CENTRAL EUROPEAN INITIATIVE
CEI Know-how Exchange Programme (KEP)

ENIGMA Project (*Ref. No. 1206KEP.008-12*)

AIR POLLUTION WITH HEAVY METALS OF ALLCHAR LOCALITY, KOŽUF AREA, REPUBLIC OF MACEDONIA

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Abstract

A study on air pollution with heavy metals in the Allchar locality (cca. 13 km^2), an antimony-arsenic-thallium mineralization, was performed. The mine is located on the north-western part of Kožuf Mt., Republic of Macedonia. The locality of Allchar is unique in its mineral composition. The distribution of 53 elements (with special attention to As, Sb and Tl) was established by applying of 69 moss samples from nine various species collected from this area. Moss samples were analysed following microwave digestion by inductively coupled plasma - mass spectrometry (ICP-MS) and inductively coupled plasma – atomic emission spectrometry (ICP-AES). It was found that the atmospheric deposition for As in the moss samples on or around the mine is >6.5 times higher and for Tl is 19 times higher compared to values for the samples from the rest of the Allchar area. By the application of Multivariate cluster and R-mode factor analyses (FA) five geochemical associations were determined: Cluster and R mode factor analysis (FA) was used to identify and characterise element associations and five associations of elements were determined by the method of multivariate statistics. F1 (Co, Cr, Fe, Sc, Li, V, Ga, Y, Ni, Mn, Al, La-Lu, Cu, Ge, Be, Bi and Hf); F2 (As, Tl, Sb and Mg); F3 (Rb, Cs and Mo); F4 (Sr, Ba, Hf, Zr, La-Lu and Bi) and F5 (Cd, Zn, Ag and Cu).

Introduction

Emissions from anthropogenic sources and those of natural origin contribute to contamination of the environment with heavy metals. Mining and smelting of ore can release large quantities of toxic and trace elements and dust particles into the atmosphere creating pollution problems (Kabata-Pendias and Mukherjee, 2007). Heavy metals are well-known for their toxic effects, and therefore information on their concentrations and distribution in the environment is important. Emissions from mine activate, mine mills, smelters and metal processing plants are the main sources of heavy metals in the environment for specific regions (Sims et al. 2013).

Biomonitoring of environmental pollution is an important way of addressing environmental impacts of mining activities. Monitoring toxic air pollutants is needed for understanding their spatial and temporal distribution and ultimately to minimize their harmful effects. Mosses provide an effective and cheap method for monitoring trends in heavy metal pollution in different geographical areas (Harmens et al., 2007, 2008). The first systematic study of heavy metals as an atmospheric pollution using moss analysis in Macedonia was undertaken in the frame of International Cooperative Programme on Effects of Air Pollution on Natural Vegetation and Crops by United Nations Economic Commission for Europe (UNECE ICP Vegetation) in 2002 and repeated in 2005 and 2010 (Barandovski et al. 2008, 2012, 2013). The results obtained from these studies show that the most important sources of pollution were related to Pb-Zn, Fe-Ni and Fe-Cr smelters near the cities of Veles, Kavadarci and Tetovo as well as copper and Pb-Zn mines in the E part of the country (Stafilov et al., 2008, 2010a, 2010b; Bačeva et al., 2011, 2012; Balabanova et al., 2010; Barandovski et al., 2008, 2012, 2013; Boev et al., 2013).

The aim of this study is to present the natural air transport and deposition of trace elements in the As-Sb-Tl Allchar locality, Republic of Macedonia, abounded mine in the last 100 years, based on moss biomonitoring technique. Special attention was given to the behavior of As, Sb and Tl and other trace elements which follow the As-Sb-Tl mineralization present in this mine. For this purpose the level of air deposition of various elements was determined by using moss samples and inductively coupled plasma-mass spectrometry (ICP-MS) as well as and inductively coupled plasma-atomic emission spectrometry (ICP-AES).

Materials and methods

Study area

The Kožuf district is a large volcanic complex situated in the south of the Republic of Macedonia. The Allchar As-Sb-Tl locality is comprised of hydrothermal volcanogenic deposits situated at the NW of the Kožuf Mts., close to the border between the Republic of Macedonia and Greece (Fig. 1). From the geotectonic point of view, ore mineralization is related to a Pliocene volcano-intrusive complex located between the rigid Pellagonian block in the west, and the labile Vardar zone in the east characterized by ring-radial structures (Boev and Jelenković 2012). From the metallogenic point of view, the Allchar deposit belongs to the Kožuf ore district as part of the Serbo-Macedonian metallogenetic region.

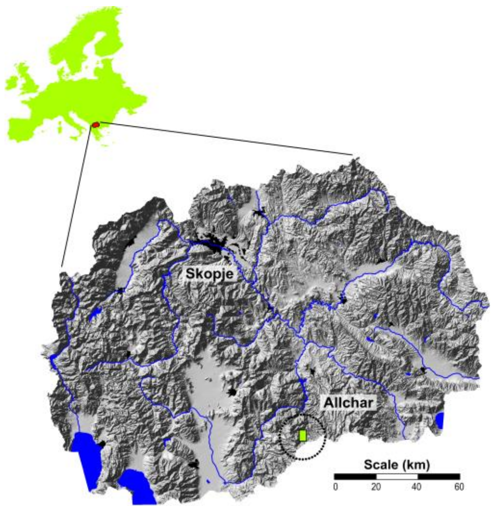

Fig. 1. The studied area in the Republic of Macedonia

Sampling and sample preparation

Samples of the different moss species [*Hypnum cupressiforme*, *Homalothecium lutescens* (Hedw.) Robins., *Lencodon scinroides* (Hedw.) Schwaegr., *Brachythecium salebrosum* (Web & Mohr.) B. S. & G.] were collected during summer in 2011 at 69 locations (Fig. 2). Sampling was carried out in accordance with European moss survey protocols (Rühling and Steinnes, 1998). In the laboratory the samples were cleaned from extraneous plant material and soil particles and air-dried at room temperature. Moss samples were digested with a mixture of concentrated HNO_3 and H_2O_2 at 180˚C in the microwave digestion system.

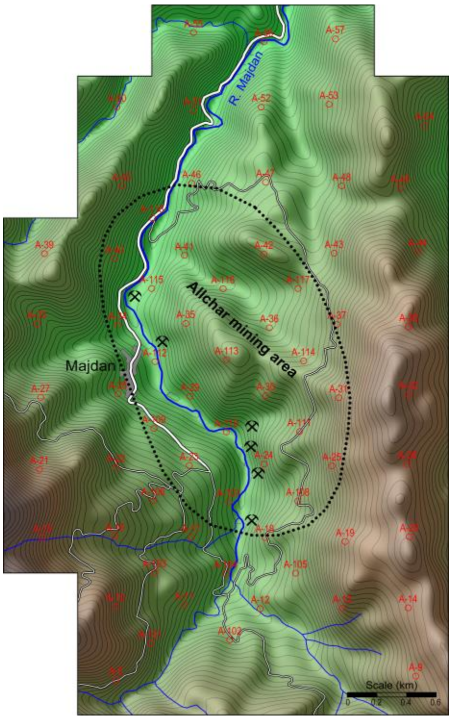

Fig. 2. Shaded relief map with sampling locations

Instrumentation

Elemental analysis was accomplished by inductively coupled plasma - mass spectrometry (ICP-MS with quadruple and single detector setup (SCIEX Perkin Elmer Elan DRC II, Canada). For this study, a NIST 2709 and NIST 1643e certified reference materials were used. The quality control was also ensured by standard moss reference materials M2 and M3, which were prepared for the European Moss Survey (Steinnes et al., 1997). All moss samples were also analysed with ICP-AES (Varian, 715-ES), for the elements with high contents (Al, Ca, K, Mg and P) with the operating conditions presented previously (Balabanova et al., 2010).

Data processing and statistical analyses

Interpretation of the geostatistical data and visualization (mapping) were performed at Geological Survey of Slovenia by using the following software packages: Statistica (Stat Soft, Inc.), Autodesk MAP 3D (Autodesk, Inc.), ArcINFO (ESRI, Inc.) and Surfer (Golden Software, Inc.). Parametric and nonparametric statistical methods were used (Zhang et al. 1998), and normality tests of data distributions were performed. The degree of association of chemical elements was assessed using the linear coefficient of correlation – Peaerson r (Cohen, 1988). Multivariate cluster and R-mode factor analyses (FA) were used to reveal associations of chemical elements (Garson, 2000, Reimann et al., 2002, Šajn, 2005, 2006). The factor analysis was performed on variables standardized to zero mean and unit standard deviation. For orthogonal rotation the varimax method has been used. The factor analysis (FA) from accurate number of variables provides smaller number of new variables, so called factors that present association of statistical significant variables. Universal kriging with linear variogram interpolation method was used for the construction of maps showing spatial distribution of factor scores, as well as maps of the distribution of all elements (Davis, 1986).

Results and discussion

The statistical data of all the 53 analysed elements in the moss samples collected from the investigated region (*n*=69), are presented in Table 1. Data obtained by ICP-MS and ICP-AES were based on nitric acid solutions, possibly leaving out fractions of the elements contained in silicate minerals in the precipitate (soil particles).

Association of chemical elements

The degree of association between the concentrations of chemical elements in the moss samples has been assessed by the Pearson correlation coefficient (r). Elements whit majority of measurements below the DL have been excluded from further statistical analyses.

On the basis of the matrix of correlation coefficients, cluster and factor multivariate statistical analysis was performed. The factor analysis (Table 2) was used to identify and characterize element associations. From 53 analysed variables (analysed elements), 12 analysed variables Br, Ca, Hg, I, K, Na, P, Pb, S, Sn, Th and W were eliminated from further analysis, because of not showing a reasonable connection with other chemical elements. Elements with low share of communality or tendency to form independent factors were excluded too. The matrix of rotated factor loadings are presented and five factors were identified Table 3: **F1** (Co, Cr, Fe, Sc, Li, V, Ga, Y, Ni, Mn, Al, La-Lu, Cu, Ge, Be, Bi, Hf); **F2** (As, Tl, Sb, Mg); **F3** (Rb, Cs, Mo); **F4** (Sr, Ba, Hf, Zr, La-Lu, Bi) and **F5** (Cd, Zn, Ag, Cu) associations, interpreted as Factors (F1 - F5), which account for 81 % of the total variability of treated elements.

F1 association (Co, Cr, Fe, Sc, Li, V, Ga, Y, Ni, Mn, Al, La-Lu, Cu, Ge, Be, Bi and Hf) includes elements that are probably naturally distributed. High concentrations of most elements of the F1 association are typical for Plio-Quaternary tuff and latite breccias and extremely low values for Pliocene andesitic. It represents a scale of the wider area, so that it cannot be interpreted locally. The regional distribution of majority of these elements is typical for the group of crucial elements predominantly supplied to the moss by windblown soil dust. The relative enrichment in La is characteristic for the volcanic rocks of Allchar, similar to the Ce content, as well as Ce/Y (Frantz et al. 1994; Boev and Jelenković 2012). The global trend of the value of F1 is the SE-NW, the influence of weak local topology.

Factor 2 (As, Tl, Sb and Mg) represents the element association which indicates natural and anthropogenic influence in the studying area. The distribution map for this geochemical association is given in Fig. 3. From the distribution map of the F2 association is clearly visible that the higher content of these elements is deposited in close vicinity of the mine. This association of elements was expected because of the mining activities in the past (ore and tailings waste is present in the open) and as a result of surface phenomena of the past in this area (Janković 1993; Frantz et al. 1994). In the case of the F2 distribution, elements were very well defined, although this distribution is not directly related to geology. For this association the influence of local topology is also low. Local thermal winds carried up and down in the valley the primary fine particles of dust from the surface layer and soil with high concentrations of As, Tl, Sb, and dispose them to the moss samples (Fig. 3).

Factor 3 (Rb, Cs and Mo). The high concentrations of these elements are present in Plio-Quaternary tuff outcrops, Triassic carbonates, the relatively high concentrations in Pliocene andesites and very low concentrations are location to Quaternary moraines. Probably such distribution is due to the same case as in F1 association, as remote impact.

Table 1. Descriptive statistics for values for the content of 53 elements in the moss samples (n=69)

Element	**Unit**	**Distribution**	**Average**	**Median**	**Min**	**Max**
Ag	µg kg^{-1}	Log	25	20	10	140
Al	%	Log	0.22	0.13	0.029	1.4
As	mg kg^{-1}	Log	2.8	0.49	<0.1	30
Ba	mg kg^{-1}	Log	38	19	3.6	200
Be	µg kg^{-1}	Log	57	30	<10	370
Bi	µg kg^{-1}	Log	20	15	<10	88
Br	mg kg^{-1}	Log	0.55	0.43	<0.01	3.4
Ca	%	Log	0.58	0.57	0.29	0.86
Cd	mg kg^{-1}	Log	0.15	0.13	0.038	0.67
Ce	mg kg^{-1}	Log	1.4	0.89	0.17	9.6
Co	mg kg^{-1}	Log	0.87	0.69	0.29	3.4
Cr	mg kg^{-1}	Log	5.7	5.0	2.2	20
Cs	mg kg^{-1}	Log	0.60	0.14	0.021	7.7
Cu	mg kg^{-1}	Log	3.2	2.7	0.021	11
Dy	µg kg^{-1}	Log	110	72	17	870
Er	µg kg^{-1}	Log	57	36	<10	420
Eu	µg kg^{-1}	Log	35	22	<10	280
Fe	mg kg^{-1}	Log	1200	730	230	6800
Ga	mg kg^{-1}	Log	0.44	0.25	0.068	3.5
Gd	µg kg^{-1}	Log	150	98	23	1200
Ge	µg kg^{-1}	N	15	14	<10	33
Hf	µg kg^{-1}	Log	23	17	<10	140
Hg	µg kg^{-1}	Log	74	40	<10	410
Ho	µg kg^{-1}	Log	21	14	<10	160
I	mg kg^{-1}	N	0.21	0.20	0.033	0.38
K	%	Log	0.46	0.45	0.22	0.83
La	mg kg^{-1}	Log	0.69	0.40	0.081	6.3
Li	mg kg^{-1}	Log	1.0	0.60	0.15	13
Mg	%	N	0.11	0.11	0.077	0.16
Mn	mg kg^{-1}	Log	71	62	16	330
Mo	mg kg^{-1}	Log	0.20	0.15	0.058	1.1
Na	mg kg^{-1}	Log	140	91	44	850
Nd	mg kg^{-1}	Log	0.71	0.45	0.083	5.0
Ni	mg kg^{-1}	Log	13	11	6.5	27
P	%	N	0.10	0.11	0.023	0.18
Pb	mg kg^{-1}	Log	11	4.0	<0.01	480
Pr	mg kg^{-1}	Log	0.17	0.11	0.021	1.2
Rb	mg kg^{-1}	Log	5.6	4.3	1.6	26
S	mg kg^{-1}	Log	680	580	290	1600
Sb	µg kg^{-1}	Log	25	10	<10	330
Sc	mg kg^{-1}	Log	0.49	0.35	0.17	2.6
Sm	µg kg^{-1}	Log	130	<100	<100	1100
Sn	mg kg^{-1}	Log	1.7	0.74	0.42	47
Sr	mg kg^{-1}	Log	21	12	4.7	120
Tb	µg kg^{-1}	Log	20	13	<10	160
Th	mg kg^{-1}	Log	0.45	0.26	<0.1	3.2
Tl	mg kg^{-1}	Log	4.8	0.12	<0.1	290
V	mg kg^{-1}	Log	2.8	1.8	0.51	17
W	µg kg^{-1}	Log	21	15	<10	95
Y	mg kg^{-1}	Log	0.55	0.35	0.091	4.0
Yb	µg kg^{-1}	Log	49	31	<10	360
Zn	mg kg^{-1}	Log	17	16	10	32
Zr	mg kg^{-1}	Log	0.76	0.60	0.19	3.3

Table 2. Matrix of rotated factor loadings (*n*=69)

Element	F1	F2	F3	F4	F5	Communality
Co	**0.90**	0.18	0.26	0.14	0.19	96.0
Cr	**0.87**	0.26	0.18	0.06	0.14	88.1
Fe	**0.85**	0.18	0.32	0.29	0.17	97.6
Sc	**0.84**	0.14	0.27	0.17	0.09	83.4
Li	**0.84**	0.19	0.31	0.22	0.07	89.3
V	**0.82**	0.16	0.30	0.33	0.22	94.9
Ga	**0.81**	0.14	0.35	0.38	0.14	97.1
Y	**0.78**	0.14	0.30	0.42	0.21	94.4
Ni	**0.78**	0.11	0.07	-0.02	0.24	68.1
Mn	**0.77**	-0.15	-0.22	0.18	0.14	72.7
Al	**0.76**	0.21	0.29	0.37	0.13	86.9
La-Lu	**0.73**	0.11	0.31	**0.52**	0.20	94.6
Cu	**0.67**	-0.09	0.13	0.05	**0.50**	71.9
Ge	**0.61**	0.14	0.28	0.37	0.29	69.5
Be	**0.59**	0.29	0.42	0.44	0.06	80.9
Bi	**0.55**	0.15	0.31	**0.50**	0.29	75.7
As	0.35	**0.87**	0.16	0.07	-0.08	90.9
Mg	0.19	**0.63**	-0.18	-0.03	-0.18	50.1
Sb	0.08	**0.76**	-0.05	-0.07	-0.13	60.4
Tl	0.02	**0.85**	0.32	-0.10	0.03	83.3
Mo	0.39	0.30	**0.60**	0.26	-0.06	67.3
Cs	0.39	-0.06	**0.83**	0.12	-0.05	86.0
Rb	0.28	-0.01	**0.85**	0.15	0.11	83.7
Hf	**0.51**	0.18	0.31	**0.63**	0.17	82.0
Zr	0.48	0.26	0.31	**0.61**	0.20	79.8
Ba	0.30	-0.21	0.09	**0.80**	0.11	78.5
Sr	0.07	-0.26	0.02	**0.83**	0.13	77.7
Zn	0.44	0.00	0.11	0.09	**0.78**	81.9
Ag	0.30	-0.26	-0.20	0.13	**0.74**	76.8
Cd	0.13	-0.19	0.08	0.26	**0.83**	82.4
Var.	36.2	11.1	11.6	13.2	9.3	81.4

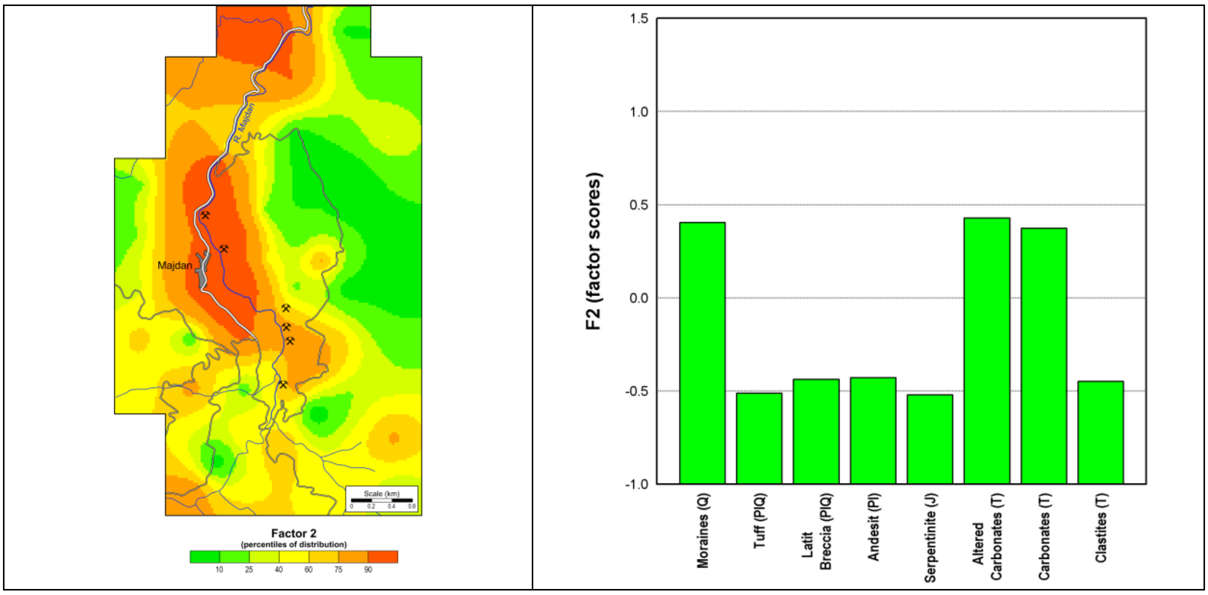

Fig. 3. Spatial distribution of Factor 2 (As, Tl, Sb and Mg) scores (above) and its levels according to basic lithological units (below)

Factor 4 (Sr, Ba, Hf, Zr, La-Lu, Bi) association is locally distributed. High values were related to quartz outcrops PLQ Latite Breccia (N and E of the study area) and a small part of the outcrops is related to Pl andesites (center). Low values of this group were in the area of Jurassic diabase and serpentines (SW part). The content of these elements depends mostly on the basic geological structure.

Factor 5 (Cd, Zn, Ag, Cu) is an association correlated typical "heavy metals" and assumed to be reason for the local distribution. The presence of high contents of these heavy metals in the atmosphere is from the relative enrichment of Cu and Zn in some ore from the Allchar deposit (Frantz et al. 1994; Boev and Jelenković 2012).

Air dispersion of As, Sb, and Tl in the Allchar area

Special attention was given to the behavior of As, Sb and Tl to investigate the anthropogenic influence in the studied area, due to the impact of the volcanic phenomena of the past and mineralization present in this mine. From descriptive statistic (Table 1), it can be seen that the median values and ranges for most of the elements obtained in this study are very similar to the median values and ranges obtained for the whole territory Macedonia (Barandovski et al. 2008; 2012; 2013). Only a few elements have slightly higher values for medians, like As, Sb, and Tl that is obviously as a result of mining activities in the past and as a result of surface phenomena of the presence of these elements in this area (Janković, 1993; Frantz et al., 1994; Volkov et al., 2006; Boev and Jelenković, 2012). However, if we were compare data for these elements in moss samples collected from the mining area (n=25) with moss samples collected from the rest of the wider area, than we can distinguish the differences in the content of As, Sb and Tl (Figs. 2 and 4).

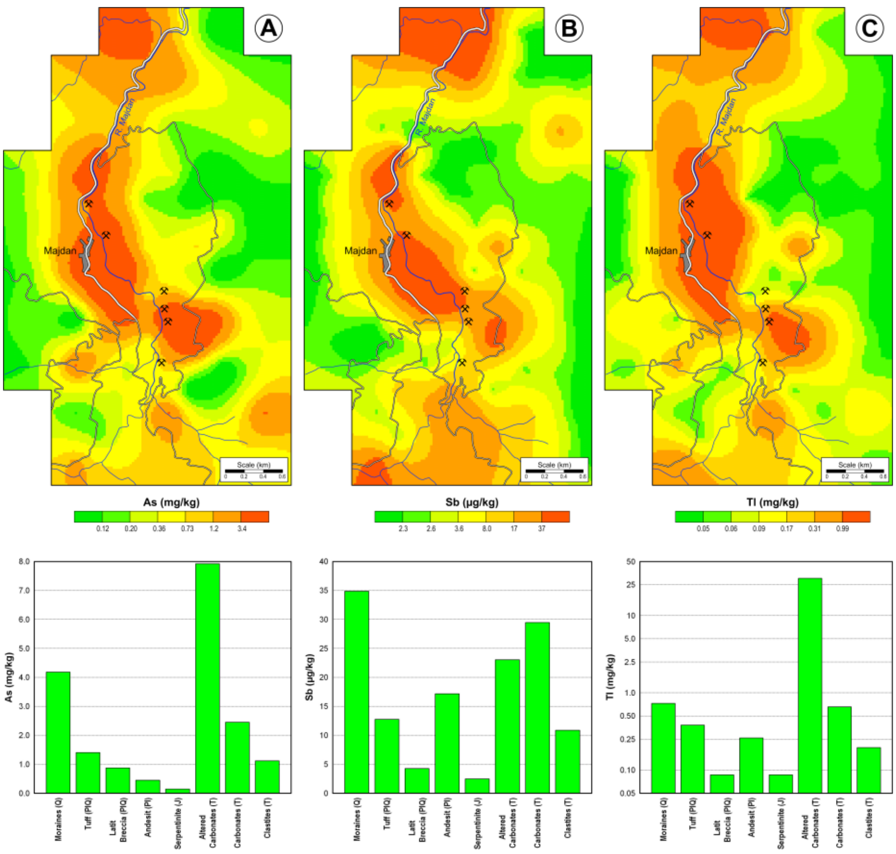

Fig. 4. Spatial distribution of As, Sb and Tl (above) and their concentration levels according to basic lithological units (below)

The median value of As in the moss samples around the Allchar mine is 2.1 mg kg^{-1}, which is almost 6.5 times higher compared to values for the samples from the rest of the Allchar area. The content of As in the moss samples around the Allchar mine varied from <0.1-30 mg kg^{-1}, with the average value of 5.7 mg kg^{-1}, compared with the rest of the Allchar area (ranges <0.1-12 mg kg^{-1}) and the average of 1.2 mg kg^{-1}. The median values for As from Allchar locality are much higher that the values obtained from the moss survey in Macedonia in 2002, 2005 and 2010 (0.80 mg kg^{-1}; 0.67 mg $kg^{-1}$and 0.50 mg kg^{-1}, respectively) (Barandovski et al. 2008, 2012, 2013). In addition, the spatial distribution of As in moss samples is closely related on lithology (Fig. 4). The highest concentrations were found on Triassic altered carbonates and Quaternary moraines.

It was found that the median for Tl in moss samples from the vicinity of the mine (0.96 mg kg^{-1}, the average of 13 mg kg^{-1}) with the moss from the rest of the Allchar area (0.10 mg kg^{-1} and the average is 0.23 mg kg^{-}1) is about 10 times higher. The content of Tl in moss samples around the Allchar mine varied remarkably from <0.10-290 mg kg^{-1}, compared with the moss samples taken from the rest of the Allchar area varied from <0.10-2.4 mg kg^{-1}. The spatial distribution of Tl is also strongly dependent on lithology and very similar to arsenic spatial distribution (Fig. 4). Very high content of Tl was also found in the endemic plant species from the Crven Dol area from this locality (Bačeva et al., 2013).

Antimony has considerably low deposition compared with As and Tl, and it has no significant variation between the Allchar areas and the moss survey in Macedonia (Barandovski et al., 2013). Similar to the distribution of As and Tl, higher Sb contents were found on Quaternary moraines and lower in Triassic and hydrothermally altered carbonates. The lowest concentrations of Sb were found on Plio-Quaternary latite breccias and Jurassic serpentinite (Fig. 4). The median values for Sb in the Allchar area (0.1 mg kg^{-1}) are significantly lower than those in moss samples from the territory of Macedonia (0.20 mg kg^{-1}; 0.15 mg kg^{-1} and 0.09 mg kg^{-1} from the survey studies in 2002, 2005 and 2010, respectively) (Barandovski et al. 2008, 2012, 2013). This is mostly due to the air pollution from the metallurgical and flotation plants (Stafilov et al., 2009; Bačeva et al. 2012). The second reason for the significantly lower Sb concentration in moss samples in comparison with recent Sb data for whole territory of Macedonia is that the Sb mineralization (mainly stibnite) is distributed in deeper layers in the mine deposit (Jelenković and Boev, 2011).

Conclusion

Moss biomonitoring technique was successfully applied in the determination of the increased content of certain toxic elements into atmosphere in the Allchar mine locality as a result of the former mining activities and their presence in the surface soil. The comparison made between the data from the samples around the Allchar mine and the rest of the Allchar area show that in the vicinity of the mine had the highest median values for As, Sb and Tl. Atmospheric deposition for As in the moss samples on or around the Allchar mine is >6.5 times higher and Tl is 10 times higher compared to values for the samples from the rest of the Allchar area. By the application of Multivariate cluster and R-mode factor analyses five geochemical associations were determined: F1 (Co, Cr, Fe, Sc, Li, V, Ga, Y, Ni, Mn, Al, La-Lu, Cu, Ge, Be, Bi and Hf); F2 (As, Tl, Sb and Mg); F3 (Rb, Cs and Mo); F4 (Sr, Ba, Hf, Zr, La-Lu and Bi) and F5 (Cd, Zn, Ag and Cu). The essence of this work is the success of the moss biomonitoring and multivariate statistical methods for small area to detect without problems the strongly expressed association of As-Sb-Tl, but also the less prominent associations. It should be noted that this method can successfully be applied for monitoring the atmospheric deposition especially in the hilly areas with complex lithology.

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