BIOMONITORING ATMOSPHERIC POLLUTION WITH HEAVY METALS IN THE COPPER MINE VICINITY LOCATED NEAR RADOVIŠ, REPUBLIC OF MACEDONIA

Biljana Balabanova[1] Trajče Stafilov[2], Katerina Bačeva[2], Robert Šajn[3]

[1]Faculty of Agriculture, Goce Delčev University, POB 201, 2000 Štip, Macedonia

[2]Institute of Chemistry, Faculty of Science, Sts. Cyril and Methodius University, POB 162, 1000 Skopje, Macedonia

[3]Geological Survey of Slovenia, Dimičeva ulica 14, 1000 Ljubljana, Slovenia

INTRODUCTION

The main object of this study was examination of atmospheric pollution with heavy metals due to copper mining Bučim near Radoviš, Republic of Macedonia (Figs. 1 and 2). The Republic of Macedonia does not deviate from the global framework of air pollution with heavy metals. In the eastern part of the country the appearance of some metals (Al, Cd, Cu, Pb, V) in the air is related to the presence of a 'Bučim' copper mine and flotation plant [1]. For that issue lichen species, *Hypogymnia physodes (Nyl.)* and *Evernia prunastri (Ach.)* were used as biomonitors. 18 elements (Al, As, Ba, Ca, Cd, Cr, Cu, Fe, Li, K, Mg, Mn, Na, Ni, Pb, Sr, V and Zn) were analysed.

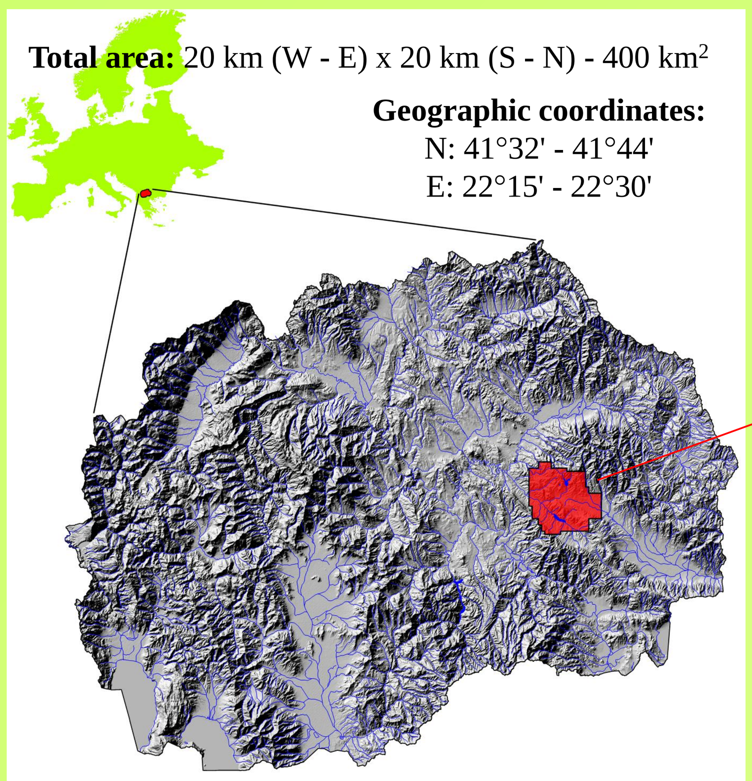

Fig. 1. Location of the study area in the R. Macedonia

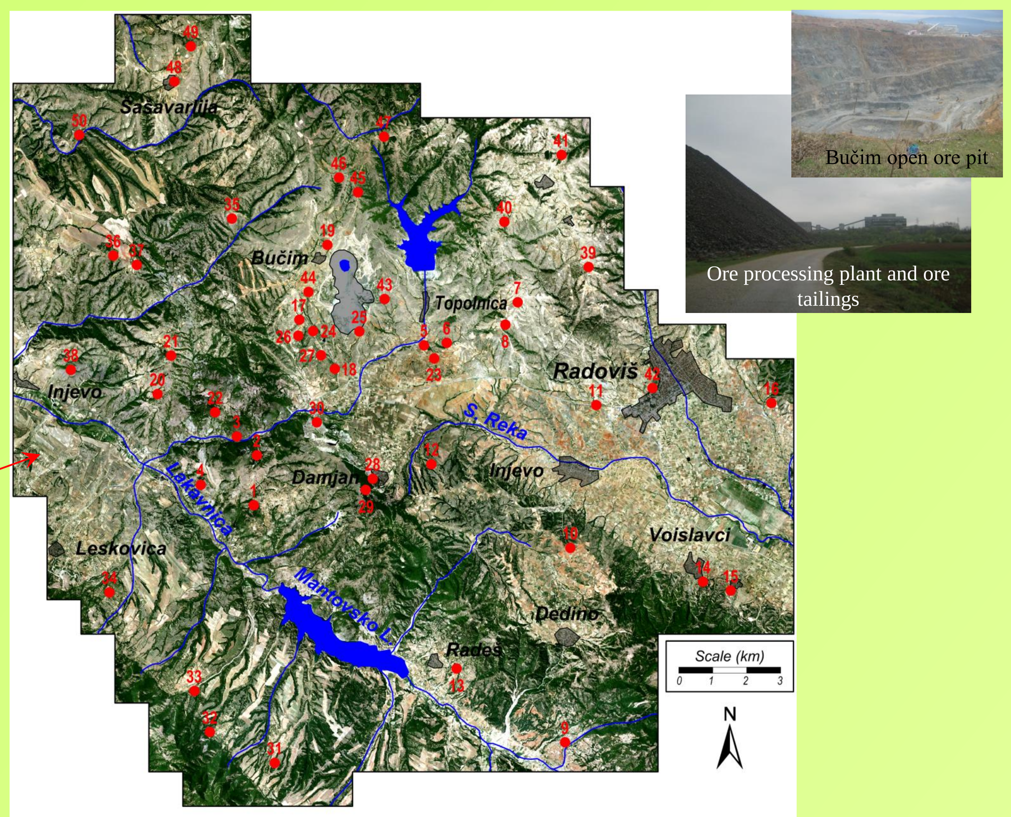

Fig. 2. Lichen samples locations

EXPERIMENTAL

Sampling

Fifty samples of lichen species *Hypogymnia physodes* **(1)** and *Evernia prunastri* **(2)** were collected from the whole study area (Fig. 2.). The collection of lichen samples was performed according to the protocol adopted within the European Heavy Metal Survey.

Sample preparation

For digestion of lichen samples, the **microwave digestion system** (CEM, model Mars) was applied. The precisely measured mass (0.5 g) of each lichen sample was measured in Teflon digestion vessels to which 5ml concentrated nitric acid, HNO_3 and 2ml hydrogen peroxide, H_2O_2 (30%, m/V) were added.

Microwave digestion program

Step	Tepmperature/°C	Time/min	Power/W	Pressure/bar
1	180	5	500	20
2	180	10	500	20

Analyses

Analyses were performed with atomic emission spectrometer with inductively coupled plasma, **ICP-AES (Varian, 715ES),** for Al, Ba Ca, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Sr, V and Zn and electrothermal atomic absorption spectrometer, **ETAAS (Varian, SpectrAA 640Z)** for Cd and As.

Data processing

The obtained values were statistically processed using nonparametric and parametric analysis. Multivariate (factor analysis) method was used to reveal the associations of the chemical elements. The universal kriging method with linear variogram interpolation was applied for the construction of the areal distribution maps.

RESULTS

Lichen species showed a strong tolerance to high contents of Cu and Pb (>0.01%)

Table 1. Descriptive statistics for elements content values in lichen samples (content values are given in mg kg^{-1})

Element	X_a	X_g	Md	min	max	s	s_X	CV	A	E
Al	580	480	440	150	2500	420	60	73	2.54	9.08
As	0.89	0.74	0.87	0.10	3.83	0.54	0.07	61	2.93	15.6
Ba	14	13	14	3.8	30.1	6.0	0.84	42	0.60	-0.03
Ca	6500	5600	5700	1300	20000	3700	530	58	1.69	3.52
Cd	0.12	0.11	0.11	0.05	0.38	0.05	0.01	46	2.82	11.4
Cr	2.34	2.11	1.9	1.01	6.92	1.10	0.16	50	1.63	3.55
Cu	**12**	**7.9**	**6.8**	**1.5**	**130**	**19**	**2.7**	**159**	**5.47**	**34.3**
Li	710	560	520	190	4500	660	93	93	4.14	22.7
Fe	2400	2300	2500	1200	3700	460	65	19	-0.07	0.79
K	0.48	0.42	0.37	0.17	1.15	0.27	0.04	55	0.94	-0.13
Mg	740	710	750	280	1600	210	30	28	1.50	5.53
Mn	57	51	49	14	150	29	4.2	52	1.49	2.26
Na	71	57	66	16	250	47	6.6	65	1.44	3.49
Ni	2.8	2.6	2.5	1.5	10	1.5	0.21	53	2.80	11.4
Pb	**6.7**	**4.3**	**4.2**	**0.61**	**120**	**17**	**2.4**	**253**	**6.98**	**49.1**
Sr	14	13	12	2.9	37	7.8	1.1	55	1.62	2.30
V	2.3	1.8	1.7	0.58	11	1.7	0.25	76	2.49	9.38
Zn	21	20	20	10	39	5.4	0.77	26	1.52	3.32

X_a – mean; X_g – geometrical mean; Md–median; min – minimum; max – maximum; s - standard deviation; s_X – standard error of mean; CV – coefficient of variation; A – skewness; E – kurtosis

The median value of copper is not a worrisome aspect (6.8 mg kg^{-1}), but the median value of samples of lichen collected in the vicinity of the mine, is showing a significantly higher value of approximately 25 mg kg^{-1} **(increased by a factor of 4 times)**

Collected lichen species more easily accumulates atmophile elements (Cd, Pb, Cu, V, Zn)

Copper showed a strong correlation with lead content (r=0.93)

Table 2. Comparative analyses of median and range values between moss and lichen element content

Element	Lichen samples Present study		Moss samples [2]		Correlation coefficients moss:lichen
	Median	Range	Median	Range	
Cu	6.84	1.50-130	10	2.1-198	**0.86**
Pb	4.20	0.61-120	6.8	2.7-40.2	**0.68**

The collected lichens species showed high retention power for accumulation of anthropogenic group of elements compared to moss species sampled from the same study area (*r*=0.86 and *r*=0.68). It was concluded that lichens are very suitable biomonitors for atmospheric distribution of anthropogenic introduced elements.

Four factors were identified, one anthropogenic (F4) and three geogenic(F1, F2 and F3), which includes 86 % of variability of treated elements (Table 3, Figs. 3 and 4)

Table 3. Matrix of dominant rotated factor loadings (F>0.60)

Element	F1	F2	F3	F4	Com
Li	**0.96**	-0.08	0.01	-0.06	94
Al	**0.96**	0.05	-0.02	0.16	95
Cr	**0.93**	0.07	0.13	0.13	90
V	**0.91**	0.08	0.02	0.31	94
Fe	**0.89**	0.10	-0.01	0.39	96
K	-0.10	**0.84**	-0.11	0.05	72
Zn	0.07	**0.80**	-0.06	0.24	71
Cd	0.22	**0.80**	0.34	0.23	86
Ca	0.04	**0.80**	0.31	-0.07	74
Sr	-0.12	0.17	**0.90**	0.05	86
Ni	0.18	0.03	**0.88**	-0.09	81
Cu	0.21	0.16	-0.17	**0.89**	89
Pb	0.29	0.16	0.13	**0.86**	87
Var	35	21	14	15	86

F1, F2, F3, F4-Factor loading; Var-Variance (%); Com-Communality (%)

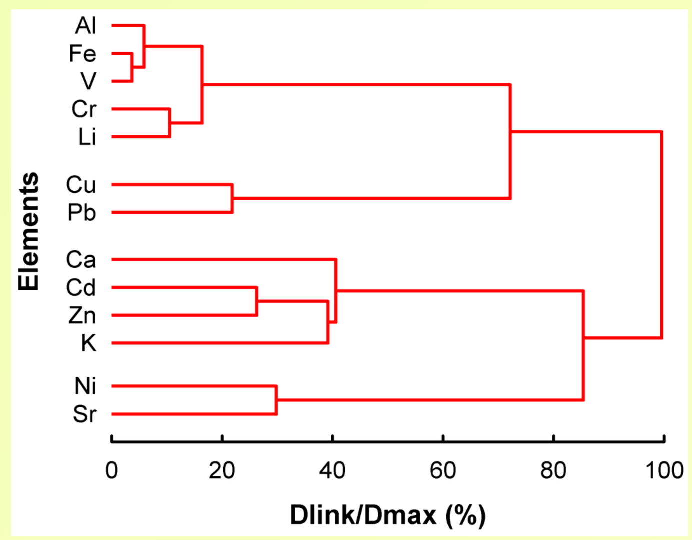

Fig. 3. Dendrogram of cluster analyses

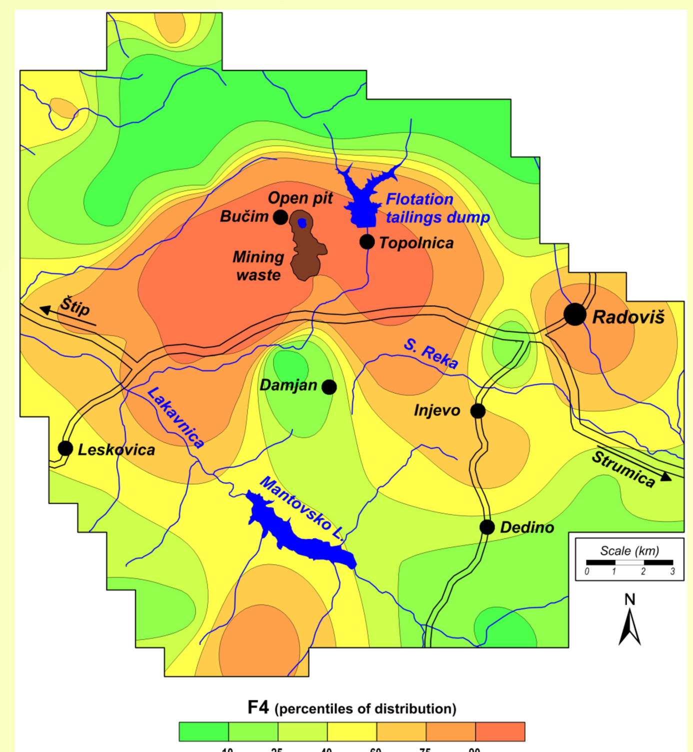

Fig. 4. Spatial distribution of Factor 4 scores (Cu and Pb) in lichen samples

Geochemical anomaly caused by the Cu mining is shown by the statistical factor 4 (Table 3). The group comprises Cu and Pb, elements that were introduced into the environment through anthropogenic activities.

The distribution of Cu and Pb at distant regions was not determined / However, it is worrying that in the close vicinity of the mine there are two settlements - the villages of Bučim and Topolnica.

CONCLUSION

The presence of an open copper ore pit and ore processing and flotation plant (Bučim mine) in the eastern region of the Republic of Macedonia leads to increased deposition of copper in its surroundings (max. value 130 mg kg^{-1}). Apart from copper, increased atmospheric deposition of Pb (120 mg kg^{-1}) was also found, singled out as anthropogenic association with copper. Lichen species (*Hypogymnia physodes* and *Evernia prunastri*) reflect the real atmospheric distribution, not only for the anthropogenic elements (Cu and Pb) , but also for those elements that are little affected by anthropogenic activities from the copper mine (Al, Ca, Cd, Cr, Fe, Li, K, Ni, Sr, Zn and V). Long distant distribution from copper mine of the anthropogenic association of elements (Cu and Pb) was not determined.

Reference

[1] Stafilov, T., Balabanova, B., Šajn, R., Bačeva, K. and Boev, B. (2010b). Geochemical at-las of Radoviš and the environs and the distribution of heavy metals in the air. Faculty of Natural Sciences and Mathematics, Skopje.

[2] Balabanova, .B, Stafilov, T., Bačeva, K. and Šajn, R. (2010). Biomonitoring of atmospheric pollution with heavy metals in copper mine vicinity located near Radoviš, Republic of Macedonia. Journal of Environmental Science and Health , Part A., 12, 1504-1518.

XXI Congress of Chemists and Technologists of Macedonia, September 23-26, 2010, Ohrid, Macedonia