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ATMOSPHERIC POLLUTION WITH COPPER AROUND THE COPPER MINE AND FLOTATION, "BUČIM", REPUBLIC OF MACEDONIA, USING BIOMONITORING MOSS AND LICHEN TECHNIQUE

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

Faculty of Agriculture, "Goce Delčev" University,
POB 201, MK-2001, Štip, Republic of Macedonia
[2]Institute of Chemistry, Faculty of Science, Sts. Cyril and Methodius University in Skopje,
POB 162, MK-1001 Skopje, Republic of Macedonia
[3]Geological Survey of Slovenia,
Dimičeva ulica 14, 1000 Ljubljana, Slovenia
trajcest@pmf.ukim.mk

A b s t r a c t: This paper has studied the atmospheric pollution with copper due to copper mining and flotation "Bučim" near Radoviš, Republic of Macedonia. The copper ore and ore tailings continually are exposed to open air, which occur winds carry out the fine particles in to atmosphere. Moss (*Hyloconium splendens* and *Pleurozium schrebery*) and lichen (*Hypogymnia physodes* and *Parmelia sulcata*) samples were used for biomonitoring the possible atmospheric pollution with copper in the mine vicinity. Moss and lichen samples were digested by using of microwave digestion system and copper was analyzed by atomic emission spectrometry with inductively coupled plasma (ICP-AES). The obtained values for the content of copper in moss and lichen samples were statistically processed using the nonparametric and parametric analysis. Maps of areal deposition of copper show an increase content of copper in the vicinity of mine, but long distance distribution of this element is not established yet.

Key words: air pollution; copper; copper mine; biomonitoring; Bučim; Macedonia

INTRODUCTION

Mine and flotation activities lead to large amounts of waste material (Salomons, 1995; Dudka et al., 1997). Most serious consequence in atmospheric terms is acid deposition, which removes other pollutants in contact within chemical reactions (Repley et al., 1996; Sengupta, 1993). Copper founds in environment as an essential element, but increase content lead to its toxicity (Flemming and Trevors, 1989).

Very useful technique for determining atmospheric pollution with copper and other heavy metals, in different geographical areas, has proved biomonitoring with different bioindicators (Buse et al., 2003; Stamenov, 2002; Frontasyeva, 2004; Coşkun, 2005; Culikov, 2005; Ermakova, 2004; Harmens et al., 2008; Markert et al., 2003). Mosses and lichen despite of all disadvantages represent suitable bioindicators, due to their occurrence in almost all terrestrial ecosystems and ability to tolerate long periods of extreme environmental condition (Gjengedal and Steinnes, 1990; Aceto et al., 2003; Bargagli, et al., 2002; Loppi and Bonini, 2000). In addition, moss and lichen elemental content can be converted into atmospheric deposition values, provided metal uptake efficiency had been previously estimated in the species used as a bioindicators (Čeburnis et al., 1999; Wolterbeek, 2002).

In the Republic of Macedonia the first systematic study for atmospheric pollution with heavy metals using moss technique was undertaken in order to assess the general situation regarding heavy metal pollution and to jointly report these results to the European Atlas of Heavy Metal Atmospheric Deposition issued by UNECE ICP Vegetation (Barandovski et al., 2006, 2008). In the eastern part of the country the appearance of increase content of copper in air is related to a presence of copper mine and flotation "Bučim" near

the city of Radoviš. In this area there has been determined also an influence from the former iron mine, Damjan (Serafimovski et al., 2005).

The Bučim mine is in operation from 1980 and process about 4 million tons of ore annually. The deposit is a porphyry copper type deposit and mineralization is related to Tertiary sub-volcanic intrusions of andesite and latite in a host of Pre-Cambrian gneisses and amphibolites (Serafimovski et al., 1995). The open ore body is approximately 500 m in diameter and 250 m in vertical extent, which actually allows direct exposure of ore particles to the atmosphere. The content of copper in ore is at on the average of 0.3 % Cu. Characteristic metallic minerals are chalcopyrite, pyrite, and bornite, with small amounts of galena, sphalerite, magnetite, hematite, and cubanite (Serafimovski et al., 1996; Alderton et al., 2005). Ore is concentrating by flotation on site and tailings are disposed to a dam in an adjacent valley near village Topolnica. Therefore, it was found that it is important to investigate the atmospheric pollution with copper due to copper mining and flotation "Bučim". For that purpose, moss and lichen biomonitoring was applied. Moss and lichen samples were digested by using of microwave digestion system and copper was analyzed by atomic emission spectrometry with inductively coupled plasma (ICP-AES).

STUDY AREA

The study area is located in eastern part of the Republic of Macedonia (Fig. 1), with largeness of 20 km (W-E) × 20 km (S-N), total 400 km^2, which is limited with coordinates N: 41°32' – 41°44' and E: 22°15' – 22°30'. The copper mine Bučim is located in the centre of the study area, concerning 10 km air line north-west from town Radoviš and 16 km air line south-east from town Štip. The region is characterized by moderate continental climate. Most frequent winds in the region are wind from west with frequency 199 ‰ and 2.7 m s^{-1} speed wind from the east to the 124 ‰ frequency and 2.0 m s^{-1} speed, which is important for the distribution of atmospheric dust with copper contained.

Fig. 1. Study area

EXPERIMENTAL

Sampling

The collection of moss samples was performed according to the protocol adopted within the European Heavy Metal Survey. The networks for moss and lichen species collection are given in Figs. 2 and 3. In the study area the dominant moss species were *Hyloconium splendens* (Hedw.) and *Pleurozium schrebery* (Brid.). As dominant lichen species were *Hypogymnia physodes* (Nyl.) and *Parmelia sulcata* (Tayl.). Moss samples were collected at 52 localities, alongside with lichen species, collected at 50 localities in period of November 2008 to March 2009. The sampling protocol was in this order: one sampling spot is formed by collecting five sub-spots in area of 50 × 50 m^2. Every spot of sampling network was in a distance of minimum 300 m from main roads, 100 m from local roads, and 200 m from villages. Collected material was stored in paper bags and air dried. After drying the moss species were cleaned from other plant species and soil. In thus way prepared, moss species were ready for digestion.

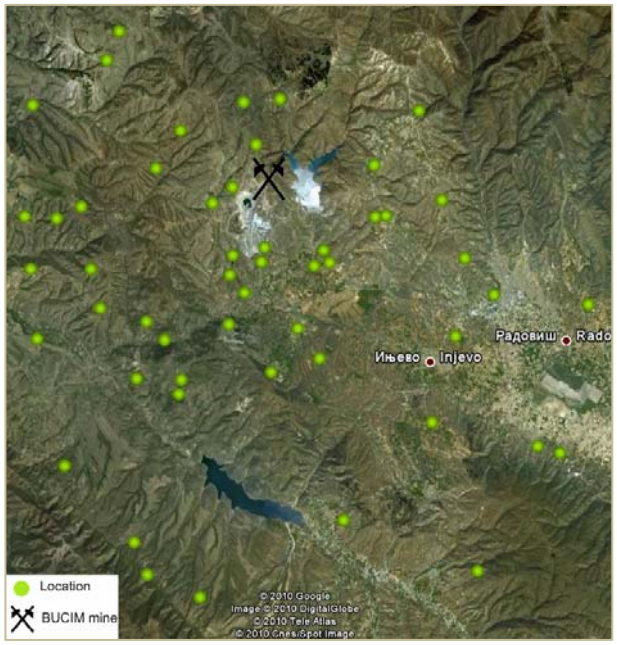

Fig. 2. Moss sampling network

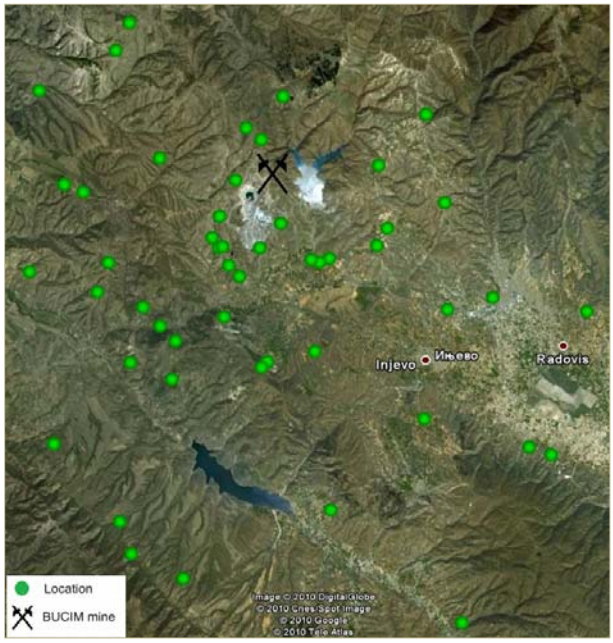

Fig. 3. Lichen sampling network

Sample preparation

For digestion of moss and lichen samples microwave digestion system was applied. Precisely measured mass of samples (0.5 g) were placed in teflon digestion vessels, 5 ml concentrated nitric acid, HNO_3 and 2 ml hydrogen peroxide, H_2O_2 (30%, m V^{-1}) were added and the vessels were closed, tightened and placed in the rotor of a microwave digestion system (Milestone, Ethos Touch Control). The digestion was carried out with two steps program: 1 step (ramp) and 2 step (hold): temperature 180 °C, 5 min ramp time, with power of 500 W and 20 bar pressure. Finally the vessels were cooled, carefully opened, and digests quantitatively transferred to 25 ml calibrated flasks.

Reagents and standards

For this study reagents with analytical grade or better were used for preparation of all solutions: nitric acid, trace pure (Merck, Germany), hydrogen peroxide, p.a. (Merck, Germany), and redistilled water. Standard solutions of metals were prepared by dilution of 1000 mg l^{-1} solutions (11355-ICP multi Element Standard).

Instrumentation

The content of copper in moss and lichen samples was analyzed by atomic emission spectrometer with inductively coupled plasma, ICP-AES (Varian, 715ES). The operating instrumental conditions are given in Table 1.

Table 1

Instrumentation and operating conditions for ICP-AES system

RF generator			
Operating frequency	40.68 MHz free-running, air-cooled RF generator.		
Power output of RF generator	700–1700 W in 50 W increments		
Power output stability	Better than 0.1 %		
Introduction area			
Sample nebulizer	V- groove		
Spray chamber	Double-pass cyclone		
Peristaltic pump	0–50 rpm		
Plasma configuration	Radially viewed		
Spectrometer			
Optical arrangement	Echelle optical design		
Polychromator	400 mm focal length		
Echelle grating	94.74 lines/mm		
Polychromator purge	0.5 l min^{-1}		
Megapixel CCD detector	1.12 million pixels		
Wavelength coverage	177 nm to 785 nm		
Wavelength for Cu measurement	324.754 nm		
Conditions for program			
RFG power	1.0 kW	Pump speed	25 rpm
Plasma Ar flow rate	15 l min^{-1}	Stabilization time	30 s
Auxiliary Ar flow rate	1.5 l min^{-1}	Rinse time	30 s
Nebulizer Ar flow rate	0.75 l min^{-1}	Sample delay	30 s
Background correction	Fitted	Number of replicates	3

RESULTS AND DISCUSION

The descriptive statistic of analyzed element is shown in Table 2. Normality tests were compared with histograms of distribution for the content of copper in moss and lichen samples, the normality was assumed on the bases of the logarithms of contents in moss and lichen samples. Median values for copper contents were compared with the median values for the same element for the entire territory of Republic of Macedonia.

Table 2

Descriptive statistic of measurements for Cu content in moss and lichen samples

Biomonitor	*n*	Dis	X_a	X_g	Md	min	max	P_{10}	P_{90}	Var	s	CV	A	E
Moss	52	Log	20.7	11.5	9.95	2.14	198	3.75	54.0	1141	33.8	163	3.69	15.6
Lichen	50	Log	12.1	7.8	6.85	1.50	134	3.55	23.5	369	19.2	159	5.47	34.3

Dis – distribution (log – lognormal; N – normal); X_a – aritmetical mean; X_g – geometrical mean; Md – median; min – minimum; max – maximum; P_{10} – 10 percentile; P_{90} – 90 percentile; Var – variance; s – standard deviation; CV – coefficient of variance; A – skewness; E – kurtosis

From descriptive statistic, median values for copper show deviation, compared with medians for this element for whole territory of Macedonia 22 mg kg^{-1} for Cu (Barandovski et al., 2008), Table 3. Smaller median for Cu was not expected in this area, because of the influence of copper mine. However, the range of values shows much higher copper content in the moss and lichen samples.

Table 3

Comparison of median values of element content in moss and lichen between data of present work and data for whole territory of Macedonia (given in mg kg^{-1})

Biomontior	Study area (present work)				Republic of Macedonia (Barandovski et al., 2008)	
	Whole area		Mine and flotation area			
	Median	Range	Median	Range	Median	Range
Moss	10	2.1–198	91.0	29.2–198	22	3–83
Lichen	7.0	1.5–134	24.5	20.4–134	–	–

The logarithmic values were used for normalization, because of the curved distribution, and the big difference of the median and arithmetical mean.

The obtained values for copper content in lichen, compared with appropriate values from moss samples, show lichen less uptake retention of copper (Table 3). This is probably because the particle absorption in lichen is influenced by acid precipitation which is characteristic for this study area, due to present acid mine drainage (Conti and Cecchetti, 2001; Pandey et al., 2007). Comparative analysis of median values for copper content in moss samples obtained from the present work with median values of copper content for whole territory of Republic of Macedonia (22 mg kg^{-1}), confirms that the atmospheric dust distribution is of short range (Table 3). Concerning the median value for copper content from moss samples collected near mine and flotation plant, it can be seen (Table 3) that the atmospheric pollution with copper is 4 times higher (91 mg kg^{-1}), in terms of median value for the country and for the whole study area (10 mg kg^{-1}). Distribution of copper in the study area was present using Google Earth program software. From the obtained maps (Figs. 4 and 5) it can be seen that the copper content in moss and lichen samples collected in the close vicinity of the mine are much higher than in the samples from the surrounding (more than 9 times). From the obtained results it can be concluded that the pollution of the atomsphere with copper is only present in the very close vicinity of the copper mine and flotation plant and flotation tailings deposit. Higher content of copper in moss and lichen samples was found near the villages Bučim and Topolnica, which could be assumed as most polluted settlements, from aspect of risk for human health.

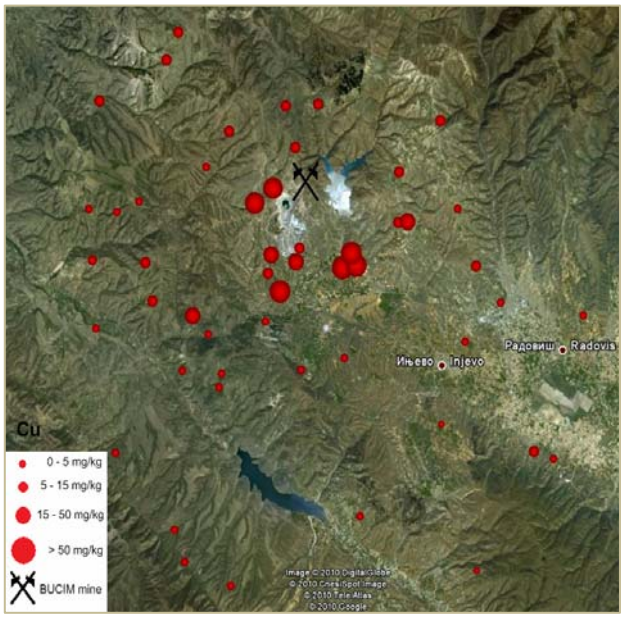

Fig. 4. Map of areal deposition of copper from moss samples

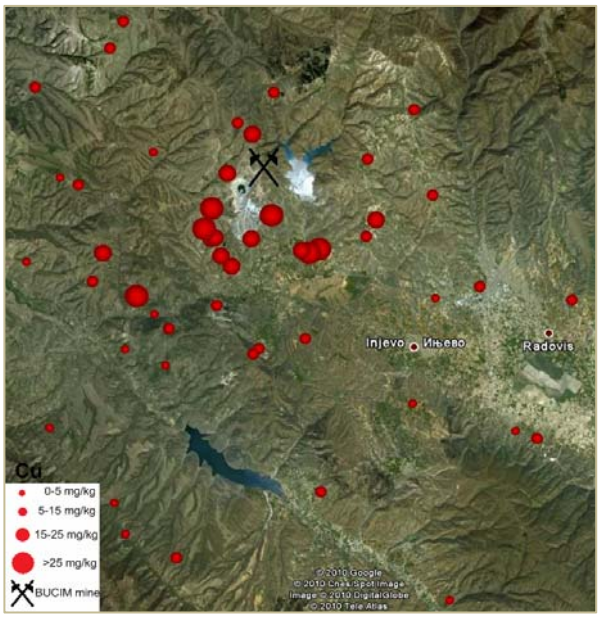

Fig. 5. Map of areal deposition of copper from lichen samples

CONCLUSION

The mining and flotation plant activities, as well as the flotation tailings from Bučim mine, near Radoviš, Republic of Macedonia, was investigated by using moss and lichen biomonitoring. It was found that the copper content in moss and lichen samples collected in the close vicinity of the mine are much higher than in the samples from the surrounding (more that 9 times). Higher content of copper in moss and lichen samples was found near the villages Bučim and Topolnica, which could be assumed as most polluted settlements, from aspect of risk for human health.

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Р е з и м е

ЗАГАДУВАЊЕ НА ВОЗДУХОТ СО БАКАР ВО ОКОЛИНАТА НА РУДНИКОТ И ФЛОТАЦИЈАТА ЗА БАКАР „БУЧИМ”, РЕПУБЛИКА МАКЕДОНИЈА, СО ПРИМЕНА НА БИОМОНИТОРИНГ СО МОВОВИ И ЛИШАИ

Биљана Балабанова[1], Трајче Стафилов[2], Катерина Бачева[2], Роберт Шајн[3]

[1]Земјоделски факултет, Универзитет „Гоце Делчев”, п. фах 201, МК-2000 Штип, Република Македонија
[2]Институт за хемија, Природно-математички факултет, Универзитет „Св. Кирил и Методиј“ во Скопје, п. фах 162, МК-1000 Скопје, Република Македонија
[3]Геолошки завод на Словенија, Димичева 14, 1000 Љубљана, Словенија
trajcest@pmf.ukim.mk

Клучни зборови: загадување на воздухот; бакар; рудник за бакар; биомониторинг; Бучим; Македонија

Во трудот се презентирани резултатите од извршените испитувања на атмосферското загадување во околината на рудникот и флотацијата за бакар „Бучим” близу Радовиш, Република Македонија. Изложеноста на рудничката и флотационата јаловина на воздух и влага доведува до појава на повисоки содржини на бакар во околината. Во студијата е применет биомониторинг со мовови и лишаи, а определувањето на бакарот е вршено со примена на атомската емисиона спектрометрија со индуктивно спрегната плазма. Целта на испитувањето е да се утврди областа на загадувањето на воздухот со бакар, кое може да се очекува како резултат на активностите на рудникот и флотацијата. За таа цел се земени примероци мов од 52 локации, како и примероци лишаи од 50 локации во испитуваниот регион. Добиените резултати покажуваат значително високи вредности на содржината на бакар во примероците од мов и лишај земени од поблиската околина на рудникот „Бучим“. Вредностите на медијаната за содржината на Cu во примероците мов од целата испитувана област (10 mg kg^{-1}) се пониски од онаа за целата територија на Република Македонија (22 mg kg^{-1}), што укажува на тоа дека поширокиот регион не е засегнат од работата на рудникот. Ако се споредат, пак, вредностите на медијаната за содржината на бакар во мововите земени во непосредната околина на рудникот и флотацијата со медијаната за бакар за Македонија, се добива фактор на зголемување од околу 5 пати (91 mg kg^{-1}). Изработените карти на депозиција го потврдуваат фактот за влијанието на активностите во рудникот врз загадувањето на воздухот во блиската околина на рудникот.