

Content of inorganic elements in honey and imago samples from different regions of Ukraine

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Received: 18.04.2021. Accepted 30.05.2021

Many recent studies have shown that bees and bee products can selectively accumulate heavy metals, radioactive substances, pesticides, and other contaminants. The work aimed to assess the ecological quality of beekeeping products and adult bees for the content of some inorganic elements. The amount of inorganic elements was determined using the method of X-ray fluorescence analysis. We experimentally proved that the qualitative and quantitative composition of inorganic elements in honey varies both in one area and when it is harvested from one species of honey plant. Sunflower honey has the ability to accumulate such inorganic elements as zinc (max 49.87 mg/kg), calcium (max 862.47 mg/kg), strontium (max 0.647 mg/kg), cobalt (max 0.147 mg/kg), chromium (max 0.589 mg/kg) and lead (max 1.09 mg/kg); in addition to the above, herbaceous honey can accumulate as most iron (max 10.27 mg/kg) and selenium (max 0.175 mg/kg); buckwheat honey has the ability to accumulate manganese (max 8.36 mg/kg). Collected from horticultural and forest crops, honey is relatively safe, as the content of most heavy metals (lead, chromium, nickel, strontium, selenium, and cobalt) was below the limit of the method but has the potential to accumulate iron and copper. The least dangerous in terms of the accumulation of inorganic elements is honey, which is collected from linden. The location of the apiary affects the accumulation of trace elements like zinc, manganese, and indirectly iron (Kirovohrad: max 22.10, 6.52, and 10.27 mg/kg, respectively, Zhytomyr: max 7.48, 8.64 and 13.20 mg/kg, respectively, Luhansk: max 7.69, 8.36 and 6.54 mg/kg according to the region). In environmental terms, the safest of the results of the analysis can be considered Poltava and Mykolayiv regions, and with the risk of heavy metal accumulation – Luhansk, Kirovohrad, Kharkiv, Sumy, Odessa, and Zhytomyr regions, as evidenced by the high content of inorganic elements in adult bees, in particular, from Luhansk and Sumy region.

Keywords: honey, adult bees, honey plant, zinc, copper, iron, manganese, selenium, strontium, nickel, lead, calcium, cobalt, chromium.

Introduction

One of the most essential branches of agriculture is beekeeping. Beekeeping is a branch of agricultural production, the basis of which is the breeding, keeping, and use of bees for pollination of entomophilic plants for agricultural purposes and increase their yield, production of food, and raw materials for industry (Turinsky & Adamchuk, 2016; Abejew & Zeleke, 2017; Dudar, 2020).

Thus, the primary function of beekeeping is to breed bees, which in turn provide various types of agricultural products, namely: honey, wax, operculum, royal jelly, merva, bee venom, dead bees, perga, pollen, propolis, and drone homogenates. Beekeeping products are widely used in more than 40 industries and in medicine and pharmacology (Stanhope et al., 2017; Ahmed et al., 2020).

Of course, the main product of beekeeping is honey. Natural bee honey, which does not contain harmful compounds, is beneficial because it strengthens the immune system, saturates the body with essential vitamins and minerals (Khan et al., 2007; Ajibola et al., 2012).

Honey quality is a concept that covers a quite wide range of characteristics and properties of this unique product. During the storage of honey, from the moment of pumping, it undergoes many natural biochemical processes. As a result, its composition is constantly changing (Mădaş et al., 2020; Zeinab et al., 2020). Like any food product, bee honey is characterized by organoleptic

and physicochemical quality indicators (Samarghandian et al., 2017). In addition, the safety indicators of honey are determined - toxicity, the content of pesticides, antibiotics, radionuclides, and heavy metals (Simanonok et al., 2020).

Bee honey is one of the most complex natural products, containing more than four hundred different components (El Sohaimy et al., 2015). It should be noted that the chemical composition of honey is not constant and depends on the type of honey plants from which nectar is collected; the soil on which they grow; the time elapsed from nectar collection to honey extraction from honeycombs; terms of storage of honey; weather and climatic conditions, but the main groups of substances in honey are constant (Soares et al., 2017; Don & Petrusha, 2019).

Some scientists argue that two global environmental problems directly affect beekeeping and the quality of bee products: global warming and changes in the living conditions of bees due to anthropogenic influences (Brovarskiy et al., 2020; El-Sofany et al., 2020). Therefore, for the sustainable development of beekeeping in Ukraine, it is necessary to analyze the factors that can negatively affect the quality and safety of bee honey and the domestic regulatory framework for all stages of production and sale of this product to harmonize with European one (Arnauta et al., 2013; Yefimova & Kasyanchuk, 2013). In addition, it is necessary to consider climate change in the context of its impact on honey quality indicators; it is necessary to systematize the results of research and the formation of a database. This, in turn, will allow assessing the relevance and compliance of quality indicators, which are enshrined in national regulations governing the quality of beekeeping products.

Qualitative and ecological indicators of honey harvest products in different localities and climatic zones differ depending on the type and safety of agricultural land, weather conditions (air temperature, precipitation), and other factors, including negative. In particular, it is the anthropogenic activity and the intensity of artificial load, which directly or indirectly affect both quantitative and qualitative indicators of beekeeping production (Karadas & Birinci, 2018).

It is known that solid, gaseous, and liquid air components can be harmful or toxic to bees. Once in the upper layers of open water bodies, rivers, streams, soils, and the trophic parts of plants, they reflect the atmospheric influence of nature on the biological systems of a particular agroecological zone, territory, or agricultural area. Studies conducted in different agroecological conditions have shown that all this diversity of organic and mineral substances is present in beehives and bee products produced under the influence of relevant environmental factors (Underwood et al., 2019).

Bee pollination, perga, and honey, as products of processing of pollen and nectar of plants by honey bees with the participation of enzymes produced by salivary glands, reflect the agroecological conditions of the feeding of these insects. The conversion of nectar into honey is associated with complex physiological and physicochemical processes in bees. As a result of the transformation of these plant components with the participation of bees, a natural product is formed, characterized by the presence of nutrients and minerals and various biologically active substances, and under certain conditions, harmful or toxic chemical elements. As a valuable food and medicinal product containing carbohydrates, enzymes, minerals, proteins, vitamins, amino acids, and hormones, honey concentrates easily digestible sugars. Under physiological conditions, small amounts corresponding to their presence in honeybees, honey contain ash elements, the concentration of most of which can increase under conditions of high levels in biological objects of the environment, which is relevant for World Beekeeping (Solayman et al., 2016). It is known that honey bees are the most sensitive to the ecological state of the environment. Recent studies have shown that bees and bee products can selectively accumulate some heavy metals, radioactive substances, pesticides, and other contaminants (Kiryanova & Ulanova, 2001; Paranyak et al., 2007). It has been found that even a small concentration of some toxic substances in water, air, nectar, or pollen of honey plants often leads to mass destruction and death of bees. The bee family, collecting raw materials for its products on a plot of 12–28 km², carries information about the ecological condition of the territory within a radius of 2–3 km around the hive (Razanov, 2007).

Pollution of the environment by heavy metals is known to pose a serious threat to ecosystems and human health. Particularly dangerous are heavy metals that exhibit high toxicity in small quantities – mercury, lead, cadmium. These substances, which are part of the emissions of industrial enterprises and road transport, get into the hive with the help of bees when they collect nectar, pollen, propolis. The migration of heavy metals occurs along the chain of soil - plants - bee products - humans. Heavy metals enter the soil with precipitation, emissions, and effluents from nearby industrial plants, exhaust gases from motor vehicles, pesticides, and fertilizers. Work on the determination of heavy metals in honey first appeared in Germany in 1935. After that, researchers in Italy, France, Germany, and other countries published numerous data showing heavy metal contamination of honey from apiaries located near highways and industrial enterprises (Sperandio et al., 2019).

Despite the declining trend of some harmful substances in the environment, the recent environmental situation in certain regions remains unfavorable for safe beekeeping products. The most contaminated products are obtained from hives located in radioactively contaminated areas near extensive forests, wet meadows and pastures, and nutrient-poor soils. Therefore, in solving the production of environmentally friendly beekeeping products, it is essential to carry out constant control of its quality and safety against contamination by toxic elements. Considering the importance of this problem, the purpose of our work was to assess the environmental quality of bee products for the content of inorganic elements.

Materials and methods

Experimental studies were conducted in specialized laboratories of the National Scientific Center "Institute of Experimental and Clinical Veterinary Medicine" (Kharkiv). Samples of honey (from 11 regions of Ukraine, from 7 different honey plants, n=94) and adult bees (from 3 regions, from 3 honey plants, n=30) were taken at exhibitions and fairs of beekeeping products held in Kharkiv and Sumy during 2017-2018 and were also delivered to the laboratory for analysis.

The content of inorganic elements in honey and imago of bees was determined using the method of X-ray fluorescence analysis (XRF) with the device "Spectroscan-Max-G" NPO "Spectron" (St. Petersburg) (Declarative patent of Ukraine for utility model № 72574).

The main parameters of the device for measuring the spectral parameters we used were: the first display – from 950 mÅ to 3150 mÅ, the second display – from 315 mÅ to 1575 mÅ. The step size of the device and the exposure time were 4. The method is based on X-ray fluorescence of elements with subsequent analysis of the spectra with the device "Spectroscan-MAX". When the sample is irradiated with X-rays, the sample, previously subjected to dry mineralization, begins to emit (fluoresce) in the X-ray range. The spectrum of this secondary fluorescence adequately reflects the elemental composition of the analyzed sample. The atom of each element has its characteristic spectral line. Certain characteristic lines in the recorded spectrum indicate the presence of the corresponding elements in the sample. The concentration of this element is judged by the change in the number of pulses along the characteristic line. The depth of penetration of X-rays into the irradiated sample (matrix) depends on its structure (material). The greater the atomic number of the material, the shallower the radiation penetrates. For heavy matrices (metal alloys), this depth is a fraction of a millimeter, and for light is a few millimeters. This layer is functional (information on the sample's elemental composition is removed from it). When fluorescent radiation (secondary) leaves the sample, it is also absorbed by the matrix. Softer longwave lines are absorbed more than hard (shortwave) lines. The wavelength of fluorescent radiation increases with decreasing atomic number of the corresponding element. The method provides measurements with a relative error not exceeding 15% with a confidence level of 0.95. The method of determining inorganic elements by X-ray fluorescence analysis differs from other methods due to the simplicity, convenience, computer data processing, wide range, and quality of the results. According to the spectrum of elements, the method allows to determine several elements simultaneously (in the range from Ca to U), including those that have crucial toxicological significance (Sr, Br, Se, Pb, Zn, Cu, Ni, Fe, Co, Mn, Cr, Ca).

To prepare honey samples for analysis, porcelain crucibles with a volume 5 times larger than the sample volume were selected. For the analysis of chemical elements by X-ray fluorescence method, an average sample of honey weighing 25.00–30.00 g was taken, and the bodies of bees – 3.00–5.00 g (with a weighing accuracy of 0.01 g). Then the honey was dried: in the first stage, the crucible and the sample were placed in an oven for 4 hours at 130 °C; in the second stage (after caramelization of the sample), the temperature was gradually raised to 150°C and dried for 4 hours.

The test material was subjected with incineration (ashed to black or gray ash). Perhydrol ($\approx 5.0 \text{ cm}^3$) was added to the crucible for more efficient combustion of the material. The crucibles were then placed in a muffle furnace with an adjustable and controlled heating system. When burning honey samples, the optimal amount of ash is formed at a temperature of 350–400°C for 4–6 hours, and bee samples – 2 hours at the same temperature.

To correct the individual fluorescence intensity of each separate matrix, an internal standard in the form of gallium silica powder was applied to each ash sample. The weight of the internal standard was selected based on the weight of ash and the concentration of the gallium element in the standard and weighed with accuracy to 0.01 g (usually 0.02–0.06 mg of internal standard was added to the ash samples of honey and bee bodies – the concentration of gallium was 5.0 mg/g). The mixture of ash and internal standard was stirred with a glass rod and ground in a mortar. The mass of ash was then determined together with the weight of the standard by weighing to 0.001 g. The crushed material was transferred to glass vials with a volume of 10–20 cm^3 , capped, and stored for analysis on the device.

Measurements were performed on the device "Spectroscan-MAX," following the instructions for its use. First, the device was calibrated by analyzing a standard matrix (silicon oxide, which contains preknown concentrations of the analyzed elements). The ash samples prepared for the study were placed in the cuvette of the instrument and thickened. The radiation intensity of an element in the sample depends on the qualitative and quantitative composition of each specific test sample. Therefore, in the quantitative calculation of the element, this shortcoming was eliminated by introducing into the basic formula the coefficient (K1), which was calculated by the fluorescence intensity of the internal standard (gallium) in each sample and the fluorescence intensity of gallium in the standard on silicon oxide.

The calculation of the coefficient K1 was performed according to the formula:

$$K1 = \frac{A1 \times CmGa \times Mz + st}{A2 \times Ga \times Mst}$$

where: A1 – the number of Ga pulses in a particular test sample;

CmGa – the concentration of Ga in the standard calibration matrix of silicon oxide, measured on the device (1.0 mg/g);

Mz+st – the mass of ash obtained after combustion of the test material in combination with the mass of the introduced internal standard of silicon oxide, g;

A2 – the number of Ga pulses in a standard calibration matrix of silicon oxide, with a concentration of 1.0 mg/g;

Ga – the concentration of gallium on silicon oxide in the internal standard (5.0 mg/g);

Mst – weighting of the internal standard included in the sample (g);

The calculation of the amount of the element determined in the sample was performed according to the formula:

$$X = \frac{Ipr \times Mz + st}{Ist \times M \times K1} \times 1000$$

where: X – the amount of element in the test sample, mg/kg of natural weight;

Ipr – the number of pulses of the element in the test sample;

Mz+st – the mass of ash obtained after combustion of the test material in combination with the mass of the introduced internal standard of silicon oxide;

Ist – the number of pulses of the element in the standard calibration matrix of silicon oxide, with a concentration of 1.0 mg/g;

M – the amount of weight of the test material, g;

K1 – conversion factor;

1000 – conversion factor to convert the element's content in milligrams per 1 kg of natural mass of honey and bees.

Each sample of honey and adult bees was examined in 3 replicates.

The results were processed by methods of variation statistics using the analysis of software package (ANOVA) StatPlus 5 (6.7.0.3) (AnalystSoft Inc., USA). The probability of the obtained results was evaluated by Tukey's criterion at a probability level of 95.0–99.9% ($p < 0.05$ – $p < 0.001$).

Results and discussion

According to the results of the study of 94 samples of honey and 30 samples of adult bees, we found that the quantitative composition of inorganic elements differed significantly both in samples from one area and in samples from one species of honey plant (Tables 1 & 2).

It should be noted at once that in two samples of honey, the presence of lead was found at the level of 1.09 mg/kg from herbaceous and 0.92 mg/kg from sunflower, which is on the border with the maximum permissible level (MPL) of 1.00 mg/kg according to DSTU 4497: 2005, also in two samples the zinc content was 45.51 mg/kg in honey from herbaceous and 49.87 mg/kg – from sunflower, which exceeded the MPL, which is equal to 30 mg/kg in food products according to SanPin 2.3.2.1078-01, indicating the impossibility of selling this honey. Given the above, these samples were not included in the overall analysis. Inorganic elements such as zinc, copper, iron, manganese, and calcium were found in all studied samples of honey, while strontium – in 71.1%, selenium – in 66.7%, nickel – in 41.1%, cobalt – in 34.4%, chromium – in 26.7%, lead – in 17.8% of samples, respectively. In the remaining relevant samples, the content of the above elements was below the limit of determination (b.l.d.) of the method (0.01 mg/kg).

Analyzing the content of zinc in honey (min-max: 0.59–22.10 mg/kg) relative to honey plant, it was found that the highest content of the element was found in honey from sunflower: the average content of zinc was 1.9 times higher than in herbaceous ($p < 0.001$), 2.5 times – than in buckwheat ($p < 0.001$) and horticultural crops ($p < 0.05$), 4.1 times – than from forest crops ($p < 0.001$), 4.4 times – than from acacia ($p < 0.001$) and 4.9 times – than from linden ($p < 0.001$). The copper content in honey ranged in the bounds (min-max: 0.57–8.63 mg/kg). The highest content of the element was found in honey from horticultural crops, while the content of copper in other honey plants was slightly lower: in honey from linden and herbaceous, the decrease was 8.8 and 2.4 times ($p < 0.001$); in sunflower and buckwheat – 1.6 and 1.5 times, respectively ($p < 0.05$), and in honey from acacia and forest crops, no significant deviations were found, although the average copper content in honey from the above honey plants was lower than in horticultural crops 1.4 and 1.3 times, respectively (Table 1).

Table 1. The content of inorganic elements in honey depends on the main honey plant in the area of the apiary ($M \pm m$, $n=90$, * – $p < 0.05$, ** – $p < 0.001$ – relative to the highest value of the element)

Element, mg/kg	The average content of inorganic elements in honey depends on the honey plant, mg/kg						
	Herbaceous, n=36	Sunflower, n=21	Buckwheat, n=8	Acacia, n=5	Linden, n=6	Horticultural crops, n=5	Forest crops, n=3
Zinc	3.649± 0.609**	6.881± 0.632	2.738± 0.326**	1.558± 0.219**	1.417± 0.129**	2.756± 0.219*	1.667± 0.076**
Copper	3.603± 0.256**	4.626± 0.270*	4.865± 0.464*	5.163± 0.441	0.840± 0.084**	7.242± 0.514	5.463± 0.530
Iron	4.365± 0.361	3.823± 0.433	3.255± 0.555	3.131± 0.611	1.218± 0.111	4.100± 1.145	5.950± 3.626
Manganese	1.381± 0.127**	1.220± 0.121**	4.923± 2.515	0.531± 0.073**	0.807± 0.165**	3.02± 1.420*	1.05± 0.268**
Calcium	245.879± 16.759*	365.379± 38.691	177.675± 76.016*	267.704± 76.016	77.26± 9.206**	298.486± 31.750	259.750± 30.666
Strontium	0.163± 0.019*	0.282± 0.041	0.122± 0.026*	0.165± 0.026	0.0483± 0.0387*	b.l.d.	0.253± 0.063
Selenium	0.0633± 0.008	0.0248± 0.0042*	0.0363± 0.0089	0.0521± 0.0097	b.l.d.	b.l.d.	b.l.d.
Nickel	0.0257± 0.0044	0.0210± 0.0056	0.0075± 0.0033	0.0041± 0.0031	b.l.d.	b.l.d.	b.l.d.
Cobalt	0.0241± 0.0053	0.0454± 0.0113	0.0183± 0.0089	0.0109± 0.0109	b.l.d.	b.l.d.	b.l.d.
Chromium	0.0677± 0.0200	0.0864± 0.0396	0.0318± 0.0138	0.0230± 0.0109	b.l.d.	b.l.d.	b.l.d.
Lead	0.0434± 0.0180	0.123± 0.044	0.0125± 0.0084	0.0034± 0.0034	b.l.d.	b.l.d.	b.l.d.

The studied samples of honey were iron content (min-max: 0.84–13.20 mg/kg). It should be noted that relative to the highest rate of honey plants, no significant deviations in the content of this element were found; the exception was the excess of iron ($p < 0.05$) in honey from forest crops and herbaceous relative to linden honey in 4.9 and 3.6 times, respectively. Analyzing the manganese content in honey (min – max: 0.32–8.64 mg/kg) relative to honey plants, it was found that the highest element content was found in buckwheat honey: the average manganese content was 9.3 times higher than that from acacia ($p < 0.001$),

6.3 times – than from linden ($p < 0.001$), 4.7 times – than from forest crops ($p < 0.001$), 4.0 times – than from sunflower ($p < 0.001$), 3.6 times – than from herbaceous ($p < 0.001$) and 1.6 times – than from horticultural crops ($p < 0.05$). In addition, a significant difference ($p < 0.05$) in the direction of increasing manganese content was found in honey from horticultural crops relative to honey from acacia, linden, sunflower, and herbaceous – in 5.7; 3.7; 2.5 and 2.2 times, respectively. The calcium content in honey was the highest of all studied elements regardless of honey plant and was (min-max: 45.89–862.47 mg/kg). Its highest content was determined in sunflower honey: the average calcium content was 4.7 times higher than that of linden ($p < 0.001$), 2.1 times higher than that of buckwheat ($p < 0.05$), and 1.5 times higher than that of herbaceous ($p < 0.05$), while reliable differences with other honey plants and between them were not observed. The selenium content in the studied samples of honey was (min-max: n.m.v.–0.175 mg/kg), and in honey from linden, horticultural, and forest crops, the microelement was not detected. The highest selenium content was determined in honey from herbaceous, but a reliable difference was found only with the indicator of selenium content in honey from sunflower (2.6 times, $p < 0.05$). No significant deviations were found in buckwheat and acacia honey, although the average content of the element in honey from the above honey plants was 1.7 and 1.2 times lower than in herbaceous honey, respectively. The studied samples of honey were strontium content (min-max: n.m.v.–0.647 mg/kg), and in honey from horticultural crops, the microelement was not detected.

The highest strontium content was determined in sunflower honey, but a reliable difference was found only with the indicator of strontium content in honey from linden, buckwheat, and herbaceous (5.8; 2.3 and 1.7 times, respectively, $p < 0.05$). No significant deviations were found in acacia and forest honey, although the average content of the element in honey from the above honey plants was 1.7 and 1.1 times lower than in honey from herbaceous, respectively. Nickel and cobalt in honey samples were detected in small amounts (min-max: b.l.d.–0.076 mg/kg) and (min-max: b.l.d.–0.147 mg/kg): mainly in honey from herbaceous, sunflower, and buckwheat, while in acacia honey – only in one sample, and in linden honey and honey from horticultural and forest crops they were not detected at all. The obtained data of the analysis concerning the content of honey plant by these elements did not have probable deviations. Chromium and lead (min-max: b.l.d.–0.114 mg/kg) and (min-max: b.l.d.–0.646 mg/kg) were detected in even fewer samples of honey, and their maximum amount accumulated in honey from sunflower and herbaceous (Table 1).

Thus, as a result of the analysis of the content of inorganic elements in honey depending on the honey harvest, it can be stated that sunflower honey can accumulate such inorganic elements as zinc, calcium, strontium, cobalt, chromium, and lead, most of which are heavy metals. In an unfavorable environmental situation, this can cause its culling and damaging consequences when consumed by humans. Herbaceous honey has a similar potential, which in addition to the above, can accumulate as most iron and selenium. Acacia and buckwheat honey has a slightly lower environmental risk by the possibility of accumulating inorganic elements; the latter can accumulate manganese. Honey, collected from horticultural and forest crops, is relatively safe, as it does not contain the most heavy metals (lead, chromium, nickel, strontium, selenium, and cobalt) but can accumulate iron and copper. The least dangerous in terms of accumulation of inorganic elements is honey, collected from linden because it has the lowest concentrations of all investigated metals.

When analyzing the content of inorganic elements in honey in different regions of Ukraine, the following results were obtained (Table 2).

The content of zinc in honey from different regions of Ukraine fluctuated within (by the total number of samples min-max: 0.59–22.10 mg/kg), and on average by region: from 2.050 ± 0.424 mg/kg in Poltava region to 10.34 ± 2.26 mg/kg in the Kirovohrad region. The highest zinc content was determined in honey from the Kirovohrad region, which is 2.4 times higher than in the Kharkiv region ($p < 0.001$); 2.5 times – than from the Kyiv region ($p < 0.001$); 3.8 times – than from the Odessa region ($p < 0.001$); 4.4 times – than from Cherkasy region ($p < 0.001$); 4.0 times – than from Mykolayiv region ($p < 0.001$); 3.8 times – than from Kherson region ($p < 0.001$); 2.0 times – than from Zhytomyr region ($p < 0.05$); 5.0 – than from Poltava region ($p < 0.001$) and 3.0 times – than from Luhansk region. It should be noted that no significant differences in zinc content in honey samples were found between other areas. According to the copper content in honey relative to the area of the apiary location, no significant differences were found between the groups, the fluctuations in the content were (min-max: 0.57–8.63 mg/kg), and on average by region: from 2.658 ± 0.532 mg/kg in Cherkasy region to 5.064 ± 0.447 mg/kg in Sumy region.

The situation was similar with the iron content – no significant differences were found between the regions, the fluctuations in the element content were (min-max: 0.84–13.20 mg/kg), and on average by region: from 2.395 ± 0.156 mg/kg in Sumy region to 5.673 ± 1.441 mg/kg in Zhytomyr region. The manganese content in different regions of Ukraine fluctuated within (by the total number of samples min-max: 0.32–8.64 mg/kg), and on average by region: from 0.767 ± 0.127 mg/kg in the Odessa region to 4.679 ± 0.943 mg/kg in the Zhytomyr region. The highest content of manganese was determined in honey from the Zhytomyr region, which is 5.4 times more than in honey from the Kharkiv region ($p < 0.001$); 4.8 times – than from Kyiv, Poltava, and Cherkasy regions ($p < 0.001$); 6.1 times – than from Odessa region ($p < 0.001$), 2.7 times – than from Mykolayiv region ($p < 0.001$); 3.4 times – than from Kherson region ($p < 0.001$) and 4.3 times – than from Sumy region ($p < 0.001$).

In addition to honey samples from the Zhytomyr region, honey samples from Kirovohrad and Luhansk regions had a high manganese content, accompanied by statistically significant deviations. In samples of honey from the Kirovohrad region (3.086 ± 0.596 mg/kg), the manganese content was 3.2 times higher than in samples from Kyiv and Cherkasy regions ($p < 0.05$); 4.0 times – from the Odessa region ($p < 0.05$); 3.1 times – from Poltava region ($p < 0.05$); 2.8 times – from Sumy region ($p < 0.05$) and 3.6 times – from Kharkiv region ($p < 0.05$).

The manganese content in samples from the Luhansk region exceeded similar ones from the Kharkiv region by 4.8 times ($p < 0.001$); Sumy, Poltava, Odessa, and Kyiv regions by 3.8; 4.2; 5.4 and 4.3 times ($p < 0.001$); and from Mykolayiv, Kherson and Cherkasy regions by 2.4; 3.0 and 4.3 times, respectively (Table 2).

Table 2. The content of inorganic elements in samples of honey from different regions of Ukraine, mg/kg (M±m, n=90, * – p<0.05, ** – p<0.001 – relative to the highest value of the element)

Zn	Cu	Fe	Mn	Ca	Sr	Se	Ni	Co	Cr	Pb
Kharkiv region (n=15)										
4.273±	4.337±	3.022±	0.867±	273.695±	0.184±	0.0701±	0.0169±	0.0338±	0.119±	0.0804±
0.593**	0.438	0.439	0.071**	38.286	0.041	0.0147	0.0061	0.0134	0.0382	0.0423
Kirovohrad region (n=8)										
10.34±	4.380±	5.001±	3.086±	341.31±	0.239±	0.0534±	0.0100±	0.0243±	0.0819±	0.0571±
2.26	0.526	1.14	0.596	93.13	0.065	0.0151	0.0049	0.0145	0.0726	0.0363
Kyiv region (n=7)										
4.076±	4.349±	4.087±	0.976±	234.47±	0.184±	0.0197±	0.0107±	b.l.d.	b.l.d.	b.l.d.
0.428**	1.01	0.736	0.107**	48.74	0.036	0.0095	0.0072			
Odessa region (n=6)										
2.703±	3.985±	3.572±	0.767±	176.28±	0.134±	0.0592±	0.0303±	0.0175±	b.l.d.	0.132±
0.492**	0.486	1.012	0.127**	44.17	0.045	0.0190	0.0138	0.0082		0.0819
Cherkasy region (n=6)										
2.372±	2.658±	3.652±	0.970±	223.79±	0.225±	0.0260±	0.0150±	0.0372±	0.0593±	b.l.d.
0.486**	0.532	0.692	0.220**	53.49	0.091	0.0070	0.0078	0.0169	0.0411	
Mykolayiv region (n=8)										
2.616±	3.795±	4.481±	1.750±	223.60±	0.124±	0.0096±	0.0183±	0.0261±	b.l.d.	b.l.d.
0.471**	0.883	0.863	0.444**	21.58	0.041	0.0050	0.0010	0.0128		
Kherson region (n=6)										
2.728±	4.405±	4.723±	1.372±	147.76±	0.113±	b.l.d.	0.0322±	0.0165±	b.l.d.	b.l.d.
0.460**	1.279	0.740	1.141**	29.85	0.040		0.0147	0.0142		
Zhytomyr region (n=7)										
5.139±	3.827±	5.673±	4.679±	259.44±	0.259±	0.0284±	0.0229±	b.l.d.	b.l.d.	b.l.d.
0.798*	0.714	1.441	0.943	24.24	0.077	0.0092	0.0012			
Poltava region (n=9)										
2.050±	4.113±	3.608±	0.981±	286.41±	0.149±	0.0616±	0.002±	0.0204±	b.l.d.	b.l.d.
0.424**	0.336	0.759	0.065**	32.13	0.032	0.0073	0.0013	0.0088		
Sumy region (n=12)										
2.318±	5.064±	2.395±	1.097±	269.81±	0.155±	0.0548±	0.0131±	0.0302±	0.1625±	0.0463±
0.441**	0.447	0.156	0.117**	27.14	0.042	0.0094	0.0055	0.0127	0.0343	0.0324
Luhansk region (n=6)										
3.402±	4.592±	3.580±	4.147±	361.93±	0.115±	b.l.d.	0.0208±	0.0377±	0.1685±	0.239±
1.15**	0.634	0.943	0.9318	107.37	0.044		0.0092	0.0172	0.0859	0.105

According to the calcium content in honey relative to the apiary location, no significant differences were found between the groups, the content fluctuations were (min-max: 45.89–862.47 mg/kg), and on average by region: from 147.76±29.85 mg/kg in Kherson region to 361.93±107.37 mg/kg in Luhansk region. The situation was similar with the strontium content – no significant differences were found between the regions, the fluctuations of the element content were (min-max: b.l.d.–0.647 mg/kg), and on average by region: from 0.113±0.018 mg/kg in Kherson region to 0.259±0.077 mg/kg in Zhytomyr region. The fluctuations of the selenium content were (min-max: b.l.d.–0.175 mg/kg), and on average by region: from 0.0096±0.0050 mg/kg in Mykolayiv region to 0.0701±0.0147 mg/kg in Kharkiv region. Selenium was not detected in honey samples from the Luhansk and Kherson regions (it was below the limit of determination). The highest content of the element was determined in samples of honey from the Kharkiv region, which reliably exceeded 7.3 times the content of selenium in honey from the Mykolayiv region (p<0.05), while between the other regions, no reliable deviations were found. The content of nickel in honey did not reveal significant differences between regions; fluctuations in the content of the element were (min-max: b.l.d.–0.076 mg/kg), and the average for the regions: from 0.002±0.0013 mg/kg in Poltava region to 0.0322±0.0147 mg/kg in Kherson region. There were also no significant changes in the cobalt content between the regions. Fluctuations in the content of the elements were (min-max: b.l.d.–0.147 mg/kg), and on average by region: from 0.0165±0.0142 mg/kg in Kherson region to 0.0377±0.0172 mg/kg in Luhansk region, and in samples of honey from Kyiv and Zhytomyr regions we did not detect cobalt (it was below the limit of determination). Chromium was detected only in samples of honey from Kharkiv, Kirovohrad, Cherkasy, Sumy, and Luhansk regions (in the rest of the samples, it was below the limit of determination), the fluctuations of the element content were (min-max: b.l.d.–0.114 mg/kg), and on average by regions: from 0.0593±0.0411 mg/kg from Cherkasy region to 0.01685±0.0859 mg/kg from Luhansk region. The lead content was detected only in samples of honey from Kharkiv, Kirovohrad, Odessa, Sumy, and Luhansk regions (in the rest of the samples, it was below the limit of determination), the fluctuations of the element content were (min-max: b.l.d.–0.646 mg/kg), and on average by regions: for 0.0463±0.0324 mg/kg from Sumy region to 0.239±0.105 mg/kg from Luhansk region (Table 2).

Thus, as a result of analysis of the content of inorganic elements in honey depending on the location of the apiary, it can be argued that the area affects the accumulation of trace elements such as zinc, manganese, and indirectly iron (Kirovohrad, Zhytomyr, Luhansk regions). In contrast, the accumulation of other inorganic elements in honey largely depends on intraregional features, anthropogenic (remoteness of the apiary from industries, roads, large settlements), and natural (geochemical provinces) nature. There is a slight dependence of the accumulation of heavy metals (zinc, copper, cobalt, chromium, and lead) on the capacity of regional centers; in particular, a significant number of them are in samples from Kharkiv Luhansk, Odessa, Sumy, and Kirovohrad regions. According to the analysis results, Poltava and Mykolayiv regions can be considered the safest in the ecological aspect, and Luhansk, Kirovohrad, Kharkiv, Sumy, Odessa, and Zhytomyr regions – with the risk of accumulation of heavy metals.

The studied inorganic elements were found in all tested samples of adult bees. According to the results of research, the highest zinc content was found in adults of bees that collected nectar from sunflower, which was 1.4 times higher than from horticultural crops ($p < 0.001$) and 1.1 times higher than from herbaceous ($p < 0.05$), fluctuations in the content of the element in adult bees was (min-max: 110.25–191.27 mg/kg). Fluctuations in the copper content in adult bees were (min-max: 11.23–26.58 mg/kg), and the highest content was determined in adult bees that collected nectar from horticultural crops, which was 1.5 times higher than in bees that collected nectar from herbaceous and sunflower, respectively ($p < 0.001$). For iron content in adult bees, no significant deviations were found relative to the honey plant; the element content fluctuations were (min-max: 315.28–436.28 mg/kg). The highest manganese content was determined in bees that collected nectar from horticultural crops, which was 1.2 times higher than from herbaceous ($p < 0.05$) and 1.1 times higher than from sunflower ($p < 0.05$), fluctuations in the content of the element in adult bees (min-max: 69.37–97.58 mg/kg). The calcium content in adult bees ranged from 1793.48 to 2997.24 mg/kg. Its highest content was determined in bees that collected nectar from sunflower, which was 1.2 times higher than from herbaceous ($p < 0.05$), while at the rate of horticultural crops, no significant difference was found. The highest strontium content was determined in bees that collected nectar from sunflower, which was 1.3 times higher than from herbaceous ($p < 0.05$) and 1.7 times higher than from horticultural crops ($p < 0.001$), in addition, the strontium content in bees from herbaceous was reliably 1.3 times higher than in horticultural crops value ($p < 0.05$); fluctuations in the content of the element in adult bees was (min-max: 3.26–8.69 mg/kg).

The nickel content in adult bees fluctuated within (min-max: 0.66–1.91 mg/kg); no significant difference was found between the groups. The highest lead content was determined in bees that collected nectar from sunflower, which was 2.4 times higher than from herbaceous ($p < 0.001$) and 11.3 times higher than from horticultural crops ($p < 0.001$), in addition, the lead content in bees from herbaceous was reliably 4.7 times higher than in bees from horticultural crops ($p < 0.001$), and fluctuations in the element content in adult bees were (min-max: 0.52–10.47 mg/kg) (Table 3).

The chromium content in adult bees fluctuated within (min-max: 0.02–0.52 mg/kg); the average content of the element in bees from sunflower exceeded the corresponding indicator from herbaceous and horticultural crops by 2.0 ($p < 0.05$) and 5.6 times ($p < 0.001$). The selenium content in adult bees fluctuated within (min-max: 0.073–0.39 mg/kg), the highest element content was determined in adult bees that collected nectar from sunflower, which is 2.2 times higher than the indicator from horticultural crops ($p < 0.05$) and 1.5 times higher than from herbaceous, but the indicator was not reliable. The content of cobalt in adult bees fluctuated within (min-max: 0.034–0.132 mg/kg), the highest content of the element was determined in adult bees that collected nectar from sunflower, which is 1.7 times higher than the indicator from horticultural crops ($p < 0.05$) and 1.2 times higher than from herbaceous, however, the indicator was not reliable, and the cobalt content in imago bees from herbaceous was 1.4 times higher than from forest crops ($p < 0.05$) (Table 3).

Table 3. The content of inorganic elements in the samples of adult bees depends on the main honey plant in the area of the apiary ($M \pm m$, $n=30$, * – $p < 0.05$, ** – $p < 0.001$ – relative to the highest value of the element)

Element, mg/kg	The average amount of inorganic elements in imago samples depending on the honey plant		
	Herbaceous, $n=16$	Sunflower, $n=7$	Horticultural crops, $n=7$
Zinc	146.48±5.32*	166.09±7.00	122.97±3.79**
Copper	15.11±0.65**	14.84±1.14**	22.87±1.00
Iron	398.36±7.94	411.53±8.48	412.87±5.46
Manganese	75.57±0.811*	78.74±1.978*	87.12±2.25
Calcium	2258.99±55.68*	2681.65±109.06	2531.07±100.09
Strontium	5.70±0.09**	7.13±0.39	4.17±0.35**
Nickel	1.31±0.04	1.32±0.16	1.20±0.11
Lead	3.79±0.22**	9.04±0.46	0.80±0.070**
Chromium	0.21±0.023*	0.41±0.034	0.073±0.022**
Selenium	0.151±0.020	0.227±0.036	0.104±0.013*
Cobalt	0.0969±0.0056	0.118±0.0043	0.068±0.0061*

Therefore, as a result of the analysis of the content of inorganic elements in adult bees depending on the honey harvest, it can be argued that the most significant potential for the accumulation of inorganic elements has sunflower, which confirms the results of their content in honey.

When analyzing the content of inorganic elements in adult bees concerning different regions of Ukraine, the following results were obtained (Table 4).

Table 4. The content of inorganic elements in imago samples depends on the location of the apiary ($M \pm m$, $n=30$, * – $p < 0.05$, ** – $p < 0.001$ – relative to the highest value of the element)

Element, mg/kg	The average amount of inorganic elements in imago samples depends On the location of the apiary			
	Kharkiv, n=8	Sumy, n=8	Odessa, n=7	Luhansk, n=7
Zinc	137.90±7.36	152.82±7.47	139.70±9.31	151.91±10.67
Copper	17.80±1.58	18.41±1.85	15.18±1.09	15.68±1.48
Iron	409.52±8.21	394.31±14.15	405.46±7.74	410.82±6.95
Manganese	75.98±0.77*	74.59±1.49*	78.56±1.40*	87.95±1.91
Calcium	2511.51±89.24	2357.14±51.41	2182.50±138.13*	2629.47±103.38
Strontium	6.60±0.38	6.09±0.33	5.10±0.33*	4.71±0.45*
Nickel	1.24±0.070	1.20±0.13	1.38±0.06	1.37±0.11
Lead	3.57±0.82	2.82±0.41	4.75±1.44	6.46±1.37
Chromium	0.162±0.0187*	0.325±0.0358	0.079±0.022**	0.343±0.059
Selenium	0.224±0.027	0.196±0.034	0.112±0.012	0.084±0.003
Cobalt	0.103±0.007	0.104±0.007	0.066±0.007*	0.105±0.010

The zinc content in adult bees ranged from 137.90±7.36 mg/kg in the Kharkiv region to 152.82±7.47 mg/kg in the Sumy region and had no significant deviations. The copper content in adult bees ranged from 15.18±1.09 mg/kg in the Odessa region to 18.41±1.85 mg/kg in the Sumy region and had no significant deviations. The iron content in adult bees on average in the region ranged from 394.31±14.15 mg/kg in the Sumy region to 410.82±6.95 mg/kg in the Luhansk region and had no significant deviations. The manganese content in adult bees ranged from 74.59±1.49 mg/kg in the Sumy region to 87.95±1.91 mg/kg in the Luhansk region. The highest content of the element was determined in samples from bees from the Luhansk region, which exceeded the indicator in Kharkiv, Sumy, and Odessa regions by 1.2; 1.2 and 1.1 times, respectively ($p < 0.05$) (Table 4). The calcium content in adult bees ranged on average from 2182.50±138.13 mg/kg in the Odessa region to 2629.47±103.38 mg/kg in the Luhansk region. The highest content of the element was determined in samples from bees from the Luhansk region, which exceeded the indicator in the Odessa region by 1.2 and 1.1 times ($p < 0.05$), while in Kharkiv and Sumy regions, no significant deviations were noted. The strontium content in adult bees ranged from 4.71±0.45 mg/kg in the Luhansk region to 6.60±0.38 mg/kg in the Kharkiv region.

The highest content of the element was determined in samples from bees from the Kharkiv region, which exceeded the indicator in Odessa and Luhansk regions by 1.3 and 1.4 times, respectively ($p < 0.05$), while relative to the strontium content in bees from the Sumy region no significant deviations were observed. The nickel content in adult bees on average in the regions ranged from 1.20±0.13 mg/kg in the Sumy region to 1.38±0.06 mg/kg in the Odessa region and had no significant deviations. The lead content in the imago samples did not differ significantly from the areas of apiary location. Moreover, the highest content of the element was determined in bees from the Luhansk region, which exceeded its average content in Kharkiv, Sumy, and Odessa regions by 1.8; 2.3 and 1.4 times, and fluctuations in lead content averaged in the regions from 2.82±0.41 mg/kg in Sumy to 6.46±1.37 mg/kg in Luhansk region. The chromium content in adult bees ranged on average from 0.079±0.022 mg/kg in the Odessa region to 0.343±0.059 mg/kg in the Luhansk region. The highest content of the element was determined in samples from bees from the Luhansk region, which exceeded the indicator for Kharkiv and Odessa regions by 2.1 ($p < 0.05$) and 4.3 times ($p < 0.001$), respectively, while relative to the indicator in Sumy region no probable deviations were found. For the chromium content, there was also found significant exceeding in content between samples from Sumy, Kharkiv, and Odessa regions ($p < 0.05$) (2.0 and 4.1 times, respectively). The selenium content in the samples of adult bees did not have a significant difference concerning the areas of apiary location. However, the highest content of the element was determined in bees from the Kharkiv region, which exceeded its average content in Sumy, Odessa, and Luhansk regions by 1.1; 2.0 and 2.7 times, and fluctuations in selenium content averaged over the regions from 0.084±0.003 mg/kg in Luhansk region to 0.224±0.027 mg/kg in Kharkiv region.

The highest cobalt content was determined in bees from the Luhansk region, which exceeded its average content in the Odessa region by 1.6 times ($p < 0.05$). The fluctuations in cobalt content averaged in the region from 0.066±0.007 mg/kg in Odessa region to 0.105±0.007 mg/kg in the Luhansk region; in addition, its content in bees from the Odessa region was 1.6 times lower than in imago samples from Kharkiv and Sumy regions ($p < 0.05$) (Table 4).

Therefore, as a result of the analysis of the content of inorganic elements in adult bees, depending on the location of the apiary, it can be argued that bees have a relatively stable elemental composition, except for manganese content. The obtained data confirm that the Luhansk region of Ukraine has the potential to accumulate inorganic elements.

Thus, according to the results of the research, it was determined that the qualitative and quantitative composition of inorganic elements in honey and samples of adult bees varied significantly both in one area and from one honey plant. These data indicate

that the content of inorganic elements in honey and adult bees largely depends on the area of honey collection: climatic conditions during nectar collection, the presence of large highways, developed chemical and metallurgical industries, chemical fertilizers, and a variety of honey plants. Higher rates in adult bee samples than in honey indicate that inorganic elements are accumulated more in bee tissues and enter honey by trophic bonds at lower concentrations, respectively. The level of intensity of technogenic load on the ecological conditions of Ukraine generally determines the pronounced complex physiological influence on the content of some mineral elements in various tissues of the body of honey bees and the transformation of these elements directly into beekeeping products.

However, the data obtained by us are consistent with the data of other researchers. Thus, determined by us zinc content in honey samples (0.59–22.10 mg/kg) was close to that in honey from China (0.59–22.85 mg/kg) (Ru et al., 2013) and India (2.50–16.77 mg/kg) (Nanda et al., 2003). The copper content (0.57–8.63 mg/kg) was close to honey from Israel (3.18–9.00 mg/kg) (Dag et al., 2006), Palestine (b.l.d.–7.60 mg/kg) (Swaileh & Abdulkhalik, 2013), Ethiopia (0.37–13.99 mg/kg) (Nigussie et al., 2012), Libya (0.80–10.40 mg/kg) (Ahmida et al., 2013). The iron content (0.84–13.20 mg/kg) was similar to that in honey from many countries around the world, but the closest values were in honey from Israel (0.90–9.30 mg/kg) (Dag et al., 2006), Turkey (0.57–8.74 mg/kg) (Silici et al., 2016), Spain (b.l.d.–7.59 mg/kg) (de Alda-Garcilope et al., 2012), Argentina (1.13–10.32 mg/kg) (Cantarelli et al., 2008) and Chile (0.78–7.66 mg/kg) (Fredes & Montenegro, 2006). The manganese content (0.32–8.64 mg/kg) was mainly similar to that in European countries (Bulgaria, Poland, Spain, Morocco), respectively (0.06–12.70 mg/kg), (0.10–8.00 mg/kg), (0.98–10.90 mg/kg), (0.08–9.76 mg/kg) and Venezuela (0.50–10.70 mg/kg) (Belouali et al., 2008; Vit et al., 2010; de Alda-Garcilope et al., 2012; Atanassova et al., 2012; Grembecka & Szefer, 2013). The calcium content (45.89–862.47 mg/kg) was similar to that in Malaysia (65.80–567.27 mg/kg) and Italy (9.10–402.60 mg/kg) (Conti et al., 2007; Moniruzzaman et al., 2014). The strontium content (b.l.d.–0.647 mg/kg) was close to the content in honey from Bulgaria (0.12–0.40 mg/kg) and Chile (0.04–22.06 mg/kg) (Fredes & Montenegro, 2006; Atanassova et al., 2012). The similarity of selenium content (b.l.d.–0.175 mg/kg) was established with honey from Iran (0.06–0.260 mg/kg) and Turkey (0.01–0.450 mg/kg) (Samimi et al., 2001; Silici et al., 2016).

Nickel in honey samples was detected in small amounts (b.l.d.–0.076 mg/kg), which was consistent with data on honey from Palestine (Swaileh & Abdulkhalik, 2013.) (b.l.d.–0.13 mg/kg); Bulgaria (Atanassova et al., 2012) (0.01–1.00 mg/kg); Spain (de Alda-Garcilope et al., 2012) (0.05–0.75 mg/kg); USA (Birge & Price, 2001) (b.l.d.–0.13 mg/kg), Chile (Fredes & Montenegro, 2006) (0.01–1.48 mg/kg) and New Zealand (Vanhanen et al., 2011) 0.02–0.65 mg/kg). The content of cobalt (b.l.d.–0.147 mg/kg) in honey was consistent with the content from countries such as Turkey (0.125–3.0 mg/kg), France (0.100–0.230 mg/kg), Poland (b.l.d.–0.300 mg/kg) and Spain (b.l.d.–0.136 mg/kg) (Devillers et al., 2002; de Alda-Garcilope et al., 2012; Grembecka & Szefer, 2013; Silici et al., 2016). The chromium content (b.l.d.–0.114 mg/kg) was close to the content in honey from Bulgaria (0.100–0.200 mg/kg) (Atanassova et al., 2012) and France (0.08–0.360 mg/kg) (Devillers et al., 2002). The lead content (b.l.d.–0.646 mg/kg) found in honey from Ukraine was close to that from France and Italy (0.28–1.08 mg/kg) and (0.10–1.53 mg/kg) (Devillers et al., 2002; Conti et al., 2007).

Regarding adult bees, there are data that the keeping of honey bees in agroecological conditions with a low level of artificial pollution is accompanied by a lower content of heavy metals in beekeeping products. Significantly lower concentrations of Fe, Zn, Cu, Cr, Ni, Pb, Cd were found in the tissues of the head of honey bees, kept at a distance of 15 and 30 km from the zone of intensive artificial load. The abdominal tissues showed a significantly lower concentration of all investigated heavy metals, except Cu. It has been established that agroecological conditions of the foothills and mountain zones of the Carpathians with different anthropogenic loads contribute to a reliable decrease in Cu and Ni in the tissues of the head, thorax, and abdomen of honey bees, as well as in honey and bee pollen against a significant decrease in Pb and Cb in products (Kovalchuk & Fedoruk, 2013).

Thus, when evaluating honey and adult bees from different regions of Ukraine, the influence of agroecological and climatic conditions on the mineral composition of beekeeping products has been proved. The obtained results will be used to form a database of honey quality indicators further and assess data stability over time. Further research of honey samples of different botanical origins in comparison with honey samples from other regions of Ukraine is considered promising. It is necessary to provide sustainable prerequisites for developing an innovative science-based methodological framework for organic beekeeping in Ukraine. It is advisable to study the content of heavy metals in the tissues of bees and the reproductive capacity of queens, which will be the subject of further research.

Conclusions

It has been experimentally proved that the qualitative and quantitative composition of inorganic elements in honey varies both in one area and when it is harvested from one species of honey plant. As a result of analysis of the content of inorganic elements in honey depending on the honey harvest, it can be stated that sunflower honey can accumulate such inorganic elements as zinc (max 49.87 mg/kg), calcium (max 862.47 mg/kg), strontium (max 0.647 mg/kg), cobalt (max 0.147 mg/kg), chromium (max 0.589 mg/kg) and lead (max 1.09 mg/kg), most of which are heavy metals, which under an unfavorable environmental situation can cause culling of honey and have negative consequences when consumed by humans. These data are confirmed by a certain maximum content of the above inorganic elements in adult bees. Herbaceous honey has a similar potential, which in addition to the above can accumulate as most iron (max 10.27 mg/kg) and selenium (max 0.175 mg/kg). Acacia and buckwheat honey has a slightly lower environmental risk due to the possibility of accumulating inorganic elements; the latter can accumulate manganese (max 8.36 mg/kg). Honey collected from horticultural and forest crops are relatively safe, as the content of most heavy metals (lead, chromium, nickel, strontium, selenium, and cobalt) was below the limit of the method but has the potential to accumulate iron and copper. The least dangerous in terms of accumulation of inorganic elements is honey, which is collected from linden because it has the lowest concentrations of all investigated metals.

As a result of analysis of the content of inorganic elements in honey depending on the location of the apiary, it can be argued that the area affects the accumulation of trace elements such as zinc, manganese, and indirectly iron (Kirovohrad: max 22.10, 6.52 and 10.27 mg/kg, respectively, Zhytomyr: max 7.48, 8.64 and 13.20 mg/kg, respectively, Luhansk: max 7.69, 8.36 and 6.54 mg/kg, respectively). There is a slight dependence of the accumulation of heavy metals (zinc, copper, cobalt, chromium, and lead) on the capacity of regional centers; in particular, a significant amount of them is in samples from the Kharkiv, Luhansk, Odessa, Sumy, and Kirovohrad regions. According to the results of the analysis, Poltava and Mykolayiv regions are considered the safest from the ecological aspect, and Luhansk, Kirovohrad, Kharkiv, Sumy, Odessa, and Zhytomyr regions are considered at risk of heavy metal accumulation, which is confirmed by the high content of inorganic elements in adult bees, in particular, from Luhansk, Kharkiv and Sumy regions.

The obtained data are consistent with the content of inorganic elements in honey from around the world.

References

- Abejew, T. A., & Zeleke, Z. M. (2017). Study on the Beekeeping Situation, the Level of Beekeepers Knowledge Concerning Local Honeybee Subspecies, Their Productive Characteristics, and Behavior in Eastern Amhara Region, Ethiopia. *Advances in Agriculture*, Article ID 6354250. <https://doi.org/10.1155/2017/6354250>
- Ahmed, Z. H., Tawfik, A. I., Abdel-Rahman, M. F., & Moustafa, A. M. (2020). Nutritional Value and Physiological Effects of Some Proteinaceous Diets on Honey Bee Workers (*Apis mellifera* L.). *Bee World*, 97(1), 26-31. <https://doi.org/10.1080/0005772X.2019.1672983>
- Ahmida, M. H., Elwerfali, S., Agha, A., Elagori, M., & Ahmida, N. H. (2013). Physicochemical, heavy metals and phenolic compounds analysis of Libyan honey samples collected from Benghazi during 2009–2010. *Food Nutr Sci.*, 4, 33-40. doi: 10.4236/fns.2013.41006
- Ajibola, A., Chamunorwa, J. P., & Erlwanger, K. H. (2012). Nutraceutical values of natural honey and its contribution to human health and wealth. *Nutrition & metabolism*, 9, 61. <https://doi.org/10.1186/1743-7075-9-61>
- Arnauta, O. V., Tomchuk, V. A., & Bernatovich, O. V. (2013). Features of regulatory quality assurance and safety of bee honey in Ukraine and the EU at the stages of its production and sale. *Scientific Bulletin of LNAU: veterinary sciences*, 53, 5-7. (in Ukrainian)
- Atanassova, J., Yurukova, L., & Lazarova, M. (2012). Pollen and inorganic characteristics of Bulgarian unifloral honeys. *Czech J Food Sci.*, 30, 520-526.
- Belouali, H., Bouaka, M., & Hakkou, A. (2008). Determination of some major and minor elements in the east of Morocco honeys through inductively coupled plasma optical emission spectrometry. *Apiacta*, 43, 17-24.
- Birge, W., & Price, D. (2001). Analysis of Metals and Polychlorinated Biphenyl (PCB) Residues in Beaver Tissue Samples Collected January 27 and February 1, 2000, from PGDP Ditches. *Environmental Science*, ID: 130156361
- Brovarskiy, V. D., Turdaliev, A. T., & Mirzakhmedova, G. I. (2020). High temperatures and their effect on plants and bees. *Scientific journal "Livestock and Food Technology"*, 11(2), 5-15. <http://dx.doi.org/10.31548/animal2020.02.005>
- Cantarelli, M., Pellerano, R., Marchevsky, E., & Camiña, J. (2008). Quality of honey from Argentina: study of chemical composition and trace elements. *J Argent Chem Soc.*, 96, 33-41.
- Conti, M. E., Stripeikis, J., Campanella, L., Cucina, D., & Tudino, M. B. (2007). Characterization of Italian honeys (Marche Region) on the basis of their mineral content and some typical quality parameters. *Chem Cent J.*, 1, 1-14. doi: 10.1186/1752-153X-1-14
- Dag, A., Afik, O., Yeselson, Y., Schaffer, A., & Shafir, S. (2006). Physical, chemical and palynological characterization of avocado (*Persea Americana* Mill.) honey in Israel. *Int J Food Sci Technol.*, 41, 387-394. <https://doi.org/10.1111/j.1365-2621.2005.01081.x>
- de Alda-Garcilope, C., Gallego-Picó, A., Bravo-Yagüe, J. C., Garcinuño-Martínez, R. M., & Fernández-Hernando, P. (2012). Characterization of Spanish honeys with protected designation of origin "Miel de Granada" according to their mineral content. *Food Chem.*, 135(3), 1785-1788. doi: 10.1016/j.foodchem.2012.06.057
- Devillers, J., Dore, J., Marenco, M., Poirier-Duchene, F., Galand, N., & Viel, C. (2002). Chemometrical analysis of 18 metallic and nonmetallic elements found in honeys sold in France. *J Agric Food Chem.*, 50, 5998-6007. doi: 10.1021/jf020497r
- Don, I., & Petrussha, Y. (2019). Physico-chemical quality indicators of different varieties of honey. *ΛΟΓΟΣ. The art of scientific thought*, 46-49. doi: 10.36074/2617-7064.07.00.010
- Dudar, T. (2020). Development of beekeeping in Ukraine: successes achieved, the need for marketing cooperation in the industry, the strategy of the honey business. *Herald of Economics*, 2(96), 36-49. <https://doi.org/10.35774/visnyk2020.02.036>
- El-Sofany, A., Naggar, Y. A., Naiem, E., Giesy, J. P., & Seif, A. (2020). Authentication of the botanical and geographic origin of Egyptian honey using pollen analysis methods. *Journal of Apicultural Research*, 59(5), 946-955. <https://doi.org/10.1080/00218839.2020.1720950>
- El Sohaimy, S. A., Masry, S. H. D., & Shehata, M. G. (2015). Physicochemical characteristics of honey from different origins. *Annals of Agricultural Sciences*, 60(2), 279-287. <https://doi.org/10.1016/j.aogas.2015.10.015>
- Fredes, C., & Montenegro, G. (2006). Heavy metal and other trace elements contents in honey bee in Chile. *Cienc Investig Agrar.*, 33, 50-58.
- Grembecka, M., & Szefer, P. (2013). Evaluation of honeys and bee products quality based on their mineral composition using multivariate techniques. *Environ Monit Assess.*, 185, 4033-4047. doi: 10.1007/s10661-012-2847-y
- Karadas, K., & Birinci, A. (2018). Identification of risk factors affecting production of beekeeping farms and development of risk management strategies: A new approach. *Revista Brasileira de Zootecnia*, 47, e20170252. <https://doi.org/10.1590/rbz4720170252>
- Khan, F. R., Ul Abadin, Z., & Rauf, N. (2007). Honey: nutritional and medicinal value. *Int J Clin Pract.*, 61(10), 1705-1707. doi: 10.1111/j.1742-1241.2007.01417.x

- Kiryanova, L. Y., & Ulanova, T. S. (2001). Honeybees and apiculture products as the bioindicators of ecological ill-being of the environment. Ecological problems of Western Ural: conference materials of students, post-graduates and young scientists, Perm, 13-15. (in Russian)
- Kovalchuk, I. I., & Fedoruk, R. S. (2013). Content of heavy metals in the bees tissues and products depending on agroecological conditions of Carpathians region. *The Animal Biology*, 15(4), 54-65. (in Ukrainian)
- Mădaş, M. N., Mărghitaş, L. A., Dezmirean, D. S., Bobiş, O., Abbas, O., Danthine, S., Francis, F., Haubruge, E., & Nguyen, B. K. (2020). Labeling Regulations and Quality Control of Honey Origin: A Review. *Food Reviews International*, 36(3), 215-240. doi: [10.1080/87559129.2019.1636063](https://doi.org/10.1080/87559129.2019.1636063)
- Moniruzzaman, M., Chowdhury, M. A. Z., Rahman, M. A., Sulaiman, S. A., & Gan, S. H. (2014). Determination of mineral, trace element, and pesticide levels in honey samples originating from different regions of Malaysia compared to Manuka honey. *BioMed Res Int.*, 2014, 1-10. doi: 10.1155/2014/359890
- Nanda, V., Sarkar, B., Sharma, H., & Bawa, A. (2003). Physico-chemical properties and estimation of mineral content in honey produced from different plants in northern India. *J Food Compost Anal.*, 16, 613-619.
- Nigusse, K., Subramanian, P., & Mebrahtu, G. (2012). Physicochemical analysis of Tigray honey: an attempt to determine major quality markers of honey. *Bull Chem Soc Ethiop.*, 26, 127-133. doi: 10.4314/bcse.v26i1.14
- Paranyak, R. P., Vasil'tseva, L. P., & Makukh, K. I. (2007). Ways how heavy metals get into the environment and their influence on viability. *Biology of Animals*, 9(1-2), 83-89. (in Ukrainian)
- Razanov, S. (2007). How to get pure honey. *Animal farming in Ukraine*, 4, 40-41. (in Ukrainian)
- Ru, Q.-M., Feng, Q., & He, J.-Z. (2013). Risk assessment of heavy metals in honey consumed in Zhejiang province, southeastern China. *Food Chem Toxicol.*, 53, 256-262. doi: 10.1016/j.fct.2012.12.015
- Samarghandian, S., Farkhondeh, T., & Samini, F. (2017). Honey and Health: A Review of Recent Clinical Research. *Pharmacognosy Research*, 9(2), 121-127. <https://doi.org/10.4103/0974-8490.204647>
- Samimi, A., Maymand, O. E., & Mehrtabatabaei, M. (2001). Determination of cadmium and arsenic pollution by bee honey based on the study on Ja'far Abad area from Saveh city from Iran. *Water Geosci*, 23, 199-202.
- Silici, S., Uluzozlu, O. D., Tuzen, M., & Soylak, M. (2016). Honeybees and honey as monitors for heavy metal contamination near thermal power plants in Mugla, Turkey. *Toxicol Ind Health.*, 32(3), 507-516. doi: 10.1177/0748233713503393
- Simanonok, M. P., Otto, C. R. V., & Smart, M. D. (2020). Do the Quality and Quantity of Honey Bee-Collected Pollen Vary Across an Agricultural Land-Use Gradient? *Environmental Entomology*, 49(1), 189-196. <https://doi.org/10.1093/ee/nvz139>
- Soares, S., Amaral, J. S., Oliveira, M. B. P., & Mafra, I. (2017). A Comprehensive Review on the Main Honey Authentication Issues: Production and Origin. *Comprehensive Reviews in Food Science and Food Safety*, 16, 1072-1100. <https://doi.org/10.1111/1541-4337.12278>
- Solayman, Md., Islam, Md. A., Sudip, P., Yousuf, A., Khalil, Md. I., Alam, N., & Gan, S. H. (2016). Physicochemical Properties, Minerals, Trace Elements, and Heavy Metals in Honey of Different Origins: A Comprehensive Review. *Comprehensive Reviews in Food Science and Food Safety*, 15(1), 219-233. <https://doi.org/10.1111/1541-4337.12182>
- Sperandio, G., Simonetto, A., Carneseccchi, E., Costa, C., Hatjina, F., Tosi, S., & Gilioli, G. (2019). Beekeeping and honey bee colony health: A review and conceptualization of beekeeping management practices implemented in Europe. *Science of The Total Environment*, 696. <https://doi.org/10.1016/j.scitotenv.2019.133795>
- Stanhope, J., Carver, S., & Weinstein, P. (2017). Health outcomes of beekeeping: a systematic review. *Journal of Apicultural Research*, 56(2), 100-111. doi: [10.1080/00218839.2017.1291208](https://doi.org/10.1080/00218839.2017.1291208)
- Swaileh, K. M., & Abdulkhaliq, A. (2013). Analysis of aflatoxins, caffeine, nicotine and heavy metals in Palestinian multifloral honey from different geographic regions. *J Sci Food Agric.*, 93, 2116-2120. doi: 10.1002/jsfa.6014
- Turinsky, V. M., & Adamchuk, L. O. (2016). Important issues of beekeeping development. *Scientific journal "Livestock and Food Technology"*, 223. <http://journals.nubip.edu.ua/index.php/Tekhnologiya/article/view/5867>
- Underwood, R. M., Traver, B. E., & López-Urbe, M. M. (2019). Beekeeping Management Practices Are Associated with Operation Size and Beekeepers' Philosophy towards in-Hive Chemicals. *Insects*, 10(1), 10. <https://doi.org/10.3390/insects10010010>
- Vanhanen, L. P., Emmertz, A., & Savage, G. P. (2011). Mineral analysis of mono-floral New Zealand honey. *Food Chem.*, 128, 236-240. doi: 10.1016/j.foodchem.2011.02.064
- Vit, P., Rodriguez-Malaver, A., Rondon, C., Gonzalez, I., Di Bernardo, M. L., & Garcia, M. Y. (2010). Bioactive indicators related to bioelements of eight unifloral honeys. *Arch Latinoam Nutr.*, 60, 405-410.
- Yefimova, O. M., & Kasyanchuk, V. V. (2013). Analysis of microbiological safety of national products of animal origin intended for export. *Veterinary medicine of Ukraine*, 1(215), 30-34. (in Ukrainian)
- Zeinab, H. A., Amer, I. T., Abdel-Rahman, M. F., & Moustafa, A. M. (2020). Nutritional Value and Physiological Effects of Some Proteinaceous Diets on Honey Bee Workers (*Apis mellifera* L.). *Bee World*, 97(1), 26-31. doi: [10.1080/0005772X.2019.1672983](https://doi.org/10.1080/0005772X.2019.1672983)

Citation:

Orobchenko, O.L., Paliy, A.P., Paliy, A.P., Petrov, R.V., Musiienko, O.V., Kysterna, O.S., Prykhodko, M.F., Furman, S.V., Lisohurska, D.V., Lisohurska, O.V. (2021). Content of inorganic elements in honey and imago samples from different regions of Ukraine.

Ukrainian Journal of Ecology, 11 (3), 188-198.



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