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ContentofHeavyMetalsinDifferentTypesofHoneyin the Municipalities of Tuzla, Lukavac, Živinice and Bihać.

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ABSTRACT:*The industrialization of agriculture has led to the great use of pesticides, which leads to huge global problems, such as the production of safe food that is safe for humans and the environment. By heavy metals we mean elements whose relative density is above 5 g cm-3, heavy metals can be divided into essential trace elements (Fe, Cu, Zn, Mo, Mn, Ni) and toxic elements (Pb, Cd, Cr, As, Hg). Heavy metals are represented 25% in the soil, and the largest percentage is occupied by K, Fe, Mg, Ca, Al, Na. In addition to anthropogenic processes such as urbanization, traffic, industrialization, heavy metals can be a consequence of natural or pedogenetic processes, ie. inheritance from the parent substrate.*
The aim of this study was to determine the content of heavy metals Lead and Cadmium in the examined samples, to compare the obtained samples with the norms of the EU and BiH and the influence of the content of heavy metals on the quality of honey. Data collection was performed on the basis of honey analysis of four producers from the area of Tuzla, Lukavac, Živinice and Bihać. The analysis was performed on February 18, 2020. to 25.02.2020. years. The analysis of the processed data was performed in the statistical program IBM SPSS.
Keywords:*heavy metals, Lead, Cadmium*

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I. INTRODUCTION

For decades, there has been a growing awareness of the negative consequences of intensive agriculture. We strive for as much production as possible, and manufacturers use various ways to achieve this. Special emphasis should be placed on the rapid rise of the chemical industry in the 1990s, which produced chemical products that were very effective in destroying pests and generally treating plant and animal diseases.

These chemical products have a beneficial effect on the prevention of diseases of flora and fauna, increase the productivity of agricultural production, but have a detrimental effect on the environment, plant diversity, the Earth's atmosphere, animals and humans. Chemical preparations have a negative effect on microorganisms in the soil.[1]

"Soil is a universal buffer that prevents (alleviates) some reactions pesticides entering the soilpass into non-toxic substances). "[2]

The soil continuously receives, binds and retains harmful substances. If the intake of these pollutants exceeds a certain limit, the soil begins to pose a health risk. Under the term soil contamination with heavy metals we mean the share of heavy metal in the soil in the amount that leads to measurable disturbances of some of the functions of the soil, and especially those related to the formation of organic matter.[3]

In biology, the term "heavy" refers to a number of metals or metalloids that can be toxic to both plants and animals, even when their concentrations are very low. Soil contamination with heavy metals is significantly different from water and air pollution, therefore the longer heavy metals are retained in the soil than in water or air.[4]

Cadmium is a non-essential, toxic element that is most often found in soil in low concentrations, below 3 mg / kg. The maximum permitted concentrations of cadmium in soil in agricultural production, depending on the type of soil, must not exceed 1 mg / kg of soil (OG 32/10). Cadmium is a metal that is naturally found in mines that contain other elements as well. The availability of cadmium in soil depends primarily on soil properties such as cadmium concentration and the form in which it is found in the soil, the content of organic

[1]Ecological beekeeping, Lovro Krnjić, Karlovac 2011
[2]Soil and water protection, Ph.D. Jasna Šoštarić, Monika Marković, B.Sc. ing., Osijek 2011
[3] https://repozitorij.ktf-split.hr/islandora/object/ktfst:234/preview
[4] https://www.sensa.hr/clanci/zensko-zdravlje/teski-metali-kako-djeluju-naorganizam-i-kako-se-od-njih-ocistiti

matter, the pH of the soil and the cation exchange capacity. Cadmium contamination can be caused by mineral fertilizers, organic fertilizers and fertilizers obtained from sewage sludge.[5]

Lead is a heavy metal found in the exhaust of cars and factories. It is the main chemical pollutant of the environment. It appears in the form of Pb2 + ions, as lead tetraethyl, lead diethyl and as other alkyl derivatives of lead. It has a high degree of absorption in soils rich in three-layer clay minerals. The usual lead content in agricultural land is 2 to 100 mg / kg.[6]

Honey may contain high levels of toxic elements, such as Hg, As, Cd, and Pb as a result of increased amounts in plant nectar. Due to large-scale mining and industrial activities, toxic metals are absorbed into the soil, atmosphere and water and consequently into plants. High concentrations of these metals are determined in honey from areas with heavy industry or near highways.[7]

By polluting the environment, heavy metals get to the pollen, so the bees come into contact with them by collecting pollen, which can have consequences for their health. This is often noticed by a change in their behavior, they are restless, aggressive and fly in front of the hive.[8]

Great attention should be paid to setting up beehives to avoid possible contamination with heavy metals. In periods when there is no flowering or when the bee colonies are dormant, they should be within 3 km from the location of the apiary so that the sources of nectar and pollen come from plants from organic production, from wild plants and plants from conventional production that are treated with organic production and at a sufficient distance from sources that can lead to contamination of bee products and endanger the health of bees.

The apiary should be away from non-agricultural sources of pollution such as populated areas, highways, industrial zones, landfills, wastewater and other environmental pollutants.

It is important to note that the composition of honey depends on the geographical location of the hives, so the above data can vary, without additional pollution, and the differences are small.[9] Larger differences in composition confirm the dependence of the content and composition of minerals in honey on the way bees feed and the state of the environment in which they live.[10]

II. MATERIAL AND METHODS

Honey samples were collected directly from honey producers (beekeepers) in the period of February 2020. The collected samples were produced in the spring / summer 2019 season.

Samples were delivered to the laboratory in glass containers, in the amount of 450 g, with information on the regional and botanical origin of honey. A total of 4 honey samples were collected, of which: three samples of acacia honey and one sample of chestnut honey. Heavy metals were analyzed by Atomic Absorption Spectrophotometry (AAS). AAS is an analytical method first used in 1955 for the purpose of determining the amounts of metallic elements in samples based on 32 absorption and emission of a certain amount of energy induced by light radiation.[11]

In plasma spectrophotometry, the sample is transferred via a thin tube to a nebulizer and then to a test tube where it is mixed with the compressed fluid, forming an aerosol with it. The side tube has a very thin tube through which only the tiniest aerosol particles pass. These particles then enter the plasma whose high temperature dries them and gradually atomizes and ionizes them. A large number of positive and neutral ions pass into the part of the device that registers mass. The next step is the electrostatic separation of positive ions from neutral ones. Positive ions then enter the tube through which helium flows.

[5]Kisić I., (2012). Remediation of contaminated soil. Textbooks of the University of Zagreb

[6]Kisić I., (2012). Remediation of contaminated soil. Textbooks of the University of Zagreb

[7]Gajek, O., M. Gdanski, and R. Gajewska (1987): Metallic impurities in imported canned fruit and vegetables and bee honey. Roczniki Panstwowego Zakladu Higieny 38, 14-20.

[8]Matašin Ž., Matašin M. 2002. Beekeeping and Poisoning, Croatian Bee.121: 104-108

[9]Huljev A., Dimač E., Huljev D. 2002. Influence of geographical area on organic composition of propolis, Croatian bee. 121: 177-178.

[10]Rashed M.N., Soltan M.E. 2004. Major and trace elements in different types of Egyptian mono-floral and non-floral bee honeys. J. Food Comp. Anal. 17, 725-735.

[11]Beaty R. D., Kerber J. 1993. Atomic Absorbtion Instrumentation, Concepts, Instrumentation and Techniques in Atomic Absorption Spectrophotometry, The PerkinElmer corporation Instrumentation and Techniques in Atomic Absorption Spectrophotometry

The role of helium in this part is to slow down the particles by colliding with them. Helium collisions re-select particles for those with high and those with low energy. Only high-energy particles continue their journey and then enter a quadrupole system of 4 metal pipes that are interconnected in pairs. A radio frequency is passed between the pairs of tubes. Frequency-induced vibrations will only withstand more stable ions, and the rest will lag in the tube colliding with its walls.

The detector then registers the mass and type of ions coming out of the quadrupole and displays their quantities in electronic form.[12]

The following equipment was used in the sample preparation procedures: spectrophotometer (AAS), analytical balance, weighing vessel, sieve and usual laboratory equipment (pipettes, flasks, beakers ...).

The procedure referred to the following procedures:

Weigh 1 g of honey sample into a porcelain pot and pour 6 mL of HCl and 2 mL of HNO3 (3: 1 gold). The mixture thus prepared was heated to boiling, and then the crucible was removed from the sieve and covered with a watch glass. The samples had to be kept covered for 2 hours and it was necessary to return them to the water bath for heating. The heated mixture was filtered through a filter into a 100 ml volumetric flask. The cooled flask should be topped up with ultra-pure water up to the mark. The solutions thus prepared were used for spectrophotometric determination.

III. RESULTS AND DISCUSSION

The analysis of the obtained research results included a descriptive analysis of the research results. Descriptive analysis included mean (arithmetic mean) and standard deviation. The arithmetic mean gives us a number that is often considered the closest in theoretical and practical terms.

On the other hand, the standard deviation tells us how close it is, that is, how far it deviates from the mean. The smaller the standard deviation, the closer the arithmetic mean is to the data. If the standard deviation is equal to 0, all values are the same, and the arithmetic mean is equal to all values.[13]

Table No. 1 General characteristics of the tested honey

	Sample 1	Sample 2	Sample 3	Sample 4
Place	Tuzlanski Canton	Tuzlanski canton	Tuzlanski canton	Unsko-sanski canton
Origin	Tuzla	Živinice	Lukavac	Bihać
Type of honey	Acacia honey	Acacia honey	Acacia honey	Chestnut honey
Physical state	Liqid	Liqid	Solid	Solid

Lead

Based on the analysis, the following data were obtained:

Table No. 2 Lead Analysis

Sample number	Sample result	Norm for BiH	Norm for EU
1	0	Do 0.10	0,02-0,8
2	0	Do 0.10	0,02-0,8
3	0	Do 0.10	0,02-0,8
4	0	Do 0.10	0,02-0,8

As can be read in the table, no traces of heavy metals lead and cadmium were found on the analyzed samples. In this regard, it can be said that the samples correspond to the set norms, both in BiH and in the EU. Also, it is statistically shown that there are no deviations between the analyzed samples, because all values are equal to zero (0).

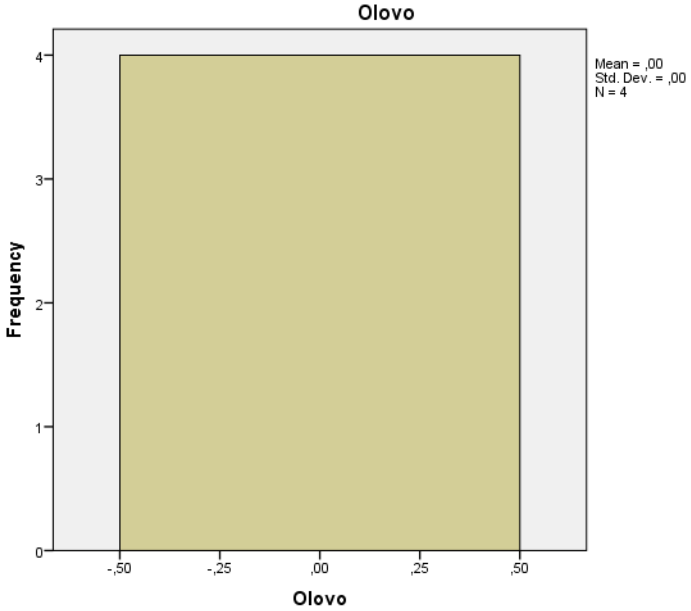
Table No. 3 Descriptive Statistics Lead

	Lead	Norm for BiH	Norm for EU min	Norm for EU max

[12] Agilent Technologies 2009. How does theICP work, Agilent Technologies, http://www.youtube.com/watch?v=MQqtV2oiC6U

[13] Tadić T., Arithmetic mean and standard deviation; available at www.hrcak.srce.hr

N	Valid	4	4	4	4
	Missing	0	0	0	0
Mean		,0000	,10000	,02000	,80000
Std. Deviation		,00000	,000000	,000000	,000000



Graph No. 1 Lead

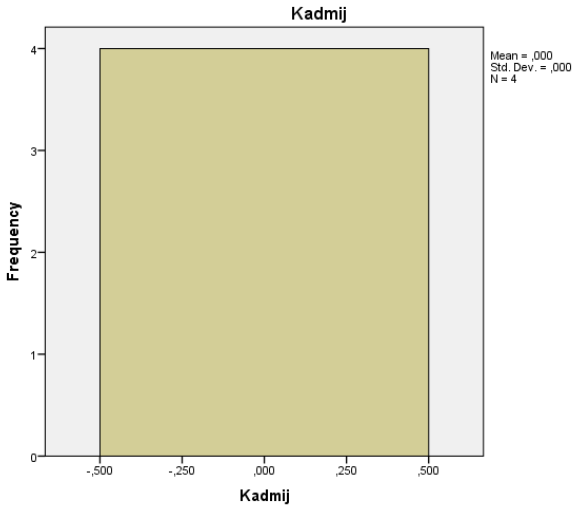
Cadmium
Based on the analysis, the following data were obtained:

Table No. 4 Cadmium analysis

Sample number	Sample result	Norm for BiH	Norm for EU
1	0	There is no data	0,005-0.15
2	0	There is no data	0,005-0.15
3	0	There is no data	0,005-0.15
4	0	There is no data	0,005-0.15

Table No. 5 Descriptive Statistics Cadmium

		Cadmium	Norm for EU min	Norm for EU max
N	Valid	4	4	4
	Missing	0	0	0
Mean		,00000	,005000	,150000
Std. Deviation		,000000	,0000000	,0000000



Graph No. 2 Cadmium

The share of heavy metals is an indicator of the degree of environmental pollution in which production takes place. As mentioned earlier, heavy metals have a very bad effect on the health of bees as well as on the quality of the product itself, so it is necessary to pay great attention to this problem.

IV. CONCLUSION

Based on the obtained results of research on the concentration of metals in honey from different locations in the Tuzla Canton, we can conclude that:

- The location of the hives themselves is of great importance for the entire beekeeping production,
- That it is necessary to examine the quality of honey before placing it on the market and consumption,
- And that the tested samples met all the criteria prescribed by the Ordinance and the team can be competitive in the market.

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