

## A COMPARATIVE STUDY ON THE EVOLUTION OF ENVIRONMENTAL AND HONEY POLLUTION WITH HEAVY METALS

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**Abstract.** *In this paper, the content of four heavy metals (Cu, Zn, Cd and Pb) in honey was determined by atomic absorption spectrometry. The main goal of this study was to relate the heavy metals contents in honey samples to the pollution of the environment as a result of the industrial activities running in this area. The honey samples were harvested between 2005 and 2012 from the neighbour area of Baia Mare city that used to be known as one of the most polluted cities in Romania. The metals concentrations in honey were compared with the metals concentrations in air, in falling dust and soil, during the investigated period of time. Our results reveal a very good correlation between the metals content in honey and air and falling dust and a less relevant correlation with the metal content in soil.*

**Keywords:** *heavy metals, honey, atomic absorption spectrometry, pollution.*

### 1. INTRODUCTION

It is well known that the honey is a bioindicator sensitive to the pollution with heavy metals [1-8] and that the honey composition shows its geographic and botanic origin [9].

Baia Mare city and its surroundings are known as one of the most polluted areas with heavy metals both in Romania and worldwide. Copper, zinc, cadmium and lead were the metals emerging from the industrial activities developed for decades in Baia Mare area. During the time, frequent exceedings of the allowed limit values for these metals were recorded in air and soil.

The main sources responsible for the historical pollution of the environment in Baia Mare area are represented by the two non-ferrous metallurgical plant Romplumb SA (primary lead producer, closed in January 2012) and Cuprom SA (secondary copper producer, already closed since October 2008), as well as the decanting ponds of the flotation plants, the tailings dams related to the extracting activities and the acidic waters coming from the former mines. Dusts with heavy metals have been emitted for more than hundred of years from the dispersion stacks of both metallurgical plants. Pollution from traffic and residential heating is obviously added.

Data from the Local Environmental Protection Agency show a continuous decrease of the pollution level, starting in 1999 until 2011, as a result of the closure of the most pollutants plants and the ongoing technological modernisation. After Romania's EU accession on 2007 January 1st, several transition periods for the industrial risk management were negotiated in

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order to meet the environmental European standards, the last one in Baia Mare city ended on December 2010 for Romplumb SA.

We choose for our study the years we considered the most significant for this period when pollution is continuously decreasing, respectively 2005 to 2012 and we assessed the trend of the four metals concentration both in environment and in honey. In our days the main pollution sources stopped working, but Baia Mare is facing a severe historical pollution of the environment with heavy metals.

Baia Mare is located in the north-western part of Romania in Baia Mare basin at an average altitude of 228 m above sea level. Sasar River flows from east to west and has Firiza River as tributary on its right side coming down from the hills and low mountains in the north-west of the basin. Firiza River forms a passageway through which the wind blows predominantly to the city. Specific meteorological features with predominant wind direction blowing from NE to SW and long periods of atmospheric calm result in preferential dispersion of the pollutants emitted from the 120m height stack of Romplumb SA, located on Firiza River. This plant is situated in Firiza valley, placed at the north-eastern part of the town, at a distance of 7 km from the city centre.

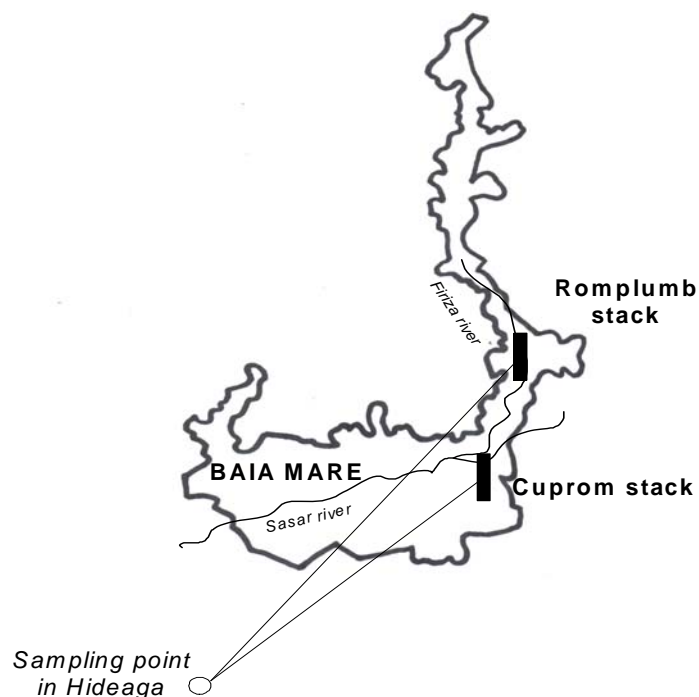
Based on the assessment of a mathematical model which is studied in a not yet published paper by the same authors, we choose for this study honey samples from one single location, 19.5 km faraway from Romplumb SA and 14.0 km from Cuprom SA, on the main direction of the air currents. We did study only one type of honey, spring poliflora honey, harvested on June, in order to eliminate most of the perturbing variables in the mathematical model concerning the relationship between the honey's composition and the level of the environmental pollution. The selected location is an opened area with a lot of vegetation, where bees can collect honey in a circular area with a radius of at least 3 km, as known from literature [10-11].

For the determination of mineral constituents in honey various methods have been developed: the reflexion X-ray fluorescence spectroscopy [12], the inductively coupled plasma optical emission spectrometry [8, 13-15], the ionic chromatography [16], the atomic absorption spectrometry [17-18] and the instrumental neutron activation analysis [19]. In the present study, we used the atomic absorption spectrometry technique in order to determine the amounts of Pb and Cd in honey samples.

## 2. MATERIALS AND METHODS

### 2.1. HONEY SAMPLES

For our study, we have chosen honey samples with the same botanical origin, poliflora type, and the same geographical origin. Fig. 1 illustrates the geographic position of the point where honey was harvested, 19.2 km faraway from Romplumb SA, as the main polluting source (closed in January 2012) and 14.0 km from Cuprom SA (closed in October 2008). The sampling point is located in Hideaga village, South West from Baia Mare city. One honey sample of poliflora type has been harvested in June of each year from 2005 until 2012, as can be seen in Fig. 1.



**Fig. 1.** The map of Baia Mare area with the polluting sources and the sampling location.

## 2.2. ANALYSIS OF HONEY SAMPLES

One gram of honey was suspended in 2 ml of 0.1M  $\text{HNO}_3$  and the mixture was thoroughly hand stirred. The acid was then evaporated on a heating plate to almost dryness. 10 ml of the same diluted acid were added and the mixture was gauged to 25 ml with ultrapure water. Nitric acid 65% (EMSURE®ISO, MERCK) was used in all works.

A Perkin Elmer AAnalyst 700 atomic absorption spectrometer was used for metals determination both in flame (for Cu and Zn determination) and with electrothermal atomization (for Pb and Cd determination). The atomic absorption spectrometer was calibrated with several working standards and the concentration of metals in each sample was measured individually. All gases used were ultra pure carrier grade. Certipur Merck standard solutions ( $1000 \text{ mgL}^{-1}$ ) were used to prepare the working standards and calibration curves were built based on five standards. The instrument was programmed to take three readings per sample and average the absorbance ( $\text{RSD} < 20\%$  for GFAAS and  $\text{RSD} < 10\%$  for FAAS). Instrument blanks (0.5%  $\text{HNO}_3$ ) and check standards were processed with all samples.

The operating conditions, the ranges of working standard concentrations used for metals determination and the quantification limits for the studied metals are summarized in Table 1.

**Table 1. Operating conditions for Pb, Cd, Cu and Zn analysis by GFAAS and FAAS.**

Metals	Wavelength (nm)	MDL (mg kg <sup>-1</sup> )	LQ (mg kg <sup>-1</sup> )	WS concentration	
				FAAS (mg L <sup>-1</sup> )	GFAAS (µg L <sup>-1</sup> )
<b>Cd</b>	228.8	0.011	0.037	-	0.4; 0.8; 1.2; 1.6; 2.0 stock solution= 2.0
<b>Pb</b>	283.3	0.088	0.293	-	10.0; 20.0; 30.0; 40.0; 50.0 stock solution= 50.0
<b>Cu</b>	324.8	0.207	0.690	0.1; 0.2; 0.5; 1.0; 2.0	
<b>Zn</b>	213.9	0.167	0.557	0.1; 0.2; 0.5; 1.0; 2.0	

MDL = method detection limit ; LQ = limit of quantification

### 3. RESULTS AND DISCUSSIONS

Table 2 and Figs. 2 and 3 are showing the contents of Pb, Cd, Cu and Zn in the honey samples harvested yearly, during the investigated period of time, that is, in the period 2005-2012 from Hideage village honey producers.

**Table 2. The amounts of Pb, Cd, Cu and Zn expressed in mg/kg of honey.**

Year	Pb			Cd			Cu			Zn		
	V mg/kg	IC	CL	V mg/kg	IC	CL	V mg/kg	IC	CL	V mg/kg	IC	CL
2005	20.34	0.99	S	0.093	0.78	M	0.24	-1.08	N	1.25	0.20	W
2006	19.22	0.99	S	0.088	0.77	M	0.28	-0.79	N	1.09	0.08	W
2007	17.31	0.99	S	0.082	0.76	M	0.32	-0.56	N	1.33	0.25	W
2008	16.87	0.99	S	0.076	0.74	M	0.25	-1.00	N	1.39	0.28	W
2009	1.23	0.84	S	<MDL	-	N	0.26	-0.92	N	1.2	0.17	W
2010	0.18	-0.11	N	<MDL	-	N	0.32	-0.56	N	1.13	0.12	W
2011	0.22	0.09	W	<MDL	-	N	0.30	-0.67	N	1.18	0.15	W
2012	0.12	-0.67	N	<MDL	-	N	0.20	-1.50	N	0.89	-0.12	N

Table 2 also contains the values for the *index of contamination* (IC) defined by the formula:

$$IC = \frac{V - MAL}{V}$$

where: V = determined value of heavy metal (in mg/kg) and MAL = maximum admitted level. In our study we adopted the maximum admitted level that is valid in Romania according to the Ordinance of the Ministry of Health O.M.S no. 975/1998, which is 0.2 mg/kg for Pb, 0.02 mg/kg for Cd, 0.5 mg/kg for Cu and 1.0 mg/kg for Zn. The computed values for ICs are given in Table 2. Their interpretation is the following one: 1) if  $IC \leq 0$ , then we have no contamination (N); 2) if  $IC > 0$ , then we have contamination. A value of IC very close to 1 indicates a strong contamination (S). Therefore, we propose the following contamination levels (CL): 1) weak contamination (W), if  $0 < IC < 0.5$ ; 2) medium contamination (M), if  $0.5 \leq IC < 0.8$ ; 3) strong contamination (S), if  $0.8 \leq IC < 1$ . The metal content in honey between 2005 until 2011 ranges from 0.18 to 20.34 mg/kg for Pb, from 0.003 to 0.093 mg/kg for Cd, from 0.24 to 0.32 mg/kg for Cu and from 1.09 to 1.39 mg/kg for Zn.

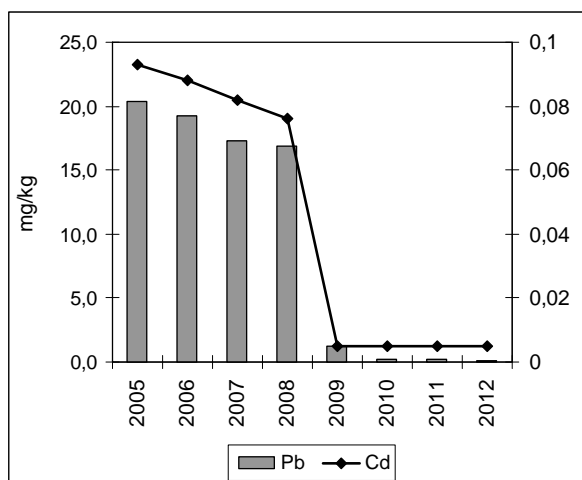


Fig. 2. Concentrations of Pb and Cd in honey samples.

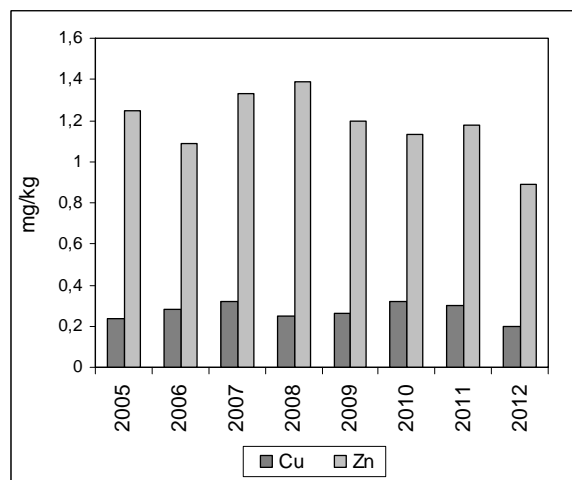


Fig. 3. Concentrations of Cu and Zn in honey samples.

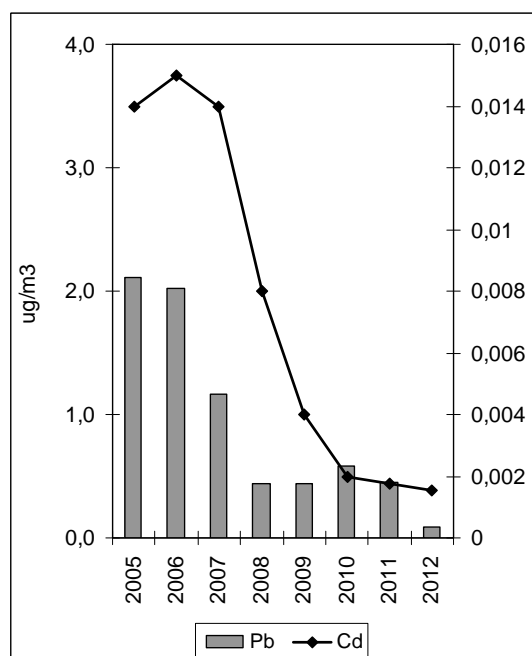


Fig. 4. Yearly average concentrations of Pb and Cd in air in Baia Mare city.

As it can be seen, the content of Pb and Cd in honey samples decreased significantly in the investigated period of time, while the content of Cu and Zn were approximately constant.

The trend of these values may be explained by the particular geographical position of Baia Mare city and of the lead smelter which is situated in a small and narrow valley of a low mountains chain, placed at the north-eastern part of the town, at a distance of 7 km from the city centre and the industrial activity of the two pollution sources. Hence, long periods of atmospheric calm and dominant north-western winds ascending/ descendant air flows in Firiza valley-where Romplumb S.A. is situated and in Sasar valley, where Baia Mare city is situated, have as a result the dispersion of the emitted pollutants mainly in the centre and south-western part of the city, like in an opening cone from the dispersion stack of Romplumb smelter. On the other hand, see Fig. 4, the content of Pb and Cd in air has significant

variations in rather short time intervals, being influenced strongly by the industrial activity itself.

There is a very good agreement between the metals content in air and in the honey sample and the metals in honey follow very well their trend in air quality. From the Local Environmental Protection Agency we know also the variation of the investigated heavy metals in air in Baia Mare as yearly means of Pb, Cd, Cu and Zn in the falling dust monitored in Baia Mare city (Figures 5 and 6), as well as in soil samples (Figure 7). The lead smelter Romplumb S.A used to emit dust with lead and cadmium. Since August 2008 until April 2009 the plant stopped the activity and implemented an important project for the mitigation of the dust emissions from the 120 m height dispersion stack. Accordingly, the lead and cadmium in air decreased after 2009. The Cu and Zn emissions in air continued to be relatively constant. The copper smelter Cuprom SA used to meet all the European environmental protection requirements still 2005, the dispersion stack of 351.5 m height was ensuring the efficient mitigation of the pollutant emissions in air.

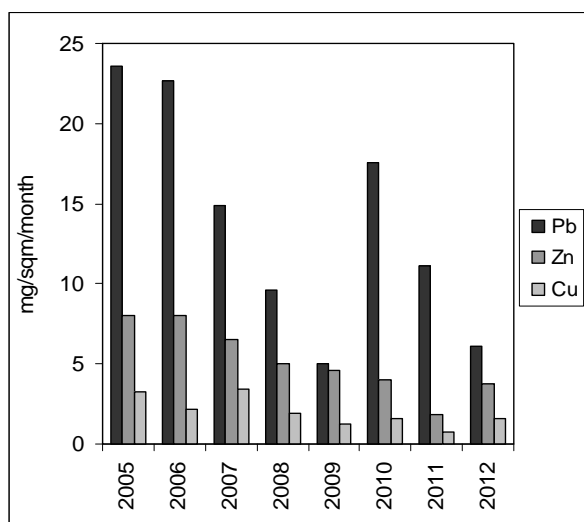


Fig. 5. Concentrations of Pb, Zn and Cu in the falling dust in Baia Mare city.

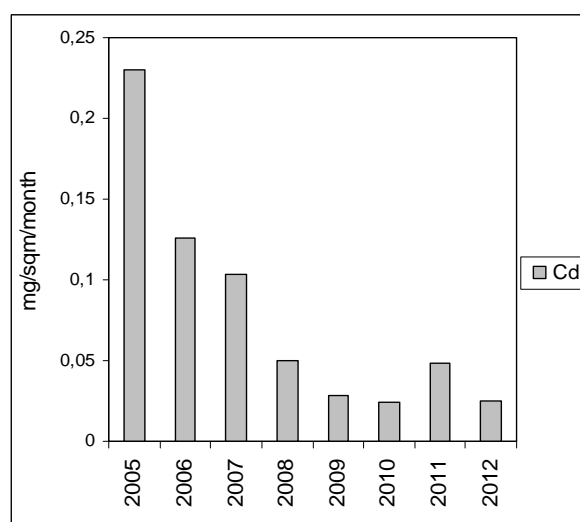


Fig. 6. Concentrations of Cd in the falling dust in Baia Mare city.

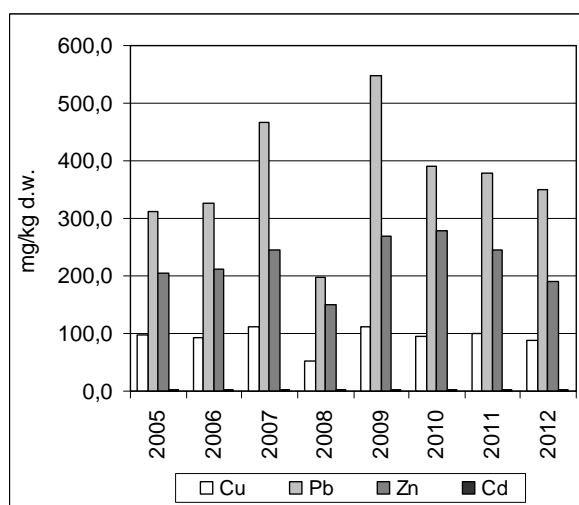


Fig. 7. Concentrations of Cu, Pb, Zn and Cd (d.w.) in soil samples in Baia Mare city.

Due to economical reasons, the copper smelter stopped the activity in 2008 October, but there is no relevant change in the Cu and Zn content in the falling dust, suggesting that these two metals comes rather from the historical pollution of the soil within the city. On the other hand, after the closure of the lead plant in 2012 January, the Pb concentration in air and in the falling dust decreased significantly, but soil contamination with metals, especially Pb, remains as an important environmental issue, due to the high risk on human health.

#### 4. CONCLUSIONS

In conditions of intensive anthropogenic impact on the environment, it is very important to control the metals level in food and environment in order to avoid intoxications.

The copper and zinc concentration both in environment (air and soil) and honey show very small fluctuation and meet the admissible limits in the investigated period of time.

The strong contamination of the honey with lead and cadmium, especially until 2008 is highly related to the emission of these metals in air from the non-ferrous metallurgical plant Romplumb SA and Cuprom SA. In 2005, lead in air far exceeded the limit value and lead in honey was 100 times higher than the maximum admitted value. After the technological improvements at Romplumb SA implemented within 2008-2009, the decrease of lead and cadmium concentrations in air (and, consequently, in honey) was remarkable.

As a final conclusion of our study, we noticed that between the observed contamination levels with heavy metals of honey, air and soil, the most relevant correlation is the one between honey and air especially in the case of lead and cadmium.

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