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Assessing the Presence of Heavy Metals in the Area of Glloogoc (Kosovo) by Using Mosses as a Bioindicator for Heavy Metals

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ABSTRACT

This study aimed at determining the level of pollution from heavy metals that are deposited from air in the area of Gllogoc. The main goal was to identify the emission sources of pollution by using mosses as bio indicators. In this study area, the mining of Fe-Ni (Industrial Ferronickel Complex) is believed to strongly influence the level of heavy metals. The mining and production activity of Fe-Ni affects the soil, water and air. As the air pollution (from liberated aerosols of Industrial Ferronickel Complex) and the deposition products of this pollution are harmful not only locally but also can pollute the environmental at extended distances, the use of mosses allows analyzing the content and origin of the pollution from heavy metals. ICP was used for the determination of heavy metals in moss samples. The use of Principal Component Analysis (PCA), dendograms and other statistical procedures, permitted to understand the source of the air pollution from heavy metals.

Keywords: heavy metals; Pb and Zn concentrates; mosses as bio indicators; soil; water; sterile; sludge; landfill; ''Ferronickel'' complex

INTRODUCTION

The main possible pollution source in this area, i.e. the Ferronickel complex, performs the technological processing of the Fe-Ni containing ore; thereby, it produces large amounts of waste that contains heavy metals and other compounds [Barandovski et al., 2013]. The inorganic parts of these pollutants are largely released into the atmosphere, not only by the Ferronickel complex but also as a result of other human industrial activities [Nriagu and Pacyna 2001]. Therefore, evaluating and monitoring the air pollution is mandatory.

The dust generated by the various technological processes that involve combustion in the Ferronickel complex is transported from the wind even at distant distances, polluting the air with various toxic elements that can be deposited in matter during their activity. In this context, the use of moss as bio indicators is a scientifically established procedure for monitoring the deposition of heavy metals from air [Canbay 2017, Walker et al., 2003]. These plants have no roots, meaning that the presence of the pollutants in them is directly related to their presence in atmosphere [Khare 2012]. The level and extent of the air pollutants depends on: emission composition, atmospheric and topographic conditions. Most of the pollutants remain near their discharge source, but some may even spread thousands of kilometres away from the pollution source [Vasconcelos et al., 1998]. The surface and groundwater pollution in this area occur as a possible result of the untreated industrial wastewater originating from the underground discharge pipelines of the Ferronickel complex that flows directly into the local river. In addition to this, the water pollution is also influenced by the urban pollution and discharges of landfill and sterile dumps [Vukojeviç et al., 2010] that lie near the river bank. Likewise, the contamination of the soil occurs as a result from the industrial discharges of the Ferronickel compound, and also from the use of pesticides and herbicides in agricultural lands and wastelands [Lazo et al., 2013]. The Earth itself serves as an environment where the continuous deposition of various inorganic and organic pollutants occurs [Mazzoni et al., 2012].

MATERIAL AND METHOD

The Hypnum cupressiforme moss was used for the research purposes. This type of moss absorbs metals from the atmospheric deposition better than other species [WHO. Regional Office for Europe, 2007].

Sampling

In order to obtain complete information on the air pollution levels, a concept map was built (a sampling network) that considered the following: a) specific pollution sources, main roads in the city, the field of urban disposal waste, or different factories and plants; and b) geographical and meteorological features related to the terrain of the area, and wind direction. This strategy of sampling is based on the European program of evaluation of heavy metals [Chen 2017, Fernandez et al., 2002]. The samples are collected about 150 m from the main roads, 100 m from the local roads, and 200–300 m from the inhabited areas (villages) Figure 1. The collection is carried out on open lawns and in the spaces between the forest trees, in order to avoid the effect of various tree crowns on the atmospheric deposition.

Each sample is provided by 3 or 5, 6 or 10 sub-samples, collected in a 50×50 m space, [Canbay H.S, et al., 2017] randomly. Submasters are mixed, forming the representative sample of each station. The samples collected were cleared in advance from foreign materials such as; soil, mix other lichens or mosses, herbs, leaves, trees or other, [Barandovski et al., 2013]. They were then put in paper envelopes and sent to the lab for further processing.

Preparation of samples

The samples obtained in the field, after being thoroughly cleaned in the laboratory from other inert materials, were are dried at the temperature at 30–40ºC for 48 hours [Canbay and Doğantürk 2017].

The green and brown parts of moss were used for analysis (they represent a period of 1–3 years of growth), so that they reflected the air metal deposits of the last three years. In order to reduce the volume of samples and to carry out homogenization, [Vukojeviç et al., 2010] the samples were hand-crushed, wearing polythene lab-free, dust-free lab coats.

Dry chemical treatment of mosses

About 0.5 g of the homogenized moss samples were placed in semi-press Teflon tubes, to which 10 ml of HNO_3 were added, [Canbay and Doğantürk 2017] (Merck for analysis) – (9 : 1). The tubes were plugged and left at room temperature for 48 hours. The temperature aftwerwards

Fig. 1. The sampling sites for collection of mosses.

was increased to 200°C for 1 hour in order to complete decomposition [Barandovski et al., 2013]. The content of the tube is evaporated until a very small volume remained. After the cooling, the samples were filtered and transferred to a normal container with the volume of 100 ml.

RESULTS AND DISCUSSIONS

The results for the heavy metal content in five different sampling positions (the samples taken in July 2016) [Barandovski et al., 2013] measured by ICP-OES are presented in the Table 1. The maximum values for heavy metals are as follows: Fe > Ni > Zn > Cu > Cr > Pb> Co.

In order to gain an understanding about the possible source of the analyzed heavy metals, the regression results between the studied heavy metals were presented in Table 2. There is a strong positive correlation (presented in yellow) between the metal couples: Cr/Co, Fe/Co/Cr, Ni/Co/Cr/Fe and Zn/Co/Cr/Fe/Ni; suggesting that these metals originate from the ultra basic rocks which are rich in iron and also contain nickel, cobalt, zinc and chromium [Ference et al., 2016]. There is no correlation for Pb and Cu suggesting a different source from the Zn/Co/Cr/Fe/Ni group.

In order to gain a better understanding about the heavy metal contents in between the sampling positions we created a dendogram for all of the sampling positions (Figure 2). The maximum similarity was found between the M2/M5 sampling positions, followed by M2/M4. Sample M3 is distinctive in regard to its chemical composition. In this context, this sample represents a possible external impact that is caused from a pollution source. This sampling position is situated near the deposited landfill of the Ferronickel Complex.

In order to better understand the differences concerning the regression results (Table 1) the Principal Component Analysis (PCA) was performed [Hyang et al., 2007]. PCA is a multivariate statistical method, originally proposed by Hotelling.

The differences among the heavy metal (Figure 3) content are explained using the first two components of the Scree plot. On the basis of the principal component scores, PCA is able to examine multivariate relationship and explain the variance in the data while reducing the number of variable to several groups of individuals [Everitt et al., 1992]. The PCA results are presented in Figure 3 (the Scree plot) and Figure 4 (loading plot).

The PCA analysis groups the heavy metals into two major entities: first group (Fe, Zn, Co, Ni and Cr) and second group (Cu, Pb). This confirms the results from the regression analysis (Table 1), meaning that these two elements (Cu and Pb) have a similar source from pollution. The concentration of heavy metals in the analyzed moss samples reflects the atmospheric deposition of the heavy metals [Lucaciu et al., 2004]. In addition to the part of pollution from directly affected areas, the contaminated dusts adsorb the slag and sterile particles as well as the aerosol particles discharged from the forest of the plant, thereby increasing their content on the moss samples [Vasconcelos et al., 1998]. Moreover, these dust particles can enter soils with other metallic particles, from the flow of the nearby river entering the groundwater layers. The other published results [Barandovski et al., 2013] indicate that this area around the Ferronickel plant is highly polluted with heavy metals.

The concentration of heavy metals in moss samples is as follows: Fe – 629+6736 mg/L; Ni – 12.30–132.50 mg/L; Cu – 1.20–103.20 mg/L; Zn – 27.50–106.40 mg/L; Co – 1.59–7.57mg/L; Cr – 0.20–17.74mg/L and Pb – 0.00–15.99 mg/L. The content of Pb is quite high, compared to the moss sample analysis performed in other countries (Table 3) [Lazo P, et al., 2013].

Table 1. Heavy metal levels in mosses samples determined by ICP-OES

Variable	Mean	Minimum	Median	Maximum
Co	4.23	1.59	4.00	7.57
Cr	7.66	0.20	8.79	17.74
Cu	24.40	1.20	5.60	103.20
Fe	2527.00	629.00	1957.00	6736.00
Ni	71.50	12.30	75.30	132.50
Pb	7.31	0.00	6.19	15.99
Zn	54.50	27.50	40.60	106.40

CONCLUSIONS

In this study, several metals (Fe, Zn, Co, Ni, Cr, Cu and Pb) were analyzed in the moss samples with the statistical methods. The following conclusions were drawn from the discussions above: (1) The difference in the content of the metals in the moss samples in strongly influenced by the local pollution source (Industrial Ferronickel Complex); (2) The correlation coefficients of the metals (between Zn/Co/Cr/Fe/Ni) in the moss samples were between 0.860 and 0.947. This indicates that these metals have a common geological source (from ultra basic rocks). The absence of correlation between Cu and Pb points out that they are directly related to a possible

Table 2. Regression results for the heavy metals in the studied sampling positions

Co	Cr	Cu	Fe	Ni	Pb
0.914					
-0.196	-0.557				
0.941	0.912	-0.229			
0.986	0.912	-0.246	0.882		
-0.126	-0.106	-0.113	-0.391	0.036	
0.909	0.933	-0.42	0.947	0.86	-0.403

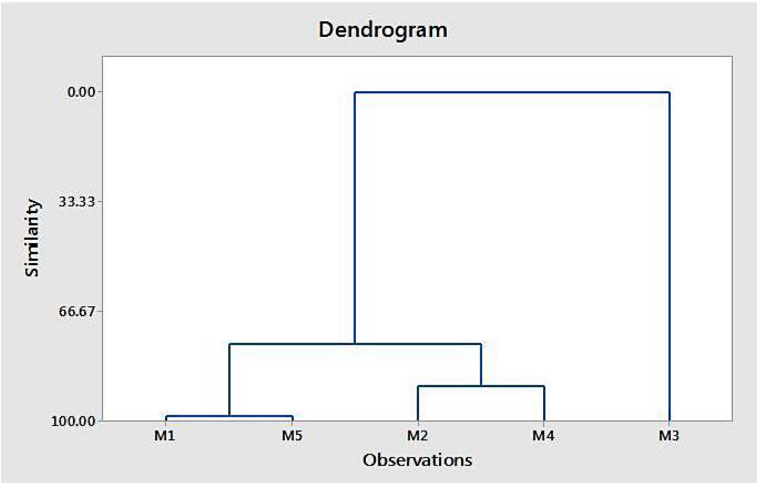

Fig. 2. Dendrogram of cluster analysis of the heavy metals in moss samples at five sampling positions

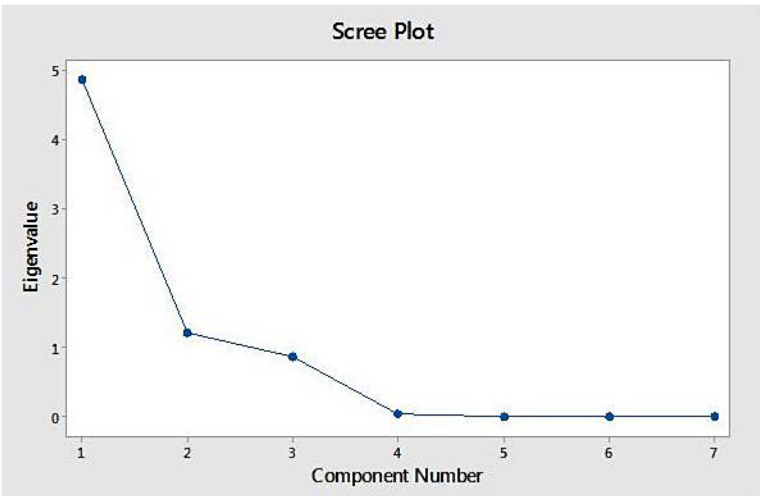

Fig. 3. Scree plot.

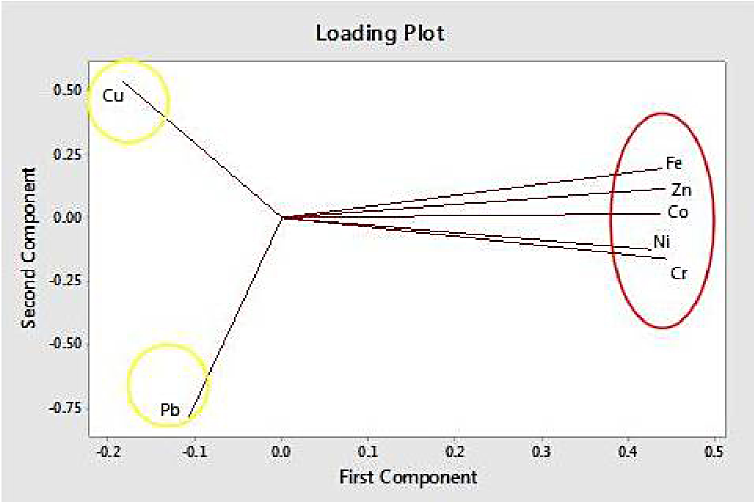

Fig. 4. PCA ordination biplots for the analyzed heavy metals in moss samples

Table 3. The range of variation of lead in moss samples of the area in the vicinity of the Ferronickel complex (Kosovo) and some other countries (* Ref. [Lazo et al., 2010])

Country	Pb, mg/kg
Kosovo (Ferronickel Complex, this work)	0.00 –15.99
Macedonia *	1.50 – 37.20
Albania *	1.34 – 5.38
Croatia *	0.06 – 82.40
Romania*	6.45 – 31.5
Norway *	0.64 – 6.12

local pollution source; (3) The first principle component groups the metals in two categories: a) Fe, Zn, Co, Ni, Cr; and b) Cu, Pb. This supports the regression results, confirming their pollution source. Generally, the above-mentioned results were able to show the metal pollution distribution within the different sampling positions. The study confirms that the use of moss can serve to monitor the heavy metals.

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