MELLIFERA RESEARCH ARTICLE

Investigation of Some Metals in Honey Samples Produced in Different Regions of Bingöl Province by ICP-MS

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Received: 17th February, 2021; accepted:15th May, 2021; published: 15th July, 2021

A B S T R A C T

Qualitative and quantitative analyzes of metals in honey are important for the quality and authenticity of honey. Therefore, in this study, the concentrations of some metals in honey samples obtained from beekeepers in 8 different regions of Bingöl province of Turkey (Merkez, Genç, Solhan, Yayladere, Karlıova, Yedisu, Adaklı ve Kığı) were determined by ICP-MS (Inductively Coupled Plasma-Mass Spectrometry). The concentrations of Al, As, Ba, Ca, Cd, Co, Cu, Fe, Hg, Mg, Mn, Se, Sr, Zn metals were investigated in honey samples. Al, Ba, Cu were not determined in Merkez and Genç honey samples, but other elements were detected. While Hg could not be determined in all honeys, other elements were detected. In honey samples, K element was detected at the highest concentration (442.56±1.8 mg/kg), while the lowest concentration was observed in As (6.0±1 µg/kg). It was observed that the As levels determined as a result of this study did not exceed the maximum limits accepted by the European Union, and the other metal concentrations were at acceptable levels. It was determined that honey samples produced in Bingöl region are rich in minerals, not completely devoid of heavy metals, but heavy metal concentrations are below the limits determined in the literature.

Keywords: ICP-MS, honey, heavy metal, mineral, Bingöl

Introduction

Honey is a natural sweet substance that honey bees collect, dry, store and leave in the honeycomb for maturation by combining them with specific substances they collect from the nectar of plants or from the secretions of living parts of plants or from the feces of plant sucking insects in the living parts of plants [1]. Honey contains many essential nutrients, especially carbohydrates, amino acids, vitamins, phenols, enzymes and minerals; therefore, it has an important place in human nutrition and medicine due to its nutritiousness and antibacterial, antifungal and antiviral effects [2]. The composition and properties of honey vary primarily depending on the botanical origin of the nectar or honey extract, climate, geographic

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regions, and honey bee species [3]. Honey is seen as a good source of essential minerals and trace elements that humans need. However, it is reported that some elements taken from food can be toxic, especially when heavy metals exceed their safety levels [4]. As a result of the accumulation of toxic heavy metals in the human body, many health disorders such as vomiting, bleeding, jaundice, anemia, kidney failure, mental disorders, skin lesions and fragile bone structure can be seen in humans depending on the type and amount of the metal. In addition, residues and contaminants, especially in our export products, negatively affect exports; this causes economic losses. Therefore, it is necessary to investigate the ways of contamination and prevention remedies for all kinds of substances (heavy metals, toxins, etc.) that may be harmful to human health [5].

Metals are divided into 4 groups by Domingo: 1. Argon (Ar), Cadmium (Cd), Lead (Pb), Mercury (Hg) 2. Essential trace metals Chromium (Cr), Cobalt. (Co), Manganese (Mn), Selenium (Se), Zinc (Zn) 3. Other metals of biological importance Nickel (Ni), Vanadium (Va) 4. Pharmacological metals Aluminum (Al), Calcium (Ca), Lithium (Li) [6].

Heavy metals; these are elements that show metallic properties, have relatively high density, and may show toxic effects even at low concentrations. In this group; there are more than 60 metals including lead, cadmium, chromium, iron, cobalt, copper, nickel, mercury and zinc. The most important feature that distinguishes heavy metals from other toxic substances is their natural presence in the earth's crust. That is, it can neither be created nor destroyed by humans. These metals, which are not necessary for the human body, are taken into the body through food, water or respiratory tract, and cause a "metal load" to form. Heavy metals are taken into the organism through the mouth, respiration and skin, and most of them cannot be excreted through the body's excretory pathways (kidney, liver, intestine, lung, skin) without special support. Therefore, most of the heavy metals accumulate in biological organisms. These metals, which concentrate in living things with their metal load, cause many chronic and degenerative diseases. In addition, these heavy metals can affect many biochemical reactions by binding to the functional groups of proteins, can take part in enzymatic activities in different pathways, and affect nuclear metabolism and ATP synthesis.

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The toxic effects of heavy metals vary according to the properties of each metal. However, all of them generally affect more than one organ and system. Toxic heavy metals; It damages nerves and bones, blocks the functions of important enzyme groups and causes cancer. Same time; As a result of studies conducted on subjects, behavioral disorders due to psychological and neurological effects, neurotransmitter production and irregularities in their functions were observed in people exposed to heavy metals. For example; when metallic mercury is taken into the body, it mixes with the blood and easily reaches all tissues including the brain and accumulates in the brain. Metallic mercury vapor is rapidly absorbed from the lung and distributed to the central nervous system; it may cause the development of central nervous system symptoms such as extreme irritability, forgetfulness, weakness, visual disturbances, tremors in the hands, arms, legs and head. The only way to help the body fight against heavy metals is to remove heavy metals from the body and eliminate the possibility of re-exposure [7].

The importance and some properties of ultra trace elements for human health in the study

Although it is generally accepted that Na (Sodium) is essential for human life, sodium salts are found in almost all foods and drinking water [8]. The formation of hypertension in different types of animals given high levels of sodium chloride in their diet is clearly demonstrated. [9]. The WHO recommends reducing sodium intake to reduce blood pressure in adults and the risk of cardiovascular disease, stroke and coronary heart disease. WHO recommends reducing sodium (5 g / day salt) by 2 g / day in adults [10].

K (Potassium) is a mineral and an electrolyte. It helps your muscles work, including those that control your heartbeat and breathing [11]. Total body potassium is approximately 3500 mmol. Approximately 98% of the total is intracellular, mainly in skeletal muscle and to a lesser extent in the liver. The remaining 2% (approximately 70 mmol) is in extracellular fluid (ECF) [12]. WHO recommends increasing potassium intake from food to reduce blood pressure and the risk of cardiovascular disease, stroke, and coronary heart disease in adults. WHO recommends a potassium intake of at least 90 mmol / day (3510 mg / day) for adults [13].

Aluminum (Al) atomic number is 13 and it has a silver appearance in color. For most

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people, aluminum is not as toxic as heavy metals. However, aluminum may rarely cause vitamin D-resistant osteomalacia, erythropoietin-resistant sufficiently high doses (>50 g / day microcytic anemia and central nervous system changes. Aluminum has been established as a neurotoxin, although the basis of its toxicity is unknown. Recently, it has been shown to alter the function of the blood-brain barrier (BBB), which regulates the exchange between the central nervous system (CNS) and peripheral circulation [14].

Arsenic (As) is a metalloid located between metal and nonmetal and has different chemical forms. Arsenic inhibits reductase enzyme activity that prevents the formation of reactive oxygen species (ROS) in the cell, causing ROS increase and damage by binding to DNA and other cell components, and various types of cancer occur [15,16]. After the International Agency for Research on Cancer (ICRA) classified arsenic as first degree carcinogens in 1980, the World Health Organization (WHO) reduced the upper limit value of arsenic allowed in drinking water from 50 ppb to 10 ppb [17].

Ba (Barium) is a soft silvery-white metal that is slightly golden when ultra pure [18]. Organs damaged by water-soluble barium compounds (i.e. barium ions) are the eyes, immune system, heart, respiratory system, and skin. In Canada, a maximum acceptable concentration (MAC) of 2.0 mg / L (2,000 µg / L) is recommended for total barium in drinking water [19].

Ca (Calcium) is the fifth element predominantly found in the body that is needed in large quantities. 99% of calcium in the body is found in the structure of bones and teeth, and 1% in intra and extracellular fluid. Calcium activates cell signaling in muscle contraction, nerve conduction, cell division, communication between cells, release of hormones [20]. The only source of calcium in the body is calcium from food. 2500 mg / day value is reported as the upper limit [21].

Cadmium (Cd) is a heavy metal that can cause serious problems in terms of human and living health due to its high mobility in soil, root and seed systems [22]. Cadmium is highly harmful in living things and is a metal that has toxic effects on almost every tissue [23]. It is known to cause reproductive and kidney disorders, hepatic toxicity, osteomalacia, cancer and cardiovascular diseases, and also affect protein, enzyme, carbohydrate and nucleic acid metabolism [66,67]. The Joint FAO / WHO Expert Committee on Food Additives has declared that 7 µg / kg body

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weight is tentatively acceptable weekly intake level [24].

Co (Cobalt) is also important in the nutrition of living things. Cobalt is the central building block of vitamin B_{12}. Cobalt is assimilated only with the intake of vitamin B_{12}, not in its ionic or metallic form. It is the most effective biocatalyst known to date. Cobalt deficiency increases the risk of anemia. The daily need for cobalt is 5 mg [68]. According to the assessment of the IARC, cobalt has a carcinogenic effect for humans. According to the report of the United States National Toxicology Program (NTP), cobalt sulfide significantly increases the incidence of lung tumors in animals compared to controls [25-27].

Cu (Copper) is one of the essential micronutrient trace elements that are abundant in various rocks and minerals. It plays an important role in iron metabolism. It is required for a wide range of metabolic processes in both prokaryotes and eukaryotes. There are at least 30 known copper-containing enzymes that have functions such as oxygen carriers (hemocyanin) or redox catalysts (cytochrome oxidase, nitrate reductase) [28]. Copper is essential as a trace dietary mineral for all living organisms as it is an essential component of the respiratory enzyme complex cytochrome c oxidase [29]. In copper deficiency, clinical disorders such as hypochromia anemia, neutropenia and ostewporosis can be seen. In the case of copper excess, clinical conditions such as Wilson (Hepatolenticular Degeneration), acute and chronic copper toxicity may occur [30]. The maximum value that copper salts can be found as particles in air is limited to 1 mg / m^3. [31].

It is necessary for the absorption of certain minerals such as Fe (Iron), copper and calcium, and for the production of red blood cells and various enzymes that carry oxygen in the blood. It also boosts the immune system. It is found in the organism hemoglobin, myoglobin, and respiratory enzymes. It is found in foods in the form of Fe 3. Excess iron is toxic to humans, because excessive intake of divalent iron (ferrous iron) reacts with peroxides in the body to form free radicals. Daily requirement is 8 - 10 mg [32]. The daily amount of iron that needs to be absorbed into the blood is around 1.5 mg in adults. Moderate to severe poisoning occurs when elemental iron intake exceeds 40 mg / kg. Intakes exceeding 60 mg / kg can be fatal [33].

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Hg (Mercury) is a metal that is liquid at room temperature. At sufficiently high doses, all types of mercury can produce toxicity [34]. Mercury vapor is monoatomic and can dissolve in lipids; therefore, 80% accumulation occurs in the organism. When metallic mercury is taken into the body, it mixes with the blood and easily reaches all tissues including the brain and accumulates in the brain [35]. The lethal mercury concentration in the air is up to 10 ppm in acute poisoning caused by inhalation in factories working on mercury. The lethal dose of mercury compounds is 1 gram [69]. It is dangerous if the maximum amount of mercury in food is more than 0.05 mg / kg [70].

Magnesium (Mg) is the fourth essential element in terms of the amount found in the human body (2000 mEq in a 70 kg human), second after potassium in terms of the amount found in the intracellular space, and is an essential element required for the function of more than three thousand enzymes [36]. 60% of the magnesium in the human body is in bones and teeth. The remaining 40% is contained in blood, tissue and other body fluids. It is more concentrated in the brain and heart than other tissues [37]. If the magnesium level in the serum is below normal, it means Hypomagnesemia. In this case, the serum magnesium concentration is below 1.6 mEq / L (< 1.9 mg / dl). [38]. If the magnesium level in the serum is above normal, it means Hypermagnesemia. Serum magnesium concentration above 2.1 mEq / L (> 2.5 mg / dl) [39].

Mn (Manganese) contains more than 300 minerals in nature that contain manganese [40]. It is among the minerals found in small amounts in the human body. In the body; there is a total of 10-20 milligrams of manganese, mainly in the kidneys, pancreas, liver and bones. Taking 2-3 milligrams of manganese a day is sufficient for health [41]. It plays a role in many processes in the body such as bone formation, hormone functions, blood sugar regulation, and immune system functions. It helps the healing of wounds, bone formation, absorption of nutrients [41].

An essential mineral, Se (Selenium) has an essential value for human life [42]. Selenium participates in the structure of many enzymes as a cofactor and plays a role in many events such as thyroid hormone mechanism, antioxidant enzyme defense, regulation of the immune system [43]. The minimum amount of selenium that should be taken to prevent deficiency symptoms in humans is 10 µg / day; The maximum

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tolerable intake is estimated at 400 µg / day [44]. Plasma selenium level should be on average 125 ng / mL [45].

Strontium (Sr) is a trace element common in nature and recommended for the treatment of osteoporosis. Its effect on bone is dose dependent. It disrupts bone mineralization in high doses. When using low doses for a long time, bone resorption decreases and formation increases. With Sr, there is an increase in both trabecular and cortical bone [71]. When strontium is administered at low doses (2-5 microg), cell differentiation and bone formation; intact nodule formation by changing mineralization at high concentration (20-100 microg); It causes the formation of hydroxyapatite when administered at a drug dose [46]. It is used in a daily dose of 2 g, it is safe and effective. Its effect on bone is dose dependent. When taken in high doses, it reduces calcitriol and bone mineralization [47].

Zn (Zinc) is an essential element for the organism. It plays a critical role for the structural and functional integrity of cells. It has functions in gene expression and growth. It protects from ultraviolet radiation, facilitates wound healing, contributes to immune and neuropsychiatric functions, and reduces the risk of cancer and cardiovascular disease. There is 1-2.5 gr of zinc in the human body [48]. Daily zinc requirement varies according to gender and age. The daily zinc requirement in adults is 15 mg [49,50].

Materials and Methods

Honey samples used in this study were obtained from beekeepers in Bingöl city (from Turkey) and its seven towns: Genç, Solhan, Karlıova, Adaklı, Yedisu, Kığı, and

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Yayladere. The location of the regions on the map is shown in Figure 1.

Figure 1. The regions where the study was conducted: Bingöl city and its seven towns

Reagents

Ultrapure distilled water (18.3 MΩ cm − 1) was used throughout the entire experiment. Multi-Element Calibration Standard (Agilent Technologies, USA) and Internal Standard Mix (Agilent Technologies, USA) were used as the calibration standard. Nitric acid, 65% Suprapure Merck (Darmstadt, Germany) brand was used.

- The natural mortality of Varroa *:* Each hive is equipped with a lange, coated with greasy material, placed on the floor (the plateau) of hives. Each lange is protected by a metal grid preventing bees from accessing it. The count of dead Varroa is done every three weeks throughout the study period.

Sample preparation and analysis method for ICP-MS

In the elemental analysis performed with ICP-MS, firstly the samples were solubilized by burning supra pure with 65% nitric acid in a microwave cracker oven (CEM MARS6 One Touch USA). Completely dissolved samples were diluted with 1% supra pure nitric acid solution using 18.3 MΩ ultrapure water (Human Power I). ICP-MS calibration solutions mix standards (Agilent Technologies, USA) were prepared in seven different concentrations (Table 1) using 1% supra pure nitric acid-ultrapure water.

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Table 1. Calibration standards

	1.Standard 1 (ppb)	2.Standard 10 (ppb)	3.Standard 25 (ppb)	4.Standard 50 (ppb)	5.Standard 125 (ppb)	6.Standard 250 (ppb)	7.Standard 500(ppb)	Internal standard
Analytes	^{23}Na, ^{24}Mg, ^{27}Al, ^{39}K, ^{43}Ca, ^{55}Mn, ^{57}Fe, ^{59}Co, ^{63}Cu							^{45}Sc
	^{66}Zn, ^{75}As, ^{82}Se, ^{88}Sr, ^{111}Cd, ^{138}Ba, ^{202}Hg							^{89}Y

ICP-MS (Agilent 7700X (Tokyo, Japan)) device was used for element analysis in the study, and ICP-MS calibration was performed before each measurement. ^{45}Sc, ^{89}Y internal standard elements were used for the control of calibration graph and element analysis. After the samples prepared and the calibration charts created, the analysis of the elements with the ICP-MS device was made as follows: The samples diluted in the standard calibration range using a peristaltic pump were sent to the cyclonic spraychember with high purity argon gas flow. High levels of helium gas have been used to prevent interference. In addition, for the reliability of the measurements, standard reading was made after each sample, and device control was provided. Operating conditions of the ICP-MS device are given in Table 2, and analytical parameters are given in Table 3.

Table 2. ICP-MS device working conditions

Parameter	Description / Value
Radio frequency power	1550 W
Radio frequency matching	1.80 V
Radio frequency	27.12 MHz
Plasma gas flow (Ar)	15 L/min
Plasma gas	Ar X50S 5.0
Makeup gas	0.9 L/min
Carrier gas (inner)	1.1 L/min
Sample intake	0.5 mL/min

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Spray chamber temperature	2°C
Nebulizer pump	0.1 rps
Resolution m/z	244 amu
Short-term stability	<3% RSD
Long-term stability	<4% RSD/2 h
Background	<5 cps (9 amu)
Cones	Ni
Rinse time	45 sec
Injector	2.0 mm

Table 3. Analytical parameters of the ICP-MS method

Element	Linear range (µg/kg)	Regression	Correlation coefficient (r)	Limit of detection (µg/kg)	Limit of quantification (µg/kg)
Na	0–500	y=0.049x+00	0.9997	0.2126	0.6982
Mg	0–500	y=0.023x+00	0.9999	0.1504	0.5248
Al	0–500	y=0.006x+00	0.9999	0.1122	0.4306
K	0–500	y=0.011x+00	0.9998	0.2012	0.6402
Ca	0–500	y=0.001x+00	0.9996	0.2015	0.6005
Mn	0–500	y=0.062x+00	0.9999	0.2200	0.6600
Fe	0–500	y=0.003x+00	0.9998	0.3006	0.9018
Co	0–500	y=0.247x+00	0.9999	0.0926	0.2896
Cu	0–500	y=0.203x+00	0.9998	0.4321	1.2894
Zn	0–500	y=0.027x+00	0.9997	0.9151	2.7526
As	0–500	y=0.004x+00	0.9999	0.2236	0.7446
Se	0–500	y=0.001x+00	0.9999	0.3685	1.2275
Sr	0–500	y=0.020x+00	0.9999	0.1242	0.4628
Cd	0–500	y=0.013x+00	0.9999	0.3255	0.8985
Ba	0–500	y=0.082x+00	0.9999	0.2018	0.6122
Hg	0–500	y=0.021x+00	0.9997	0.4186	1.2948

Values expressed are means ±standard deviation of three parallel measurements ($p < 0.05$).

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Results and Discussion

In this study, elemental analysis of honey samples obtained from 8 different regions of Bingöl province was performed. The results of the elemental analysis are given in Table 4 with their three parallel mean and standard deviation values.

Table 4. Elemental analysis results of honey

Sample Id	Na 23 (mg/kg)	K 39 (mg/kg)	Al 27 (µg/kg)	As 75 (µg/kg)	Ba 138 (µg/kg)	Ca 43 (mg/kg)	Cd 111 (µg/kg)	Co 59 (µg/kg)
Bingöl City	15,78±0,5	432,15±2	<LOD	6,5±0,3	<LOD	20,2±1,1	285,0±5	506,2±13
Genç	23,43±1,1	412,52±1,9	<LOD	6,0±0,1	<LOD	11,7±0,2	251,1±54	544,1±45
Solhan	19,62±1	442,56±1,8	2686,0±112	6,9±0,3	27,4±1,1	16,6±0,3	223,8±23	656,4±39
Yayladere	16,21±0,9	401,12±2	8183,3±442	6,9±0,3	766,8±29	42,4±1,9	232,0±49	800,2±69
Karlıova	10,25±0,7	298,55±1,4	1903,0±62	6,4±0,2	57,7±2,1	21,1±1,6	198,7±41	936,1±28
Yedisu	25,11±1,2	320,15±1,8	1831,6±507	7,5±3	67,4±12	30,6±4,6	171,1±18	994,1±8
Adaklı	26,21±1	391,52±1,5	48053,8±1175	5,8±2	1716,9±87	56,7±5,1	177,1±57	1024,6±39
Kığı	24,02±0,9	333,58±1,9	1520,5±256	6,7±2	117,3±11	18,3±1,1	265,9±18	955,9±34

Sample Id	Cu 63 (µg/kg)	Fe 57 (µg/kg)	Hg 202 (µg/kg)	Mg 24 (mg/kg)	Mn 55 (µg/kg)	Se 82 (µg/kg)	Sr 88 (µg/kg)	Zn 66 (µg/kg)
Bingöl City	<LOD	849,1±85	<LOD	29,2±0,9	1190,3±75	468,1±45	595,68±35	208,9±49
Genç	<LOD	438,8±69	<LOD	17,5±0,8	612,8±71	593,1±30	266,75±34	364,2±94
Solhan	636,7±70	5065,4±530	<LOD	56,4±1,9	921,2±87	323,9±36	425,44±33	4205,1±81
Yayladere	946,8±140	7566,5±317	<LOD	113,8±3	5306,7±126	319,4±65	1524,65±147	4927,3±176
Karlıova	439,7±66	2615,0±46	<LOD	33±1,4	631,7±57	348,2±110	367,09±22	1943,7±133
Yedisu	<LOD	2827,5±351	<LOD	67,6±2,3	2430,3±43	377,6±4	598,68±43	2206,2±110

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Adaklı	3464,2±157	3282,5±136	<LOD	117,7±1,9	12328,3±137	349,5±27	1487,15±83	1792,7±21
Kığı	<LOD	3007,2±115	<LOD	36,4±1,2	1509,9±41	281,6±72	615,33±39	1046,9±39

Since the concentrations of K, Na, Mg, and Ca are high, the results are given in mg/kg (ppm), and the concentrations of the other elements are given as µg/kg (ppb). In this study, Na, K, As, Ca, Cd, Co, Fe, Mn, Se, Sr, and Zn elements were detected in all honey samples, whereas Hg was not detected in any honey samples (<LOD). In the study, the minimum value of Na element in honey found in different regions is 10.25 ppm and the maximum value is 26.21 ppm. They found the amount of Na element between 0.0657-0.2791 ppm in the study by Bengü and Kutlu (2020) "Analysis of Some Basic and Toxic Elements in Honey Supplied from Bingöl with ICP-MS" [51]. In another study, the amount of Na in honey was found between 11.7 and 52 ppm [52]. Kek et al. (2017) found the minimum and maximum values of Na amount as 375.2-944.5 ppm, respectively, in their study on 8 different honey samples [53]. In another study, Na was found in the range of 52.38–289.20 ppm. The amount of K in our honey samples is in the range of 298.55- 442.56 ppm. Kek et al. (2017) found the minimum and maximum values of K amount as 95.4-1643.9 ppm, respectively, in their study on 8 different honey samples. In another study, the amount of K was found in the range 104.40-878.70 ppm [54]. They found the amount of K element between 2,612-6,871 ppm in the study "Analysis of Some Basic and Toxic Elements with ICP-MS in Honey Supplied from Bingöl" by Bengü and Mutlu (2020). In another study, the amount of K in honey is between 277-7382 ppm [52]. The minimum value of the Al amount found in honey samples is 1,520 ppm and the maximum value is 48,053 ppm. Tutun et al. (2019) found the amount of Al in the range of 1.00-25.80 ppm [55]. In another study in which element analysis was performed in honey samples, the amount of Al was found in the range of 2.11-8.04 ppm [56]. The amount of As in honey samples was determined as 7.5-5.8 ppb. Aghamirlou et al. (2015) found the amount of As in the honey sample as 4.68 ppm [57]. In the study conducted on Iranian honey, the amount of As was found in the range of 0.1-0.001 ppm [58]. Roman et al. (2011), the minimum amount of As in honey samples is 0.087 ppm and the maximum value is 1.238 ppm [59]. The amount of Ba we found in the

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study is in the range of 1716.9-27.4 ppb. Tutun et al. (2019) found the amount of Ba in the range of 0.03 ppm on average. In another study, they found the amount of Ba in honey 0.75 ppm [60]. Staniškienė et al. (2006) found the amount of Ba in the range of 5.8-71.3 ppb in their study [61]. The amount of Ca we find in honey samples is 56.7-11.7 ppm. In a study, the amount of Ca in honey was found to be 219.38 ppm [54]. They found the amount of Ca element between 52.90-199.97 ppb in the study "Analysis of Some Essential and Toxic Elements with ICP-MS in Honey Supplied from Bingöl" by Bengü and Kutlu (2020). In another study, the amount of Ca was determined as 113-858 ppm [52]. In the study conducted by Tutun et al. (2019), they found the amount of Ca in the range of 0.03-0.12 ppm. Kek et al. (2017) the amount of Ca in honey 157.1 ppm, Silva et al. (2013) found it in the range of 10.28-93.37 ppm [62]. In this study, the amount of Cd was found in the range of 171.1-285.0 ppb. Kek et al. (2017) Cd amount in honey 0.001-0.004 ppm, Bayır (2019) 4.301-6.898 ppb, Tutun et al. (2019) 0.20 ppb, Aghamirlou et al. (2015) found it to be 27.62-125.88 ppb, while Yücel and Sultanoğlu (2013) found it to be 0.008–0.12 ppm [72]. The amount of Co determined in our study is 506.2-1024.6 ppb. Yücel and Sultanoğlu (2013) found that Co amount 10–120 ppb, Tutun et al. (2019) found 0.17 ppb. In this study, Cu amount was found between 439.7- 3464.2 ppb. Kek et al. (2017), the amount of Cu in honey 0.621-2.931 ppm, Bayır (2019) 0.395 -0.950 ppm, Altundağ et al. (2016) 0.45-2.15 ppm, Tutun et al. (2019) 0.38-1.52 ppm, and Kasapoğlu (2006) determined it as 0.15-0.71 ppm. The amount of Fe detected in our study is 438.8-7566.5 ppb. Kasapoğlu (2006), Fe amount in honey 1.15-13.18 ppm, Bengü and Kutlu (2020) 10.90-61.15 ppb, Yücel and Sultanoğlu (2013) 7.40-92.38 ppm and Bayır (2019) found it as 6,266 -14,500 ppm. The amount of Mg we detected in honey samples is 17.5-117.7 ppm. Kek et al. (2017) determined the amount of Mg in honey 13.72-71.04 ppm, Tutun et al. (2019) found it as 9.28- 117.16 ppm, and Bengü and Kutlu (2020) found it as 71.84- 179.91 ppb. The amount of Se detected in the study is in the range of 281.6-593.1 ppb. In the study conducted by Altunatmaz et al. (2018), the amount of Se in honey was found to be 0.096-29.496 ppm, while Costa-Silva (2011) found 1.0-2.91 μg / 100 g [63, 64]. In our study, the amount of Sr was determined as 266.75-1524.65 ppb. Studies have found that the amount of Sr in honey samples is 0.12–2.46 ppm, 0.03 ppm and 1.45 ppm [54, 55] [65]. The amount of

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Zn detected in our study is in the range of 208.9-4927.3 ppb. In their studies, Kasapoğlu (2006) 0.72-9.8 ppm, Kek et al. (2017) 1.258- 4.566 ppm, Bayır (2019) 1.039-1.635 ppm, Altundağ et al. (2016) found it to be 0.80-64.49 ppm.

Conclusion

It is inevitable that our analysis results differ from the results in the literature, as the element content of honey may be affected by the plants visited by the bees, the difference in the raw materials they collect to produce honey, the environment, exhaust gases, industrial activities, and even bee races. The results obtained showed that Bingöl honey consumption will not cause any problem in terms of metal concentrations. Metal concentrations of the studied honeys were found to be in accordance with the limits of the foods consumed according to the WHO data and other literature data. In this study, it was determined that honeys are rich in minerals. It is evaluated that Bingöl honey, which is especially rich in Fe and Zn content, can be used as an important food supplement considering the importance of these minerals in terms of health. It is also pleasing that some of the metals such as As, Cd and Hg, which are considered to be the most dangerous heavy metals, were not detected or found in low amounts in Bingöl honeys. This situation can be considered as a result of the lack of industrial facilities that will cause environmental pollution in Bingöl province and the protection of its natural flora. This study is expected to contribute to the literature on the element analysis of honey.

Bingöl İlinin Farklı Bölgelerinde Üretilen Bal Örneklerinde Bazı Metallerin ICP-MS ile Araştırılması

Öz: Balda bulunan metallerin kalitatif ve kantitatif analizleri, balın kalitesi ve güvenilirliği açısından önemlidir. Bu nedenle, bu çalışmada Türkiye'nin Bingöl ilinin 8 farklı bölgesindeki (Merkez, Genç, Solhan, Yayladere, Karlıova, Yedisu, Adaklı ve Kığı) arıcılardan temin edilen bal örneklerinde bazı metallerin konsantrasyonları ICP-MS (İndüktif Eşleşmiş Plazma-Kütle Spektrometresi) ile belirlenmiştir. Toplanan bal örneklerinde Al, As, Ba, Ca, Cd, Co, Cu, Fe, Hg, Mg, Mn, Se, Sr, Zn metallerinin konsantrasyonları araştırıldı. Merkez ve Genç'ten toplanan bal örneklerinde, Al, Ba, Cu metalleri belirlenmezken diğer elementler ise tespit edildi. Balların

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tamamında ise Hg belirlenemezken diğer elementler tespit edilmiştir. Bal örneklerinde K elementi en yüksek konsantrasyonda (442,56±1,8 mg/kg) tespit edilirken, en düşük konsantrasyon ise As’de (6,0±1 µg/kg) görüldü. Bu çalışma sonucunda belirlenen As düzeylerinin Avrupa Birliği tarafından kabul edilen maksimum limitleri aşmadığı, diğer metal konsantrasyonlarının ise kabul edilebilir düzeylerde olduğu görüldü. Bingöl bölgesinde üretilen bal örneklerinin mineral yönünden zengin olduğu, ağır metallerden tamamen yoksun olmadığı ancak ağır metal konsantrasyonlarının literatürde belirlenen limitlerin altında olduğu tespit edilmiştir

Anahtar Kelimeler: ICP-MS, bal, ağır metal, mineral, Bingöl

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