THE CUMULATION OF SELECTED CHEMICAL ELEMENTS OF TOXIC PROPERTIES IN BEE HONEY ORIGINATING FROM THE INDUSTRIAL AND RURAL-FOREST AREAS

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SUMMARY

The aim of the investigation was determining accumulation level of selected chemical elements of toxic properties (Pb, Cu, Cd, Zn), in bee honey coming from the industrial and rural-forest areas. In honey samples there detected different levels average concentration values of the examined elements in honey originating from copper industry region were low and they amounted as follows: copper – 0,484, cadmium – 0,059, zinc – 3,343 and lead – 0,059 $mg \cdot kg^{-1}$ d.m. The samples coming from rural-forest region showed higher copper concentration – 1,353, lead – 0,147 and cadmium – 0,373 $mg \cdot kg^{-1}$ d.m., while zinc concentration was lower – 3,179 $mg \cdot kg^{-1}$ d.m. Statistically significant differences (at $P_{0,05}$) in copper and lead concentration there were recorded between the areas subjected to examination. In honey samples from both areas there were obtained significant (at $P_{0,01}$) correlations between cadmium and lead concentration level. Similarly significant (at $P_{0,05}$) correlations were proved between copper and cadmium concentration in honey collected from Legnica and Głogów copper district and between copper and zinc concentration in honey originating from the control region.

Keywords: honeybee, bee's honey, heavy metals, toxic elements

INTRODUCTION

Bee's honey is a product made by a honeybee from flower nectar or honeydew. Obtained from beehives, it constitutes a final product, without aim necessity of its technological processing. Yet, the raw materials from honey production brought by bees contain contamination coming from different sources. Therefore, bees and their product have been used to estimate the degree of environmental pollution through determination of heave metals concentration and other chemical elements of toxic properties [Muszyńska, 1995, Topolska et al. 2004]. In this way there are obtained the data regarding average contamination of particular area included within the range of bee flying, I.E. about 20 km^2, which is equal approximately 2,5 km from a beehive [Muszyńska, 1997]. Legnica and Głogów copper district is situated in Silesia Lower province and it covers an area of about 2200 km^2. Yearly output of copper ores amounts about 26 mln tons. Copper industry came into being in an agricultural region and in the vicinity of urban agglomerations, which compelled introduction of proecological undertakings. Main sources of pollution emission to the atmosphere in copper metallurgy are metallurgical furnaces, refining processes technologies. Connected with waste utilizing and transport devices.

The purpose of this investigation was estimation of the level of contamination with selected chemical elements possessing toxic properties (Pb, Cu, Cd, Zn) of bee's honey originating from copper industry and rural-forest region.

MATERIAL AND METHODS

The investigation was conducted in 2005 in two regions differing in the degree of anthroporession on natural environment:

1. copper industry – Legnica and Głogów copper district – experimental region
2. agricultural and forest – the Kłodzko basin – control region.

The material for examination were the samples of multiflower honey collected, after centrifuging, as average samples from particular apiaries. Sample collection took place in July and August 2005. Total number of honey samples collected from those regions was 24. After sample unification out of each sample there was prepared a weighed portion of 1000 mg ($\pm$0.10 mg). Those honey portions underwent chemical decomposition with concentrated nitric acid, spectrally pure (Merck company, Germany), 10 ml per each sample, and then they were mineralized under high pressure in microwave oven, Mars 5 by CEM firm, where sample decomposition was conducted in closed non-stick containers. Quantitative analysis of multiflower honey regarding the content of trace elements such as: copper, cadmium, lead and zinc was done using ICP plasma spectrometer operated by P-3202 computer cooperating with analytical device Philips Scientific model PU-7000 and CETAC-5000 AT supersonic nebuliser. Calibration curves for particular chemical elements were drawn using the patterns ICP class, featuring special purity. The results obtained were statistically worked out using computer program Statgraphics version 5.1 – there were calculated average contents of metals in particular regions of investigation, standard deviations and correlations between content levels of particular elements. Difference significance in chemical elements content between the regions under examination were estimated according to Duncan multiple spread test.

RESULTS AND DISCUSSION

The results of our examination proved that the level of heavy metals content in honey samples coming from copper industry region was lower than permissible norm (tab. 1). Copper is a dominating chemical element in Legnica and Głogów copper district, yet the examinations proved that its average concentration was the lowest just in the honey from the mentioned region and it amounted 0.484 $mg \cdot kg^{-1}$ d.m. (tab. 1). It was higher, however, in control samples – 1,353 $mg \cdot kg^{-1}$ d.m. Low copper content in bee's honey also confirm Lipińska and Zalewski [1989]: from 0,69 to 2,33 $mg \cdot kg^{-1}$. Buliński et al. [1995] proved that mean copper content ranging from 0,14 $mg \cdot kg^{-1}$. Comparable data were reported by Szkoda and Żmudzki [2002], as well as by Przybyłowski et al. [2003]. Perużyński [2003] also observed significantly low copper content – 0,320 $mg \cdot kg^{-1}$ d.m. in the honey collected from the area situated about 30 km away from chemical plant in Police. Dobrzański et al. [1994] detected low level of copper concentration in the honey from copper industrial region – 0.194 $mg \cdot kg^{-1}$, while Roman [1997] recorded maximum copper concentration in the same region amounting 15.820 $mg \cdot kg^{-1}$ d.m.

Elevated cadmium content can occur in the honey from typical agricultural regions, where high consumption of mineral fertilizers and plant pesticides often takes place. That fact can be average 0.373 mg·kg^{-1} d.m. (tab. 1). In copper industrial region mean cadmium concentration was significantly low – 0.041 mg·kg^{-1} d.m. In the available literature similar low values were obtained by Migula et al. [1992] – 0.043 mg·kg^{-1} ore-bearing area, Perużyński [2003] and Stein and Umland [1986] – 0.014–0.052 mg·kg^{-1}. Low cadmium content was also recorded by Roman [1997 and 2000] in the samples from copper industry region. Higher level of cadmium accumulation was reported by Przybyłowski [2003] in nectar honey – 0.113 mg·kg^{-1}, while in honeydew ones it amounted 0.346 mg·kg^{-1}.

Zinc belongs to microelements, which are indispensable for appropriate course of live processes, as it is a component or activator of numerous enzymes. Yet its excessive amounts can be harmful to people and animals, or even toxic [Kabata-Pendias and Pendias 1999]. Our investigation proved that in honey samples from copper industry region zinc content ranged average 3.343 mg·kg^{-1} d.m. and maximum valve – 11.891 mg·kg^{-1} d.m. (tab. 1). Lower mean concentration value of this metal was recorded in control region honey – 3.179 mg·kg^{-1} d.m. In the available literature there are reported considerable discrepancies regarding zinc level in honey. Perużyński [2003] proved average 1.242 mg·kg^{-1} d.m., while Buliński et al. [1995] – 9.90 mg·kg^{-1} d.m. (the highest value – 30.0 mg·kg^{-1} d.m.). Similarly, Lipińska and Zalewski [1989] report of zinc content amounting 19.70 mg·kg^{-1}, while Gajewska et al. [1984] – even 49.1 mg·kg^{-1}. Roman [1997] detected average 19.53 mg·kg^{-1} d.m. in the honey from copper industrial region and maximum value ranged 177.91 mg·kg^{-1} d.m.

Our investigation proved that the highest lead content occurred in the honey from control region, where mean value was 0.147 mg·kg^{-1} d.m. and maximum – 0.980 mg·kg^{-1} d.m. (tab. 1). In Honey samples from copper industry region there was determined very low lead concentration, ranging 0.062 mg·kg^{-1} d.m. Comparable lead values in bee's honey were reported by Szkoda and Żmudzki [2002]: 0.001 to 0.251 mg·kg^{-1}. Similar results were obtained by Buliński et al. [1995] – 0.115 mg·kg^{-1} according to Lipińska and Zalewski [1989] lead content in nectar honey ranged from 0.057 to 0.370 mg·kg^{-1}. Madras-Majewska and Jasiński [2003] recorded lead vale from 0.005 to 0.1469 mg·kg^{-1}. Perużyński [2002] also obtained low lead amounts in bee's honey originating from West Pomeranian region – 0.216 mg·kg^{-1} d.m. Accorti et al. [1990] recorded mean lead concentration 0.210 mg·kg^{-1} and Bogdanov et al. [1986] 0.09 mg·kg^{-1} in honey samples coming from Italy. Increased values of lead in copper industry region were detected by Dobrzański et al. [1994] average values ranged from 0.369 to 1.025 mg·kg^{-1} d.m., I.E. they were higher than those obtained in our own investigation regarding that region. Also in the work by Roman [1997] lead accumulation level in the honey from Legnica and Głogów copper district proved to be higher and mean values ranged from 0.465 to 1.097 mg·kg^{-1} d.m.

On the basis of the results obtained there were proved statistically significant differences (at $P_{0,05}$) in copper and cadmium concentration between the regions examined (tab. 1). In honey samples from both regions there were recorded significant correlations (at $P_{0,01}$) between the level of cadmium and lead concentration. Similarly significant correlations (at $P_{0,05}$) were proved between the level of copper and cadmium concentration in the honey from Legnica and Głogów region and between copper and zinc concentration in control region honey (tab. 2). The results of our investigation proved that in experimental region mean contents of the examined chemical elements were lower (except for zinc) than those obtained from control region (tab. 1). It can be concluded that the mentioned situation resulted from considerable improvement of the state of natural environment in Legnica and Głogów region in the recent years, as well as from high ability of purification of honey raw material from trace metals in the course of its processing into honey performed by bees themselves [Roman and Demeńczuk 2003].

CONCLUSIONS

1. In the examined honey samples different concentration there was recorded of selected chemical elements bearing toxic properties (Cu, Pb, Cd and Zn).
2. Average content of particular metals in the honey coming from copper industry region did not exceed permissible concentration set by The Polish Norm.
3. In agricultural and forest region dominating element in bee honey occurred to be cadmium – its mean concentration was three times higher than the norms in force.
4. Regarding bee honey as a bioindicator of environmental pollution with heavy metals it should be stated that the region under copper industry effect can be regarded as not endangered ecologically.

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Table 1. Concentration level of the examined heavy metals in multiflower honey (in $mg \cdot kg^{-1}$ s.m.)

Sample number	Cu		Cd		Pb		Zn	
	LGOM	Control	LGOM	Control	LGOM	Control	LGOM	Control
1	1,375	1,152	0,025	0,516	0,020	0,010	4,678	2,260
2	0,131	1,067	0,070	0,044	0,048	0,032	1,557	1,679
3	0,115	1,347	0,017	0,087	0,035	0,023	1,247	2,385
4	0,126	2,203	0,064	1,978	0,105	0,980	1,770	3,269
5	0,323	0,116	0,093	0,055	0,081	0,080	2,213	1,619
6	0,116	0,100	0,061	0,099	0,076	0,115	1,254	0,823
7	1,565	0,122	0,045	0,080	0,067	0,054	1,618	2,851
8	1,256	0,693	0,023	0,122	0,042	0,089	2,478	6,613
9	0,324	4,651	0,064	0,087	0,039	0,077	8,396	7,762
10	0,134	2,115	0,080	0,099	0,045	0,042	11,891	4,111
11	0,222	1,448	0,102	1,218	0,105	0,203	1,356	2,331
12	0,124	1,224	0,070	0,096	0,076	0,061	1,652	2,447
Minimum	0,115	0,100	0,017	0,044	0,020	0,010	1,247	0,823
Maximum	1,565	4,651	0,102	1,978	0,105	0,980	11,891	7,762
Average	**0,484**^{A}	**1,353**^{B}	**0,059**^{A}	**0,373**^{B}	**0,062**	**0,147**	**3,343**	**3,179**
SD	0,560	1,203	0,027	0,582	0,027	0,256	3,393	1,974
NDS [1)]	12,00		0,12		0,50		18,00	

[1)] The highest permissible concentration (The Polish Norm, 1988)
A, B – statistically significant differences at $P_{0,01}$

Table 2. The values of correlation coefficient between the examined elements (n=12)

Chemical elements	Region under investigation	
	Copper industry region	Agricultural and forest region
Cu → Cd	–0,556 *	0,198
Cu → Pb	–0,367	0,204
Cu → Zn	–0,053	0,686 **
Cd → Pb	0,667 *	0,887 **
Cd → Zn	0,126	–0,070
Pb → Zn	–0,440	0,013

* – significant coefficient of correlation at $P_{0,05}$ level
** – highly significant coefficient of correlation at $P_{0,01}$ level.