Distribution of Chemical Elements in Attic Dust as Reflection of Their Geogenic and Anthropogenic Sources in the Vicinity of the Copper Mine and Flotation Plant

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Abstract   The main aim of this article was to assess the atmospheric pollution with heavy metals due to copper mining Bučim near Radoviš, the Republic of Macedonia. The open pit and mine waste and flotation tailings are continually exposed to open air, which leads to winds carrying the fine particles into the atmosphere. Samples of attic dust were examined as historical archives of mine emissions, with the aim of elucidating the pathways of pollution. Dust was collected from the attics of 29 houses, built between 1920 and 1970. Nineteen elements (Ag, Al, As, Ba, Ca, Cd, Co, Cr, Cu, Li, Fe, K, Mg, Mn, Na, Ni, Pb, Sr, and Zn) were analyzed by atomic emission spectrometry with inductively coupled plasma. The obtained values of the investigated elements in attic dust samples were statistically processed using nonparametric and parametric analysis. Factor analysis revealed three factors governing the source of individual chemical elements. Two of them grouping Ca, Li, Mg, Mn, and Sr (Factor 1) and Co, Cr, and Ni (Factor 2) can be characterized as geogenic. The third factor grouping As, Cu, and Pb is anthropogenic and mirrors dust fallout from mining operation and from flotation tailings. Maps of areal deposition were prepared for this group of elements, from which correlation of these anthropogenic born elements was confirmed.

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Atmospheric pollution with heavy metals is a global process, which is initiated by the world technology progress and human exploitation of natural resources (Athar and Vohora 1995; Järup 2003; West et al. 1997). Mining works have significant influences on this occurrence, because of the direct exposition of metal to the atmosphere. Mines produce large amounts of waste because the used ore and concentrates are only a small fraction of the total volume of the mined material (Dudka and Adriano 1997; Salomons 1995). Atmospheric emissions attributed to the extraction stage of mining come mainly from the action of wind on disturbed land and stockpiles of ore and waste material. As a result of these processes, dust is permanently introduced into the atmosphere (Repley et al. 1996; Sengupta 1993). Continuous monitoring of the content of heavy metals and other toxic components contained in dust is possible through implementation of monitoring by using samples of dust from attic beams (Ilacqua et al. 2003; Tye et al. 2006). Attic dust is derived primary from external sources through aerosol deposition and as a result of soil dusting, and less from household activities (Šajn 2003). Usefulness of attic dust as a suitable long-term monitor for the determination of the status and content of heavy metals in air is proven by numerous studies (Cyrys et al. 2003; Gosar et al. 2006; Jeffrey et al. 2005; Šajn 2005, 2006; Žibret 2008; Žibret and Šajn 2008a, b).

As a result of anthropogenetic activities, the Republic of Macedonia is affected by atmospheric pollution with heavy metals. Significant emission sources that contribute to atmospheric pollution with heavy metals for the territory of the Republic of Macedonia appear to be all mines and drainage systems and smelters near the cities of Veles, Kavadarci, and Tetovo (Barandovski et al. 2006, 2008; Stafilov et al. 2003, 2010a, b). In the eastern part of the

country, the occurrence of some metals (Au, Mg, Al, Sc, Ti, V, and Cu) in air is related to a presence of a copper mine and flotation near Radoviš.

The Bučim copper mine, as the primary emission source of heavy metals in the area, is located in the central part of eastern Macedonia, near the city of Radoviš (Fig. 1). The mine has functioned since 1980 and processes 4 million tons of ore annually. The deposit is a porphyry copper-type deposit and mineralization is related to tertiary subvolcanic intrusions of andesite and latite in a host of Pre-Cambrian gneiss and amphibolite (Serafimovski et al. 1995). The main ore body is ∼500 m in diameter and 250 m deep and has been worked in a large open pit, which actually allows direct exposure of ore particles to the atmosphere. The ore contains the following: 0.3% Cu, 0.3 g/ton Au, 1 g/ton Ag, 13 g/ton Mo, and 1–4% pyrite; the igneous rocks have been sericitized and argillitized. The important minerals are chalcopyrite, pyrite, and bornite, with small amounts of galena, sphalerite, magnetite, hematite, and cubanite (Alderton et al. 2005; Serafimovski et al. 2005). Ore is treated by flotation on site and flotation tailings are disposed at a dump site in an adjacent valley near Topolnica (Fig. 2). On the other hand, the ore wastes are disposed in the vicinity of an open pit (Fig. 2). Exposure of ore waste and flotation tailing to air and moisture leads to slow transformation of copper sulfide into copper oxide and sulfuric acid. This acid can dissolve heavy metals found in waste rock and tailings such as Pb, Zn, As, Se, Hg, and Cd

(Pandey et al. 2007). The fine particles from soil surface carried by the winds are introduced into the atmosphere (Kabata-Pendias and Pendias 2001).

The main object of this study was the assessment of atmospheric pollution with heavy metals due to copper mining activities near the mine using attic dust collected from houses in the investigated region. Nineteen elements (Ag, Al, As, Ba, Ca, Cd, Co, Cr, Cu, Li, Fe, K, Mg, Mn, Na, Ni, Pb, Sr, and Zn) were analyzed by atomic emission spectrometry with inductively coupled plasma (ICP-AES).

Study Area

The study area is located in the eastern part of the Republic of Macedonia (Fig. 1), with an area of 20 km (W-E) × 20 km (S-N) (total: 400 km^2), which is limited within the coordinates N: 41°32′–41°44′ and E: 22°15′–22°30′. The copper mine is located in the center of the study area, 10 km air line northwest from Radoviš and 16 km air line southeast from Štip. The region is characterized by a moderate continental climate. The average annual temperature is around 10°C. The warmest months of the year are July and August, with an average temperature of 23°C, and the coldest month is January, with an average temperature of 1.2°C. The average annual rainfall amounts to 563 mm, with large variations from year to year. In terms of the total annual number of sunny hours, for this

Fig. 2 Sampling network and generalized geological map
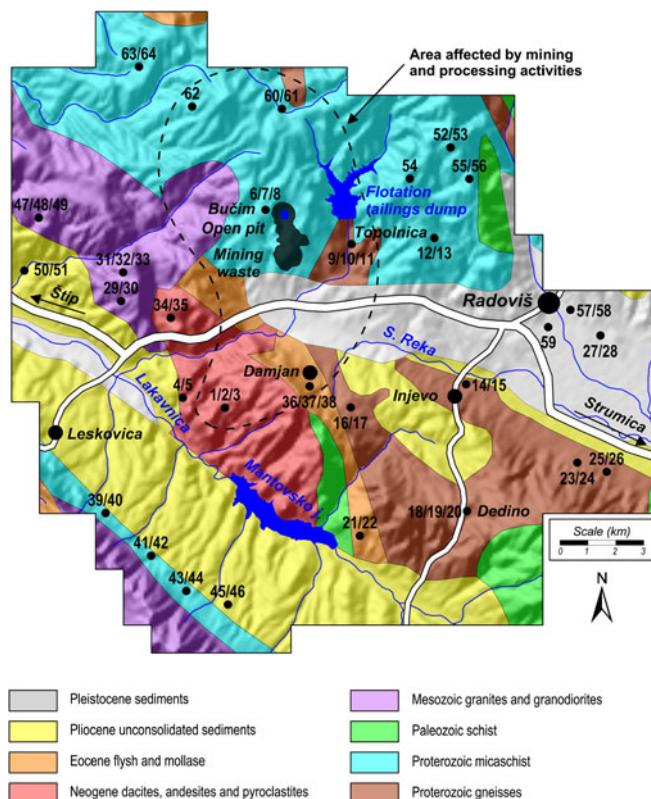
location it is ∼6.4 h per day. The most frequent winds in the region are wind from the west with frequency 199‰ and 2.7 m/s speed wind from the east to the 124‰ frequency and 2.0 m/s speed, which is important for the distribution of atmospheric dust with content of heavy metals.

The geological map of the investigated area (Fig. 2) was made on the basis of data given by Rakićević et al. (1968, Basic geological map of SFRJ, 1965). As can be seen from this map, in the northern part of the study area Proterozoic micashists with Proterozoic gnaisses and mesozoic granites and granodiotites are dominant formations, whereas in the southern part, dominant formations are Neogene tacites, andesites and pyroclastites, Proterozoic gnaisses, and Pliocene and consolidates sediments.

Materials and Methods

Sampling

Attic dust was sampled from old rural houses from 29 settlements in the vicinity of the Bučim mine. The houses were of similar age (built from 1920 to 1970), construction style, and height. In every settlement, attic dust was collected from two or three houses on different sites. The collection of attic dust samples was performed according to the adopted protocol (Šajn 2003). Attic dust was collected with a plastic brush in polyethylene bags. The surface from

the attic timber was thrown away and the finest dust was collected. The fraction of attic dust smaller than 0.125 mm in size was prepared by sieving. In that form, samples of attic dust were ready for digestion.

Sample Preparation

For digestion of attic dust samples, open wet digestion with a mixture of acids was applied. Precisely measured mass of dust samples (0.5 g) was placed in Teflon vessels and 5 ml concentrated nitric acid (HNO_3) was added until brown vapors came from the vessels. Nitric acid is a 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 a clear solution, 2 ml of $HClO_4$ was added. Perchloric acid was used for the total digestion of organic matter. After cooling the vessels for 15 min, 2 ml of HCl and 5 ml of H_2O were added for total dissolving metal ions. Finally, the vessels were cooled and digests were quantitatively transferred to 50-ml calibrated flasks.

Reagents and Standards

For this study, reagents of analytical grade (or better) were used: Nitric acid, trace pure (Merck, Germany), hydrofluoric acid, p.a. (Merck, Germany), perchloric acid, p.a. (Merck, Germany), hydrochloric acid, p.a. (Merck,

Germany), and redistilled water was used for the preparation of all solutions. Standard solutions of metals were prepared by dilution of 1000-mg/l solutions (11355-ICP multi Element Standard).

Instrumentation

The following elements were determined: Ag, Al, As, Ba, Ca, Cd, Co, Cr, Cu, Li, Fe, K, Mg, Mn, Na, Ni, Pb, Sr, and Zn. Analyses were performed with an atomic emission spectrometer with inductively coupled plasma (Varian, 715ES).

The quality control of ICP-AES determinations was performed by the standard addition method, and it was found that the recovery for the investigated elements ranged between 97.5 and 100.8%. The same method was applied for the determination of some trace elements in the reference standard materials JSAC 0401 (soil) and SARM 3 (rock), yielding values very close to those certified.

Data Processing

For the statistical analysis of data, parametric and non-parametric statistic methods were used (Davis 1986; Hollander and Wolfe 1999). Percentiles, minimum and maximum, median, geometrical mean, and arithmetical

mean were calculated and histograms were drawn to show the distribution features. Data distribution was examined with the application of a normality test. Analyzing of variance (ANOVA) was used for the determination of significant differences within selected populations. The application of bivariate statistics showed how chemical elements correlate between their content in attic dust samples. For that issue, the linear coefficient of correlation was used, and the absolute values $r > 0.50$ indicate good association between variables. The multivariate statistic method was used to reveal the associations of the chemical elements. The factor analysis (FA) from an accurate number of variables provides smaller number of new variables, so-called factors that present the association of statistical significant variables (Davis 1986; Filzmoser et al. 2005; Reimann et al. 2002; Šajn 2006; Yongming et al. 2006; Žibret and Šajn 2010).

Results

The descriptive statistics of analyzed elements are shown in Table 1. Values of all elements are given in milligrams per kilogram. Normality tests were compared with histograms of distribution for the content of all analyzed elements in attic dust samples. The normality was assumed for

Table 1 Descriptive statistic of measurements for attic dust samples (given in mg/kg)

Element	n	Dis.	X_a	X_g	Md	Min	Max	P_{10}	P_{90}	s	CV	A	E
Ag	64	log	0.24	0.10	0.05	0.009	1.12	1.09	13.4	0.83	17.8	0.90	−0.62
Al	64	N	11,040	10,292	10,886	1,787	21,957	6,407	16,085	3,797	34.4	0.26	0.39
As	64	log	11.3	8.34	9.58	0.50	51.6	2.13	18.8	9.29	82.2	−0.29	−1.42
Ba	64	log	4,635	361	146	3.95	38,676	24.2	21,121	10,533	227	0.43	−0.83
Ca	64	N	6,049	4,681	5,950	342	18,833	1,380	10,609	3,624	59.9	0.79	1.30
Cd	64	log	2.02	1.97	1.98	1.09	3.11	1.39	2.64	0.46	22.8	−0.24	−0.07
Co	64	log	6.26	5.95	5.63	2.42	11.3	4.03	9.95	2.10	33.6	0.19	0.05
Cr	64	log	38.7	34.8	31.1	16.7	110	23.8	78.1	21.3	55.2	1.19	0.80
Cu	64	log	52.1	33.4	26.8	10.9	415	15.5	116	75.8	142	1.51	2.18
Li	64	log	4.82	3.98	4.10	1.20	15.9	1.61	8.72	3.09	64.1	−1.31	1.48
Fe	64	N	11,966	10,525	13,228	1,131	18,350	5,986	16,080	4,120	34.4	0.10	−0.34
K	64	N	8,846	8,741	8,613	5,560	11,612	7,161	10,876	1,362	15.4	0.02	−0.79
Mg	64	log	1,321	642	715	24.6	5,859	94.3	3,414	1,399	106	−0.43	−0.66
Mn	64	log	211	201	195	113	454	143	302	70.4	33.3	0.40	−0.17
Na	64	log	6,846	5,024	4,784	326	28,682	2,348	15,810	6,336	92.5	−0.24	1.95
Ni	64	log	23.1	20.2	17.2	8.94	58.7	11.5	41.4	12.5	54.3	0.43	−1.11
Pb	64	log	28.8	21.4	20.4	3.12	121	7.49	53.3	23.9	83.1	−0.20	−0.07
Sr	64	log	36.1	28.4	32.1	3.64	141	10.3	60.9	25.2	69.8	−0.74	0.92
Zn	64	log	50.9	48.7	49.5	21.4	92.9	34.3	72.9	15.1	29.8	−0.20	0.11

Dis distribution (*log* log-normal, *N* normal); *n* number of observation, X_a aritmetical mean, X_g geometrical mean, *Md* median, *Min* minimum, *Max* maximum, $P_{10} = 10$ percentile, P_{90} 90 percentile, *s* standard deviation, *CV* coefficient of variance, *A* skewness, *E* kurtosis

natural values of Al, Ca, Fe, and K. For the rest of the elements, the normality was assumed on the basis of the logarithms of their contents.

Results from bivariate statistic are shown in the matrix of the correlation coefficient (Table 2). The correlation coefficient is a statistical parameter that describes the degree of similarity (linear dependence) between two random variables or sets of random variables. The content of every element was correlated to the content of the other elements separately, from which the values for the correlation coefficients (r) were represented in the matrix. Because of the large number of variables (19 elements) a clear and generalized relation between the elements could not be singled out. The principal component analysis was applied for the grouping of separate statistically significant associations.

The universal method kriging with linear variogram interpolation was applied for the construction of the areal distribution maps of the factor scores (F1–F3) in attic dust samples (Figs. 3, 4, 5). The anthropogenic association of the elements As, Cd, Cu, and Pb was the most significant area of interest. Distribution maps for these elements are shown in Figs. 6, 7, 8, 9. Seven classes of the following percentile values were selected: 0–10, 10–25, 25–40, 40–60, 60–75, 75–90 and 90–100.

Discussion

Factor analysis was done based on the matrix of the correlation coefficients. Principal component factor analysis was used to identify and characterize associations of elements. From the 19 analyzed variables, seven elements (Ag, Al, Ba, Fe, K, Na, and Zn) had a low factor loading or tendency to form an independent factor and therefore do not belong to any factor group. However, these elements are generally naturally present in the environment, so they can be considered geogenic. The matrix of dominant rotated factor loadings is presented in Table 3. Three factors were identified—two geogenic and one anthropogenic—interpreted as Factor 1, Factor 2 and Factor 3, which include 67% of the variability of treated elements.

Factor 1 (Ca, Li, Mg, Mn, and Sr)

These elements are naturally found in soil as macroelements (Fig. 3). The 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. Occurrence of this factor is typical for the oldest formations in the Republic of Macedonia (Proterozoic micaschist and Proterozoic gneisses).

Factor 2 (Co, Cr, Ni)

This factor presents a geogenic factor (Fig. 4). These determined elements are considered "natural" because their origin is primarily crustal—soil particles suspended and transported by wind. High factor loadings are related to some old formation such as Neogene dacites, andesites, and pyroclastites and Pliocene unconsolidated sediments.

Factor 3 (As, Cu, Pb)

Factor 3 associates chemical elements that indicate anthropogenic influence in the studied area (Fig. 5). This association of elements was expected because of the studied area's geology and the open pit mining and flotation activities. The acid drainage rapidly dissolved the elements, leading to increased content in soil. The open ore pit and flotation tailings dump allow direct exposure of the finest ore particles to the atmosphere. Corpuscle dust from the surface layer of the ore body and soil is spread in the atmosphere by the winds, thus performing atmospheric distribution of these elements in the vicinity of the mine. The high loading value for this factor was for Cd (0.47). That is because the higher content of this element is introduced to the environment as a result of anthropogenic activity. Urban elements and those related to mine activities in dust are associated with fine particles, which are preferentially mobilized by wind and trapped in attics (Miguel et al. 1999).

From the distribution map of Factor 3 scores and distribution maps for all elements from this factor (Figs. 6, 7, 8, 9), it is clearly visible that the higher content of these elements is deposited in close vicinity to the mine (Fig. 5). Maps of areal element deposition from Factor 3 scores results from principal factor analysis (Fig. 5 and Table 3), which shows that attic dust samples with an increased content of Cu have an increased content for the rest of the elements from this factor; this confirms the influence of the present copper mine and flotation plant on the increase of the content of these metals in the atmosphere. In addition, chemical analyses of the ore concentrate and tailings were performed (Table 4) and the obtained results proving the previous conclusion; namely, it is obvious that the content of As (860 mg/kg), Pb (775 mg/kg), and especially Cu (20.4 %) are significantly increased in Cu concentrate. It is also evident that the Cu content is high in flotation tailings (614 mg/kg).

The maximum values for the content of As, Cd, Cu, and Pb are obtained from attic dust samples collected from old houses in Bučim (situated 1 km from the mine and 2.5 km

Table 2 Matrix of correlation coefficients (r)

	Ag	Al	As	Ba	Ca	Cd	Co	Cr	Cu	Fe	K	Li	Mg	Mn	Na	Ni	Pb	Sr	Zn
Ag	1.00																		
Al	0.03	1.00																	
As	−0.10	0.04	1.00																
Ba	0.36**	−0.04	−0.16	1.00															
Ca	0.13	0.36**	−0.14	0.40**	1.00														
Cd	−0.18	0.57**	0.21	−0.03	0.15	1.00													
Co	−0.24	0.22	0.19	0.01	0.07	0.57**	1.00												
Cr	−0.27*	0.16	−0.06	0.03	0.02	0.40**	0.84**	1.00											
Cu	0.12	−0.02	0.40**	−0.02	−0.05	0.22	0.04	−0.19	1.00										
Fe	−0.07	0.21	0.04	0.29*	0.25*	0.24	0.26*	0.38**	−0.09	1.00									
K	−0.07	0.10	0.07	−0.16	0.24	−0.00	−0.21	−0.34**	0.05	−0.23	1.00								
Li	0.34**	0.30*	0.07	0.48**	0.51**	−0.03	−0.06	−0.18	−0.22	0.11	0.29*	1.00							
Mg	−0.01	0.23	−0.16	0.39**	0.72**	0.28*	0.34**	0.30*	−0.23	0.40**	0.09	0.44**	1.00						
Mn	0.09	0.47**	0.01	0.22	0.44**	0.39**	0.43**	0.25*	−0.22	0.27*	0.07	0.49**	0.52**	1.00					
Na	0.14	0.10	0.16	0.24	−0.03	−0.17	−0.02	−0.15	0.10	−0.05	0.05	0.39**	−0.10	0.05	1.00				
Ni	−0.19	0.20	0.06	0.09	0.04	0.45**	0.68**	0.77**	−0.22	0.47**	−0.28*	0.06	0.34**	0.46**	−0.10	1.00			
Pb	−0.12	0.15	0.39**	−0.02	0.28*	0.27*	0.04	−0.14	0.26*	0.14	0.24	0.27*	0.15	0.37**	−0.05	0.21	1.00		
Sr	−0.03	0.63**	0.08	0.11	0.55**	0.53**	0.25*	0.11	−0.09	0.32**	0.24	0.40**	0.55**	0.64**	0.03	0.39**	0.47**	1.00	
Zn	0.34**	0.00	−0.01	0.44**	0.34**	−0.07	−0.38**	−0.52**	0.27*	0.05	0.10	0.44**	0.11	0.15	0.10	−0.21	0.38**	0.20	1.00

* Significance at $p < 0.05$

** Significance at $p < 0.01$

Fig. 3 Spatial distribution of Factor 1 scores (Ca, Li, Mg, Mn, Sr) in attic dust samples
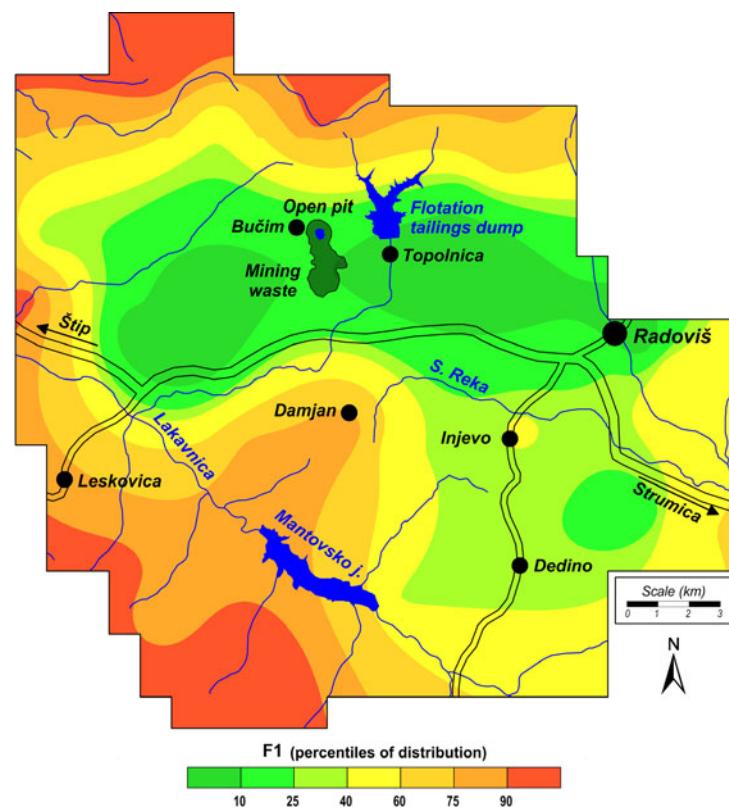

Fig. 4 Spatial distribution of Factor 2 scores (Co, Cr, Ni) in attic dust samples
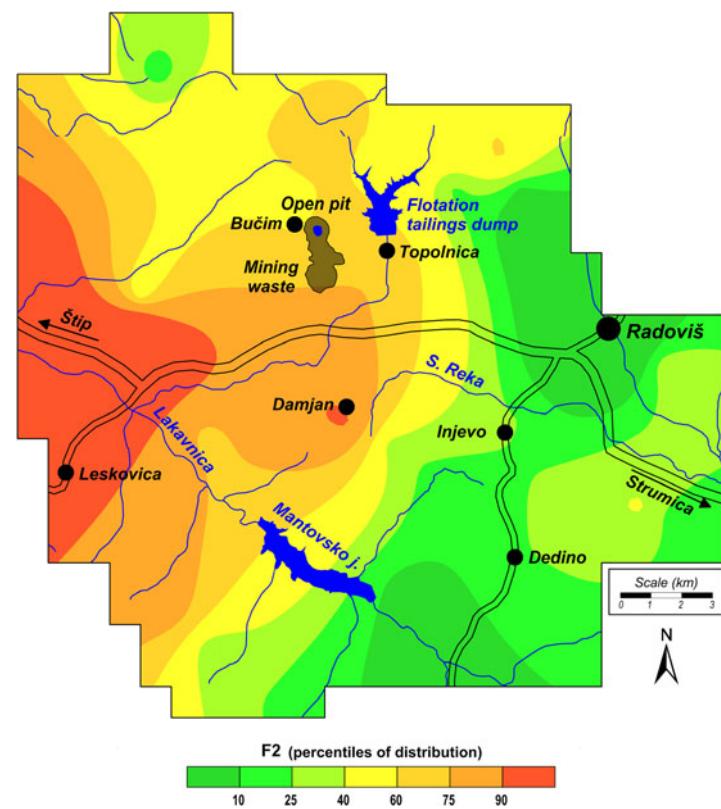
from the flotation tailings dump) and Topolnica (situated 1 km from the flotation tailings dump and 2.5 km from the mine site (Figs. 2, 5). The median values for the content of

these elements in samples taken from the houses of the settlements in close mine vicinity separated from other samples from a distant area of the mine (Table 4) are as

Fig. 5 Spatial distribution of
Factor 3 scores (As, Cd, Cu, Pb)
in attic dust samples
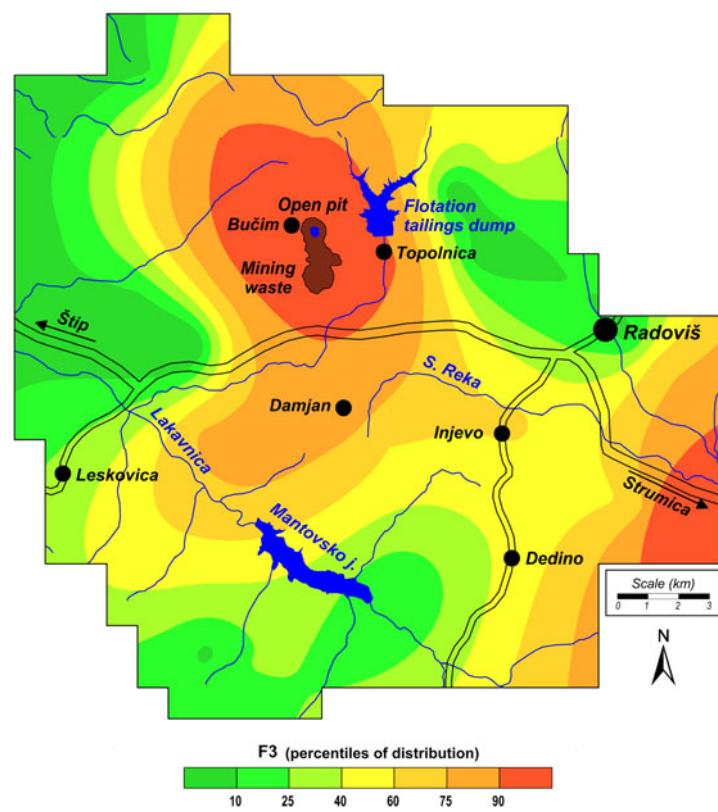
Fig. 6 Spatial distribution of
As
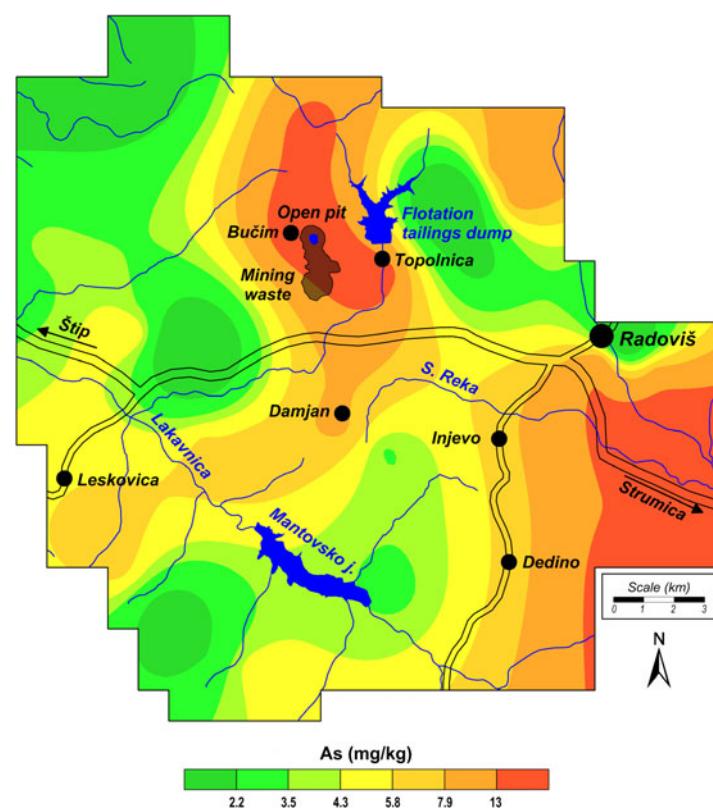
Fig. 7 Spatial distribution of Cd

Cd (mg/kg)
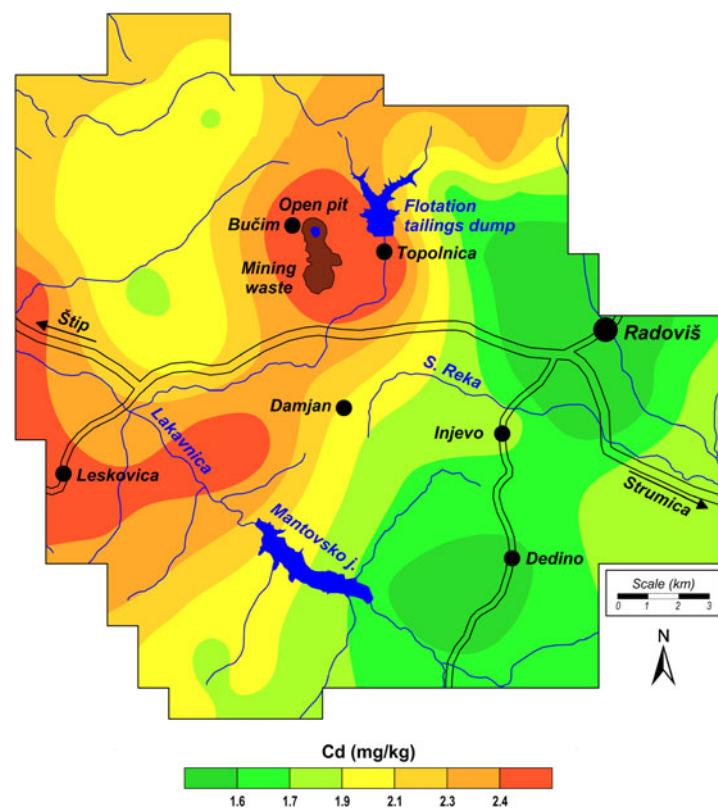
Fig. 8 Spatial distribution of Cu

Cu (mg/kg)
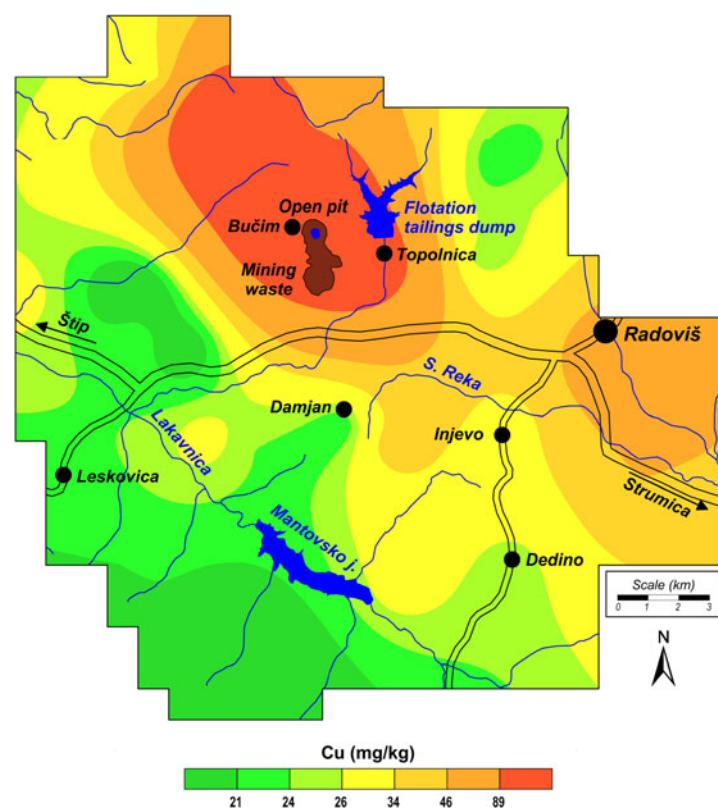
Fig. 9 Spatial distribution of
Pb

Pb (mg/kg)

| 12 | 16 | 22 | 29 | 34 | 41 |
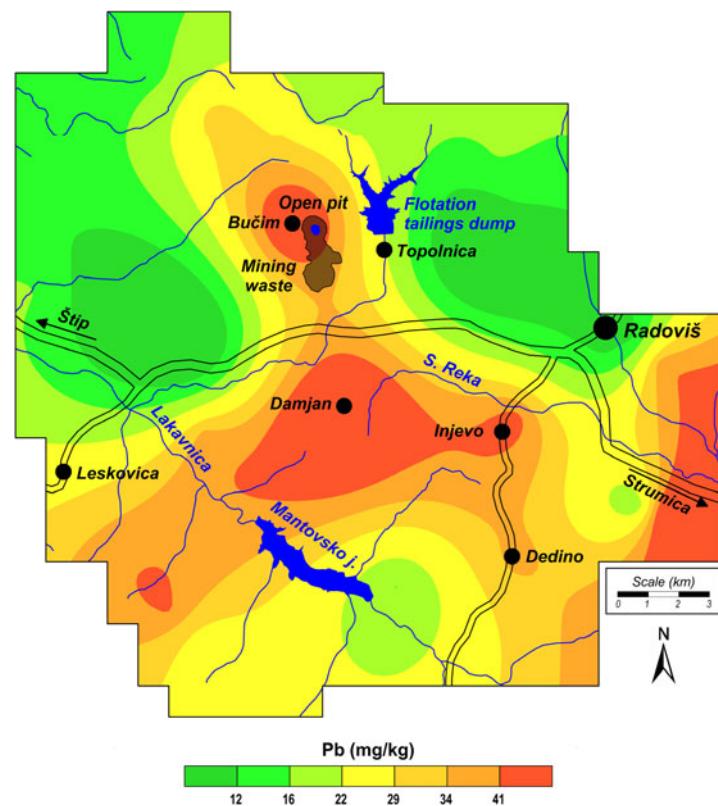
Table 3 Matrix of dominant rotated factor loadings (F > 0.60)

	F1	F2	F3	Com
As	−0.08	−0.06	**0.78**	62
Ca	**0.80**	−0.03	−0.09	70
Cd	0.27	0.51	0.47	67
Co	0.04	**0.89**	0.09	89
Cr	−0.07	**0.90**	−0.23	89
Cu	−0.18	−0.07	**0.70**	57
Li	**0.81**	−0.18	0.04	80
Mg	**0.78**	0.21	−0.22	79
Mn	**0.76**	0.34	0.11	80
Ni	0.19	**0.85**	0.04	65
Pb	0.27	0.09	**0.70**	81
Sr	**0.72**	0.11	0.19	66
Var	**31**	**19**	**16**	**67**

F1, F2, F3 factor loading, *Var* variance (%), *Com* communality (%)

Numbers in bold correspond to the dominant rotated factor loadings
with a value over 0.60

follows: 14 mg/kg for As; 2.6 mg/kg for Cd; 110 mg/kg
for Cu, and 37 mg/kg for Pb compared with those for
whole investigated area, which are 3.9 mg/kg, 1.9 mg/kg,
26 mg/kg, and 17 mg/kg for As, Cd, Cu, and Pb,
respectively.

Table 4 Average contents of investigated chemical elements in flo-
tation tailings and Cu concentrate

Element	Flotation tailings	Cu concentrate
In percent		
Al	1.25	0.48
Ca	0.44	0.67
Fe	1.90	23.22
K	2.40	0.11
Na	1.74	0.54
Mg	0.54	0.50
In mg/kg		
Ag	<1	19.2
As	31.4	860
Ba	234	66.9
Cd	0.10	36.8
Co	8.55	67.0
Cr	32.8	6.1
Cu	614	204,176
Mn	177	975
Ni	10.4	54.9
Pb	20.1	775
Sr	46.2	12.0
Zn	26.4	959

Table 5 Descriptive statistic, ER, and ANOVA test regarding to surveyed areas

	Affected area ($n = 15$)				Rest of studying area ($n = 49$)				ER	F
	X_g	Md	Min	Max	X_g	Md	Min	Max		
As	10.4	14.2	1.29	32.7	2.62	3.89	0.50	51.6	3.66	11.8*
Cd	2.43	2.6	1.73	3.09	1.85	1.87	1.09	3.11	1.36	21.0*
Cu	74.0	110	14.4	415	26.2	26.0	10.9	68.8	4.23	28.1*
Pb	36.0	37.4	10.3	104	18.2	17.0	3.12	121	2.20	9.39*

n number of observation, X_g geometrical mean, Md median, min minimum, max maximum, ER affected area/rest of area enrichment ratios (Md), F continuous probability distribution (ANOVA)

* Significance at $p < 0.05$

The enrichment ratio for As, Cd, and Pb is between 1.4 and 3.7 times, but the highest enrichment ratio is found for Cu (4.2) (Table 5). A significant difference of population is additionally verified with the ANOVA test. This is because of the presence of the mine and mining Cu minerals, which result in the introduction of a higher Cu content in the environment.

Conclusion

The activities carried out in the copper mine and flotation lead to increased content of certain heavy metals in the atmosphere, which was determined through the monitoring of attic dust samples. The enforcement of statistical factor analysis singled out one anthropogenic group of elements (As, Cd, Cu, and Pb). The fine particles from the mining operation are spread in the atmosphere carried by wind. Microparticles penetrate the human body through inhalation via the respiratory system. The second potential emission source of heavy metals is flotation tailings, which is a dominant pollutant to the soil. The acid drainage system dissolves heavy metals present in the soil such as those contained naturally in soil minerals and concentrates of it. From here, the fine particles from the soil surface are taken back into the atmosphere.

The highest values for As, Cd, Cu, and Pb were obtained from attic dust samples from Bučim and Topolnica houses (52 mg/kg for As; 3.1 mg/kg for Cd; 415 mg/kg for Cu, and 121 mg/kg for Pb). Median values for the investigated elements did not indicate a significant anthropogenic effect on the environment. However, the values obtained for the content of As, Cd, and Pb in attic dust samples from the nearest mine settlements show values 1.4–3.7 times higher compared with the corresponding medians; for Cu, it is 4.2 times higher.

Maps of areal deposition of heavy metals in the area around the Bučim mine show that these metals have an increased content in close vicinity of the mine. The high content of Cu in attic dust was collected in close vicinity of the mine. The population from Bučim and Topolnica is directly exposed to the presence of these heavy metals in the atmosphere, which is certainly worrisome from the aspect of human health risk.

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