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STUDIES OF CHOSEN TOXIC ELEMENTS CONCENTRATION IN MULTIFLOWER BEE HONEY

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ABSTRACT

The aim of the study was to determine the bioaccumulation level of chosen toxic elements (Zn, Cu, Pb, As and Cd) in multiflower honey collected from Brzeg area. Biological material (honey) was mineralized using the microwave technique at an elevated pressure in the microprocessor station of pressure in the type Mars 5. Quantitative analysis of elements (As, Cd, Cu, Pb and Zn) was performed by plasma spectrometry method using a Varian ICP-AES apparatus. The presence of toxic elements was determined in examined biological materials. The elements fallowed the fallowing decreasing order with respect to their content of honey: Zn>Cu>Pb>As>Cd. The average concentrations of studied elements observed in multi-flower honey were as follows: 6.24 mg.kg-1 of zinc, 2.75 mg.kg-1 of copper, 0.53, 0.071, 0.042 mg.kg-1of lead, arsenic and cadmium, respectively. Lead was the most problematic in bee honey because its average content exceeded the maximum acceptable concentration. Additionally, this metal concentration was 60% higher in studied samples than allowable standard of lead content.

Keywords: honey, heavy metals, arsenic, cadmium, copper, lead, zinc, accumulation

INTRODUCTION

Among many pollutants accumulating in the environment, there are elements of toxic properties like a cadmium, copper, lead, zinc and arsenic. These heavy metals may cause vascular diseases, kidney or bones damages, irregular functioning of human and animal reproductive system. They can easily penetrate to the cell membranes and internal organs as well as cause denaturation of proteins in the blood or mucous membranes and penetrate to the tissues. The most toxic elements are lead, cadmium and arsenic. In the nature they often occur in higher concentration than the allowable maximum concentrations and may contribute to the formation of tumors in human organism **(Kabata-Pendias and Pendias 1999)**.

Honey bees (*Apis mellifera* L.) are 100% dependent on the flowering plants which provide them with nectar and pollen. The pollutants occurring within area where bees are working can be accumulated in honey bees organism and also in the raw material collected by bees **(Roman 2009 and 2010)**.

Honey is a natural product produced by bee workers from the nectar or honeydew, without any human interference. It consists 80% of dry weight, which is dominated by (98-99% of dry weight) carbohydrates (mainly glucose and fructose). The remaining part consists 0.2-3.0% of protein and 0.25-1.0% of minerals. Raw material for honey production is obtained by honey bees from the external environment, therefore, it also contains pollutants characteristic for the relevant environment (Roman 1997). However, bee workers partly purify raw material from some part of heavy metals during processing. **(Jabłoński et al. 1995, Roman and Demeńczuk 2003)**.

The aim of the study was to determine the accumulation degree of chosen toxic elements (As, Cd, Cu, Pb and Zn) in multi-flower honey collected from bee colonies located in Brzeg area.

MATERIAL AND METHODS

The research material for the investigation comprised samples of multi-flower honey that came from stationary apiaries situated in Brzeg area (Opole province, Poland). Material was collected from May to August 2009. The study contained 10 apiaries, honey was collected from 3 bee colonies in each apiary (n=3x10=30). Each individual sample weighted about 100 g.

The samples were homogenized by mixing and about 1000 mg (±0,1 mg) of material from each sample was weighted and diluted with 20 ml concentrated, spectrally pure, nitric acid solution. Next, samples were mineralized using the microwave technique at an elevated pressure in the chip-type Mars 5.

Quantitative analysis of elements studied (arsenic, cadmium, copper, lead, and zinc) were conducted using Varian ICP-AES plasma spectrometer with mass detection and CETAC-5000 AT ultrasonic nebulizer. All analysis were conducted in Analytical Laboratory of Wrocław University of Environmental and Life Science (Poland).

The results of the study were elaborated statistically by ANOVA. The mean concentrations of elements, standard deviations and correlations between elements were calculated. Level of significance was taken as $P < 0.01$ or $P < 0.05$.

RESULTS AND DISCUSSION

The multi-flower honey used in the study showed low levels of zinc. Its average value was 6.24 $mg \cdot kg^{-1}$. The content of this metal in all honey samples was below the permissible standards for honey, i.e. <15.00 $mg \cdot kg^{-1}$ and ranged from 1.13 to 13.92 $mg \cdot kg^{-1}$ (Table 1). Comparable level of zinc (mean amounted 3.14 $mg.kg^{-1}$) accumulation in honey was noted by **Conti (2000)**. Przybyłowski and **Wilczyńska (2001)** demonstrated slightly higher content of zinc in honey where average ranged 7.76 $mg \cdot kg^{-1}$. Very similar results were noted by **Tuzen et al. (2007) and Yazgan et al. (2006). Caroli et al. (2000)** found in their study of honey very low (0.405 $mg \cdot kg^{-1}$) level of zinc concentration. However, although zinc is one of the heavy metals it fulfills important physiological function in human organisms **(Kabata-Pendias and Pendias 1999)**. Therefore this is a reason why this element is called "bio-element" and its small quantity in food products should be included.

Table 1 Concentration of chosen elements in bee honey (N=30)

No. of sample	Chemical Elements (in mg·kg^{-1})				
	As	Cd	Cu	Pb	Zn
Min.	0,005	0,001	1,03	0,11	1,13
Max.	0,204	0,110	7,72	1,12	13,92
Average	**0.071** Aa	**0.042** Ab	**2.75** B	**0.53** C	**6.24** D
SD	0.055	0.032	1.56	0.31	3.02
Variation coefficient (%)	76.7	77.6	56.8	58.6	48.4
NDS	0.20	0.10	10.00	0.4 0	15.00

NDS – maximum acceptable concentration according to Polish Standards PN-88/A-77626 „Bee honey"

Similarly, copper is considered a heavy metal but it participates in humans and animals physiological functions and belongs to bio-**elements (Kabata-Pendias and Pendias 1999)**. The present study demonstrated that the average accumulation of copper in the honey amounted to 2.75 mg·kg^{-1}. Even the maximum content of that metal was below the acceptable standards (10.00 mg.kg^{-1}) and recorded on 7.72 mg·kg^{-1} level (Table 1). Comparable amounts of copper in honey were shown by **Yazgan et al. (2006)**, by **Tuzen et al. (2007)** and by **Fernández-Torres et al. (2005)**. Slightly lower (0.696 mg·kg^{-1}) copper concentration in multiflower honey was obtained by **Stankovska et al. (2008)**. Significant lower copper content in honey was noted by **Forte et al. (2001), Sodré et al. (2007) and Conti (2000)**. Only **Roman (1997)** demonstrated a higher concentration of Cu up to 6.178 mg.kg^{-1} on average in honey from the copper industry region.

Another heavy metal which was found in high concentration in bee honey was lead. The average level was 0.53 mg·kg^{-1}. This value is much higher than the permissible standard for honey which average 0.40 mg.kg^{-1} (Table 1). Additionally, this metal concentration was 60% higher in studied samples than allowable standard of lead content. Therefore, lead should be considered as the most burdensome toxic pollution of the bee honey. Two time larger concentration of lead, which amounted an average of 1.097 mgPb.kg^{-1}, was observed by **Roman (1997)** in honeys from the region of Głogów, and by **Sodré et al. (2007)** - 0.863 mg.kg^{-1}. On the other hand, **Jones (1987)** showed in British honeys low levels of lead accumulation ranged from 0.002 to 0.20 mg.kg^{-1}. Very low content of this metal in honeys from Rome suburbs was also found by **Conti and Botrè (2001)** and also by **Przybyłowski and Wilczyńska (2001)**.

Arsenic is an element which has a strong toxic properties. It doesn't fulfill any physiological function in humans organism. Therefore, its presence in the products which can't be utilised by the digestive system is completely undesirable. The average content of this element in honey was below the maximum allowable standards (NDS) and amounted to 0.071 mg.kg^{-1} (Table 1). Only in one sample concentrations of arsenic exceeded the limits (0.20 mg.kg^{-1}). In British honey samples significant wide range of arsenic content as the coefficient of variation, i.e 76.7% was observed. Significantly lower concentration of this element in honey, i.e 0.00318 mg·kg^{-1} and 0.00599 mg·kg^{-1} was obtained by **Caroli et al. (2000)** and by **Forte et al. (2001)**, respectively. **Roman (1997)** in his earlier studies showed that an average concentration of arsenic in honey derived from the cement industry region was to 0.156 mg.kg^{-1}. In turn, the level of As in honey from the copper industry area was to 0.368 mg.kg^{-1}.

Cadmium, similar like lead and arsenic, is an undesirable element in human and animal organisms. It doesn't fulfill any physiological functions because it shows strong toxic properties **(Kabata-Pendias and Pendias 1999)**. The average level of cadmium in present research was demonstrated as a 0.042 mg.kg^{-1} (Table 1). Of all honey samples 10% has exceeded the allowable limits (0.10 mg.kg^{-1}) of this element. **Tuzen et al. (2007)** as well as **Przybyłowski and Wilczyńska (2001)** found significant lower cadmium content, i.e 0.0179 and 0.015 mg·kg^{-}1, respectively. Very low concentrations of this heavy metal in honey were obtained by **Caroli et al. (2000), Yazgan et al. (2006), Conti and Botrè (2001)** and **Forte et al. (2001)**. Only **Jones' (1987)** study demonstrated a very high concentration of Cd in honey (0.30 mg.kg^{-1}).

The study was demonstrated that the most problematic toxic element in bee honey was lead. Only in this case the mean concentration was much higher than the acceptable limits. The elements fallowed the fallowing decreasing order with respect to their content of honey: Zn>Cu>Pb>As>Cd. No significant correlation between the concentration of particular elements in bee honey was observed (Table 2). However, **Frías et al. (2008)** found such a correlation between cadmium and zinc as well as cadmium and lead content in honey harvested in Tenerife.

Table 2 The values of correlation coefficient (r) between concentration of each element in honey (n=150)

Elements	Cd	Cu	Pb	Zn	As
Cd	-	-0.094	-0.282	0.027	-0.058
Cu	-0.094	-	0.006	-0.081	-0.308
Pb	-0.282	0.006	-	-0.135	0.075
Zn	0.027	-0.081	-0.135	-	0.071
As	-0.058	-0.308	0.075	0.071	-

A. B. C. D - differences between the elements assessed highly significant on a level of $p<0.01$, a. b - differences between the elements assessed significant on a level of $p<0.05$

CONCLUSIONS

In multiflower honey the sequence of examined elements concentration level was the same: Zn > Cu > Pb > As > Cd.

The most problematic element in bee honey was lead. Its average concentration was 60% higher in studied samples than allowable standard of lead content.

In all honey samples cooper and zinc weren't exceed the maximum permissible concentration for these heavy metals.

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