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RESEARCH ARTICLE

Determination of the Metal Contents of Honey Samples from Orumieh in Iran

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Summary

In this study the concentrations of metals in 89 different honey samples were collected, from four different areas of Orumieh City, in Iran from September of 2009 were investigated. Most of the samples were obtained from beekeepers located at a distance of 10 km from the roadside, to their accommodation. Pb, Co, Cr, Fe, Mn, Zn, As and Ni were detected in all of the honey samples. The contents of metals in honey samples were found to be in the range of 0.04±0.1 ppm, 0.001±0.002 ppm, 7.09±9.4 ppm, 0.6±0.9 ppm 0.06±0.1 ppm, 9.99±26.5 ppm, 0.0008±0.0011 ppm, 0.003±0.005 ppm for Pb, Co, Cr, Fe, Mn, Zn, As and Ni respectively. At the end of the study the Pb levels were found to be lower than the maximum residue limits of the European Union. Other metal levels were within acceptable levels. It was detected that the honey which was collected was of good quality from the point of metal contents.

Keywords: *Atomic absorption spectrometry, Honey, Iran, Metal, Orumieh*

İran'ın Orumieh Şehri'nden Toplanan Ballarda Metal Düzeylerinin Belirlenmesi

Özet

Bu çalışmada İran'ın Orumieh Şehri'nin 4 farklı bölgesinden (Tergever, Mergever, Sero ve Merkez) 2009 Eylül ayında toplanan 89 farklı bal örneklerinde metal kalıntı (Pb, Co, Cu, Fe, Mn, Zn, As, Ni) düzeyleri araştırıldı. Örneklerin çoğunluğu yol kenarlarına en az 10 km mesafede konaklayan arıcılardan sağlandı. Pb, Co, As, Ni analizleri Grafit Fırınlı Atomik Absorpsiyon Spektrometre cihazı ile, Fe, Cu, Mn ve Zn analizleri ise Alevli Atomik Absorpsiyon Spektrometre cihazı ile yapıldı. Analizler sonucunda bütün bal örneklerinde Pb, Co, Cu, Fe, Mn, Zn, As ve Ni tespit edildi. Analiz edilen bal örneklerinde Pb 0.04±0.1 ppm, Co 0.001±0.002 ppm, Cu 7.09±9.4 ppm, Fe 0.6±0.9 ppm, Mn 0.06±0.1 ppm, Zn 9.99±26.5 ppm, As 0.0008±0.0011 ve Ni 0.003±0.005 düzeyinde tespit edildi. Bu çalışma sonucunda belirlenen Pb düzeylerinin Avrupa Birliği tarafından kabul edilen maksimum kalıntı limitlerini aşmadığı, diğer metal düzeylerinin ise kabul edilebilir düzeylerde olduğu görüldü. Metal kalıntı yönünden balların iyi kalitede olduğu tespit edildi.

Anahtar sözcükler: *Atomik absorpsiyon spektrometresi, Bal, İran, Metal, Orumieh*

INTRODUCTION

Honey has been used for different aims such as a whole food in all parts of the world, treatment for various ailments and diseases, in medicine and also as a biological monitor for the determination of heavy metals, radioactivity in the region and to determine environmental quality in polluted environments [1-4]. There are various reviews about honey which used as a method for determining the amount of heavy metals of the region. Beekeeping is considered to be one of the most important agricultural activities in the world. Nowadays it is estimated that are 56 million bees

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worldwide and that 1.2 million tons honey is produced by them in one year [5-7].

Iran is the one of the most important honey producers country in the world. According to official statistics in 2007, 2% of world's total honey production came from Iran with 36.000 tons. Approximately 10.000 tons of honey is produced in Orumieh City yearly [8,9]. The aim of this study is to determine the residue of some heavy metals (Pb, Co, Cr, Fe, Mn, Zn, As and Ni) in honey samples collected from four different regions of Orumieh City and to determine potential health risks to humans.

MATERIAL and METHODS

In total eighty-nine samples were collected, made up from the following regions Tergever (26 samples), Mergever (22 samples), Serow (19 samples) and Center region (22 samples) of Orimieh in 2009 September *(Fig. 1)*. Natural honey, natural + sweet honey, wax honey were collected from Tergever and Mergever regions. Natural honey and natural + sweet honey were collected from Serow and Center regions. The honey samples were stored in plastic molds and kept at room temperature (25°C) until analyzed.

One gram of honey samples from each region were mixed with magnesium acetate (1 mg/mL). The mixture was placed in a porcelain crucible. After drying at 100°C for 2 h, the samples were ashed at 600°C. Care was taken during heating so that no excess foaming took place. The ash was extracted with nitric acid (HNO_3) 2N and was diluted to 30 mL. The contents of lead (Pb), cobalt (Co), chrome (Cr), iron (Fe), manganese (Mn), zinc (Zn), arsenic (As) and nickel (Ni) were determined directly in the ash solution using atomic absorption spectroscopy (GF 3000 model AAS, Graphite Furnace GF 3000, Auto Sampler GBC PAL 3000, GBC Scientific Equipment Pty Ltd, Australia). The accuracy of the instrument was periodically checked with a known standard. Calibration curves were prepared using dilutions of stock solutions. The results were read three times and the mean values and the relative standard deviations were computed.

Data was analyzed statistically by one-way analysis of variance (ANOVA). When significant treatment effects were detected, DUNCAN'S multiple range test was used to identify specific differences between treatment means at a probability level of $P<0.05$.

RESULTS

The means and standard deviation of the ash contents of 89 honey samples for Pb, Co, Cr, Fe, Mn, Zn, As and Ni were founds as 0.04±0.1 ppm, 0.001±0.002 ppm, 7.09±9.4 ppm, 0.6±0.9 ppm 0.06±0.1 ppm, 9.99±26.5 ppm, 0.0008±0.0011 ppm, 0.003±0.005 ppm, respectively.

Statistical comparisons were calculated for regional differences and varieties of honey (*Table 1* and *Table 2*). Pb, Mn and Fe levels were statistically similar in terms of natural + sweet honey with natural honey while wax

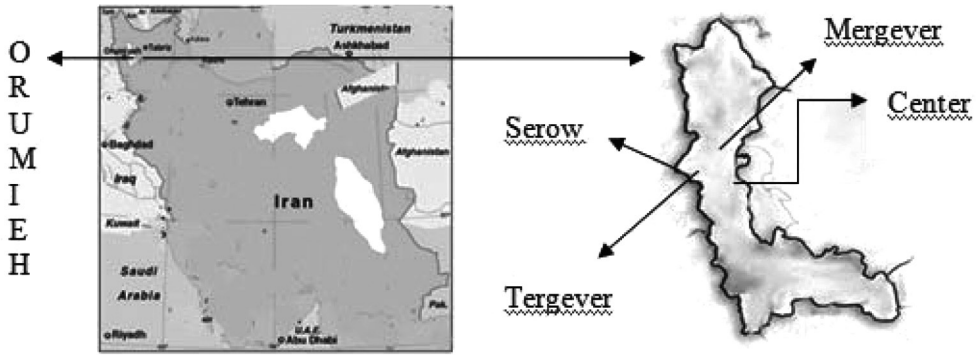

Fig 1. Locations of study areas: Tergever, Mergever, Serow and Center

Şekil 1. Çalışmanın yapıldığı bölgeler: Tergever, Mergever, Serow ve Merkez

Table 1. *Metal concentration according to different honey samples**
Tablo 1. *Farklı bal örneklerine göre metal konsantrasyonları**

Honey Samples	Pb	Co	Mn	Fe	Cr	Zn	As	Ni
natural + sweet (n:33)	0.07±0.04[a] (0.394-0.190)	0.001±0.0008 (0.0006-0.003)	0.08±0.02[a] (0.026-0.116)	0.7±0.3[a] (0.344-2.542)	8.4±3.5 (3.642-17.314)	24.3±19.2[cb] (0.953-42.490)	0.0006±0.00063 (0.0000028-0.0028)	0.003±0.001 (0.0011-0.0086)
natural honey (n:40)	0.07±0.04[a] (0.383-0.253)	0.002±0.001 (0.0003-0.005)	0.1±0.05[a] (0.018-0.305)	0.7±0.2[a] (0.378-1.935)	8.1±5.3 (3.369-33.765)	19.9±15.07[b] (0.702-68.49)	0.0011±0.00105 (0.0000264-0.0038)	0.006±0.01 (0.0015-0.068)
waxy honey (n:16)	0.1±0.08[b] (0.048-0.389)	0.002±0.001 (0.0007-0.007)	0.06±0.05[b] (0.031-0.222)	1.1±1.04[b] (0.341-4.349)	7.6±3.4 (2.968-13.635)	11.4±17.9[ab] (0.896-70.55)	0.0009±0.00065 (0.000131-0.0025)	0.005±0.004 (0.0019-0.017)

**as ppm:* *mean±Standard deviation and range*
[a,b] Mean within in the same columns with different letters are statistically significant (P<0.05)

Table 2. *Metal concentration according to different regions**
Tablo 2. *Farklı bölgelere göre metal konsantrasyonları**

Regions	Pb	Co	Mn	Fe	Cr	Zn	As	Ni
Tergever (n:26)	0.08±0.03[a] (0.048-0.20)	0.002±0.001[a] (0.0009-0.073)	0.09±0.04[a] (0.032-0.222)	0.8±0.4 (0.485-2.721)	7.6±4.07 (2.968-18.597)	14.6±9.8[c] (0.896-38.14)	0.0009±0.00086 (0.000071-0.0032)	0.005±0.003 (0.002-0.017)
Mergever (n:22)	0.1±0.07[b] (0.038-0.38)	0.001±0.001[a] (0.0005-0.0037)	0.06±0.06[b] (0.026-0.30)	0.6±0.3 (0.34-1.62)	7.09±2.4 (3.69-12.98)	9.9±12.9[ac] (0.70-52.95)	0.0008±0.00046 (0.0000448-0.00195)	0.004±0.002 (0.0022-0.098)
Serow (n:19)	0.04±00.01[c] (0.039-0.389)	0.001±0.0007[b] (0.0003-0.0035)	0.09±0.02[a] (0.03-0.16)	0.9±0.5 (0.48-2.54)	8.8±3.5 (4.27-19.33)	23.7±10.9[c] (8.02-60.58)	0.0011±0.0012 (0.0000264-0.0034)	0.004±0.005 (0.0018-0.068)
Center (n:22)	0.07±0.04[a] (0.039-0.253)	0.002±0.001[a] (0.0008-0.0044)	0.1±0.02[a] (0.018-0.17)	0.8±0.1 (0.49-1.14)	9.4±6.3 (3.369-33.765)	26.5±12.2[bc] (0.90-68.49)	0.0008±0.0009 (0.0000028-0.0038)	0.003±0002 (0.0011-0.013)

**as ppm:* *mean±Standard deviation and range*
[a.b] Mean within in the same columns with different letters are statistically significant (P<0.05)

honey showed statistically difference from the others. Furthermore significant differences were found between natural+sweet honey and wax honey samples for Zn levels *(Table 1)*. On the other hand regional comparisons were examined in this study. Significant differences were also found for Pb, Co, Mn and Zn levels in different regions. Tergever and Central regions showed similarities for these four metals *(Table 2)*.

DISCUSSION

Heavy metals are natural components of the Earth's crust. They cannot be degraded or destroyed. To a small extent they enter our bodies via food, drinking water and air as trace elements. Some heavy metals (e.g., copper, selenium, zinc) are essential to maintain the metabolism of the human body. In this study, heavy metals were analyzed and measured by atomic absorption spectrophotometer. The results indicated that Zn had highest concentration followed by Cr, Fe, Mn, Pb, Ni, Co and As.

Demirezen and Aksoy [3] reported that the ranges of the metal contents of honey samples from Kayseri as 0.11-0.18 ppm for cadmium, 0.15-0.66 ppm for copper, 2.2-11 ppm for zinc, 0.2-0.8 ppm for nickel and 0.1-0.85 ppm for lead. Fredes and Montenegro [10] determined that the contents of Pb, Cd, Cu, Fe and Mn in honey as 0.02±0.03 ppm, 0.01±0.01 ppm, 0.91±0.66 ppm, 3.13±1.44 ppm, 1.26±1.29 ppm, respectively. Frazzoli et al.[11] reported that Cd and Pb contents ranged from 0.2 to 1.37 ng g^{-1} and from 4.6 to 30.5 ng g^{-1} in flower honey, while the highest concentrations were presented by honeydew honey.

Pb, Cd, Cu, Fe and Zn contents in honey were determined as 0.10005 ppm, 0.25005 ppm, 5.00005 ppm and 3.105 ppm, respectively [12]. Erbilir and Erdogrul [4] found that the means of Cd, Mn, Fe and Mg in honey as 0.32 ppm, 0.03 ppm, 0.36 ppm and 10.45 ppm, respectively. On the other hand, Ni was not detected in the honey samples in the same study.

Devillers et al.[13] reported that the means (ranges) of Pb, Cd, Cu, Fe, Mn and Zn contents in honey from France as 0.793 ppm (0.28-1.08 ppm), 0.152 ppm (0.08-0.25 ppm), 0.305 ppm (0.06-1.71 ppm), 11.03 ppm (0.56-86.76), 3.685 ppm (0.11-42.81 ppm) and 1.343 ppm (0.17-6.42 ppm) respectively. Also, Adebiyi et al.[14] determined the means (ranges) of Cu, Fe, Mn and Zn contents in honey from Nigeria as 21 ppm (10-35 ppm), 220,6 ppm (136-407 ppm), 3 ppm (0-5 ppm) and 63.4 ppm (31-106 ppm).

The results of this study revealed that the Pb levels were higher than the results of Frazzoli et al.[11], but lower than those of Demirezen and Aksoy [3] and Devillers et al.[13], and similar to Antonescu and Mataescu [12] and Fredes and Montenegro [10]. Moreover, Fe levels that were found in this study were lower than the results of Antonescu and Mataescu [12], Devillers et al.[13], Adebiyi et al.[14], Fredes and Montenegro [10] and Erbilir and Erdogrul [4]. The levels of Mn were higher than Erbilir and Erdogrul's [4] results, but lower than results of Fredes and Montenegro [10], Devillers et al.[13] and Adebiyi et al.[14]. Results from this study for Zn were higher than the results of Demirezen and Aksoy [3], Devillers et al.[13] and Antonescu and Mataescu [12], however, lower than those of Adebiyi et al.[14]. Results from this study for Ni were lower than the results of Demirezen and Aksoy [3]. European Union (EU) maximum residue limit for Pb in honey is 1 mg/kg. The maximum residue limit for other metals in honey are not defined by EU, therefore it is difficult to evaluate the metal residues in honey from a toxicological aspect [15].

It was concluded that a little metal residue in honey samples collected from Orimieh city and the level of the residues were below the permitted limit. These results showed that the honey samples collected from Orimieh city were far from the polluted sources (i.e. highways with intense traffic, mining, industry, different botanical origins). Therefore, it is recommended that the beekeeping activities must be far from pollution. With regards to other studies, our results are in accordance with the acceptable limits of EU standards for lead. Thus the present study showed that analyzed honey samples were good quality.

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