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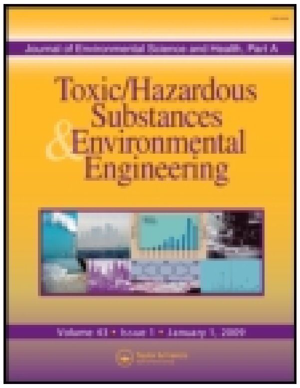

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Biomonitoring of atmospheric pollution with heavy metals in the copper mine vicinity located near Radoviš, Republic of Macedonia

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This investigation was undertaken to determine the atmospheric pollution with heavy metals due to copper mining Bučim near Radoviš, the Republic of Macedonia. Moss samples (*Hyloconium splendens* and *Pleurozium schrebery*) were used for biomonitoring the possible atmospheric pollution with heavy metals in mine vicinity. Sixteen elements (Al, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mn, Na, Ni, Pb, Sr, and Zn) were analysed by application of flame and electrothermal atomic absorption spectrometry (FAAS and ETAAS) and atomic emission spectrometry with inductively coupled plasma (ICP-AES). The obtained values were statistically processed using nonparametric and parametric analysis. The median value for copper obtained from moss samples (10 mg kg^{-1}) was much lower compared with the same values for the whole territory of the Republic of Macedonia (22 mg kg^{-1}). The range of values (2.1–198 mg kg^{-1}) shows much higher content of this element in the samples taken from the study area compared to the appropriate values for the whole territory of Macedonia. The association of elements As, Cd, Cu, Fe, Pb, and Zn was singled out by factor analysis as a characteristic anthropogenic group of elements. Maps of area deposition were made for this group of elements, wherefrom correlation of these anthropogenic born elements was confirmed.

Keywords: Air pollution, heavy metals, copper mine, biomonitoring, Bučim, Macedonia.

Introduction

Emissions of heavy metals to the environment go through several processes or pathways, including air, water and soil.[1] Atmospheric emissions of heavy metals tend to be of greatest concern in terms of human health, because of the quantities involved and the widespread dispersion and exposure to them.[2] Because of the increasing content of the elements in the atmosphere which is the indication of some human health problems, they are considered to be pollutants.[3] Atmospheric pollution with heavy metals is a global process initiated by the world technology progress and human exploitation of natural resources.[4] Because of their direct metal emission into the atmosphere mines have great influence on this occurrence.

Most of the studies based on atmospheric pollution explore metal absorption by atmospheric particles wherefrom they deposit in soil. Mines produce large amounts of waste; the used ore and concentrates are only a small fraction of the total volume of the mined material.[5,6] The ore and ore tailings are continually exposed to open air, so wind carries the fine particles into the atmosphere. The most serious consequence in atmospheric terms is acid deposition, which removes other pollutants in contact with chemical reactions.[7,8]

Moss biomonitoring is one of the most useful techniques for determining deposition of heavy metals and atmospheric pollution with heavy metals in different geographical areas.[9] The moss technique for the first time was introduced in Scandinavian countries and has been proven as very suitable for study the atmospheric deposition of heavy metals and other trace elements.[10,11] Mosses represent suitable monitors because of their occurrence in almost all terrestrial ecosystems and their ability to tolerate long periods of extreme environmental conditions.[12] Mosses uptake metal cations though ionic exchange and formation of complex compounds. Exchange and chelating of metals

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in mosses is made possible by the chemical constituents of the moss structure, which consists of a variety of organic functional groups capable of chelate formation and ion exchange.[13] In addition, moss elemental concentration can be converted into atmospheric deposition values, provided that metal uptake efficiency had been previously estimated in the species used as a biomonitor.[14] That is why the moss technique is being used now as part of monitoring programs for air pollutants worldwide.

Many European countries have used mosses since the beginning of 1960s in national and multinational surveys of atmospheric metal deposition.[15,16] Although in Northern Europe, mosses have been used as bioindicators for over 30 years, the countries in southern Europe have initiated participatation in the European program on heavy metal atmospheric deposition in Europe measured from mosses since 1995.[17−23]

In the Republic of Macedonia the first systematic study of atmospheric pollution with heavy metals using moss technique was undertaken to assess the general situation regarding heavy metal pollution and to joint the report of these results to the European Atlas of Heavy Metal Atmospheric Deposition issued by UNECE ICP Vegetation.[24,25] The most important Macedonian metal deposits are linked to regional magmatic activity which occurred in the southern parts of the Carpatho-Balkanides from the Eocene to the Pliocene.[26] Significant emission sources that contribute to atmospheric pollution with heavy metals for the territory of Republic of Macedonia appear to be all mines and drainage systems and smelters near the cities of Veles, Kavadarci and Tetovo.[25] In the eastern part of the country the appearance of some metals (Au, Mg, Al, Sc, Ti, V, Cu) in air is related to the presence of a copper mine and flotation "Bučim" near the city of Radoviš. In this area an influence from the former iron mine, Damjan has also been determined .[27,28]

The Bučim copper mine, as primary emission source of heavy metals in the area, is located in the central part of

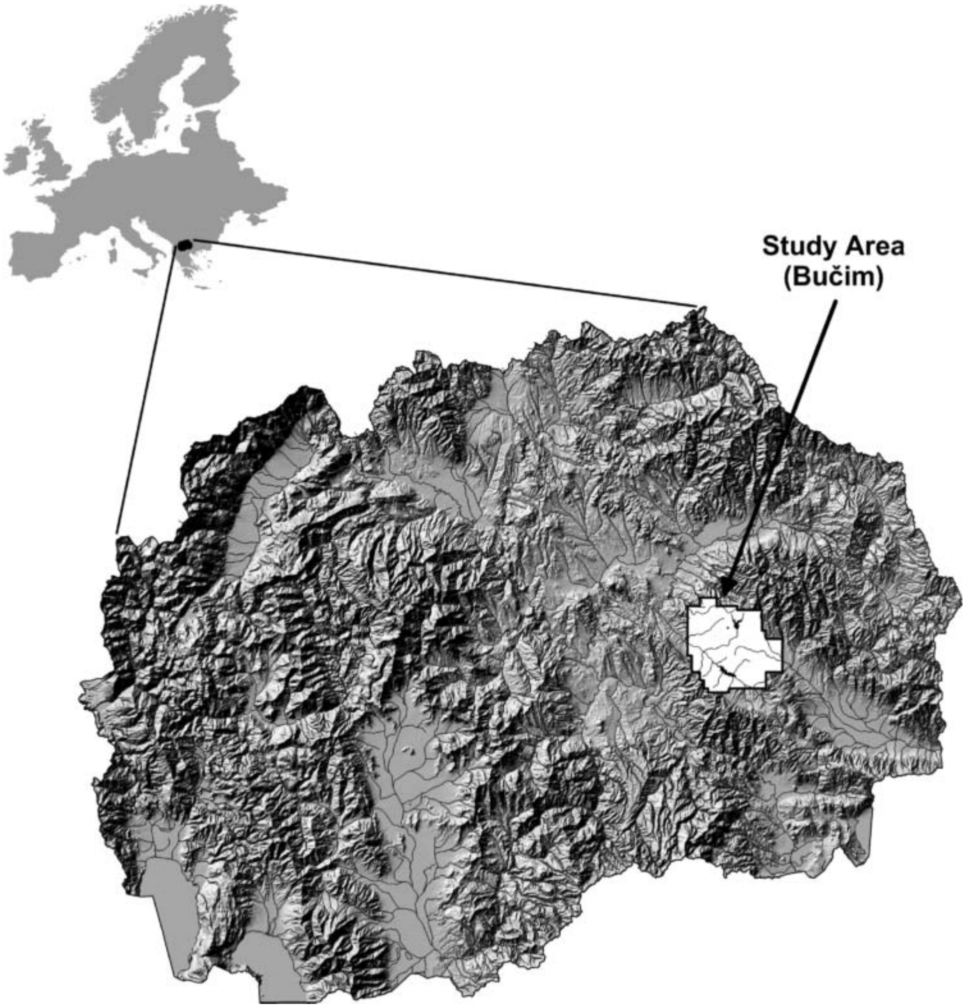

Fig. 1. Study area.

Eastern Macedonia, near the town Radoviš (Fig. 1). The mine is in function from 1980 and processes 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.[26] The main ore body is approximately 500 m in diameter and 250 m in vertical and has been worked in a large open pit, which actually allows direct exposure of ore particles to the atmosphere. The ore contents: 0.3 % Cu, 0.3 g t^{-1} Au, 1 g t^{-1} Ag, 13 g t^{-1} Mo, and 1-4 % pyrite; the igneous rocks have been altered into clays and micas. The important metallic minerals are chalcopyrite, pyrite, and bornite, with small amounts of galena, sphalerite, magnetite, hematite, and cubanite.[29]

Ore was concentrated by flotation on site and tailings were disposed to a dam in an adjacent valley near village Topolnica (Fig. 1). Exposure of ore tailing and flotation tailing to air and moisture leads to slow transformation of copper sulphide into copper oxide and sulphuric acid. This acid can dissolve heavy metals found in waste rock and tailings such as lead, zinc, arsenic, selenium, mercury and cadmium.[30] On the other hand, the copper oxide and sulphuric acid react, forming copper sulphate, which is very toxic for the environment.[31]

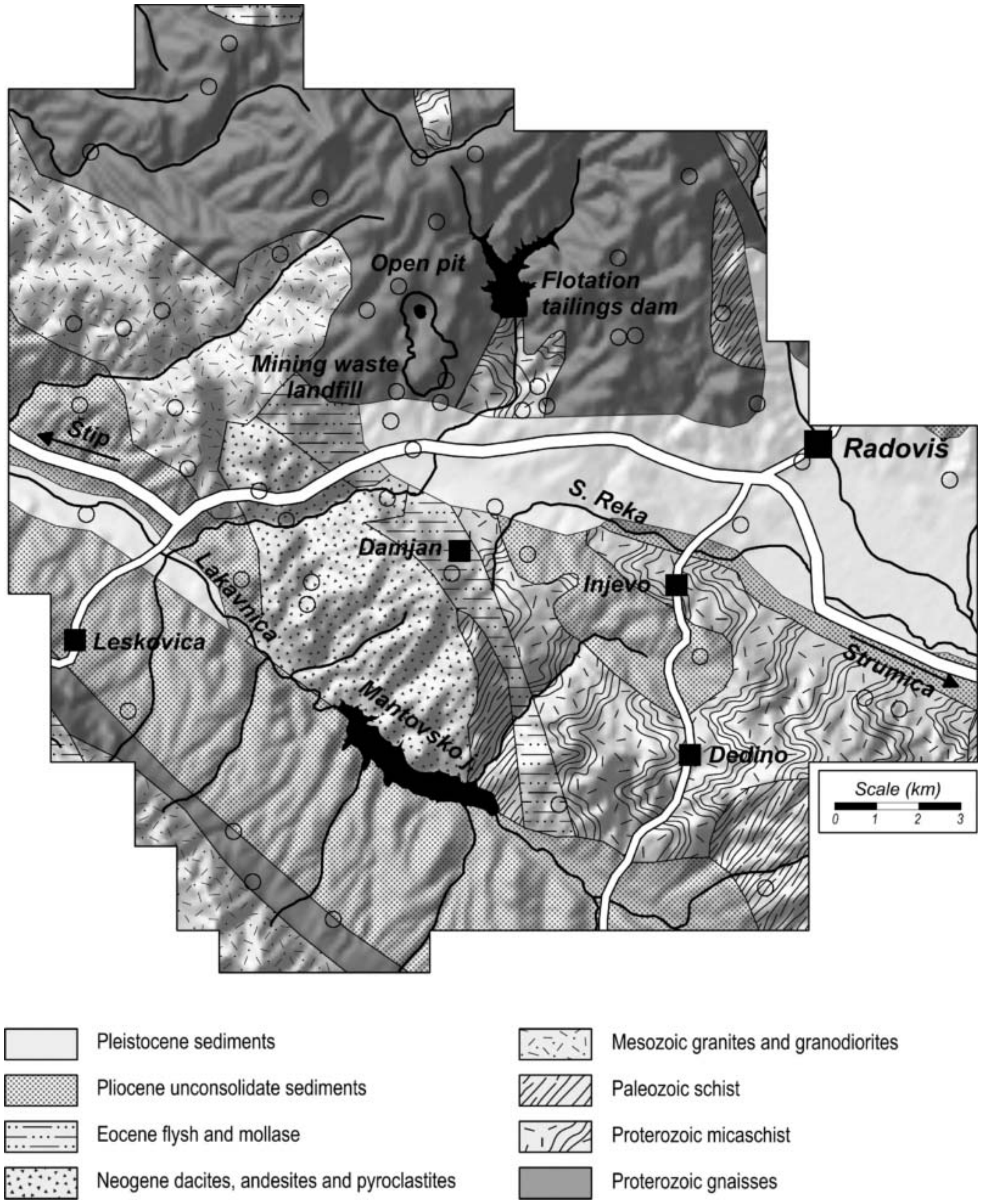

Fig. 2. Geological and sampling network map.

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^{-1}		
Polychromator purge	0.5 L min^{-1}		
Megapixel CCD detector	1.12 million pixels		
Wavelength coverage	177 nm to 785 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

Element	*Wavelength, nm*	*Element*	*Wavelength, nm*	*Element*	*Wavelength, nm*
Al	396.152	K	766.491	Pb	220.353
Ba	455.403	Mn	257.610	Sr	407.771
Ca	370.602	Na	589.592	Zn	213.857
Cr	267.716	Ni	231.604		
Fe	238.204	Cu	324.754		

Materials and methods

Study area and sampling

The study area is located in eastern part of the Republic of Macedonia (Fig. 1), with largeness of 20 km (W - E) x 20 km (S − N), total 400 km^2, 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, covering 10 km air line north-west from the town Radoviš and 16 km air line south-east from the town Štip. The region is characterized by moderate continental climate. The average annual temperature is around 10°C. The warmest months of the year are July and August with the average temperature of 23°C, and the coldest month is January with 1.2°C. The average annual rainfall amounts to 563 mm with large variations from year to year. In terms of total annual number of sunny hours, for this location it is approximately 6.4 hours per day. Most frequent winds in the region are the wind from the west with frequency 199‰ and 2.7 m s^{-1} speed, and 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 a content of heavy metals.

Table 2. Instrumentation and operating conditions for ETAAS system.

Parameter	*Co*	*Cd*	*As*
Wavelength	242.5 nm	288.8 nm	193.7 nm
Spectral width slit	0.2 nm	0.5 nm	0.2 nm
Calibration mode	Peak height		
Lamp current	7.0 mA	4.0 mA	10 mA
Dry			
Temperature	120°C	120 °C	120°C
Ramp time	55 s	55 s	55 s
Pyrolysis			
Temperature	400°C	250 °C	1400°C
Ramp time	5 s	5 s	10 s
Hold time	22 s	15 s	35 s
Atomizing			
Temperature	2300°C	1800 °C	2600°C
Ramp time	1 s	1 s	1 s
Hold time	2 s	2 s	2 s
Cleaning			
Temperature	2650°C	1800 °C	2600°C
Time	5 s	2 s	2 s
Ramp time	–	–	–
Sheath Gas	Argon		

Table 3. Descriptive statistic of measurements for moss samples (in mg kg^{-1}).

	n	*Dis*	X_a	X_g	*Md*	*min*	*max*	P_{10}	P_{90}	*Var*	*s*	*CV*	*A*	*E*
Al	52	log	2.12	1.83	1.72	0.47	8.51	1.10	3.68	1.77	1.33	62.8	0.31	0.59
As	52	log	2.62	1.54	1.55	0.14	13.7	0.39	6.46	9.36	3.06	117	0.09	−0.36
Ba	52	N	32.4	29.7	30.6	11.5	66.0	14.8	47.3	166	12.9	39.7	0.45	0.05
Ca	52	log	6.43	6.30	6.24	4.53	10.6	4.96	7.84	1.87	1.37	21.3	0.81	0.88
Cd	52	log	0.54	0.48	0.49	0.18	1.75	0.28	0.83	0.08	0.28	51.2	0.04	0.30
Co	52	log	1.09	0.72	0.70	0.12	7.60	0.30	2.31	1.94	1.39	128	0.57	1.15
Cr	52	log	3.14	2.70	2.63	1.00	10.8	1.44	5.17	4.41	2.10	66.8	0.81	0.78
Cu	52	log	20.7	11.5	9.95	2.14	199	3.75	54.0	1141	33.8	163	0.99	1.35
Fe	52	log	3.29	2.85	2.63	0.74	12.4	1.38	5.95	3.86	1.96	59.7	0.10	0.20
K	52	log	3.22	3.17	3.16	1.93	4.51	2.59	3.96	0.30	0.54	16.9	−0.25	0.37
Mn	52	log	165	153	144	59.0	439	95.2	238	4888	69.9	42.3	0.06	0.09
Na	52	log	46.3	44.6	45.8	25.1	81.5	31.2	61.8	164	12.8	27.6	0.06	−0.51
Ni	52	log	7.37	6.53	6.21	2.10	30.1	4.05	10.2	21.0	4.58	62.1	0.80	1.93
Pb	52	log	8.82	7.36	6.81	2.68	40.2	4.05	14.7	46.1	6.79	76.9	0.89	0.96
Sr	52	log	26.1	24.7	24.1	12.9	55.4	15.8	34.4	83.0	9.11	34.9	0.32	0.16
Zn	52	log	29.2	28.4	28.3	17.3	53.7	22.4	37.3	46.5	6.82	23.4	0.08	0.49

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.

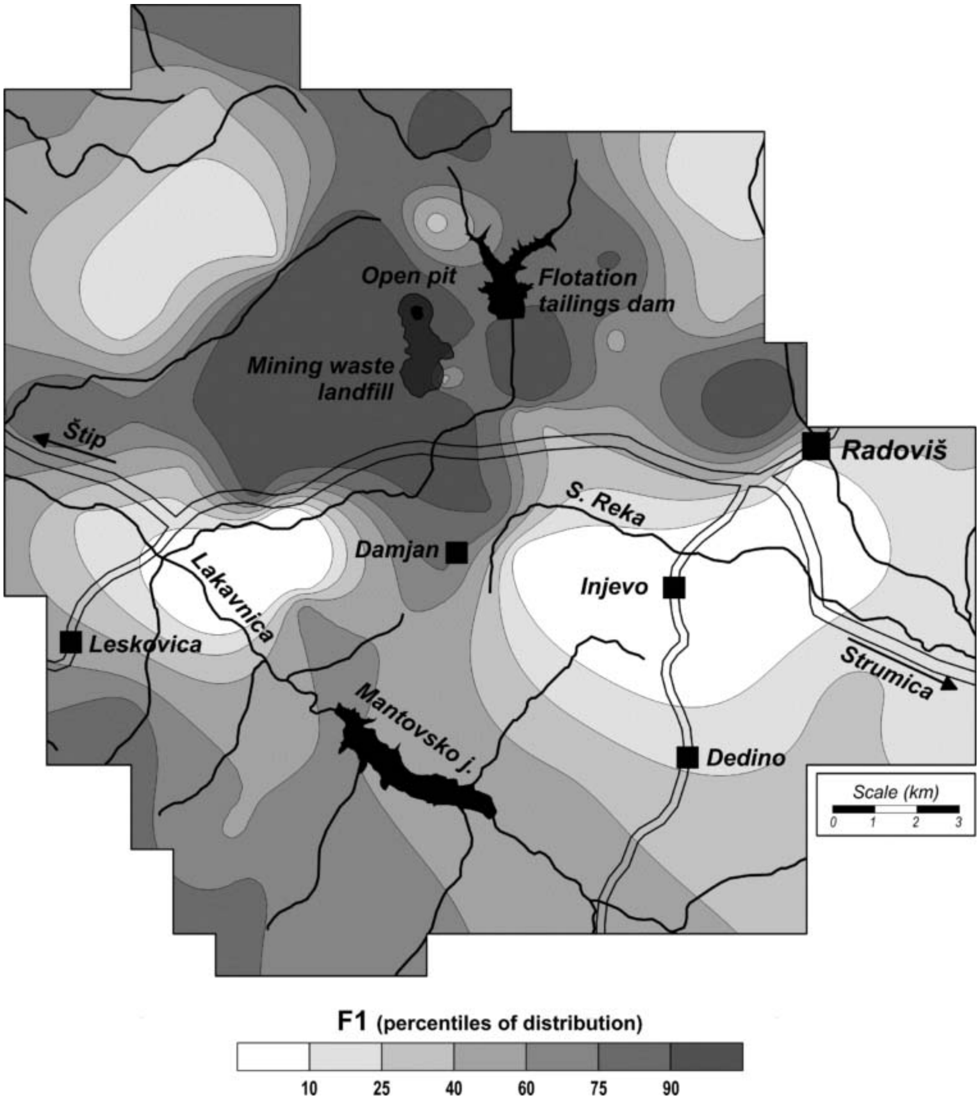

Fig. 3. Spatial distribution of Factor 1 scores (Al, As, Cd, Cu, Fe, Pb and Zn).

Table 4. Matrix of correlation coefficients (r).

Al	1.00															
As	**0.67**	1.00														
Ba	0.24	0.23	1.00													
Ca	0.21	0.15	−0.03	1.00												
Cd	**0.90**	**0.59**	0.15	0.04	1.00											
Co	**0.54**	0.31	0.13	0.16	**0.55**	1.00										
Cr	**0.58**	0.45	0.04	0.11	**0.55**	0.45	1.00									
Cu	**0.54**	0.45	0.09	−0.13	**0.65**	0.42	0.39	1.00								
Fe	**0.97**	**0.63**	0.25	0.13	**0.93**	**0.57**	**0.56**	**0.61**	1.00							
K	0.08	0.07	0.32	0.31	−0.07	0.14	0.14	0.03	0.11	1.00						
Mn	0.38	0.16	−0.09	0.14	0.27	0.01	0.05	0.09	0.30	−0.02	1.00					
Na	0.35	0.18	0.31	−0.12	0.35	0.15	0.34	0.36	0.42	0.41	0.08	1.00				
Ni	0.36	0.29	−0.03	0.27	0.26	0.30	**0.69**	0.06	0.28	0.03	0.11	0.04	1.00			
Pb	**0.60**	0.48	−0.15	0.26	**0.60**	0.38	0.41	**0.55**	**0.56**	−0.09	0.38	0.14	0.15	1.00		
Sr	0.22	0.26	0.26	0.19	0.11	0.10	**0.52**	−0.15	0.15	0.17	−0.07	−0.01	**0.63**	0.06	1.00	
Zn	**0.70**	**0.52**	0.27	0.18	**0.59**	0.34	0.40	0.36	**0.68**	0.21	**0.51**	0.45	0.14	**0.66**	0.11	1.00
	Al	As	Ba	Ca	Cd	Co	Cr	Cu	Fe	K	Mn	Na	Ni	Pb	Sr	Zn

*Numbers in bold correspond to the correlation coefficients with a value over 0.5.

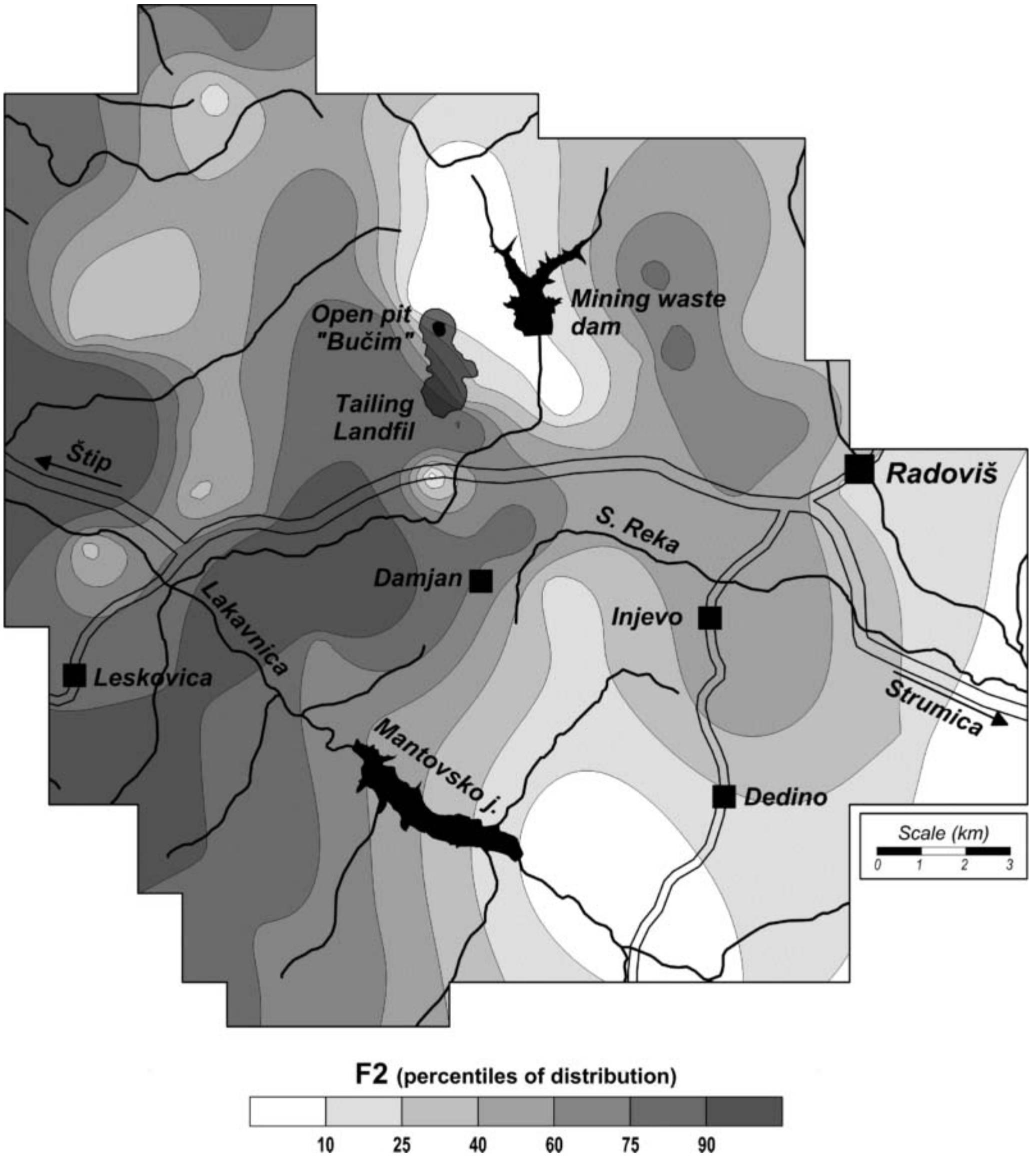

Fig. 4. Spatial distribution of Factor 2 scores (Cr, Ni and Sr).

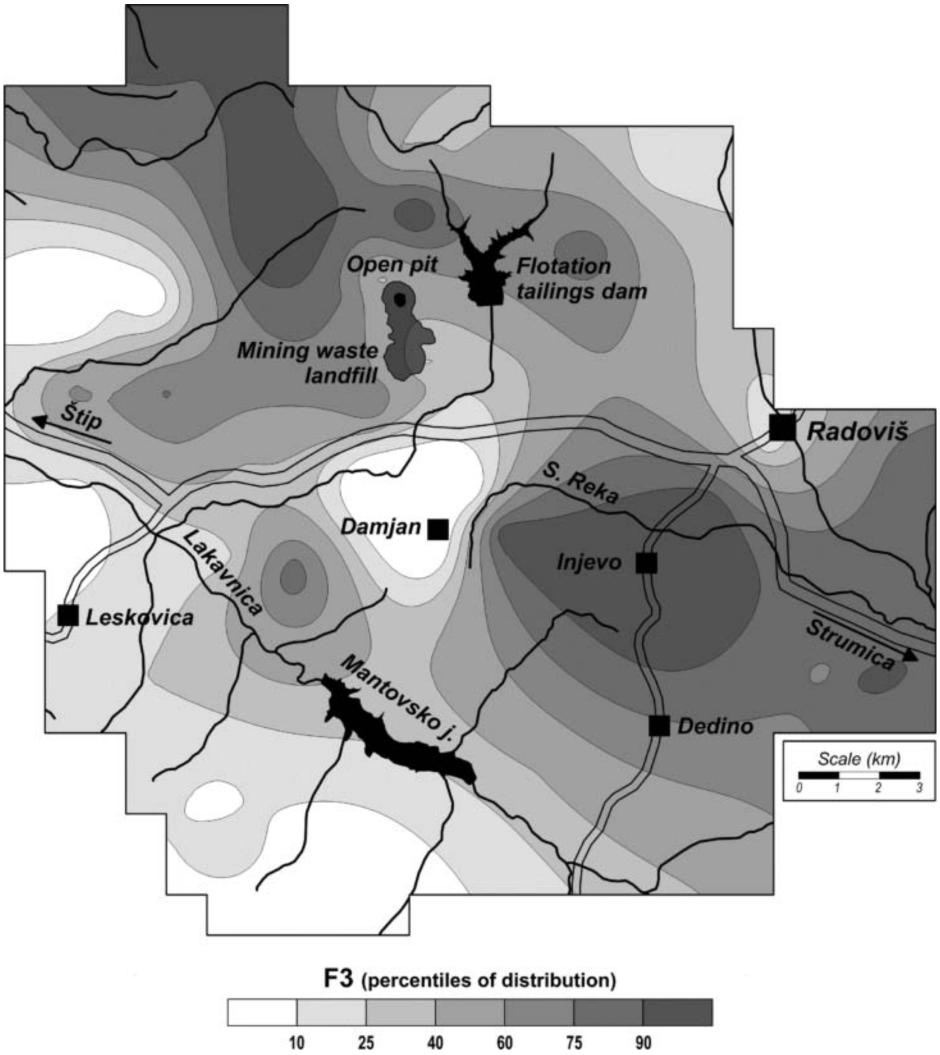

Fig. 5. Spatial distribution of Factor 3 scores (Ba, K and Na).

The geological map of the investigated area is given in Figure. 2 and was made on the basis of data given by Rakićević et al.[32,33] As it can be seen on the northern part of the study area Proterozoic micashists with Proterozoic gnaisses and mesozoic granites and granodiotites are dominant formations, while on the southern part dominant formations are Neogene tacites, andesites and pyroclastites, Proterozoic gnaisses and Pliocene and consolidated sediments.

The collection of moss samples was performed according to the protocol adopted within the European Heavy Metal Survey. Moss species were collected according to previously defined sampling network around the copper mine Bučim in an area of 400 km^2 (Fig. 2). In this study area the dominant moss species were *Hyloconium splendens* (Hedw.) and *Pleurozium schrebery* (Brid.). Samples of these moss species were collected at 52 localities in the period from November 2008 to March 2009. The sampling protocol was in this order: one sampling spot was formed by collecting five sub-spots in area of 50 × 50 m^2.

Table 5. Matrix of dominant rotated factor loadings (F > 0.60).

	F1	*F2*	*F3*	*Com*
Al	**0.89**	0.30	0.19	97.5
As	**0.60**	0.28	0.14	55.2
Ba	0.06	0.04	0.65	53.7
Ca	0.07	0.37	−0.02	49.3
Cd	**0.90**	0.15	0.09	90.9
Co	0.51	0.25	0.12	47.9
Cr	0.47	**0.65**	0.15	74.2
Cu	**0.71**	−0.12	0.11	72.7
Fe	**0.90**	0.20	0.26	97.9
K	−0.05	0.14	**0.64**	57.3
Mn	0.41	−0.02	−0.14	52.2
Na	0.34	−0.07	**0.60**	56.0
Ni	0.15	**0.83**	−0.04	72.4
Pb	**0.78**	0.12	−0.23	80.6
Sr	−0.05	**0.78**	0.19	67.1
Zn	**0.73**	0.09	0.28	79.7
Var	52.1	22.1	15.6	89.9

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

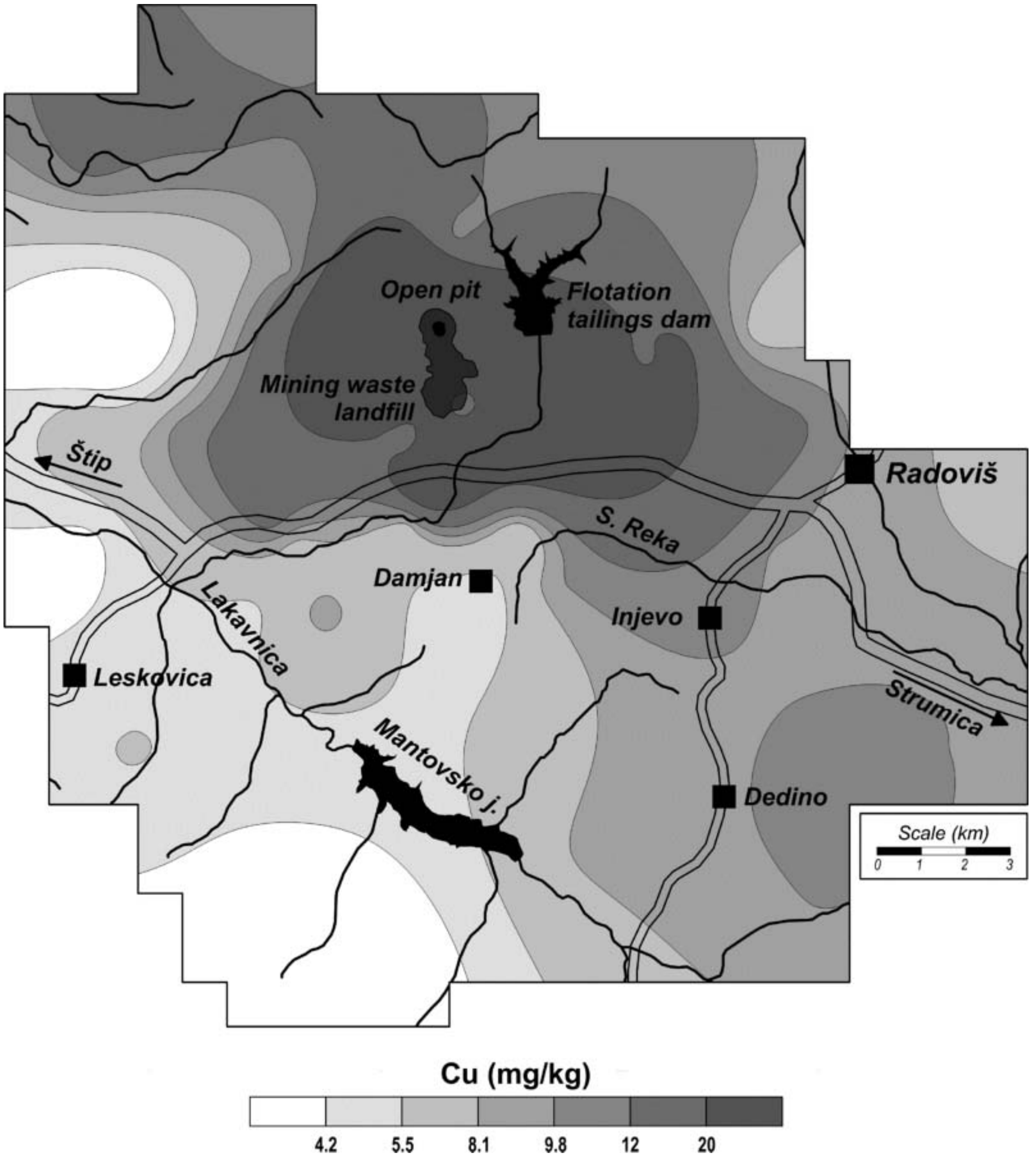

Fig. 6. Spatial distribution of copper.

Every spot of sampling network must be in a distance of minimum 300 m from main roads, 100 m from local roads, and 200 m from settlements. Collected material was stored in paper bags and air dried. After drying the moss species were cleaned from other plant species and soil. Prepared in that way, moss species were ready for digestion.

Sample preparation

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

For the digestion of moss samples microwave digestion system was applied. Precisely measured mass of moss sam-

Table 6. Comparison of median values of element content in moss between data of present work and data of the whole territory of Macedonia (in mg kg^{-1}).

	Bučim mine region (present work)		*Republic of Macedonia (Barandovski et al., 2008)*	
Element	*Median*	*Range*	*Median*	*Range*
Al	1721	472–8511	3736	825–17600
As	1.6	0.1–13.7	0.80	0.12–8.0
Cd	0.49	0.18–1.75	0.16	0.0016–2.95
Cu	10	2.1–198	22	3–83
Fe	2630	742–12356	2458	424–17380
Pb	6.8	2.7–40.2	6.0	1.5–37.2
Zn	28.3	17–53	39	14–203

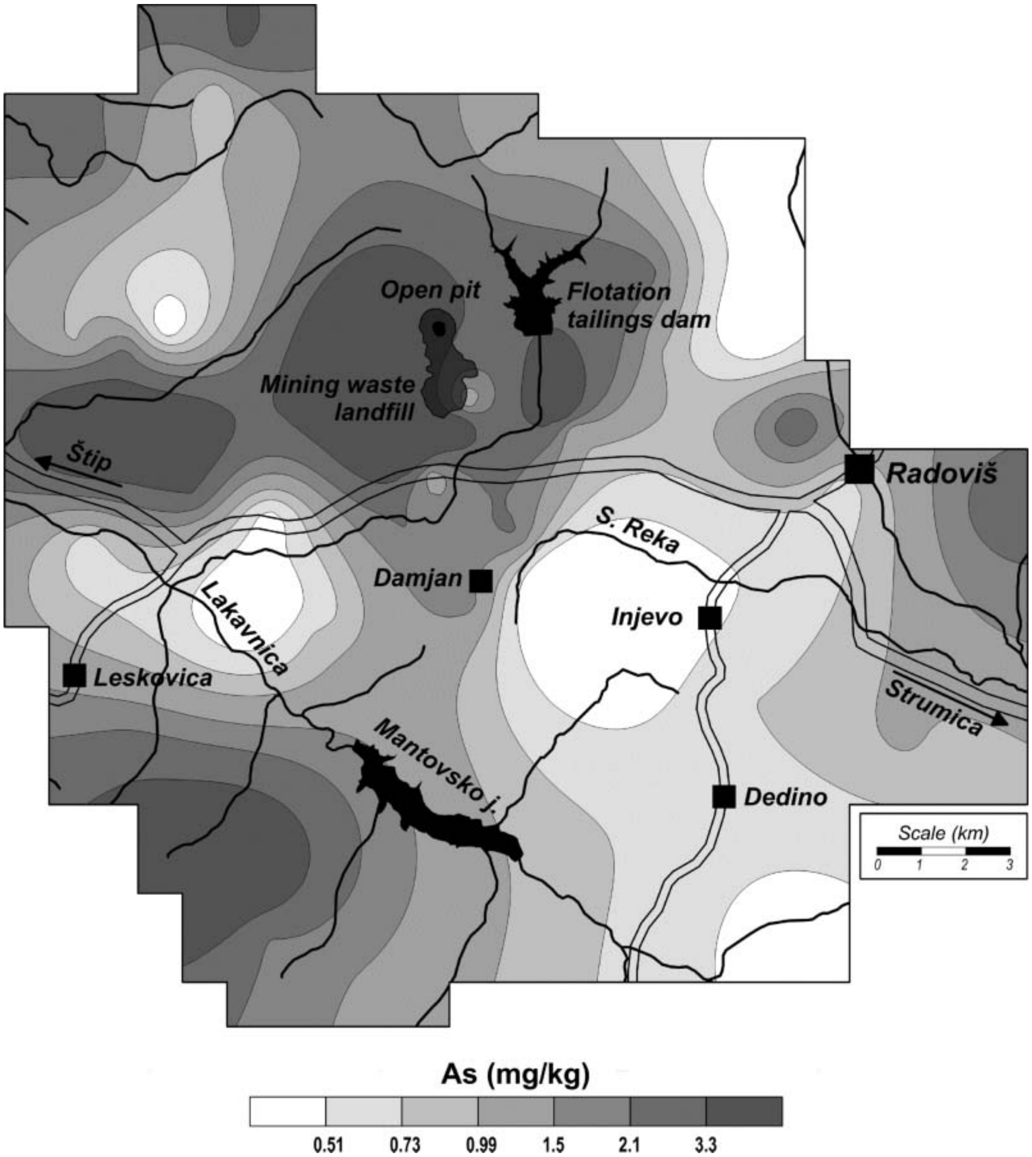

Fig. 7. Spatial distribution of arsenic.

ples (0.5 g) was 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 the following program: 1 step: temperature 180°C, 5 min ramp time, with power of 500 W and 20 bar pressure; 2 step: temperature 180°C, 5 min hold time, with power of 500 W and 20 bar pressure. Finally, the vessels were cooled, carefully opened, and digests quantitatively transferred into 25 mL calibrated flasks.

Instrumentation

The following elements were determined: Al, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mn, Na, Ni, Pb, Sr, and Zn. Analyses were performed with atomic emission spectrometer with inductively coupled plasma, ICP-AES (Varian, 715ES), for Al, Ba Ca, Cr, Cu, Fe, K, Mn, Na, Ni, Pb, Sr, Zn. Electrothermal atomic absorption spectrometer, ETAAS (Varian, SpectrAA 640Z), for Cd, Co, As. The operating conditions for all applied techniques are given in Table 1 and Table 2, respectively.

Data processing

Data processing was performed on a PC using the statistical software Stat Soft (Version 9) for the interpretation of elements deposition. All field observations, analytical data and measurements were introduced to the data matrix. For each observation there were a few variables: sample identification number, locality, geographic coordinates, sample type and concentration level for 16 elements.

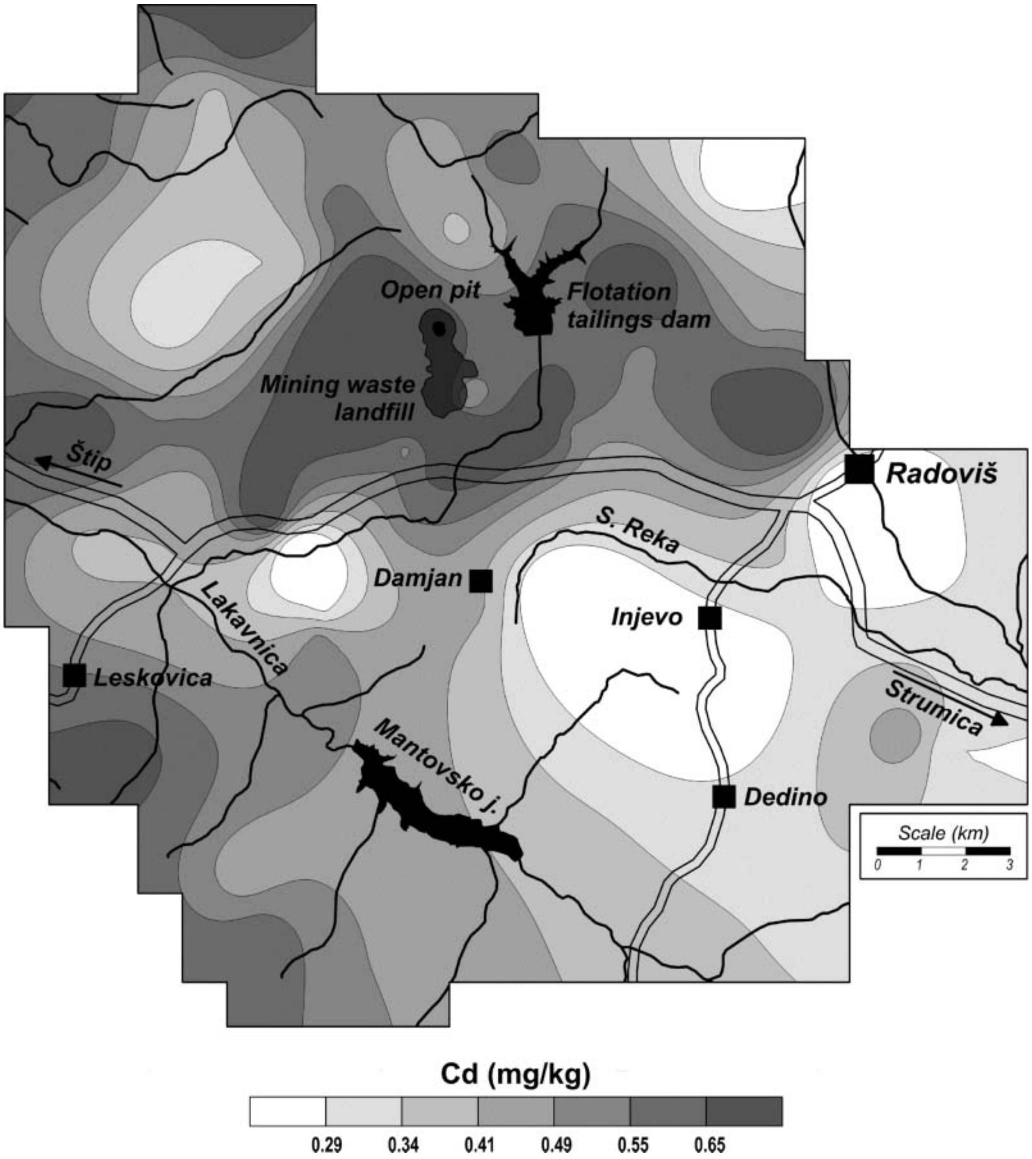

Fig. 8. Spatial distribution of cadmium.

Parametric and nonparametric statistic was used for statistical analysis of data.[34] Percentiles, minima and maxima, mean calculation method of median, geometrical mean and arithmetical mean were calculated and histograms were drawn to show the distribution features. Data distribution was examined with an application of normality test. Bivariate statistic showed the correlation of the content of chemical elements in moss samples. For that issue the linear coefficient of correlation was used, and the absolute values $r > 0.50$ indicated good relation between variables. Multivariate statistic method was used to reveal the associations of the chemical elements. The factor analysis (FA) provides smaller number of new variables from a definite number of variables, so called factors that present the association of statistical significant variables.

Results and discussion

Statistical analysis

The descriptive statistics of analysed elements are shown in Table 3. Values of Al, Ca, Fe, and K are given in % and the remaining elements in mg kg^{-1}. On the basis of the normality tests compared with histograms of distribution for the content of all analyzed elements in moss, the normality was assumed for naturally values of Ba, Fe, K, Sr and Zn. For the rest of the elements, the normality was established on the bases of the logarithms of their contents. Median values for all contents of the elements were compared with the median values for the same elements for the entire territory of Republic of Macedonia.[25]

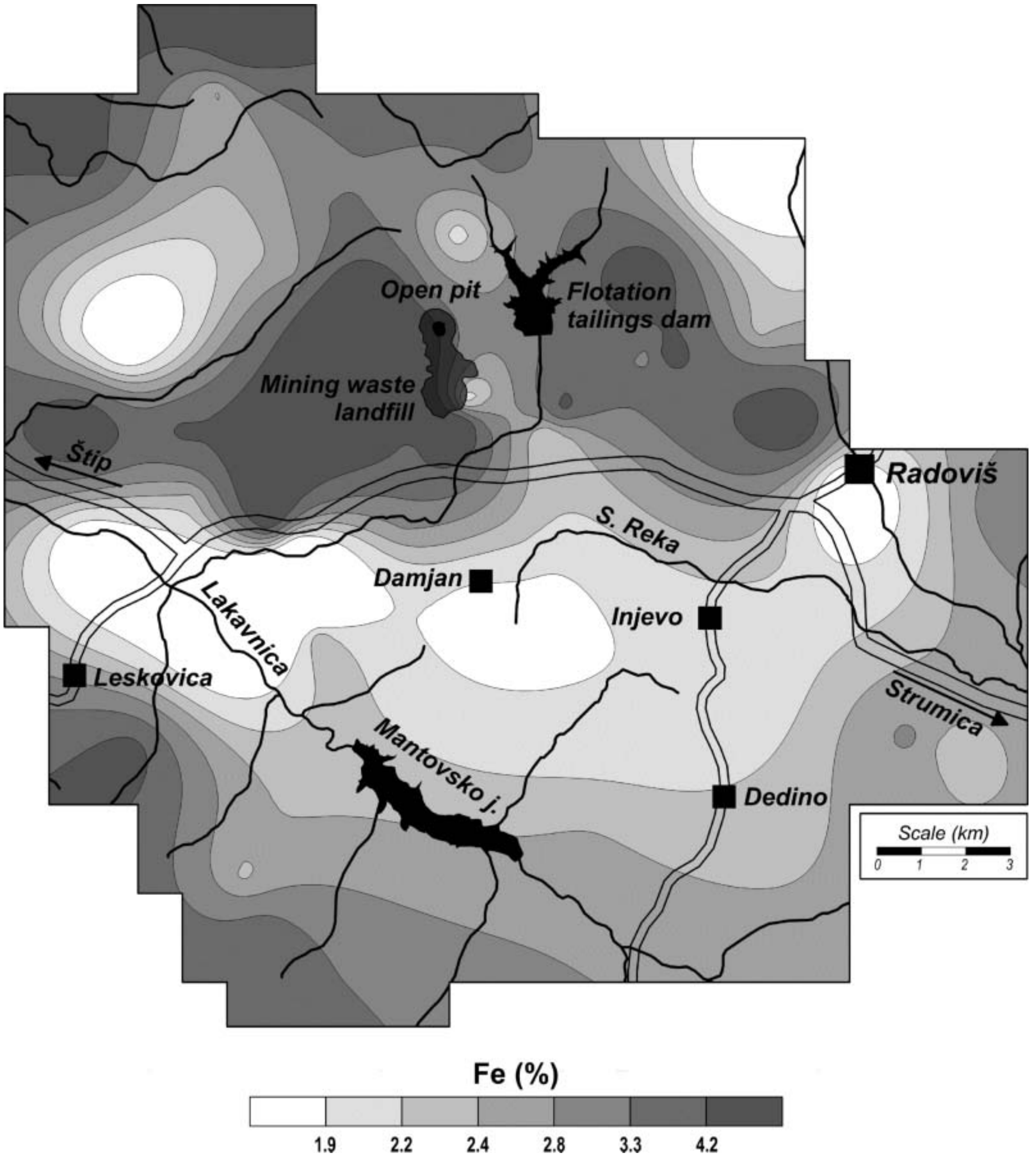

Fig. 9. Spatial distribution of iron.

From descriptive statistic, median values for Cu, and As show deviation, compared with medians for these elements for the whole territory of Macedonia 20 mg kg^{-1} for Cu, and 0.8 mg kg^{-1} for As.[25] Smaller median for Cu was not expected in this area, because of the influence of the copper mine. However, the range of values shows much higher content of this element in the samples from this area. The logarithm of values was used for normalisation, because of the curved distribution, and the big difference of the median and arithmetical mean. Similar results are obtained for the distribution of values for As, thereby the median value and the range of the values indicate increase in the content of this element compared to the whole territory of the Republic of Macedonia. For the rest of elements there are no significant differences between the median values for this region and the entire territory of Republic of Macedonia.

The results from bivariate statistic are shown in matrix of the correlation coefficient, Table 4, for better visibility. The correlation coefficient is a statistical parameter, which describes the correlation degree (linear dependence) between two random variables or sets of random variables.[35] The content of every element was correlated to the content of other elements separately.

On the basis of the matrix of correlation coefficients, factor analysis was done. Principal component factor analysis was used to identify and characterise element associations.[36] From 16 analysed variables (analyzed elements), 3 variables (Co, Ca and Mn), had very low factor loading, or tendency to form independent factor and therefore do not belong to any factor group. But these elements generally are present in the plant structure and found in high content in soil, so they can be considered as geogenic elements. The matrix of dominant rotated factor loadings is

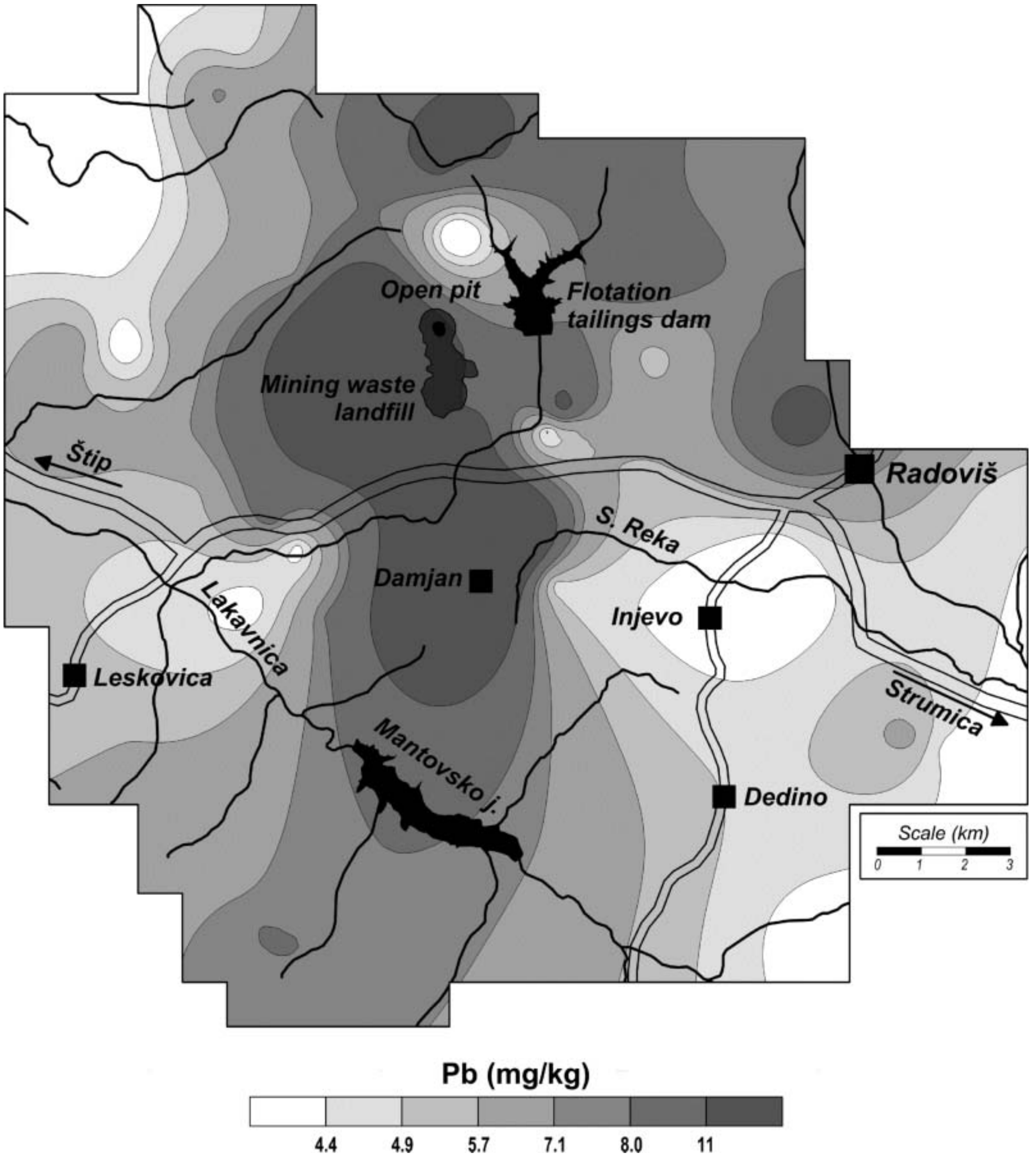

Fig. 10. Spatial distribution of lead.

presented in Table 5. Three factors were identified, one anthropogenic and 2 geogenic, interpreted as Factor 1, Factor 2 and Factor 3, which includes 90% of variability of treated elements.

Factor 1. (Al, As, Cd, Cu, Fe, Pb, Zn) associates chemical elements that indicate anthropogenic influence in the study area (Fig. 3). This association of elements was expected because of the study area geology and the open pit mining and flotation activities.[37,38] The acid drainage rapidly dissolved the elements, providing increasing content in soil. The open ore pit and flotation tailings dam allow direct exposure of the finest ore particles to the atmosphere. Corpuscle dust from the surface layer of ore body and soil is spread in the atmosphere by the winds, through which atmospheric distribution of these elements in the vicinity of the mine is performed.

Factor 2. (Cr, Ni, Sr) presents typical geogenic factor (Fig. 4). These elements are biogenic trace elements and are essential for moss issue. High factor loadings are related to the parts of Pleistocene sediments and Neogene dacites, andesites and pyroclastites.

Factor 3. (Ba, K, Na). These elements are naturally found in soil and moss as macro elements (Fig. 5). Contents of these elements are variable and are not related to any anthropogenic activities. Their sources are mainly natural phenomena such as rock weathering and chemical processes in soil. This Factor is connected to the clay which is a product of disintegration mostly of feldspar and gneisses and micaschists. This means that the occurrence of this Factor is typical for the oldest formations in the Republic of Macedonia (Proterozoic micaschist and Proterozoic gneisses).

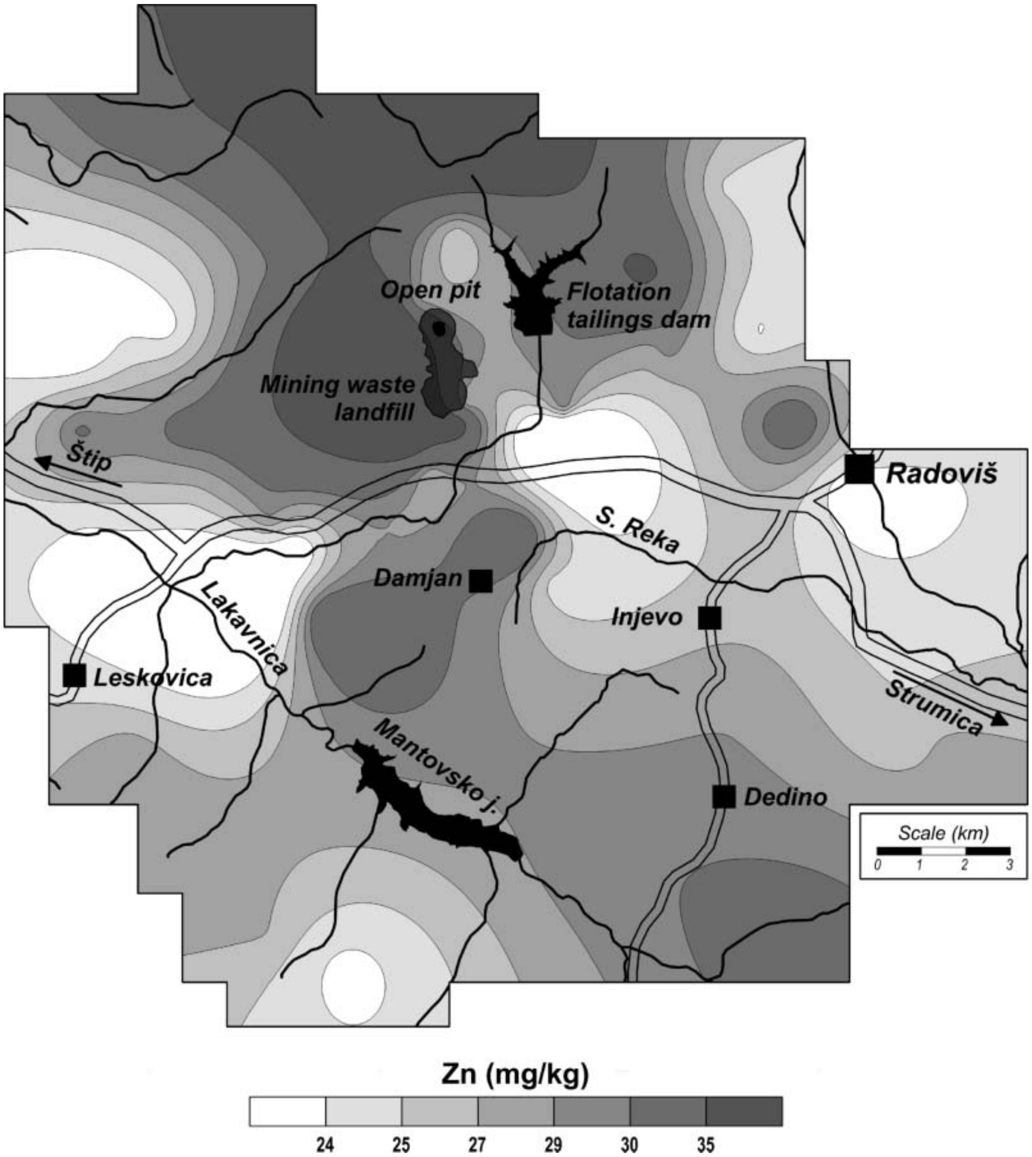

Fig. 11. Spatial distribution of zinc.

Maps of areal elements deposition

The universal method kriging with linear variogram interpolation[39] was applied for the construction of the areal distribution maps of the 16 particular elements and the factor scores (F1–F3) in moss samples (Figs. 3–5). Seven classes of the following percentile values were selected: 0–10, 10–25, 25–40, 40–60, 60–75, 75–90 and 90–100.

From the distribution map of Factor 1 scores and distribution maps for all elements from this Factor (Figs. 6–11) it is clearly visible that the higher contents of these elements are deposited in close vicinity of the mine (Fig. 3). Distribution of these elements at greater distances from the mine is not determined. The content of these elements in moss samples around the mine asserts increased median values for the same metals in moss for the whole territory of the Republic of Macedonia.[25] The deposition of aluminium is not presented because of presence of this element naturally in soil, mostly as geogenic element. Compared values for elements from Factor 1, of study area with corresponding values for the whole territory of the Republic of Macedonia, are presented in Table 6.[25]

Maps of areal element deposition from Factor 1 (Fig. 3), also confirm principal factor analysis (Table 5), which show that moss samples with an increased content of copper have an increased content for the rest of the elements from this factor. This confirms the influence of the presence of the copper mine and flotation plant on increasing content of these metals in the atmosphere. Increasing content of anthropogenic elements in moss samples in the close vicinity of the mine, precisely near villages Bučim and Topolnica, assumed as most polluted settlements, concerning human health's risk. Maximum values for the content of As, Cd, Cu, Fe, Pb and Zn are obtained from moss samples close to village Bučim.

Conclusion

Any anthropogenic activity of exploiting natural resources contributes more or less to the disruption of natural balance. A similar issue was the subject of examination of the present study. The activities carried out in a copper mine and flotation lead to an increased content of certain heavy metals in the atmosphere, which was determined through the conducted biomonitoring using the moss technique. The application of statistical multivariate analysis, more concretely factor analysis, singled out one anthropogenic group of elements. The factor group consists of these heavy metals: arsenic, cadmium, copper, iron, lead and zinc.

The contents of these heavy metals in moss were compared with the median moss content of these elements for the whole territory of The Republic of Macedonia in order to determine whether there was an increased content of each in the study research area. Copper and arsenic were singled out. The presence of high contents of these heavy metals in the atmosphere has impact on the population's health. The presence of copper mine leads to the increasing of the content of these heavy metals in the atmosphere, primarily because of the direct exposure of ore particles and ore tailings in the atmosphere. The fine particles from ore are spread in the atmosphere carried by wind. Microparticles penetrate into the human body through inhalation of respiratory system. The second potential emission source of heavy metals is flotation tailings, the dominant pollutant to the soil. The acid drainage system dissolves the heavy metals present in the soil and concentrates them. From here the fine particles from the soil surface are taken back into the atmosphere.

Maps of areal deposition of heavy metals in the area around the Bučim mine provide evidence that these metals have an increased content in the close vicinity of the mine. Distribution of these heavy metals in distant areas was not determined. But there are two settlements in the close vicinity of the mine, villages Bučim and Topolnica, where the population is directly exposed to the presence of these heavy metals in the atmosphere, which is certainly worrisome.

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