requirements for honey quality indicators, the research of Estonian honey shows that all analyzed honeys comply with European legislation in all respects (Kirs, E. et al. 2011).

An assessment of the area's honey resources indicates that several plant species can be identified that play the most important role in honey harvesting in apiaries. These are different types of willow trees, medicinal dandelion, fruit and berry honey plants of the garden, clover. These types of plants are characterized by abundant and stable nectar release, widespread distribution and, most importantly, occupy large areas.

In the course of research, it was found that the content of heavy metals (lead and cadmium) in the soils of the studied apiaries varied. The most contaminated with lead was the apiary soil of Vinnytsia National Agrarian University (2-experimental) – 2,032 mg/kg, compared to a similar sample of private apiary (1-control) at 0,823 mg/kg[1] less, agricultural apiaries (3- experimental) by 0.712 mg/kg less. This is natural since the apiary of the 2-pilot group is near the highway and the industrial centre. Accordingly, the lowest level of lead in the soil (1,209 mg/kg) was found in a private apiary (2-experimental group), located at a considerable distance from large motorways and the industrial centre. The lead content of the soil in all three samples was significantly lower than the maximum permissible concentration (0.6 mg/kg) (Table 1).

Table 1. *Lead concentration in soil and melliferous vegetation, mg/kg*

Investigated material	Group		
	1-control	2-experimental	3-experimental
Soil	1.209	2.032	1.320
The maximum permissible concentration	6.0		
Spring honey plants	0.021 ± 0.0013	0.041 + 0.0018	0.027 ± 0.0089
Summer honey plants	0.032 ± 0.0025	0.064 ± 0.0077	0.042 + 0.0056
Plants (average)	0.027 ± 0.0021	0.053 ± 0.0054	0.035 ± 0.0072
Transition level from soil into plants, %	2.2	2.6	2.5

Lead contamination of soil directly affected its concentration in plants. Accordingly, the maximum concentration of lead in honey plants was also determined in the apiary located in Vinnytsia.

In spring plants, there is less accumulation of lead than in flowering plants in summer. Thus, the average concentration of lead in the spring honey plants of the control group was 0.021 mg/kg, and in the elderly – 0.032 mg/kg, which is 0.011 mg/kg, or 34.3% less. In the samples of the experimental groups, the concentration was significantly higher honey plants of the summer flowering period, in particular, higher in the second group – by 0.023 mg/kg, or by 56.1%, the third – by 0.015 mg/kg, or 55.5%. Lead content in plants of the spring flowering period was the lowest in the control group compared to the second and third experimental groups by 0.02 mg/kg or 1.9 times by 0.06 mg/kg, or 22.2%. A similar increase in lead concentrations in plants of the summer flowering period was observed in the apiaries of the study groups, namely, 0.032 mg/kg, or 2 times in the second group and 0.01 mg/kg, or 1.2 times.

The honey plants on average in the apiary of the second experimental group contained more than 0.053 mg/kg of lead, which is higher than the apiary of the first group by 0.026 mg/kg, or 1.9 times and the apiaries of the farm (3 experimental group) by 0.016 mg/kg, or 1.4 times.

The lead is not a biogenic metal and is not used by plants for nutrition. The table shows that the level of lead transfer from soil to plants is negligible – 2.2–2.6%. The level of lead transfer from soil to melliferous plants was highest in the apiary near the highway and industrial center (2.6). In the apiaries of the Tyvriv district this indicator was lower than the highest by 0.1 and 0.4%.

Lead enters the leaves, flowers and nectar of plants through the air. It should be noted that the most wild honey plants are evenly distributed within the bee flight radius, planting tree gardens in the immediate vicinity of the roads. Dandelion also grows on the roadside. This can be explained by the increased lead content in the flowers of spring honey plants in the apiaries of the study groups.

Analyzing the concentration of lead in the honey obtained from the apiaries studied, we can conclude that its level of concentration did not exceed the established standards. Of the six honey samples examined, only one did not contain lead. It was honey from spring plants from a private apiary of the control group, where the contamination of soil and melliferous plants was less than on the other two apiaries. The level of contamination of honey samples from the apiaries of the second and third lead groups was insignificant (Table 2).

Table 2. *The lead concentration in honey and parameters of its transition in the soil – honey plants chain –honey, mg/kg*

Investigated material	Group		
	1-control	2-experimental	3-experimental
Honey (pumping 15.06)	Not found	0.0034	0.0018
Honey (pumping 15.08)	0.0012	0.0045	0.0021
Honey, on average	0.0012	0.0039	0.0019
MPC in honey	1.0		
Plants, on average	0.032 ± 0,0021	0.053 ± 0.0054	0.035 ± 0.0072
Transition level from soil to plants, %	2.2	2.6	2.5
Transition level from plants to honey, %	3.7	7.4	5.6

The lead concentration in summer honey from the apiary near the highway was 32.4% higher than in the spring, and from the apiary of the farm of the third experimental group – by 16.7%. However, in both groups these values are well below the maximum allowable concentration for lead (1.0 mg/kg).

The level of transition of the studied metal from honey plants to honey was 7.4, which is significantly higher than from soil to plants – by 4.8, according to the data in the second group. In the third group, this level of transition to honey was 5.6, which is 3.1 more than in plants. In the first control group, the level of lead transfer from honey plants flowering in summer to honey was the lowest, up to 3.7%.

Thus, the content of lead in honey is significantly influenced by its concentration in soil and honey plants. But an important factor is the proximity of the apiary to highways and industrial facilities. In the apiary, where melliferous plants grow far from highways, the lead content in honey will be less. The risk of producing honey containing lead exists in the apiaries where arrays of melliferous plants are located adjacent to highways.

The content of cadmium in soils in the apiaries studied was on average 0.053 mg/kg, which is several times lower than the maximum permissible concentration (0.7 mg/kg) (Table 3).

Table 3. *Cadmium concentration in soil and melliferous vegetation, mg/kg*

Investigated material	Group		
	1-control	2-experimental	3-experimental
Soil	0.035	0.039	0.068
The maximum permissible concentration	0.7		
Spring honey plants	0.003±0.0001	0.005±0.0001	0.017±0.001
Summer honey plants	0.038±0.0001	0.061±0.0003	0.069±0.002
Plants (average)	0.021±0.0001	0.033±0.0002	0.043±0.015
Transition level from soil into plants, %	60.0	84.6	63.2

Although according to a number of apiary parameters, Agroetalon company is located in an ecologically safe area, but the cadmium content in the soil was highest – 0.068 mg/kg. At the same time, the cadmium content in the soil of the apiary of the control and second experimental groups was low. The level of cadmium in the soil of the third experimental group was higher than in the control group, namely, by 0.033 mg/kg, or 1.9 times and by 0.029 mg/kg, or 1.7 times against the private apiary in Vasylivka (2 experimental).

Cadmium, like lead, is not a biogenic metal and is not used by plants as a nutrient. Therefore, the most important thing is getting cadmium into honey plants through the air, penetrating the flowers.

The increased level of cadmium in soils affected its content in plants. In spring in honey plants, the level of cadmium was the lowest in the apiary samples of the control group (0.003 mg/kg), compared to the indicators of the second and third apiaries less by 0.002 mg/kg, or 40.0% and 0.014 mg/kg, respectively, or 82, 4%.

In summer in honey plants, the level of cadmium was the lowest in the samples of private apiary in Vasylivka (0.038 mg/kg), less than the indexes of the training apiaries of the second and third groups by 0.023 and 0.031 mg/kg, or by 37.7 and 11.6% respectively.

There is a difference between the accumulation of cadmium in spring and summer honey plants. Comparing cadmium concentrations in summer and spring honey plants, the latter was lower.

The active transition of cadmium from soil to plants is revealed. The average level of transition was 60.0–84.6%, which is significantly higher than the same indicator for lead. The level of transition of cadmium into melliferous plants in the apiaries of the control and the second experimental group was approximately the same.

Table 4. *Concentration of cadmium in honey and parameters of its transition (soil – honey plants – honey), mg/kg*

Investigated material	Group		
	1-control	2-experimental	3-experimental
Honey (pumping 15.06)	Not found	0.002	0.003
Honey (pumping 15.08)	0.001	0.0024	0.0045
Honey, on average	0.001	0.0022	0.0038
MPC in honey	0.05		
Plants, on average	0.038±0,0013	0.033±0.0024	0.043±0.0151
Transition level from soil to plants, %	60.0	84.6	63.2
Transition level from plants to honey, %	2.6	6.6	8.8

In the study of 6 honey samples, cadmium was not detected in only one of them – from the apiary of a private apiary in Vasylivka. The content of cadmium in plants influenced its concentration in honey. However, the level of transition of cadmium from plants to honey was small – 2.6–8.8%. In the private apiary, the level of transition was the lowest – 2.6% (in honey from summer honey plants), near the motorway – 6.6%, and the level of transition in the apiary of the company Agroetalon – 8.8%. The highest concentration of cadmium was found in the honey of summer pumping from the apiary of the third experimental group – 0.0045 mg/kg, which is 9.0% of the maximum allowable concentration. Compared with the data of the second experimental group in the third group, they were higher by 0.0023 mg/kg, or 2-fold. Cadmium was found the most in the honey spring pumping from the apiary of the village Vasylivka is 0.003 mg/kg, but this indicator is also much lower than the MPC.

We would like to note that the samples of honey comply with international regulatory standards for its quality indicators. The obtained results will be used for further formation of the database of honey quality indicators and assessment of data stability over time.

CONCLUSIONS

Summarizing the results obtained, it can be concluded that the content of lead and cadmium in honey depends on the composition of honey plants and their flowering period, as well as on the content of heavy metals in the soil. There is also a difference between the accumulation of heavy metals by spring and summer melliferous plants, and a correlation is found between its content in honey and flowering melliferous plants.

The content of cadmium and lead in honey does not exceed the maximum permissible levels regulated by the requirements of the standard. The content of lead in the experimental samples is in the range from 0.0012 to 0.0045 mg / kg, cadmium - from 0.001 to 0.0045 mg / kg. The average level of transition of cadmium from soil to plants was 60-84.6, from plant to honey - 2.6-8.8, lead - respectively 2.2-2.6 and 3.7-7.4%.

Honey meets the safety indicators, namely for the content of lead and cadmium. Therefore, the monitoring data give grounds to assert the ecological suitability of the Vinnytsia region of central Ukraine for the production of quality beekeeping products.

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