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BIOINDICATION ABILITY OF *Hypnum cupressiforme* AND *Homolothecium lutescens* FOR DETERMINATION OF ARSENIC DISTRIBUTION IN ENVIRONMENT

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Abstract

Atmospheric dust emissions can be a threat for the environmental and human health. Long-term emission occurs in this area due to the Pb-Zn hydrothermal exploitation (*Sasa* and *Zletovo* mines) and copper ore exploitation and flotation (Bučim mine), in the area of Bregalnica river basin. The present study proposes a combined model based on: bioindication with moss species (*Hypnum cupressiforme* and *Homolothecium lutescens*), and universal kriging mapping for determination of arsenic distribution. For that purpose, 149 moss samples were collected from the area, and both moss species were used interchangeably. At the same sampling points, soil samples from the surface layer were also collected. Mass spectrometry with inductively coupled plasma (ICP-MS) was used for determination of total arsenic content in moss and soil samples. Prior to analysis, the samples were totally digested with the application of microwave system for samples digestion for moss samples and open wet digestion was used for total dissolution of soil samples. Spatial distribution maps were constructed for determination and localizing of narrower areas with higher contents of arsenic. The content of arsenic in moss tissue (regarding air-born dust) ranges from 0.05 mg/kg to 4.28 mg/kg, while distribution of arsenic in soil samples ranges from 3 to 261 mg/kg. Dominant lithogenic occurrence of arsenic was correlated with areas of Neogene pyroclastites (volcanism).

Key words: *moss, biomonitors, air pollution, ICP-MS*

INTRODUCTION

Atmospheric pollution represents solutions or suspensions of minute amounts of harmful compounds in the air (Valero, 2014). The degree and the extent of environmental changes over the last decades has given a new urgency and relevance for detection and understanding of environmental changes, due to human activities, which have altered global biogeochemical cycling of heavy metals and other pollutants (Greenwood and Earnshaw, 2005; Acton, 2013). Arsenic is one of the most prevalent toxic elements in the environment. The toxicity, mobility, and fate of arsenic in the environment are determined by a complex series of controls dependent on mineralogy, chemical speciation, and biological processes (Alloway, 1990). As a chemical element, arsenic is widely distributed in nature and can be concentrated in many different ways. In the Earth's crust, arsenic is concentrated by magmatic and hydrothermal processes and has been used as a "pathfinder" for metallic ore deposits, particularly gold, tin, copper, and tungsten (Alloway, 1990; Greenwood and Earnshaw, 2005; Keller et al., 2015). Monitoring toxic air pollutants is needed for understanding their spatial and temporal distribution and ultimately to minimize their harmful effects. In addition, to direct physical and chemical methods of air pollution monitoring, *bioindication* has also been used to evaluate air pollution risk (Aboal et al., 2010; Ares et al., 2012; Valero, 2014).

Mosses have been frequently used to monitor time-integrated bulk deposition of metals/semimetals as a combination of wet, cloud, and dry deposition, thus eliminating some of the complications of precipitation analysis due to the heterogeneity of precipitation (Harmens et al., 2004, 2008, 2010, 2015). Moss data provides a better geographical coverage than measured deposition data and reveals more about actual atmospheric pollution at a local level (http://icpvegetation.ceh.ac.uk/). Latest data reported from Harmens et al. (2015) and Barandovski et al. (2015) indicates on the significant enrichments of some toxic elements.

The investigated area is characterized by several significant pollution sources of potentially toxic metals and other chemical elements in the environment: the copper mine and flotation "Bučim" near the town of Radoviš, the lead and zinc mines "Sasa" near the town of Makedonska Kamenica and "Zletovo" near the town of Probištip (Serafimovski et al., 2004; Alderton et al., 2005; Rogan et al., 2006; Dolenec et al., 2007; Rogan et al., 2008; Rogan-Šmuc et al., 2009; Serafimovski et al., 2011a, 2011b; Vrhovnik et al., 2013; Alderton et al., 2014; Serafimovski and Tasev, 2015; Vrhovnik et al., 2016; Stafilov and Šajn, 2016). The excavation of the copper minerals is carried out from an open ore pit, while in the lead-zinc mines the exploitation is underground, and the ore tailings are stored outdoors.

The focus of this research is on the uses of the two moss species *Hypnum cupressiforme* (Hedw.) and *Homalotecium lutescens* (Hedw.) Schimp. for monitoring atmospheric deposition of arsenic in mine environs. Sharing the same common name "fern moss" with other monitoring mosses, these species similarly have extensive branching allowing for a large exposed surface area for ion exchange. These features make *Hypnum cupressiforme* and *Homalotecium lutescens* likely candidates for use as a biomonitors. The primary objective of this study was to evaluate the suitability of two moss species as a bioindicator of arsenic on a regional landscape scale in potentially polluted area. Mosses as pollution bioindicators only give an overview of the areas where we found the presence of higher content of arsenic in atmospheric dust, but not a real measurement of the content in the ambient air.

MATERIAL AND METHODS

Moss/soil sampling protocol

Samples of the pleurocarpous moss species *Homalotecium lutescens* and *Hypnum cupressiforme* were collected in the investigated area. Researchers while setting up large-scale survey often face the problem that the location of the predicted sampling spot becomes subordinate to the presence/absence of the selected species (Fernández et al., 2015). This problem can be overcome by using more than one moss species within the same survey; however, it is clear that the concentrations of elements may vary considerably between species thus precluding comparison of the results obtained (Boquete et al. 2013). Interspecies comparison has been made by Balabanova et al. (2017b) improving the insignificant variation for arsenic accumulation between both moss species. Depending on the conditions and the accessibility of the locations the species which are available and typical for the region were collected. Random samples (in the very close vicinity of the pollution source) and samples according to sampling network (5 x 5 km) were collected from total of 149 sample locations, as presented in Figure 1. Detailed description of the collection of samples (according officially accepted techniques) is given by Fernández et al. (2015). At each location for moss sampling, topsoil (0-5 cm) samples were collected also according to the standard protocol given by Salminen et al. (2005).

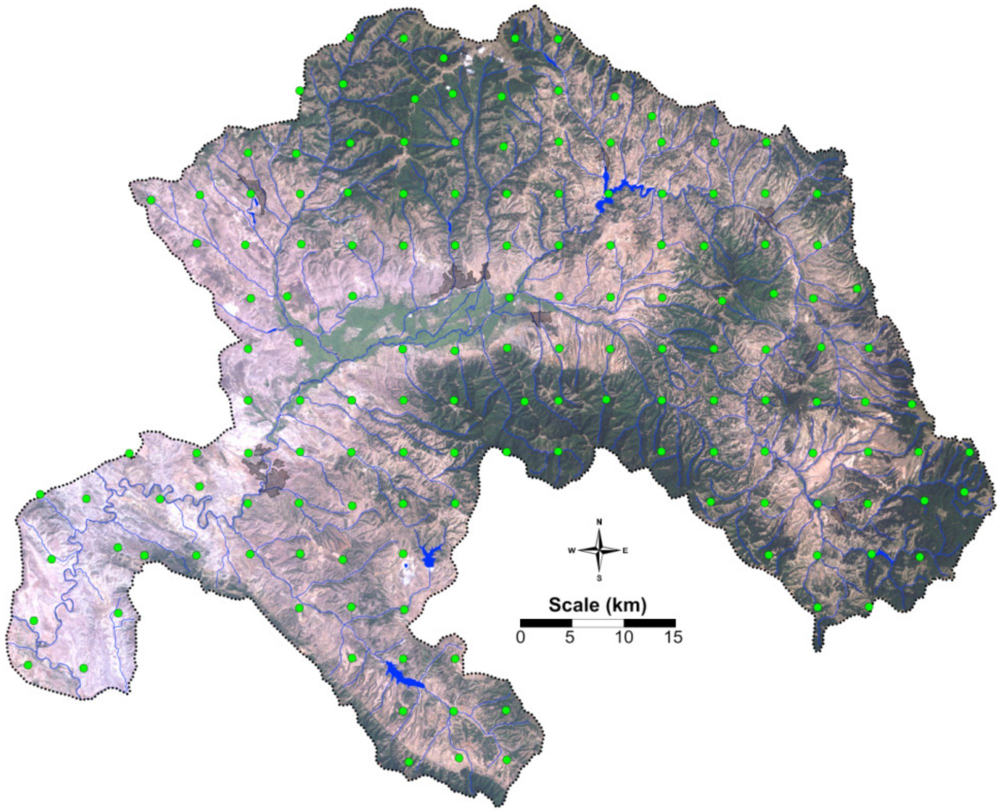

Figure 1. Moss/soil sampling network

Sample preparation protocol and spectroscopy analysis

Total digestion of moss samples was performed with application of microwave digestion system (CEM, model Mars). Precisely measured mass (0.5000 g) of moss samples was introduced into Teflon microwave vessels, than 5 mL concentrated HNO_3 (trace pure), and 2 mL H_2O_2 (30%, *m/V*) were added. The Teflon vessels were carefully closed and the microwave digestion method was applied. Digestion method was performed in to two steps for total digestion of moss tissue as previously given by Balabanova et al. (2010). After the digestion method was finished, digests were quantitatively transferred into 25 mL volumetric flaks.

For digestion of soil samples, open wet digestion with mixture of acids was applied. Precisely measured mass of soil sample (0.5 g) was placed in Teflon vessels and 5 mL concentrated nitric acid, HNO_3 was added, until the brown vapours came out from the vessels. Nitric acid is very suitable oxidant for digestion of environmental samples. For total digestion of inorganic components, 5-10 mL hydrofluoric acid was added. When the digest became clear solution, 2 mL of $HClO_4$ was added. Perchloric acid was used for total digestion of organic matter. After 15 minutes cooling the vessels, 2 mL of HCl and 5 mL of H_2O were added for total dissolve of metal ions. Finally the vessels were cooled and digests quantitatively transferred to 50 mL volumetric flaks.

In this way the digested moss and soil samples were prepared for determining the contents of the different elements using mass spectrometry.

Mass spectroscopy analysis

SCIEX Perkin Elmer Elan DRC II (Canada) inductively coupled plasma mass spectrometer (with quadrupole as single detector) was used for measurement of the arsenic concentration in digested samples. Optimization was first performed using the normal mode, and then using the collision cell mode. Before the parameters of the collision cell were optimized, the cell was flushed with collision gases (5 mL/min) for at least 1 hour. Two certified reference materials M2 and M3 (Steinnes et al., 1997) and spiked intra-laboratory sample were analyzed at a combined frequency of 20% of the samples. The recoveries for arsenic content in all control samples were obtained as: 85.6%, 109%, respectively. The detection limits (DL) were calculated using the following equation: DL = ($3\times\sigma bl/S$), where σbl is the standard deviation of the background and S the sensitivity. The quantum mode for arsenic was found for ^{75}As isotope and the calculated DL was 0.0013 mg/kg.

Data processing

The obtained values for the arsenic contents in moss and soil samples were statistically processed using basic descriptive statistics. Data processing was performed using the statistical software Stat Soft (Version 11) (StatSoft, Inc., Tulsa, OK, USA). Using field observations, analytical and measurement data matrix was created. For each observation, the following variables were extracted: sample identification number, location, geographic coordinates, sample type. Since many statistical techniques are sensitive to non-normally distributed data, the Box-Cox transformation was performed. The Box-Cox transformation improves the feature better, especially for the skewness and normality of the data sets (Box and Cox, 1964). Line and bar/colon plots were constructed for better visibility of data distribution according to defined zones. The universal method kriging with linear variogram interpolation was applied for the construction of spatial distribution map for arsenic deposition/distribution in the investigated area. Seven classes of the following percentile values were selected: 0–10, 10–25, 25–40, 40–60, 60–75, 75–90 and 90–100.

RESULTS AND DISCUSSION

The basic statistics of analysed moss and soil samples (surface soil layer) for arsenic content is presented in Table 1. The distribution of arsenic in the analyzed samples ranges from 0.05 mg/kg to 4.28 mg/kg. Compared to data available from Barandovski et al. (2015) from the survey for the whole territory of the Republic of Macedonia, indicates significant enrichments (EF=2.25, regarding maximum values). The median value for the whole territory of the Republic of Macedonia (0.48 mg/kg) did not show significant variation from the same value from the present investigation (0.49 mg/kg). The minimum arsenic content was obtained for sample collected in the area with dominant occurrence of Paleogene flysh where the topsoil layer contains 17.3 mg/kg of arsenic. In order to monitor the lithogenic affect from the natural distribution of arsenic in soil, data for arsenic content in moss tissue were compared with the data for arsenic content in topsoil layer. The distribution of arsenic in surface soil samples ranges in 3.02-261 mg/kg (Tab. 1). Four sampling spots, where the soil samples were enriched with arsenic content (104, 105, 121 and 261 mg/kg) were not characterized with higher content of arsenic in moss samples (0.35, 1.15, 1.29 and 0.15 mg/kg, respectively). This encourages the fact that soil dusting does not significantly affect the air-introduced particle distribution in the investigated area. In order to reveal a significant enrichment of arsenic, maximum value was compared with maximum values from moss survey in other countries, such as Albania, Croatia, Bulgaria and Norway (Qarri et al., 2013; Špirić et al., 2013; Harmens et al., 2013; Steinnes et al., 2011). The calculated enrichments factors, regarding the maximum value for arsenic content in moss, are given as follow: 1.49, 4.28, 0.42 and 0.88, respectively.

Table 1. Descriptive statistics for elements content values in moss samples, N=149 (given in mg/kg)

Sample	Min	P_{10}	P_{25}	P_{40}	Md	P_{60}	P_{75}	P_{90}	Max
Moss	0.050	0.25	0.33	0.42	0.49	0.57	0.75	1.03	4.28
Topsoil	3.02	6.62	9.80	13.4	16.9	20.8	28.7	53.9	261
	X	**X(BC)**	**S**	**Sx**	**CV**	**A**	**E**	**A (BC)**	**E (BC)**
Moss	0.70	0.48	0.71	0.058	100	3.06	11.5	-0.02	0.46
Topsoil	26	17	26	2.1	100	3.91	23.6	0.001	0.27

Min – minimum; P_{10} – 10 percentile; P_{25} – 25 percentile; P_{40} – 40 percentile; Md – median; P_{75} – 75 percentile; P_{90} – 90 percentile; Max – maximum; X – mean; S –standard deviation; CV – coefficient of variation; A – skewness; E – kurtosis; BC-Box/Cox transformed data.

The data for arsenic content in moss samples additionally were processed according to different lithological units in the investigated area. Data were also processed and analyzed according to the generalized geological map given by Balabanova et al. (2016). Several lithological units were identified as dominant in the investigated area: Quaternary sediments, Neogene sediment and pyroclastite, Paleogene flysch, Pleozoic schist, Rifeous schist, Proterosoic schist, gneisse and granite. Mainly, arsenic do not participate significantly in the composition of the Earth's crust, although several minerals containing as its major constituents (Alderton et al., 2014). Dumurdžanov et al. (2004) explained that natural enrichment of arsenic may occur in areas where the Neogene vulcanite's are dominant geological units. The calculated median values of Box-Cox transformed data, according to the lithological units are given as follow: in area with dominance of Quaternary sediments - 0.73 mg/kg, for Neogene sediments the median value was 0.43 mg/kg and for Neogene pyroclastites was obtained the maximum value regarding the lithological units - 0.95 mg/kg. In the area with dominant occurrence of Paleogene flysch the median value was 0.49 mg/kg, which was very similar with arsenic distribution in areas with dominant occurrence of Pleozoic schist (0.44 mg/kg), Rifeous schist (0.55 mg/kg), Proterozoic schist (0.51 mg/kg) and Proterozoic granite (0.46 mg/kg). Lower median value was obtained for moss samples collected from area with dominant occurrence of Proterozoic gneisse (0.34 mg/kg). For better visualization of data distribution according to different lithological units bar plot was constructed (Fig. 2). Ohnuki et al., (2002) introduces data that suggest strongly correlation of As with Fe, Si and Ca in mine areas. Weathering of the rocks containing As probably generates the powder rock containing As and other elements (Alderton et al., 2014). They found that As accompanies Fe in the spatial distributions in moss; small particulates containing As and Fe are associated with the lower plants in a similar manner to the trapped silicate minerals (Ohnuki et al., 2002). However, in the area where the anthropogenic introducing of arsenic is not significantly enriched, this element can shows different distribution pathways correlated with the dust weathering. From the summary data available from Balabanova et al. (2017a) the distribution of arsenic in air-distributed dust, is strongly correlated with distribution of Co, Ge and V. The long-time deposition monitoring using attic dust, suggest very stable geochemical occurrence of arsenic in areas with polymethalic enrichments (Balabanova et al., 2010, 2011; Balabanova et al. 2016; Angelovska et al., 2016; Balabanova et al., 2017a; 2017b).

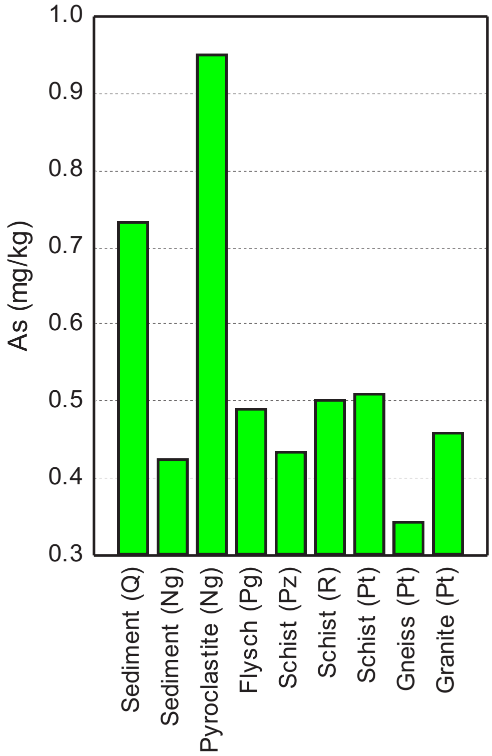

Figure 2. Arsenic distribution according to different lithological units in the investigated area

The constructed kriging map visualizes the areal distribution of arsenic in the Bregalnica River basin (Figs. 3 and 4). Arsenic deposition is with predominant occurrence on Neogene pyroclastites (Fig. 3). According to the generalized geology map (Balabanova et al 2017a), Kratovo-Zletovo region is the unique district in the region located along the continental margin and is closely related to the Tertiary volcanoes and hydrothermal activities in this area. Pb-Zn mine *Zletovo* is located in the area with dominantly presence of the Neogene volcanism appears sequentially and in several phases forming sub-volcanic areas. According to Dumurdžanov et al. (2004) the pyroclastites are most frequently found in the Kratovo-Zletovo volcanic area, where the dacites and andesites are the oldest formations. These polyphasal Neogene deformations through the insignificant movements associated with the volcanic activities had direct influence on the gradual formation of the reefs and the formation of deposits in the Zletovo area. Spatial patterns are extended in eastern direction, due to the most common winds from western direction with frequency of 199‰ and speed of 2.7 m/s (Lazarevski, 1993). This kind of geochemical *fingerprinting* occurs along the whole course of the Bregalnica river. Accordingly, the resulting areal distribution map used to support with high certainty the assessment for poly-metallic enrichments as ascribed to urbanization, including vehicular emissions and incinerators and industry. This area is characterised with poly-metallic enrichments (Ag-Bi-Cd-Cu-In-Mn-Pb-Sb-Te-W-Zn) for long-time air-dust deposition (Balabanova et al., 2017a). Furthermore, there is a strong interconnection between the anthropogenic and lithogenic fingerprinting. Arsenic distribution in topsoil layer of soil is strongly emphasised in the same area (Fig. 4). Basically, the element geochemistry intermediate between atmospheric emissions and lithogenic wind-blow dusting. Therefore, arsenic distribution can be used as proposed mechanism for possible tracking of anthropogenic poly-metallic enrichments in areas with dominant occurrence of old volcanism (Figs. 3 and 4). In the area where dominant lithological units relays on Paleogene volcanic sedimentary rocks (the area of Pb-Zn hydrothermal exploitation, Sasa mine) atmospheric emissions are significantly intensified (wind-blow dusting) compared to lithogenic enrichments in top-soil. Spatial attention also should be given for the area so called Vladimirovo-Berovo, where arsenic contents in moss samples reaches more than 1 mg/kg (Fig. 3). Almost twenty years ago, Arsovski (1997) drew attention to poly-metallic enrichment in this area so called Vladimirovo-Berovo, during the tectonic investigation. The present investigation also interpolates this area as metallic's/metalloids enriched zone, with emphasis on the anthropogenic elements. This area is characterized by dominant occurrence of Neogene clastites, and this natural anomaly correlated with arsenic distribution continues along the whole course of the river Bregalnica. Enriched atmospheric depositions of arsenic also were found in the area of hydrothermal exploitation of cooper ore (Cu-mine "Bučim" near the town of Radoviš). This area was monitored in 2010, and authors reveal the occurrence of poly-metallic association Al-As-Cd-Cu-Fe-Pb-Zn as dominant anthropogenic marker for air-pollution (Balabanova et al., 2010).

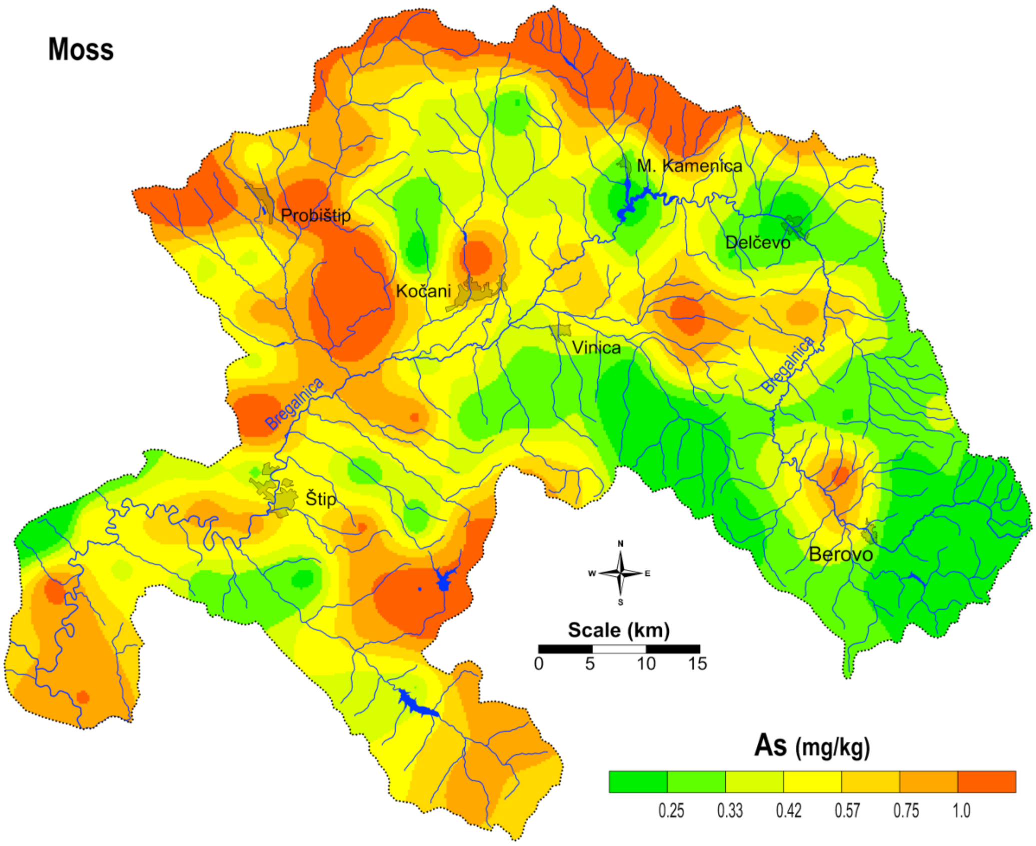

Figure 3. Areal distribution of arsenic in moss samples

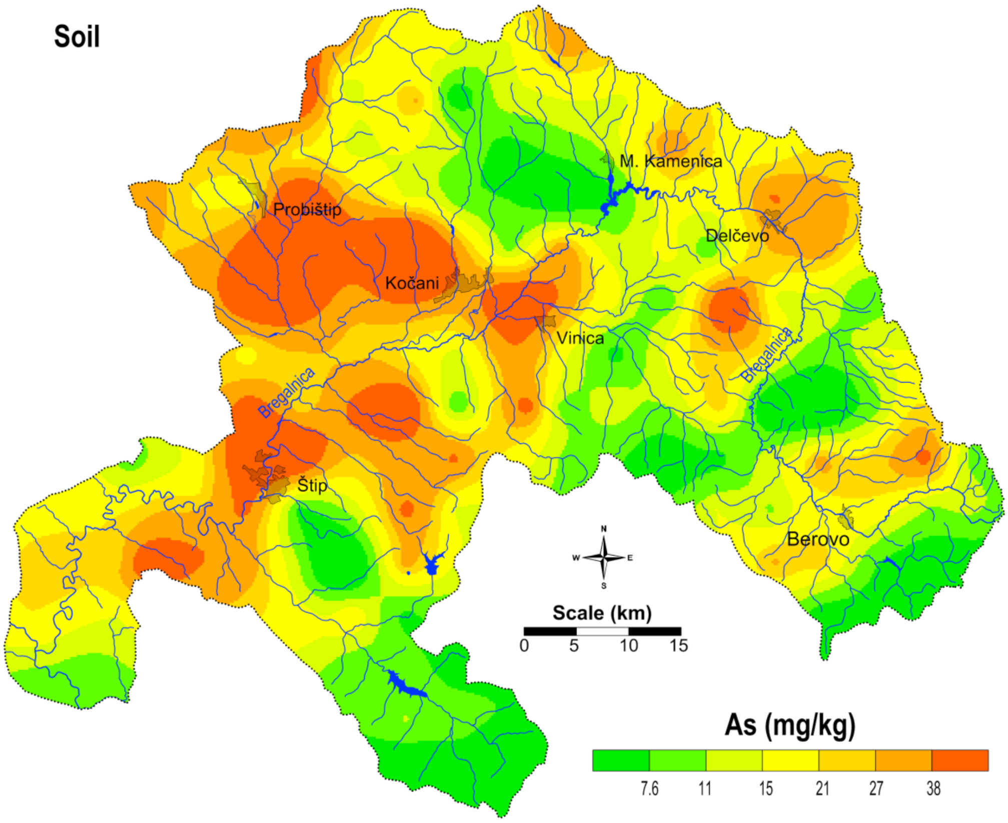

Figure 4. Areal distribution of arsenic in top-soil samples

CONCLUDING REMARKS

The present investigation points to strongly correlation of the lithogenic and anthropogenic atmospheric distribution of arsenic in the area of Bregalnica River basin. Both of the terrestrial moss species, *Hypnum cupressiforme* and *Homolothecium lutescens* were improved as a sensitive bio-indicative model for enriched arsenic deposition in air. This environmental media contain a mixture of material derived from in situ weathering of parent material and atmospheric input dominated by continental dust. The anthropogenic activities carried out in the areas of poly-metallic hydro-thermal exploitation (*Sasa*, *Zletovo* and *Bučim* mines) lead to increased content of arsenic. Atmospheric distribution of arsenic reaches to the maximum value of 4.28 mg/kg. Mainly, intensified atmospheric deposition of arsenic occurs in area with dominant occurrence of Neogene pyroclasites and clastites and Paleogene flysch. This indicates that arsenic distribution can be strongly correlated to the poly-metallic enrichments, which are due to hydro-thermal exploitation. The both moss species (*H. cupressiforme* and *H. lutescens)* were introduced as dominant bioindicator markers in the investigated area.

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БИОИНДИКАЦИСКА СПОСОБНОСТ НА *HYPNUM CUPRESSIFORME* И *HOMOLOTHECIUM LUTESCENS* ЗА СЛЕДЕЊЕ НА ДИСТРИБУЦИЈАТА НА АРСЕН ВО ЖИВОТНАТА СРЕДИНА

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Резиме

Атмосферските емисии на прашина во одредени услови претставуваат закана за животната средина и здравјето на луѓето. Во областа на сливот на реката Брегалница е утврдена долгорочна емисија на атмосферска прашина, којашто се должи на хидротермалната експлоатација на Pb-Zn руда (рудниците *Саса* и *Злетово*), како и експлоатација и флотација на бакарната руда (рудник *Бучим*). Ова истражување предложува примена на комбиниран модел базиран на биоиндикации со видови на мов (*Hypnum cupressiforme* и *Homolothecium lutescens*) и *кригинг* мапирање за одредување на дистрибуцијата на арсен. За таа цел беа собрани 149 примероци на мов од испитуваната област. И двата вида на мов беа собирани наизменично. На локациите каде што се собираа примероци на мов, исто така, беа собрани и примероци од почва од површинскиот слој. Масена спектрометрија со индуктивно спрегната плазма (ИСП-МС) беше користена за одредување на вкупната содржина на арсен во примероците на мов и почва. Пред да бидат анализирани, примероците беа целосно разложени со примена на микробранов систем за разложување на примероци (за примероците мов), додека за примероците на почва беше применет методот на отворена дигестија со смеша од киселини (мокро разложување). Карти на просторна дистрибуција беа конструирани заради одредување и локализирање на потесните области со повисока содржина на арсен. Содржината на арсен во мовното ткиво (во однос на прашината во воздухот) се движи од 0,05 mg/kg до 4,28 mg/kg, додека дистрибуцијата на арсен во примероците на почвата се движи од 3 до 261 mg/kg. Литогената дистрибуција на арсен значајно е поврзана за области со доминантно појавување на неогенски пирокластити (вулканизам).

Клучни зборови: *мов, биомонитори, загадување на воздухот, ИСП-МС*