THE CONTENT OF HEAVY METALS IN POLLEN FROM DAMBOVITA REGION

ION V. POPESCU[1,2,3], GABRIEL DIMA[1], SERGIU DINU[1]

[1]*Valahia University of Targoviste, Faculty of Sciences and Arts, 130082, Targoviste, Romania*

[2] *Valahia University of Targoviste, Multidisciplinary Research Institute for Sciences and Technologies, 130082, Targoviste, Romania*

[3]*Academy of Romanian Scientists, 050094, Bucharest, Romania*

Abstract: *The purpose of the study is to evaluate the use of the pollen as bio-indicator of environmental pollution. The content in Fe, Mn, and Zn from pollen samples uniformly distributed in Dambovita region was determined. We have collected samples during April 2009 from 18 bee houses from private farms, kipped in industrial-urban and non industrial-rural areas. The samples were analyzed with an Elvax ED-XRF spectrometer having a solid state Si-pin-diode detector with thermo-electrical cooling with 165 eV at 5.9 keV (Fe^{55} isotope) energy resolution. We found differences between the two kinds of samples and we concluded that the pollen can be used for bio-monitoring of environment for Fe, Mn, and Zn.*

Keywords: *heavy metal, pollen, bees*

1. INTRODUCTION

Areas with intensive industry are associated with heavy metal pollution of the environmental, which is a first step of contamination of food sources. On the other hand, iron, manganese and zinc are essential elements, very important for biological systems, which can have a harmful effect when their concentration exceeds well known quantities. The excess of iron in food is correlated, in principal, with degenerative brain diseases, such as Parkinson and Alzheimer [1]. A higher concentration of zinc in human diet can interfere with white blood cells and other defense systems against infections and cancers [2]. An increase of the doses of manganese in food can produce the nervous system disturbances [3][6]. Because the pollen is a good source of carbohydrates many producers selling in our day's pollen for human consumption in two forms: like food and like diet supplement. Metal pollution of pollen can produce a higher content of metals in pollen like aliment and in honey due to bee's activity.

The rich vegetation and the climate in Dambovita region (Romania) provide a good environmental for apiculture. On the other hand, Dambovita region is a high industrialized zone, having a Cement factory at Fieni, a Special Steel Factory at Targoviste and a Cool Thermal power plant at Doicesti, based on coal burning.

The purpose of the study is to determine the content on iron, manganese and zinc in pollen samples collected from Dambovita region in order to evaluate the possibility of the use of the pollen as bio-indicator. A starting point for our study is the work of Muller and Agthe performed in 1988 in Germany [4] who considers the pollen to be a good bio-indicator for Cd and Pb environmental pollution.

2. EXPERIMENTAL

The pollen samples were collected in April 2009 from 18 bee houses of private farmers (Runcu, Fieni, Pucioasa, Branesti, Doicesti, Moreni, Targoviste 1,2,3,4, Hulubesti,

Bucsani, Gaesti, Salcioara, Cojasca, Contesti, Titu and Uliesti) kipped in industrial and urban and non industrial and rural areas from Dambovita region (Fig. 1).

In order to collect pollen samples we use plastic gloves and a plastic cutter for cutting a 3×3 cm piece of comb containing on both sides pollen. The samples were stored in plastic bags on a freezer at -18^{0}C. At this temperature, the pollen can be extracting from combs by breaking the comb. After the pollen - wax separation the samples are dried at 45^{0}C in a Lalal dehumidifier for 3 days and then powdered and pressed in pellets for EDXRF analysis. For analytical purposes we use an ElvaX desktop energy-dispersive X-ray fluorescence (EDXRF) analyzer which does not require liquid nitrogen cooling for storage and use. This analyzer is proper to use for quantitative and qualitative analysis of the elemental composition of liquids, food and biological samples, in the element range from Cl (Z=17) to U (Z=92) in a wide range of element concentrations. Analyzer's detecting limit is better than 1 ppm for most elements in light matrix.

Fig. 1. Collection points on Dambovita region map

The data acquisition time can be set between 10 and 1200 s. The ElvaX spectrometer use an X ray tube with W anode and a 140 μm Be window air-cooling. The X-ray generator has a voltage between 4 and 50 kV, adjustable in 100 V steps and the current between 0 and 100 μA, adjustable in 0.2 μA steps under a maximal power of 5 W. The **s**tability of the X-ray generator is 0.1% per 8 hours. For X-rays detection we use a solid state Si-pin-diode with thermo-electrical cooling, with a 6 mm^2 active area and a 165 eV at 5.9 keV (Fe^{55} isotope) energy resolutions. In front of the X-rays detector is a Be window with 8 μm thickness.

The accuracy of the method was checked by NIST SRM 1515 Apple leaves for the interest elements and we find a good concordance between our values and certified values (Table 1).

Table 1. Concentrations of Fe, Mn and Zn obtained on NIST SRM 1515 Apple leaves with our experimental set-up

Element	Certified value [ppm]	Experimental concentration [ppm]
Fe	83	81.5 ± 5.0 %
Mn	54	52.3 ± 4.8 %
Zn	12.5	12.7 ± 0.7 %

3. RESULTS AND DISCUSSIONS

The results are presented in Table 2. It can be observed major differences between the content of heavy metals in samples collected from the study area: higher concentrations for heavy metals in pollen samples collected from urban and industrial sites and lower concentrations in pollen samples collected from rural and non- industrial sites.

Table 2. Concentrations of Fe, Mn and Zn obtained on pollen samples collected from Dambovita region

Location	Type of the site	Fe [ppm]	Mn [ppm]	Zn [ppm]
Runcu	rural non industrial	43	52	29
Fieni	urban industrial	62	82	45
Pucioasa	urban industrial	54	65	25
Branesti	rural non industrial	45	34	28
Doicesti	Industrial	52	65	33
Moreni	urban industrial	55	43	29
Targoviste 1	urban industrial	89	104	52
Targoviste 2	urban industrial	123	118	49
Targoviste 3	urban industrial	115	134	55
Targoviste 4	urban industrial	113	127	58
Hulubesti	rural non industrial	21	32	28
Bucsani	rural non industrial	34	21	24
Gaesti	urban industrial	67	76	37
Salcioara	rural non industrial	41	35	22
Cojasca	rural non industrial	36	28	25
Contesti	rural non industrial	45	25	28
Titu	urban industrial	76	64	37
Uliesti	rural non industrial	45	34	22

The lower and higher iron level were found as 21 ppm in pollen samples collected from Hulubesti area and 123 ppm in pollen samples collected from Targoviste 2 area. Iron concentrations in pollen samples have been reported in the range of 44-120 ppm for industrial and urban sites and 48-69 ppm in rural, non industrialized sites [5]. In the present study the concentrations of Fe in pollen samples from industrial and urban sites were in the range 52 – 123 ppm and in the range 21 – 45 ppm in samples collected from rural and non industrial sites. It can be observed lower values than that reported in literature from the second set of samples.

Manganese concentrations in pollen have been reported in the range of 21-73 ppm for industrial and urban sites and 68-110 ppm in rural, non industrialized sites from Finland [5]. The lower Mn concentration was found in Bucsani (21 ppm) and the higher Mn concentration in pollen was found in Targoviste 3 (134 ppm). The range of the values in our study was 43 – 134 ppm for Mn content in pollen samples collected from urban and industrial sites from Dambovita region and 21 – 52 ppm in samples collected from rural and non industrial sites. It is easy to see that in the case of industrial and urban zones the concentrations of manganese have higher values than the reported values from other similar studies and in the case of non industrial and rural zones the concentrations of manganese have lower values than that from other zones (Finland).

The lower zinc concentration was found in pollen collected from two sites, Salcioara and Uliesti at the level of 22 ppm. The higher zinc concentration was found in pollen collected from Targoviste 4 site at the level of 58 ppm. The reported values found in the literature were in the range 29 – 49 ppm for industrial and urban sites and 34 – 49 ppm for rural and non industrial sites [5]. In this study the concentrations of Zn in pollen samples collected from industrial and urban sites were in the range 25 – 58 ppm and in the range 22 – 29 ppm in samples collected from rural and non industrial sites. It can be observed lower values than that reported in literature from the second set of samples and light higher values for the first set of samples.

4. CONCLUSIONS

ED-XRF proved to be a good analytical method useful for determinations of Fe, Mn and Zn from pollen samples collected from bee hives.

It can be observed that the lower concentrations for Fe, Mn and Zn in rural sites have lower values in comparison with the values reported from other similar sites. Because of the higher content for heavy metals in pollen samples collected from urban and industrial sites and lower content in pollen samples collected from rural and non- industrial sites we can say that the pollen is a biological material who can be used for bio-monitoring of heavy metals levels in environmental studies.

The concentrations for all samples do not exceed the mean values for Fe, Mn and Zn accepted for food stuff. The mean values in pollen samples were at the same level with values obtained in other studies [5, 6].

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