J. Elem. s. 437–444 DOI: 10.5601/jelem.2011.16.3.08

CONTENT OF BIOELEMENTS AND TOXIC METALS IN HONEY OF VARIOUS BOTANICAL ORGIN FROM LOWER SILESIA

Lech Nowak[1], Halina Dzie¿yc[2], Maciej Piotrowski[1]

[1]Institute of Landscape Architecture
[2]Department of Spatial Economy
Wroc³aw University of Environmental and Life Sciences

Abstract

Analyzing the content of bioelements and toxic metals in honeys of various botanical origin is important for the consumers' health. In addition, many authors notice that results of such analyses can help to identify the botanical and geographical origin of honey and to use the product as a bioindicator of the overall contamination of the environment.

The content of As, Cd, Pb, Zn, Cu, Mn, Ni, Mg, Fe, Cr was determined in samples of nectar honey (acacia, linden, goldenrod, multifloral, buckwheat, oilseed rape) originating from some areas in the Province of Lower Silesia unexposed to industrial and traffic emissions. In order to demonstrate differences in concentrations of the metals in particular honey samples, one-factor analysis of variance or the Kruskal-Wallis test was applied, and the correlation between levels of individual metals in the honeys was investigated. Similarities between the honeys with regard to the metal content were determined using Ward's method of cluster analysis.

Among the analyzed nectar honeys from Lower Silesia, the content of zinc was the highest in linden flower honey (13.41 mg kg^{-1}), copper and manganese – in buckwheat (1.50 mg kg^{-1} and 9.40 mg kg^{-1}, respectively), nickel – in multifloral (1.03 mg kg^{-1}) and buckwheat (1.25 mg kg^{-1}), magnesium – in goldenrod (29.6 mg kg^{-1}) and iron – in linden flower (2.11 mg kg^{-1}) and goldenrod (2.00 mg kg^{-1}) honeys. The content of arsenic, cadmium and lead did not exceed the permissible values, i.e. 0.20, 0.03 and 0.30 mg kg^{-1}. The correlation analysis performed on the concentrations of the metals in the honeys demonstrated that manganese was positively correlated with copper and nickel, while iron correlated with zinc.

prof. dr hab. Lech Nowak, Institute of Landscape Architecture, Wroc³aw University of Environmental and Life Science, pl. Grunwaldzki 24A, 50-363 Wroc³aw, e-mail: lech.nowak@up.wroc.pl

Oilseed rape and acacia, as well as multifloral and goldenrod honeys were most similar to each other in the accumulation of the metals. Using the accumulation of metals in honey as a bioindicator of environmental pollution should be verified on material originating from areas where there are differences in the content of especially dangerous metals, cadmium and lead in particular.

Key words: honey, honey variety, bioelements, metals, bioindicator.

ZAWARTOŒÆ BIOPIERWIASTKÓW I METALI TOKSYCZNYCH W MIODACH O RÓ¯NYM POCHODZENIU BOTANICZNYM Z DOLNEGO ŒL¥SKA

Abstrakt

Badanie zawartoœci biopierwiastków i metali toksycznych w miodach o ró¿nym pochodzeniu botanicznym ma przede wszystkim znaczenie z uwagi na zdrowie konsumentów. Wielu autorów zauwa¿a te¿ mo¿liwoœæ kategoryzacji na tej podstawie pochodzenia botanicznego i geograficznego miodu, a tak¿e stosowania tego produktu jako bioindykatora ³¹cznego ska¿enia œrodowiska.

W próbkach miodów nektarowych: akacjowego, lipowego, naw³ociowego, wielokwiatowego, gryczanego i rzepakowego pochodz¹cych z terenów województwa dolnoœl¹skiego w niewielkim stopniu nara¿onych na oddzia³ywanie emisji przemys³owych i komunikacyjnych okreœlono zawartoœæ: As, Cd, Pb, Zn, Cu, Mn, Ni, Mg, Fe, Cr. Do wykazania ró¿nic w zawartoœci metali w poszczególnych odmianach miodu zastosowano test jednoczynnikowej analizy wariancji lub test Kruskala-Wallisa. Zbadano korelacje miêdzy zawartoœci¹ poszczególnych metali w miodach. Do okreœlenia podobieñstwa odmian miodów pod wzglêdem gromadzenia metali zastosowano analizê skupieñ, u¿ywaj¹c metody Warda.

Spoœród miodów nektarowych pochodz¹cych z Dolnego Œl¹ska najwiêcej cynku zawiera³ miód lipowy (13,41 mg kg^{-1}), miedzi i manganu – gryczany (odpowiednio 1,50 mg kg^{-1} i 9,40 mg kg^{-1}), niklu – wielokwiatowy (1,03 mg kg^{-1}) i gryczany (1,25 mg kg^{-1}), magnezu – naw³ociowy (29,6 mg kg^{-1}), a ¿elaza – lipowy (2,11 mg kg^{-1}) i naw³ociowy (2,00 mg kg^{-1}). Zawartoœæ arsenu, kadmu i o³owiu nie przekroczy³a dopuszczalnych wartoœci, tj. odpowiednio 0,20, 0,03 i 0,30 mg kg^{-1}. Analiza korelacji zawartoœci poszczególnych metali w miodach pozwoli³a stwierdziæ, ¿e zawartoœæ manganu by³a dodatnio skorelowana z zawartoœci¹ miedzi i niklu, a ¿elaza z cynkiem.

Najwiêksze podobieñstwo, jeœli chodzi o kumulacjê metali, wykaza³y miody rzepakowy i akacjowy oraz wielokwiatowy i naw³ociowy. Wykorzystuj¹c ten fakt do bioindykacji ska¿enia œrodowiska, nale¿a³oby zweryfikowaæ go na materiale pochodz¹cym z obszarów, gdzie wyst¹pi³yby ró¿nice w zawartoœci metali szczególnie niebezpiecznych, zw³aszcza kadmu i o³owiu.

S³owa kluczowe: miód, odmiana miodu, biopierwiastki, metale, bioindykator.

INTRODUCTION

In recent years, there has been an increasing interest in analyzing metallic elements in bee honey, reflected by a growing body of the relevant literature (Pohl 2009). The research is stimulated by the importance of honey in human diet. Honey is a source of many vital elements (Kot, Zarêba 2008). However, when present in excessive amounts, some of these elements may become a health hazard.

The content of mineral components in honey is affected by the soil in the area where the nectar is collected and by the plant speciation. Studying the content of elements in honeys may therefore be useful for classification of honeys with respect to their geographical and botanical origin, and for verification of the information given by the producers (Bogdanov et al. 2007, Madejczyk, Baralkiewicz 2008, Pohl 2009).

The metals in honey are also of anthropogenic origin (mines, smelters, industrial and urbanized areas, transportation routes). Hence, the product may serve as a bioindicator of the overall contamination of soil, plants, water and air of the area where bees collect the nectar (Pohl 2009, Yazgan et al. 2006, Spodniewska, Romaniuk 2007). Cadmium and lead are among the most toxic elements in honey that have an anthropogenic origin (Bogdanov et al. 2007). However, these authors indicate difficulties in using honey for bioindication due to differences in its botanical origin.

In view of the above, it seemed recommendable to determine whether honeys of various botanical origin produced in Lower Silesia were safe for consumers, and to compare their content of bioelements, thus finding the varieties which accumulate metals to a similar extent.

MATERIAL AND METHODS

Tests have been performed on honeys made in 2007 at movable apiaries set in areas very slightly exposed to industrial and traffic emissions and situated in Lower Silesia. The content of arsenic, zinc, copper, manganese, nickel, magnesium, iron, chromium, cadmium and lead was determined in samples of acacia, linden, goldenrod, multifloral, buckwheat and oilseed rape honeys.

Honey samples were mineralized in concentrated nitric acid under pressure, in a CEM Mars 5 mineralizer. The content of the metals was assayed with the plasma spectrometry method (emission) ICP-AES and the results were expressed as mg kg^{-1} of dry mass.

In order to determine the differences in the content of the metals between the honey types, one-way analysis of variance (Fisher's test) was applied. The means were compared using Tukey's test. When the data did not meet the criteria of the classical variance analysis (a negative result of the variance homogeneity test), the non-parametric Kruskal-Wallis test was used (Statistica 7).

Correlation between the levels of individual metals in the honeys was investigated, i.e. correlation coefficients were found at the corresponding probability levels.

Similarities between the honey types in the accumulation of the metallic elements were determined by the cluster analysis of standardized data, using Ward's method and the Euclidean distance.

RESULTS AND DISCUSSION

None of the honey samples contained arsenic, cadmium and lead in excess of the allowable levels of contamination, i.e. 0.20, 0.03 and 0.30 mg kg^{-1}, respectively (*Regulation of the Minister for Health 2003*) – Table 1. Hence, in this respect, they can be deemed as safe for the health.

The highest mean content of zinc (13.41 mg kg^{-1}) was found in linden flower honey. The content of Zn in the other honey types ranged from 1.54 to 2.87 mg kg^{-1}. Significantly less zinc than in linden honey appeared in buckwheat and oilseed rape honeys (Table 1). Linden honey was found to contain more zinc than acacia or oilseed rape honey in a study conducted in Switzerland by Bogdanov et al. (2007). In unpolluted areas of Romania, the zinc content was the highest in linden honey and the smallest in oilseed rape honey (Bratu, Georgescu 2005), analogously to our tests completed in Lower Silesia. In honey samples collected in various regions of Poland, the Zn content was the largest in oilseed rape and linden honeys (Kot, Zarêba 2008). The zinc content in linden, buckwheat and oilseed rape honeys collected in Pomerania was on average: 4.33, 6.66 and 4.17 mg kg^{-1}, respectively (Przyby£owski, Wilczyñska 2001).

Significantly the highest amounts of copper (on average 1.40 mg kg^{-1}) were in buckwheat honey, compared to all the other varieties. Less copper in honeys was found by Bogdanov et al. (2007): 0.180 mg kg^{-1} in acacia, 0.382 mg kg^{-1} in linden and 0.265 mg kg^{-1} in oilseed rape honey. The experiment conducted in Poland by Kot and Zarêba (2008) showed that buckwheat honey accumulated the largest amounts of copper (0.30 mg kg^{-1}), with linden, oilseed rape and acacia honeys to follow. A high content of copper in buckwheat honey may be due to buckwheat's ability to absorb from the soil some hardly available elements, including copper, which in soil occurs in its hardly mobile forms.

The highest content of manganese (9.40 mg kg^{-1}) was characteristic for buckwheat honey, being significantly lower in acacia (0.27 mg kg^{-1}) and oilseed rape honeys (0.45 mg kg^{-1}). Similarly to our experiment in the Lower Silesia, Bogdanov et al. (2007) found a higher content of manganese in linden than in acacia and oilseed rape honeys, whereas Kot and Zarêba (2008) reported the highest manganese content in acacia and buckwheat honeys.

The content of nickel in multifloral (1.03 mg kg^{-1}) and buckwheat honey (1.25 mg kg^{-1}) was significantly higher than in oilseed rape honey (0.54 mg kg^{-1}). The study in Switzerland (Bogdanov et al. 2007) showed less nickel (on average 0.152 mg kg^{-1}) in nectar honeys than in those of Lower Silesia.

Table 1

Range, mean and significant differences in the content of elements in various types of honey collected in the Province of Lower Silesia (mg kg^{-1})

Element	Type of honey						Mean	Significant statistical differences
	acacia (A)	linden (L)	golden-rod (GR)	multifloral (MF)	buckwheat (B)	rape (R)		
Cadmium	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02		
Lead	<0.17	<0.17	<0.17	<0.17	<0.17	<0.17		
Arsenic	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14		
Zinc	1.69-2.21 1.96	11.64-15.20 13.41	2.70-3.07 2.87	1.74-2.20 1.92	1.41-1.67 1.55	1.32-1.79 1.54	3.87	L → B. R*
Copper	0.31-0.56 0.44	0.37-.70 0.52	0.51-0.81 0.65	0.43-0.89 0.65	1.02-1.89 1.40	0.63-1.14 0.85	0.75	B → A. L. GR. MF. R**
Manganese	0.23-0.34 0.27	1.07-1.74 1.39	1.94-2.86 2.37	2.51-3.40 2.98	8.11-11.03 9.40	0.39-0.53 0.45	2.80	B → A. R*
Nickel	0.71-0.98 0.85	0.68-1.10 0.89	0.74-1.00 0.87	0.84-1.26 1.03	0.97-1.83 1.25	0.42-0.67 0.54	0.90	MF. B → R**
Magnesium	12.4-15.2 13.8	11.8-14.4 13.0	26.4-32.8 29.6	24.1-26.5 25.4	13.6-15.2 14.4	14.3-20.5 17.4	18.93	GR → A. L. MF. B. R; MF → A. L. B. R R → L**
Iron	0.86-1.30 1.08	1.78-2.44 2.11	1.87-2.13 2.00	0.98-1.32 1.15	0.93-1.37 1.15	1.16-1.70 1.43	1.49	L. GR → A. MF. B. R**
Chrome	0.071-0.137	<0.005	<0.005	<0.005	<0.005	<0.005		

Explanation: *Kruskal-Wallis test used, **Fisher test used
a → b – content of the element significantly higher in a than in b honey

The highest content of magnesium was characteristic for goldenrod (29.6 mg kg^{-1}), multifloral (25.4 mg kg^{-1}) and oilseed rape (17.4 mg kg^{-1}) honeys. More detailed information on the differences in the Ni content between honeys of different botanical origin can be found in Table 1. Higher magnesium content in nectar honeys (38.1 mg kg^{-1} on average) was found in the Czech Republic (LACHMAN et al. 2007).

Significantly more iron was determined in linden and goldenrod honeys (2.11 and 2.00 mg kg^{-1}, respectively) than in the other varieties. KOT and ZARÊBA (2008) found the highest Fe content in linden honey and the lowest - in acacia one. The Swiss experiment (BOGDANOV et al. 2007) demonstrated that acacia honey was the poorest in iron.

The content of chromium exceeded 0.005 mg kg^{-1} only in acacia honey. BOGDANOV et al. (2007) obtained values lower than 0.005 mg kg^{-1} for all the honey varieties they studied.

Differences in the content of metals between particular honey types from areas only slightly exposed to pollution are a result of the differentiated accumulation of metals in nectars of the respective varieties, which depends on the species-specific physiology of plants and the environmental conditions, especially the properties of the soil on which the nectar-bearing plants grow.

Our analysis of the correlations between the concentrations of the metals in the honeys demonstrated that manganese was positively correlated with the content of copper and nickel, while iron correlated with zinc (Table 2).

Table 2

Correlation between the analyzed elements

Element	Zn	Cu	Mn	Ni	Mg	Fe
Zn	x	-0.29	-0.22	-0.03	-0.33	**0.67**
Cu	x	x	**0.75**	0.21	-0.10	-0.18
Mn	x	x	x	**0.63**	-0.05	-0.23
Ni	x	x	x	x	0.03	-0.12
Mg	x	x	x	x	x	0.34
Fe	x	x	x	x	x	x

Explanation: in bold – significant at 0.05

The cluster analysis showed that oilseed rape and acacia honeys were the most similar varieties in terms of the content of the analyzed metals, followed by multifloral and goldenrod honeys. In this respect, buckwheat honey differed the most (Figure 1). This fact may be taken into account when verifying the botanical origin of honey and when using honey as an environmental bioindicator.

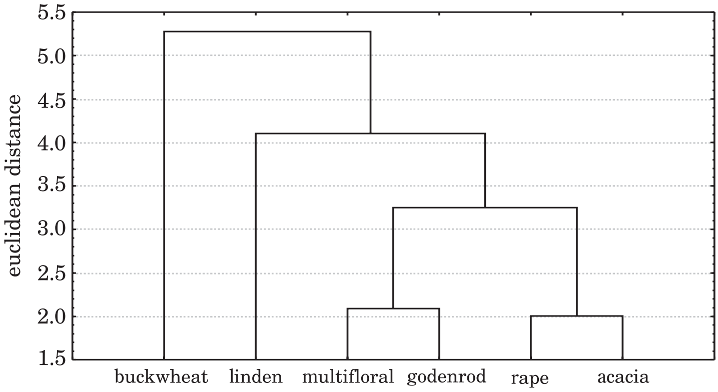

Fig. 1. Dendrogram of cluster analysis for types of honey

CONCLUSIONS

1. Among the analyzed nectar honeys made in Lower Silesia, the content of zinc was the highest in linden honey, copper and manganese – in buckwheat, nickel – in multifloral and buckwheat, magnesium – in goldenrod, and iron – in linden and goldenrod honey. The content of arsenic, cadmium and lead did not exceed the permissible values.

2. With respect to the accumulation of metals, oilseed rape and acacia honeys were most similar to each other, followed by multifloral and goldenrod honey types. Using the accumulation of metals in honey as a bioindicator of environmental pollution should be verified on material originating from areas where there are differences in the content of especially dangerous metals, cadmium and lead in particular.

REFERENCES

BBRATU I., GEORGESCU C. 2005. *Chemical contamination of bee honey – identifying sensor of the environment pollution.* J. Central Europ. Agric., 6 (1): 95-98.

BOGDANOV S., HALDIMANN M., LUGINBÜHL1 W., GALLMANN P. 2007. *Minerals in honey: environmental, geographical and botanical aspects.* J. Apicultural Res. Bee World, 46(4): 269-275.

KOT A., ZARÊBA S. 2008. *The content of copper, zinc, iron and manganese in honey*. Ann. UMCS, Pharmacia, 21: 77-80.

LACHMAN J., KOLIHOVÁ D., MIHOLOVÁ D., KOŠATA J. ,. TITERA D,. KULT K. 2007. *Analysis of minority honey components: Possible use for the evaluation of honey quality.* Food Chem., 101: 973-979.

MADEJCZYK M., BARALKIEWICZ D. 2008. *Characterization of Polish rape and honeydew honey according to their mineral contents using ICP-MS and F-AAS/AES*. Anal. Chim. Acta, 617: 11-17.

POHL P. 2009. *Determination of metal content in honey by atomic absorption and emission spectrometries*. TrAC-trend Anal. Chem., 28: 117-128.

PRZYBYŁOWSKI P., WILCZYŃSKA A. 2001. *Honey as an environmental marker*. Food Chem. 74: 289-291.

Regulation of the Minister for Health of 13th of January 2003. Journal of Law of the Poland. No 37. (*Rozporządzenie Ministra Zdrowia z dnia 13 stycznia 2003 r*. D.U. Nr 37 (in Polish).

SPODNIEWSKA A., ROMANIUK K. 2007. *Concentration of lead and cadmium in honey in randomly chosen apiaries of the Warmia and Mazury province*. Med. Wet., 63(5): 602-603). (in Polish)

YAZGAN S., HORN H., ISENGARD H.D. 2006. *Honey as a bio-indicator by screening the heavy metal content of the environment.* Deutsche Lebensmittel-Rundschau, 102(5): 192-194.