Available online at www.sciencedirect.com
ScienceDirect
Food Chemistry 103 (2007) 325–330
Food Chemistry
www.elsevier.com/locate/foodchem

Trace element levels in honeys from different regions of Turkey

M. Tuzen [a], S. Silici [b,*], D. Mendil [a], M. Soylak [c]

[a] Gaziosmanpasa University, Chemistry Department, 60250 Tokat, Turkey
[b] Erciyes University, S. Cikrikcioglu Vocational College, Department of Animal Science, 38039 Kayseri, Turkey
[c] Erciyes University, Department of Chemistry, 38039 Kayseri, Turkey

Received 24 May 2006; received in revised form 29 June 2006; accepted 25 July 2006

Abstract

A survey of 25 honey samples from different botanical origin, collected all over the Turkey was conducted to assess their trace element contents. The aim of this study was to determine the levels of cadmium (Cd), lead (Pb), iron (Fe), manganese (Mn), copper (Cu), nickel (Ni), chromium (Cr), zinc (Zn), aluminium (Al) and selenium (Se) in honey samples from different regions of Turkey. Trace element contents were determined by a flame and graphite furnace atomic absorption spectrometry technique after dry-ashing, microwave digestion and wet-digestion. The accuracy of the method was corrected by the standard reference material, NIST-SRM 1515 Apple leaves. The contents of trace elements in honey samples were in the range of 0.23–2.41 μg g^{-1}, 0.32–4.56 μg g^{-1}, 1.1–12.7 μg g^{-1}, 1.8–10.2 μg g^{-1}, 8.4–105.8 μg kg^{-1}, 2.6–29.9 μg kg^{-1}, 2.4–37.9 μg kg^{-1}, 0.9–17.9 μg kg^{-1}, 83–325 μg kg^{-1} and 38–113 μg kg^{-1} for Cu, Mn, Zn, Fe, Pb, Ni, Cr, Cd, Al and Se, respectively. Iron was the most abundant element while cadmium was the lowest element in the Turkish honeys surveyed. The results showed that trace element concentrations in the honeys from different regions were generally correlated with the degree of trace element contamination of the environment.

Keywords: Atomic absorption spectrometry; Microwave digestion; Trace element; Turkish honeys

1. Introduction

Honey is produced by honeybees from nectar of different plants, as well as from honeydew. It is one of the most complex foods produced by nature, and is the only sweetening agent that can be used by humans without processing. As a foodstuff used for healing purposes, honey must be free any of objectionable contents, and it should contain only small amounts of pollutants, such as heavy metals. Despite the fact that the mineral content of honey is very low when compared with other components, great variability has been reported in honey contents of sodium, calcium, magnesium, iron and copper. Metals such as chromium, cobalt, copper, iron, manganese and zinc (among others) are essential for humans, and they may play an important role in a number of biochemical processes (Falco, Gomez-Catalan, Llobet, & Domingo, 2003; Garcia, Garcia, Latorre, Martin, & Crecente, 2005). However, these elements can also be toxic to humans when ingested in high doses (Domingo, 1994). In contrast, elements such as cadmium, lead and mercury are well-known toxic elements for humans. The presence of heavy metals can pose human health risks and their presence in honey has not been much studied in contrast to other hazardous compounds, such as pesticides and antibiotics (Fredes & Montenegro, 2006).

Minerals can be highly indicative of the geographical origin of honey and can be used as environmental indicators (Przybylowski & Wilczynska, 2001; Uren, Serifoglu, & Sarikahya, 1998). Honeybees may continuously be exposed to contaminants present in the area surrounding the apiary for the duration of their foraging activity (Conti & Botre, 2001). Therefore honeybees and their products can be considered representative bioindicators of the environmental pollution (Conti & Botre, 2001; Leita,

* Corresponding author. Tel.: +90 3524374901x41503; fax: +90 35243 71383.
E-mail address: silicis@erciyes.edu.tr (S. Silici).

0308-8146/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.foodchem.2006.07.053

Muhlbachova, Cresco, Barbattini, & Mondini, 1996; Yazgan, Horn, & Isengard, 2006). The honeybee's area of foraging activity generally extends over a surface of more than 7 km^2. It is because of this large surface area that honey bees and their products (mainly honey and pollen) have been proposed as suitable bioindicators of chemical pollution (Crane, 1984; Leita et al., 1996; Raes, Cornelis, & Rzeznik, 1992). Apiaries located near polluted areas (because of intense traffic, industrial contaminants) can help in monitoring of the heavy metals from the various sources. However, honey may not be the most sensitive tool for evaluating environmental contamination with heavy metals due to the low concentration present, and the great variability caused by several factors, e.g. botanical origin, floral density, season of the year and rainfall (Fredes & Montenegro, 2006).

The mineral and heavy metal contents of honey have been the subject of many studies using different methods. For instance, Rodriguez-Otero, Pasrio, Simal, and Cepeda (1994) analyzed the mineral contents of some honeys from Galicia using flame atomic absorption spectrometry. Poiana, Fudo, Manzini, Postarino, and Mincione (1996) used high-performance ionic chromatography to quantify minerals in some unifloral honeys of Italian origin. Feller-Demalsy, Vincent, and Beaulieu (1989) analyzed the minerals in honeys from Canada by the neutron activation technique. Terrab, Gonzalez, Diez, and Heredia (2003) used flow injection analysis, coupled with atomic spectroscopy, to determine the metal ions in honeys from Spain.

In Turkey, thanks to geographical and climatic conditions that provide a suitable environment for apiculture, honey production has been well developed. The beekeeping that has been sustained in Turkey for thousands of years is an important agricultural activity. According to the data given by the State Statistics Institute (DIE, 1988), there are about 2,984,000 hives in Turkey, and two third of them are modern hives and Turkey produces about 80,000 tons of honey per year (Anonymous, 1997). Again there have been around 35,000 beekeepers in Turkey, managing 4 million colonies of bees, and Turkey makes a contribution of 5.7% to the total world honey production.

Mineral contents of Turkish honey have been studied by different researchers (Sevimli, Bayulgen, & Varinlioglu, 1992; Uren et al., 1998) but very limited data are available on the trace element contents of Turkish honeys. The aims of this research can be summarized under two headings: (a) to study trace element contents of Turkish multifloral honeys and (b) to compare trace element contents of honey samples from different regions of Turkey, using three different methods.

2. Materials and methods

2.1. Sampling

This study was conducted on 25 multifloral honey samples produced in 2005 and from different regions of Turkey (Table 1, Fig. 1). The honey samples were taken directly from the beekeepers, and the extraction of honeys from combs was done by centrifugation. All samples were unpasteurised and were taken no more than three months after extraction, stored in glass holders and immediately transferred to the laboratory and kept at 4–5 °C. Analyses were done within a six-month time period after harvesting. The declared botanical origin by the producers was considered, and one sample was from each sampling point.

2.2. Apparatus

A Perkin–Elmer Analyst 700 atomic absorption spectrometer (FAAS), equipped with HGA graphite furnace and with deuterium background corrector, was used in the experiments. For flame measurements, a 10 cm long slot-burner head, a lamp and an air–acetylene flame were used. For graphite furnace measurements, argon was used as inert gas. The operating parameters for the working elements were set as recommended by the manufacturer. Pyrolytic-coated graphite tubes (Perkin–Elmer part no. B3 001264) with a platform were used. Samples were injected into the graphite furnace using a Perkin–Elmer AS-800 auto sampler.

A Milestone Ethos D closed vessel microwave digestion system (maximum pressure 1450 psi, maximum temperature 300 °C) of teflon reaction vessels was used in all the digestion procedures. The reaction vessels were cleaned using 5 ml of concentrated nitric acid before each digestion.

Table 1
Honey samples from different region of Anatolia

Samples	Location	Geographical origin
H01	Bursa	Marmara Region (West Anatolia)
H02	Bursa	Marmara Region (West Anatolia)
H03	Bursa	Marmara Region (West Anatolia)
H04	Muğla	Aegean Region (West Anatolia)
H05	Izmir	Aegean Region (West Anatolia)
H06	Kayseri	Central Anatolia
H07	Yozgat	Central Anatolia
H08	Kayseri	Central Anatolia
H09	Sivas	Central Anatolia
H10	Ankara	Central Anatolia
H11	Sanliurfa	East and Southeast Anatolia
H12	Bitlis	East and Southeast Anatolia
H13	Bingol	East and Southeast Anatolia
H14	Erzurum	East and Southeast Anatolia
H15	G.Antep	East and Southeast Anatolia
H16	Adana	Mediterranean region
H17	Adana	Mediterranean region
H18	Adana	Mediterranean region
H19	Mersin	Mediterranean region
H20	Antalya	Mediterranean region
H21	Samsun	Black Sea Region
H22	Sakarya	Black Sea Region
H23	Ordu	Black Sea Region
H24	Artvin	Black Sea Region
H25	Giresun	Black Sea Region

Fig. 1. Honey samples collected from different region of Turkey.

2.3. Reagents

All reagents were of analytical grade unless otherwise stated. Double-deionised water (Milli-Q Millipore 18.2 MΩ-cm resistivity) was used in all dilutions. HNO_3 and H_2O_2 were of suprapure quality (E. Merck, Darmstadt). All the plastic and glassware were cleaned by soaking in dilute HNO_3 (1 + 9) and rinsed with distilled water prior to use. The element standard solutions used for calibration were prepared by diluting stock solutions of 1000 mg/l of each element supplied by Sigma.

2.4. Digestion procedures

2.4.1. General

Three different types of digestion procedures were applied to the digestion of honey samples: dry, wet and microwave digestions. The procedures are given below.

2.4.2. Dry ashing

One gramme of sample was placed in a high form porcelain crucible. The furnace temperature was slowly increased from room temperature to 450 °C in 1 h. The samples were ashed for about 8 h until a white or grey ash residue was obtained. The residue was dissolved in 5 ml of HNO_3 (25% v/v) and the mixture, when necessary, was heated slowly to dissolve the residue. The solution was transferred to a 10 ml volumetric flask and made up to the volume. A blank digest was also carried out in the same way.

2.4.3. Wet-ashing

Wet-digestion of honey sample was performed using an oxi-acidic mixture of 2:1, HNO_3:H_2O_2 (12 ml for 1.0 g sample). This mixture was heated for 4 h to dry and made up to a volume of 10 ml with deionized water. Blank digestions were also carried out in the same way.

2.4.4. Microwave digestion

The Microwave digestion procedure was applied to honey samples. One gramme of each sample was digested with 3 ml of HNO_3 (65%) and 1 ml of H_2O_2 (30%) in a microwave digestion system and diluted to 5 ml with deionized water. A blank digest was carried out in the same way. All sample solutions were clear. Digestion conditions for the microwave system applied were: 2 min for 250 W, 2 min for 0 W, 6 min for 250 W, 5 min for 400 W, 8 min for 550 W, vent: 8 min.

2.5. Analytical procedure

Detection limit is defined as the concentration corresponding to three times the standard deviation of ten blanks. Detection limit values of elements (as mg/l) in flame AAS were 0.009 for Zn and 0.005 for Fe. However, Pb, Cd, Cu, Cr, Ni, Al, Se and Mn were below this detection limit of the flame AAS. These elements were determined using graphite furnace AAS. During the analyses, internal argon flow rate through the graphite tube was 250 ml min^{-1}; gas flow was interrupted during atomization. Sample volume, ramp and hold times for the drying, ashing, atomization and cleaning temperatures were optimized before analysis to obtain maximum absorbance and minimum background.

Matrix modifiers were added: 200 μg $NH_4H_2PO_4$ for Pb; 15 μg Pd + 10 μg $Mg(NO_3)_2$ for Cd and Se; 50 μg $Mg(NO_3)_2$ for Al, Ni, Cr, Mn and Cu. Most of the matrix was removed before the atomization step and less interference occurred during atomization. Each graphite furnace atomic absorption spectroscopic analysis calls for 20 μl of solution and 5–10 μl of the matrix modifier were added if necessary. The signals were measured as peak area. The absolute sensitivity is defined by the mass of an element, which gives a peak absorbance of 0.0044; it was 10 pg for Pb, 0.5 pg for Cd, 2.0 pg for Mn, 4.0 pg for Cu, 22 pg for Se, 14 pg for Al, 13 pg for Ni and 3.0 pg for Cr.

3. Results and discussion

The accuracy of all the digestion methods was checked by standard reference material (NIST-SRM 1515 Apple leaves). The results are given in Table 2. There was a good

Table 2
Observed and certified values (μg g^{-1}) of elemental concentrations in NIST-SRM 1515 Apple Leaves as average ±S.D, $N = 4$

Element	Certified value	Observed values					
		Dry ashing	Recovery, %	Wet digestion	Recovery, %	Microwave digestion	Recovery, %
Cu	5.64	5.20 ± 0.25	92	5.35 ± 0.20	95	5.70 ± 0.12	101
Mn	54	48.4 ± 4.3	90	51.3 ± 2.6	95	53.1 ± 1.8	98
Zn	12.5	11.1 ± 0.8	89	11.9 ± 0.9	95	12.8 ± 1.1	102
Fe	83[a]	77.8 ± 6.5	94	79.6 ± 5.3	96	81.8 ± 4.2	99
Pb	0.47	0.42 ± 0.04	89	0.43 ± 0.03	92	0.45 ± 0.02	96
Ni	0.91	0.79 ± 0.07	87	0.85 ± 0.07	93	0.90 ± 0.05	99
Cr	0.3[a]	0.28 ± 0.03	93	0.29 ± 0.03	97	0.30 ± 0.02	100
Cd	0.013	0.011 ± 0.001	85	0.012 ± 0.001	92	0.013 ± 0.001	100
Al	286	260.4 ± 20.2	91	267.8 ± 17.6	94	276 ± 10.4	96
Se	0.05	0.02 ± 0.002	40	0.04 ± 0.004	80	0.05 ± 0.003	100

[a] Not certified.

harmony between the certified values and our values for the analyte ions. Also, recovery tests for the analyte ions were performed by microwave-digested honey samples. Table 3 shows the results of the metal contents of all the samples by using three different digestion methods. When the dry-ashing method was compared to other digestion methods, it was observed that the differences among the results were significant ($P < 0.05$). The recovery rate of trace elements was the highest with microwave-digestion method. Therefore, the microwave-digestion method was preferred for the digestion of all honey samples.

In the analysis of individual trace element contents, ten elements were identified and then quantified (Table 4): cadmium (Cd), lead (Pb), iron (Fe), manganese (Mn), copper (Cu), nickel (Ni), chromium (Cr), zinc (Zn), aluminium (Al) and selenium (Se). Iron was the most abundant element present in all the honey samples while cadmium was present in the lowest amount.

The lowest and the highest aluminium concentrations were 83 μg kg^{-1}in the honey sample from Ankara (Central Anatolia) and 325 μg kg^{-1} in the honey sample from Kayseri (Central Anatolia), respectively. In this study, aluminium, quantitatively, was the most abundant toxic metal compared to other metals tested. Possible interpretation of this amount might be that the honeys of Turkish origin may be contaminated by beekeeping equipment during the processing of honeys, e.g. aluminium honey extractor, aluminium containers.

The lowest selenium content was 38 μg kg^{-1} in the sample of Antalya (Mediterranean Region) honey (Table 4) while the highest selenium content was 113 μg kg^{-1} in the honey sample from Bursa (West Anatolia). Aluminium and selenium contents in the honeys have, to date, received little attention. Therefore, no reference was available on levels of aluminium and selenium in the honeys from other countries or Turkey.

Lead, nickel and chromium levels ranged from 8.4 to 106, 2.6–29.9 and 2.4–37.9 μg kg^{-1} in the honey samples, respectively. The honey sample from Samsun (8.4 μg kg^{-1}) had the lowest lead content, while the highest lead content was 106 μg kg^{-1} in the honey sample from Erzurum (East Anatolia). The mean lead content in the honeys was lower than those in previous reports (Przybylowski & Wilczynska, 2001; Tuzen & Duran, 2002). The chromium levels were between 2.4 and 37.9 μg kg^{-1} for blossom honeys. The chromium levels of our samples were lower than that of the reported honey samples from Italy (Conti & Botre, 2001). The lowest nickel content was 2.6 μg kg^{-1} in the honey from Adana (Table 4). In a previous study, Erbilir and Erdoğrul (2005) did not detect Ni in honey samples from Kahramanmaras city in Turkey. Contact with stainless steel surfaces during the harvesting, processing and/or preparation of honey for the market can generate a high Cr content, due to the corrosive effect of honey acidity (Fredes & Montenegro, 2006). In this study, the highest nickel content was 29.9 μg kg^{-1} in the honey samples from Bursa (Marmara Region).

The relative concentrations of other heavy metals tested in the honey samples decreased in the following order: Fe > Zn > Mn > Cu > Cd.

The minimum and maximum cadmium levels observed were 0.9 μg g^{-1} in honey samples from Samsun and 17.9 μg g^{-1} in the Adana sample. Cadmium content was lower than those reported by Przybylowski and Wilczynska (2001), Conti and Botre (2001) and Tuzen and Duran (2002). However, average cadmium levels were higher than those reported by Erbilir and Erdoğrul, 2005 in Turkish honeys from Kahramanmaras city.

Table 3
Comparison of trace element contents in honey samples (Bursa) using three different methods (Cu, Mn, Zn, Fe) (μg g^{-1}), others (μg kg^{-1}), $N = 4$

Method	Cu	Mn	Zn	Fe	Pb	Ni	Cr	Cd	Al	Se
Microwave-digestion	2.41 ± 0.10	1.10 ± 0.10	2.8 ± 0.1	7.4 ± 0.5	30.6 ± 2.1	15.2 ± 1.1	26.3 ± 1.4	11.2 ± 0.9	315 ± 17	62 ± 5
Wet-digestion	2.10 ± 0.18	1.06 ± 0.10	2.7 ± 0.2	6.9 ± 0.6	28.5 ± 2.7	14.9 ± 1.4	23.2 ± 2.1	10.8 ± 1.1	299 ± 24	50 ± 5
Dry-ashing	1.99 ± 0.19	1.01 ± 0.10	2.5 ± 0.2	6.6 ± 0.5	27.3 ± 2.6	13.2 ± 1.3	21.4 ± 2.1	10.1 ± 1.1	273 ± 26	25 ± 3

Table 4
Trace element contents in microwave digested honey samples (Cu, Mn, Zn, Fe) (μg g^{-1}), others (μg kg^{-1}), $N = 3$

Sample no	Cu	Mn	Zn	Fe	Pb	Ni	Cr	Cd	Al	Se
1	2.41 ± 0.10	1.10 ± 0.10	2.8 ± 0.1	7.4 ± 0.5	30.6 ± 2.1	15.2 ± 1.1	26.3 ± 1.4	11.2 ± 0.9	315 ± 17	62 ± 5
2	0.62 ± 0.03	1.45 ± 0.12	3.2 ± 0.2	8.1 ± 0.6	40.1 ± 3.4	29.9 ± 2.3	12.7 ± 1.1	12.6 ± 0.8	94 ± 8	113 ± 10
3	0.95 ± 0.05	0.55 ± 0.04	1.5 ± 0.1	3.4 ± 0.3	22.2 ± 1.6	10.7 ± 0.9	10.7 ± 0.9	8.6 ± 0.7	90 ± 7	41 ± 4
4	0.73 ± 0.04	0.98 ± 0.08	2.4 ± 0.2	8.1 ± 0.5	10.1 ± 0.9	11.5 ± 0.9	12.4 ± 0.8	5.1 ± 0.5	199 ± 13	53 ± 5
5	1.26 ± 0.10	1.80 ± 0.13	4.1 ± 0.3	10.2 ± 0.9	28.4 ± 2.6	29.1 ± 2.1	7.9 ± 0.5	7.2 ± 0.6	172 ± 14	82 ± 7
6	0.92 ± 0.06	1.23 ± 0.10	3.2 ± 0.3	4.6 ± 0.4	22.5 ± 1.5	25.1 ± 2.2	8.6 ± 0.7	17.9 ± 1.5	325 ± 23	59 ± 5
7	0.34 ± 0.03	0.47 ± 0.04	1.2 ± 0.1	2.8 ± 0.2	31.1 ± 1.7	15.7 ± 1.3	7.4 ± 0.6	1.1 ± 0.1	109 ± 10	45 ± 4
8	0.48 ± 0.02	0.55 ± 0.05	1.4 ± 0.1	2.2 ± 0.2	11.9 ± 1.1	9.2 ± 0.8	6.9 ± 0.7	4.1 ± 0.4	112 ± 9	60 ± 5
9	0.41 ± 0.03	1.21 ± 0.10	3.1 ± 0.3	5.1 ± 0.4	17.1 ± 1.5	16.1 ± 1.2	5.1 ± 0.5	2.1 ± 0.2	153 ± 12	54 ± 5
10	0.50 ± 0.04	0.95 ± 0.07	2.3 ± 0.2	2.1 ± 0.1	32.9 ± 2.6	16.6 ± 1.5	4.3 ± 0.4	5.8 ± 0.5	83 ± 5	59 ± 4
11	0.23 ± 0.02	0.62 ± 0.05	1.5 ± 0.1	2.4 ± 0.2	15.2 ± 1.4	14.6 ± 1.3	4.7 ± 0.3	1.1 ± 0.1	138 ± 12	59 ± 5
12	0.35 ± 0.03	0.32 ± 0.02	1.1 ± 0.1	5.1 ± 0.5	15.1 ± 1.5	10.2 ± 0.9	4.5 ± 0.4	3.5 ± 0.3	188 ± 13	96 ± 8
13	0.27 ± 0.02	0.41 ± 0.03	1.2 ± 0.1	2.2 ± 0.2	9.6 ± 0.8	5.8 ± 0.5	2.5 ± 0.2	3.8 ± 0.3	122 ± 9	73 ± 7
14	0.33 ± 0.03	1.20 ± 0.10	3.1 ± 0.3	2.1 ± 0.1	106 ± 9.7	5.9 ± 0.4	4.6 ± 0.4	6.8 ± 0.5	128 ± 10	72 ± 6
15	0.65 ± 0.05	0.99 ± 0.08	2.8 ± 0.2	7.1 ± 0.5	35.7 ± 2.5	12.8 ± 1.1	3.9 ± 0.3	2.8 ± 0.2	185 ± 15	42 ± 3
16	0.52 ± 0.04	1.56 ± 0.12	3.9 ± 0.3	4.2 ± 0.4	44.1 ± 3.9	9.5 ± 0.9	9.1 ± 0.8	6.5 ± 0.5	178 ± 12	84 ± 6
17	0.44 ± 0.02	0.82 ± 0.06	2.5 ± 0.2	4.9 ± 0.3	20.7 ± 1.5	12.5 ± 0.8	37.9 ± 2.5	1.1 ± 0.1	109 ± 10	63 ± 5
18	0.28 ± 0.03	1.86 ± 0.15	4.5 ± 0.4	4.3 ± 0.4	13.6 ± 1.1	2.6 ± 0.2	5.9 ± 0.5	1.2 ± 0.1	209 ± 19	74 ± 4
19	0.24 ± 0.02	0.38 ± 0.02	1.1 ± 0.1	1.8 ± 0.1	13.8 ± 0.9	5.9 ± 0.4	3.2 ± 0.3	1.8 ± 0.1	151 ± 15	59 ± 5
20	0.52 ± 0.05	0.83 ± 0.05	2.5 ± 0.2	4.7 ± 0.3	18.7 ± 1.2	9.6 ± 0.3	8.1 ± 0.7	1.7 ± 0.2	156 ± 11	38 ± 3
21	0.71 ± 0.06	1.45 ± 0.10	3.7 ± 0.3	4.2 ± 0.2	8.4 ± 0.5	6.5 ± 0.5	2.4 ± 0.2	0.9 ± 0.1	138 ± 13	40 ± 4
22	0.77 ± 0.07	4.56 ± 0.26	12.7 ± 1.1	6.9 ± 0.5	11.7 ± 1.1	5.3 ± 0.4	5.9 ± 0.5	4.5 ± 0.3	169 ± 14	67 ± 6
23	0.23 ± 0.02	1.89 ± 0.14	4.8 ± 0.4	2.5 ± 0.2	12.6 ± 0.8	25.5 ± 1.4	16.4 ± 1.5	6.3 ± 0.5	103 ± 10	68 ± 5
24	1.26 ± 0.11	3.25 ± 0.21	9.3 ± 0.5	4.6 ± 0.4	58.2 ± 3.6	11.3 ± 1.1	7.2 ± 0.7	2.9 ± 0.2	128 ± 12	61 ± 6
25	0.59 ± 0.04	3.47 ± 0.28	9.9 ± 0.7	2.8 ± 0.2	34.1 ± 2.1	7.3 ± 0.6	8.3 ± 0.6	4.5 ± 0.4	144 ± 13	84 ± 8

The minimum and maximum iron levels observed were 1.8 μg g^{-1} in the honey sample from Mersin (Mediterranean region) and 10.2 μg g^{-1} in Izmir (Aegean Region), respectively. Iron values in honey samples are reported to be in the range 0.40–52.51 μg g^{-1} in the honeys from Canary Island, 0.97–1.91 μg g^{-1} in Saudi honeys and 8.86–13.3 μg g^{-1} in Indian honeys (Al-Khalifa & Al-Arify, 1999; Hernandez, Fraga, Jimenez, Jimenez, & Arias, 2005; Nanda, Sarkar, Sharma, & Bawa, 2003). On the other hand, the levels of iron in honeys from Italy and Spain were generally about the same as our samples (Conti, 2000; Rodriguez-Otero, Paseiro, Simal, Terradillos, & Cepeda, 1992). Turkish honeys also had lower iron contents than had the Irish and Indian honeys (Downey, Hussey, Kelly, Walshe, & Martin, 2005; Nanda et al., 2003).

Concentrations of the last three metals ranged from 1.1 to 12.7 μg g^{-1} for zinc; 0.32–4.56 μg g^{-1} for manganese and 0.23–2.41 μg g^{-1} for copper in the honey samples. The lowest zinc content, 1.1 μg g^{-1} was for the honey sample from Bitlis (East Anatolia) (Table 4). The highest zinc content was 12.7 μg g^{-1} in the honey sample from Sakarya (Black Sea region). Keeping honey in galvanized containers might be the source of Zn contamination in honeys (Paramas et al., 2000). The zinc level in the Turkish honeys was very similar to that of reported by Conti for the Lazio region (Conti, 2000), but it was lower than that of reported by Przybylowski and Wilczynska, 2001 in Pomeranian honeys.

The minimum and maximum copper levels observed were 0.23 μg g^{-1} and 2.41 μg g^{-1} in honey samples from Sanliurfa (East and Southeast Anatolia) and Bursa, respectively. Average values for copper were slightly higher than those reported in the literature for the Lazio region (0.3 μg g^{-1}) honeys (Conti, 2000). Previously, copper values in the literature were reported to be 0.3–1.45 mg kg^{-1} for the honey samples from Turkey, 1.8 μg g^{-1} for the samples from south-eastern Turkey, 1.74–2.9 mg kg^{-1} for Indian and 0.1–0.23 mg 100 g^{-1} for Irish honeys, respectively (Downey et al., 2005; Nanda et al., 2003; Tuzen & Duran, 2002; Yilmaz & Yavuz, 1999). On the other hand, the levels of copper in the honeys from Spain were generally at the same level as our samples (Rodriguez-Otero et al., 1992).

The lowest manganese content was 0.32 μg g^{-1} in Bitlis (East Anatolia) honey (Table 4) while the highest manganese content was 4.56 μg g^{-1} in the honey sample from Sakarya (Black Sea region). Manganese levels were in agreement with the literature data (Conti, 2000; Rodriguez-Otero et al., 1992; Tuzen & Soylak, 2005), but this level was higher than that of reported by Tuzen and Duran (2002) and Downey et al. (2005).

It was noticeable that the honeys from the Marmara region (West Anatolia) showed high levels of Cu, Mn, Zn, Ni, Se and Fe. The reason might be that the industry has been well developed in this area and possibly apiaries are located at a distance not far from the polluted habitat. In contrast, honeys from East Anatolia showed lower contents of Cu, Mn, Zn, Fe and Pb than did the other honeys, due to the fact that this region does not have industrially polluted apiaries. In conclusion, honey can be considered to be a reliable biological marker for the assessment of heavy metal pollution. The present work was planned to detect significant variations in the values of trace element

concentrations among the samples collected from different regions of Turkey. The results showed that trace element concentrations in the honeys from different regions were generally correlated with the degree of trace element contamination of the environment.

Acknowledgements

The authors would like to thank Ms.K.O. Saygi for help in the experimental studies and the Scientific and Technological Research Council of Turkey (TUBITAK) for financial help (Project No. 104T448). The authors are also grateful for the financial support of the Unit of the Scientific Research Projects of Gaziosmanpasa University and the Unit of the Scientific Research Projects of Erciyes University.

References

Al-Khalifa, A. S., & Al-Arify, I. A. (1999). Physicochemical characteristics and pollen spectrum of some Saudi honeys. *Food Chemistry, 67*, 21–25.

Anonymous. (1997). Annual statistics of Republic of Turkey for 1997. DIE Ankara, Turkey.

Conti, M. E. (2000). Lazio region (central Italy) honeys: a survey of mineral content and typical quality parameters. *Food Control, 11*, 459–463.

Conti, M. E., & Botre, F. (2001). Honeybees and their products as potential bioindicators of heavy metals contamination. *Environmental Monitoring and Assessment, 69*, 267–282.

Crane, E. (1984). Bees, honey and pollen as indicators of metals in the environment. *Bee World, 65*(1), 47–49.

Domingo, J. L. (1994). Metal induced developmental toxicity in mammals: a review. *Journal of Toxicology and Environmental Health, 42*, 123–141.

Downey, G., Hussey, K., Kelly, J. D., Walshe, T. F., & Martin, P. G. (2005). Preliminary contribution to the characterization of artisanal honey produced on the island of Ireland by palynological and physicochemical data. *Food Chemistry, 91*, 347–354.

Erbilir, F., & Erdoğrul, O. (2005). Determination of heavy metals in honey in Kahramanmaras city, Turkey. *Environmental Monitoring and Assessment, 109*, 181–187.

Falco, G., Gomez-Catalan, C., Llobet, J. M., & Domingo, J. L. (2003). Contribution of medicinal plants to the dietary intake of various toxic elements in Catalonia, Spain. *Trace Elements and Electrolytes, 20*, 120–124.

Feller-Demalsy, M. J., Vincent, B., & Beaulieu, F. (1989). Teneur en mineraux et origine geographique des miels du Canada. *Apidologie, 20*, 77–91.

Fredes, C., & Montenegro, G. (2006). Heavy metals and other trace elements contents in Chilean honey. *Ciencia e Investigacion Agraria, 33*(1), 50–58.

Garcia, J. C. R., Garcia, J. B., Latorre, C. H., Martin, S. G., & Crecente, R. M. P. (2005). Comparison of palladium–magnesium nitrate and ammonium dihydrogen phosphate modifiers for lead determination in honey by electrothermal atomic absorption spectrometry. *Food Chemistry, 91*, 435–439.

Hernandez, O. H., Fraga, J. M. G., Jimenez, A. I., Jimenez, F., & Arias, J. J. (2005). Characterization of honey from the Canary Islands: Determination of the mineral content by atomic absorption spectrometry. *Food Chemistry, 93*, 449–458.

Leita, L., Muhlbachova, G., Cresco, S., Barbattini, R., & Mondini, C. (1996). Investigation of the use of honeybees and honey bee product to assess heavy metals contamination. *Environmental Monitoring and Assessment, 43*, 1–8.

Nanda, V., Sarkar, B. C., Sharma, H. K., & Bawa, A. S. (2003). Physicochemical properties and estimation of mineral content in honey produced from different plants in Northern India. *Journal of Food Composition and Analysis, 16*, 613–619.

Paramas, A. M. G., Barez, J. A. G., Garcia-Villanova, R. J., Pala, T. R., Albajar, R. A., & Sanchez, JS. (2000). Geographical discrimination of honeys by using mineral composition and common chemical quality parameters. *Journal of the Science of Food and Agriculture, 80*, 157–161.

Poiana, A., Fudo, S., Manzini, E., Postarino, S., & Mincione, B. (1996). Ricerche sui mieli commercializzatti in Italia: la componente minerale. *Ind Alim, 35*, 522–530.

Przybylowski, P., & Wilczynska, A. (2001). Honey as an environmental marker. *Food Chemistry, 74*, 289–291.

Raes, H., Cornelis, R., & Rzeznik, U. (1992). Distribution, accumulation and depuration of administered lead in adult honeybees. *Science of the Total Environment, 113*, 269–279.

Rodriguez-Otero, J. L., Paseiro, P., Simal, J., Terradillos, L., & Cepeda, A. (1992). Determination of Na, K, Ca, Mg, Cu, Fe, Mn and total cationic milliequivalents in Spanish commercial honeys. *Journal of Apicultural Research, 31*(2), 65–69.

Rodriguez-Otero, J. L., Pasrio, P., Simal, J., & Cepeda, A. (1994). Mineral content of honeys produced in Galicia (north-west Spain). *Food Chemistry, 49*, 169–171.

Sevimli, H., Bayulgen, N., & Varinlioglu, A. (1992). Determination of trace elements in honey by INAA in Turkey. *Journal of Radioanalytical and Nuclear Chemistry Letter, 165*, 319–325.

Terrab, A., Gonzalez, A. G., Diez, M. J., & Heredia, F. J. (2003). Mineral content and electrical conductivity of the honeys produced in Northwest Morocco and their contribution to the characterization of unifloral honeys. *Journal of the Science of Food and Agriculture, 83*, 637–643.

Tuzen, M., & Duran, M. (2002). analysis of Tokat region (Turkey) honeys. *Advances in Food Sciences, 24*(3), 125–127.

Tuzen, M., & Soylak, M. (2005). heavy metal levels in microwave digested honey samples from middle Anatolia, Turkey. *Journal of Food and Drug Analysis, 13*(4), 343–347.

Uren, A., Serifoglu, A., & Sarikahya, Y. (1998). Distribution of elements in honeys and effect of a thermoelectric power plant on the element contents. *Food Chemistry, 61*, 185–190.

Yazgan, S., Horn, H., & Isengard, H. D. (2006). Honey as bio indicator by screening the heavy metal content of the environment. *Deutsche Lebensmittel-Rundschau, 102*, 192–197.

Yilmaz, H., & Yavuz, O. (1999). Content of some trace metals in honey from south-eastern Anatolia. *Food Chemistry, 65*, 475–476.