

Spatial Distribution and Characterization of Some Toxic Metals and Lithogenic Elements in Topsoil and Subsoil from Copper Mine Environs

Soil Monitoring for Anthropogenic and Lithogenic Elements Distribution

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Abstract- Monitoring using soil samples (topsoil-TS and subsoil-SS) was conducted in area where copper minerals are intensively exploited. Characterization was conducted based on 18 elements: Al, As, Ba, Ca, Cr, Cu, Ga, Li, Fe, K, Mg, Mn, Na, Ni, Pb, Sr, V and Zn. The main pollutant was Cu (average value 190 mg kg⁻¹; max. value 1200 mg kg⁻¹ and the enrichment factor of TS/SS of ~10). The lithogenic elements (Al, Ga, Fe, Li, Mg, Mn, Na, Sr) showed stability in the vertical direction (TS/SS); but in a across direction the element concentrations fluctuated according to the geology of the region. The element contents were also characterized according to land use. Maximum values for Cr, Ni and Pb were found in cultivated area (290 mg kg⁻¹, 190 mg kg⁻¹ and 130 mg kg⁻¹, respectively). Using factor analysis, the distribution was reduced to three synthetic variables, which showed linkage in terms of geochemical similarities: F1 (Al-Ca-Cr-Fe-Mg-Mo), F2 (Li-Mn-Na-Ni-Pb) and F3 (Ba-Sr), accounting for 77% of the variability of analyzed elements. Spatial distribution of As, Cu, Pb, V and Zn showed that these elements are preferentially deposited in mine vicinity; due to dust deposition from ore and flotation tailings.

Keywords- Copper Mine; Toxic Metals; Spatial Distribution; Soil Pollution

I. INTRODUCTION

Toxic metals are introduced into the terrestrial environment from different sources such as industrial and municipal waste, automobile emissions and mining activities. Distribution and deposition of some heavy metals is the most evident characteristic and an inevitable process in areas where a copper mine with open ore pit is presented [1]. The main sources for releasing the pollutants are the extraction, concentration and separation of waste at the open pit. The level of the environmental pollution depends on proper control of anthropogenic activities in the mentioned processes [2]. Fine dust generated during blasts and excavation of mining minerals is distributed by the wind. These dust particles vary in size and density, which may deposit in the ground or may be retained in the atmosphere. The rate of deposition is faster for particles of larger size [3, 4]. Deposition (dry and wet) of fine dust prevails close to the emission source or (depending from intensity of wind and rain frequency) from distant sources. Rains also contribute to the erosion processes of opencast surfaces and ore tailings: the effect known as “natural rinsing” [5, 6]. Such erosion processes contribute to the increasing content of certain toxic metals from ore minerals into the soil. Some potentially risk toxic metals contained in the surface layers of soil are carried by the wind as fine dust. On the other hand, soil is the medium for the production of food, where indirect risk impact on human health occurs [7].

In order to assess the potential health risks, this study focuses on the monitoring of distribution and characterization of metals and some lithogenic elements in soil in the copper mine environs for a long period of time. The results quantified the effects on topsoil pollution and possible land degradation in vertical order from enrichment factors for top and subsoil (TS/SS). Higher contents of certain toxic metals such as Cu, Cd, Pb and Zn [8] in the topsoil (TS) in cultivated areas indicate pollution not only in the soil but also in a potential risk of contamination of the food produced [8]. Thus, using a data processing model for spatial distribution areas where food cannot be grown and it is undesirable for consumption can be narrowed down. The investigated area was previously monitored for atmospheric pollution (higher contents of As, Cd, Cu, Pb and Zn) using cross moss and lichens [9, 10]. Their results exposed the need of a soil pollution study that would focus on certain toxic metals, as well as on the distribution of lithogenic elements as a function of the emission source.

II. STUDY AREA

A total of 400 km² (20 km West–East direction × 20 km South–North direction), was used as monitored area, located in the eastern part of the Republic of Macedonia, and constrained by coordinates N: 41 °32' – 41 °44' and E: 22 °15' – 22 °30' (Fig. 1). The region is characterized by moderate continental climate. The average annual temperature is around 10 °C. The average annual rainfall amounts to 563 mm with large variations from year to year. Prevailing winds in the region are those from the west with frequency of 199% and 2.7 m s⁻¹ speed, and winds from the east with frequency of 124% and 2.0 m s⁻¹ speed [11]. The Bucim copper mine is located in the north-west part of the study area. The mine environs encompasses ten villages and it

is 14 km air distance from the first major urban settlement, the town of Radoviš. Mine activities cover 7 km² of total mine surfaces, 4 km² for the placement of ore tailings and the rest of the land belongs to the open ore pit and to the plant for ore processing. The important metallic minerals mined are chalcopyrite, pyrite, and bornite, with small amounts of galena, sphalerite, magnetite and hematite [12].

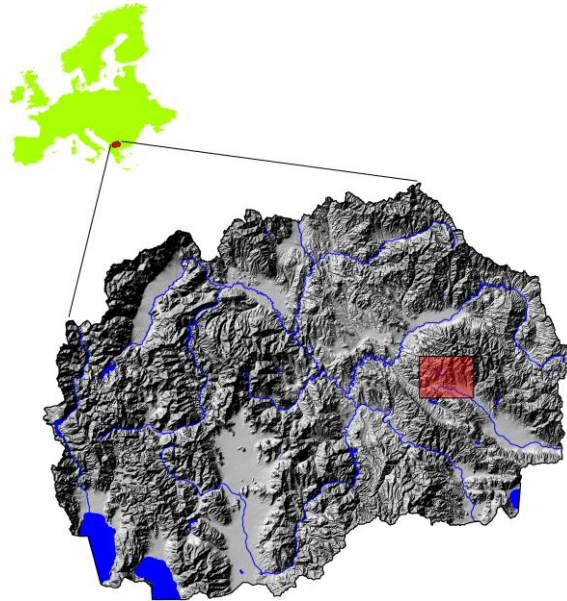


Fig. 1 Location of the study area

In geological terms, the investigated area belongs to the Vardar structural zone, separated from the other structural zones during the Caledonian, and subjected to strong tectonic processes, during the Herzynian orogenesis. The structural relations were further complicated by the Alpine orogenesis [13]. The study area anticline represents the eastern boundary of Vardar zone towards the Serbian-Macedonian mass. These two large structural units are separated by a deep, NW-SE fault [14]. The Bucim-Damjan-Borov Dol area is divided into two tectonic blocks. The Bucim tectonic block and the southern tectonic block Damjan are a part of the Vardar zone. The blocks are divided by a fault of first order with SE direction. Despite the disposition in two different tectonic blocks, the metallogenic area is unified based on the similarities of Tertiary magmatism and the analogous ore mineralization. In the northern block the Bucim copper-porphyry deposit is emplaced, with additional gold mineralization [15]. The generalized geology of the study area is presented in Fig. 2.

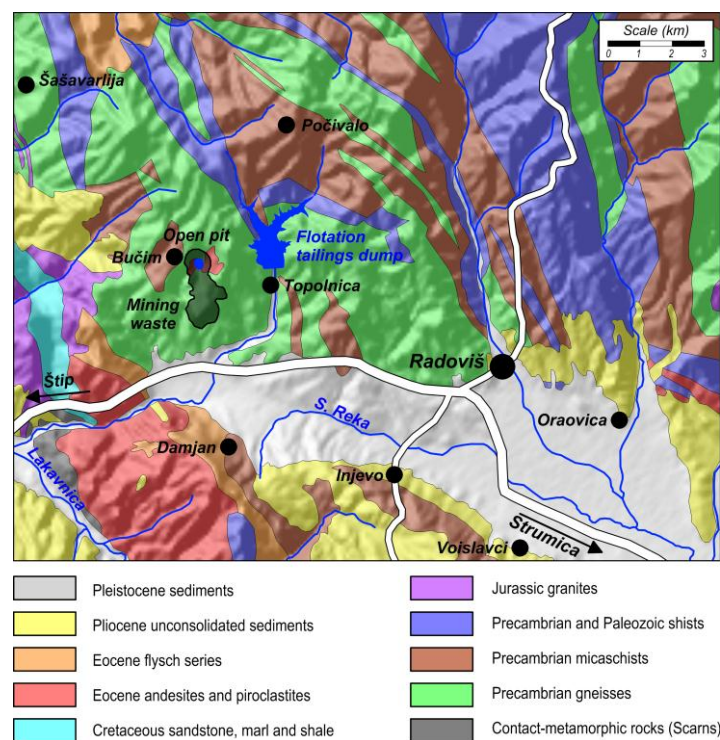


Fig. 2 Generalized geology map of the study area

Nearly half of the study area is cultivated land, most frequent crops being tobacco and potato plants (close to mine environs) as presented in Fig. 3. The rest of the study area represents the land cultivated with early garden plants as tomato and pepper. As most common fruits trees are cherry, plum and pear, agricultural production supplies the local population, with fewer activities towards manufacturing output and distribution at larger scale.

III. METHODS AND MATERIALS

A. Sample Collection and Pre-treatment

The soil samples were collected using a previously adapted sampling network ($5 \times 5 \text{ km}^2$). Two soil samples were taken at each location: a sample from the surface layer of soil - topsoil (0–5 cm) and a deep soil layer - subsoil (20–30 cm). Soil samples were collected according to soil sampling standards [16]. Each sample was a composite of five samples collected in the area within $10 \times 10 \text{ m}^2$. Topsoil samples and subsoil samples were collected at the same location. For the purpose of this study, a total of 40 samples were collected: 20 samples of topsoil and 20 subsoil (Fig. 3).

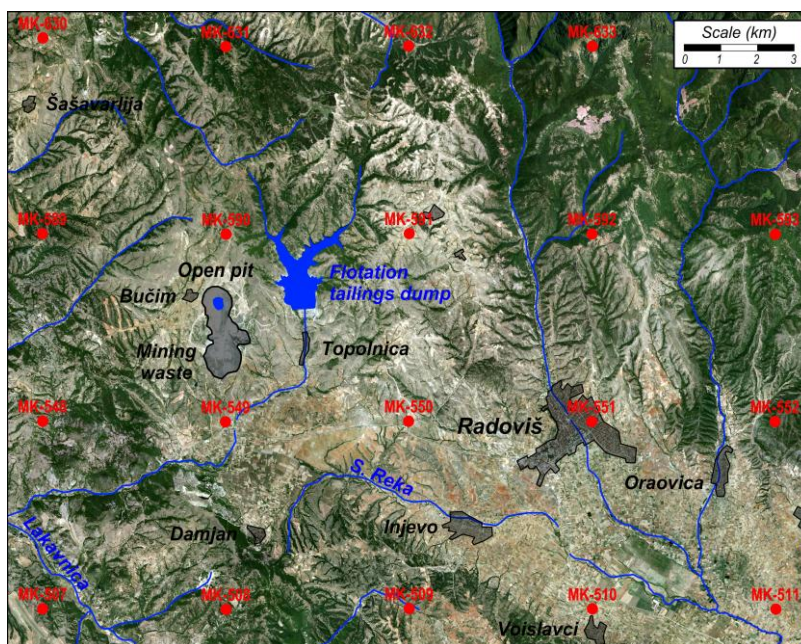


Fig. 3 Soil sample locations with landuse map of the study area

For digestion of soil samples, wet digestion with mixture of acids was applied. The digestion was carried out in this order: precisely measured mass of dust samples (0.5 g) with the accuracy of 0.0001 g was placed in teflon vessels. After this 5 ml concentrated nitric acid was added, until the brown vapors came out from the vessels. For total digestion of inorganic components, 5–10 ml of HF were added. When the digest became a clear solution, 2 ml of HClO_4 were added. Perchloric acid was used for total digestion of organic matter. After cooling the vessels for 15 min., 2 ml of HCl were added for total dissolving of metal ions. Finally, the vessels were cooled and digests quantitatively transferred to 50 ml calibrated flasks.

B. Instrumentation and Analysis of the Elements Contents

In this study, reagents with 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 were used for preparation of all solutions. Standard solutions of metals were prepared by dilution of 1000 mg l-1 solutions (11355-ICP multi Element Standard). The analyses of digested samples were performed with an atomic emission spectrometry with inductively coupled plasma, ICP-AES, Varian 715-ES. Optimization of instrumental condition for each element was previously done [17]. Total contents of 18 elements were analyzed: Al, As, Ba, Ca, Cr, Cu, Ga, Li, Fe, K, Mg, Mn, Na, Ni, Pb, Sr, V and Zn.

The quality control of the applied techniques was performed by standard addition method, and it was obtained that the recovery for the analysed elements ranges for ICP-AES between 98.5% and 101.2%. 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.

C. Data Processing

Statistical analyses were performed using Statistica 8.0. Basic statistics and multivariate exploratory techniques were used for data processing. Multivariate statistical method (R-mode factor analysis) was used to reveal the associations of the

chemical elements. The factor analysis was performed on variables standardised to zero mean and unit standard deviation. For orthogonal rotation the varimax method was used.

The universal kriging method with linear variogram interpolation was applied for the construction of spatial distribution maps for individual elements and for the factor associations [18, 19, 20].

IV. RESULTS AND DISCUSSION

All field observations, analytical data and measurements were introduced to the data matrix. For each observation there were few variables: sample identification number, locality, geographic coordinates and elements contents. The values obtained for the contents of the elements were statistically processed using basic descriptive statistics (Table 1). Based on normality tests and distribution histograms for independent variables (elements content), normality in the distribution of data was determined only for the elements Al, Fe, Ga, Na, V, Zn (for the contents in topsoil and sub soil samples). For the rest of the elements logarithms were used for the normalization of the variables.

TABLE 1 DESCRIPTIVE STATISTICS FOR ELEMENTS CONTENT VALUE IN SOIL SAMPLES

Element	Unit	Dis	X_a	X_g	Md	min	max	P_{10}	P_{90}	s	s_x	CV	A	E
Al	%	N	2,1	1.8	1.8	0.59	5.3	0.77	3.8	1.2	0.18	54	0.79	0.06
As	mg/kg	Log	23	8.8	12	0.50	160	0.50	44	34	5.4	150	-0.21	-1.61
Ba	mg/kg	Log	280	220	250	27	980	73	480	200	31	70	-0.76	1.31
Ca	%	Log	0.89	0.46	0.41	0.042	4.3	0.10	2.6	1.1	0.17	120	0.05	-0.81
Cr	mg/kg	Log	73	58	55	16	290	28	150	60	9.4	82	0.55	0.57
Cu	mg/kg	Log	59	28	23	9.3	1200	11	54	190	30	320	2.76	11.92
Fe	%	N	2.6	2.4	2.6	0.61	4.7	1.6	4.1	0.93	0.15	35	0.27	0.59
Ga	mg/kg	N	12	12	13	7.2	20	10	15	2.4	0.38	19	0.28	1.25
K	%	N	1.1	0.93	0.88	0.32	2.3	0.50	1.8	0.56	0.09	53	0.03	-0.90
Li	mg/kg	N	13	11	12	3.2	43	6.0	22	7.6	1.2	60	0.04	0.08
Mg	%	Log	0.76	0.63	0.71	0.19	2.6	0.23	1.2	0.52	0.08	68	-0.07	0.15
Mn	mg/kg	Log	510	430	440	77	1800	220	820	330	53	65	-0.18	1.28
Na	%	N	1.4	1.2	1,3	0.36	2.9	0.64	2.2	0.62	0.10	46	0.82	0.71
Ni	mg/kg	Log	36	28	27	11	190	13	63	36	5.6	99	1.21	2.45
Pb	mg/kg	Log	30	23	23	1.0	130	9.0	65	26	4.2	87	-1.01	4.03
Sr	mg/kg	Log	66	37	39	3.7	470	9.0	130	99	16	150	0.09	0.78
V	mg/kg	Log	73	53	59	0.35	170	23	150	48	7.6	66	0.74	-0.71
Zn	mg/kg	Log	70	65	71	23	120	36	110	25	3.9	35	0.08	-0.69

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

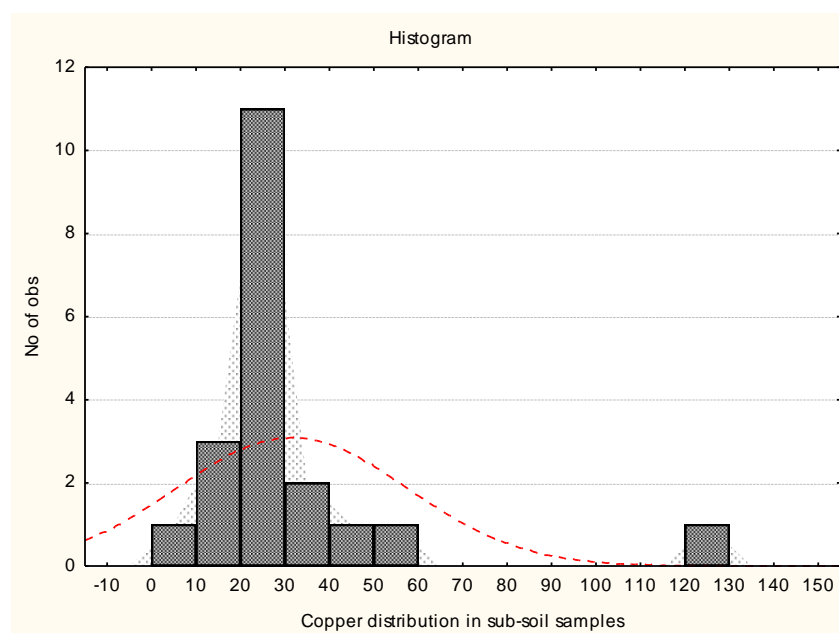


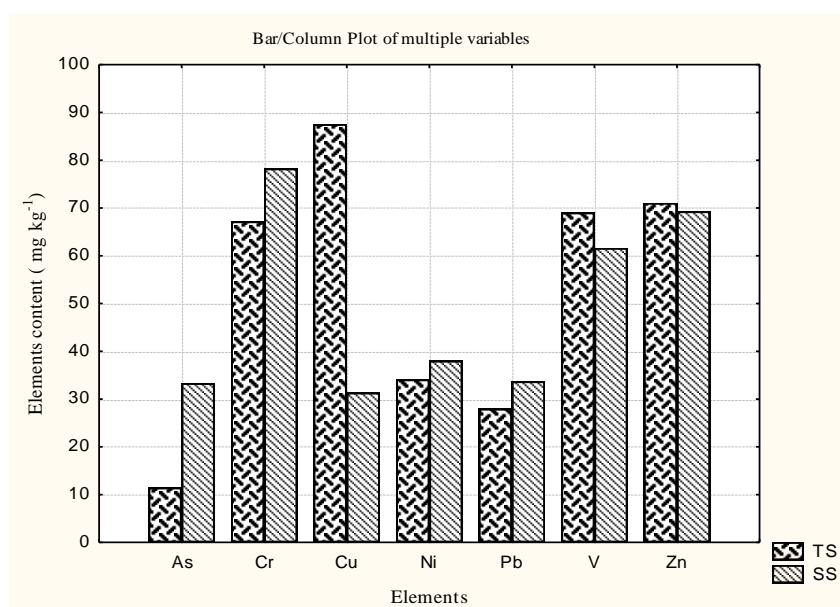
Fig. 4 Histogram for Cu distribution in subsoil samples

From descriptive statistics, median values for all elements were obtained. Relatively small median for Cu (23 mg kg^{-1}) was not expected in this area, because of the influence from the copper mine. However, the range of values shows much higher content of this element in the samples from the study area ($9.3\text{--}1200 \text{ mg kg}^{-1}$). The logarithm of values was used for the normalization, because of the skewed distribution, and the significant difference of the median and arithmetical mean was found ($Md=23.0 \text{ mg kg}^{-1}$; $Xa=59 \text{ mg kg}^{-1}$). The enrichment factor of TS/SS for Cu was 2.8 for whole study area and 10 for close mine environs. This is because of large amount of continuous and uncontrolled distribution of fine dust from ore waste and flotation tailings surface. Wind distribution of copper high contented dust follows the wind rose for the region. The copper distribution in subsoil samples followed normal distribution and was analysed separately (Fig. 4) based on the assumption that the area is bearing copper minerals. For the rest of the potentially anthropogenic elements (Pb, Ni, V and Zn), no significant enrichment factors were found. The lithogenic elements (Al, As, Cr, Ga, Fe, Li, Mg, Mn, Na, Ni, Sr) content showed stability in the vertical direction (TS/SS); but in an across direction they varied according to the geology of the region (as explained by factor distribution).

Variability in the elements contents was determined considering the type of land use (Table 2). The median value for copper in cultivated area was 26 mg kg^{-1} , in the uncultivated area was 25 mg kg^{-1} , in the urban area was 22 mg kg^{-1} and in the mine environs was 19.3 mg kg^{-1} . Because of the wide range values of the copper content in mine environs, the average amount was although considered (190 mg kg^{-1}). Compared with average amount of Cu in World soils 30 mg kg^{-1} and European soils 17 mg kg^{-1} , it can be classified as a significantly contaminated area [21, 22]. Besides the copper, several other elements showed variability with respect to the land use of the study area. Considering land use, maximum values for Cr, Ni and Pb were found in the cultivated area (290 mg kg^{-1} , 190 mg kg^{-1} and 130 mg kg^{-1} , respectively). For these elements, comparative analysis was conducted in order to test the variability of the TS/SS relation, and it was found that only Cu contents vary with respect to their TS/SS relation, likely due to anthropogenic mine impact (Fig. 5).

TABLE 2 BASIC STATISTICS FOR POTENTIALLY RISK ELEMENTS IN SOIL DEPENDING OF LAND USE

Elements		As	Cr	Cu	Ni	Pb	V	Zn
Unit		mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}
	Median	6.2	38.4	19.3	15	31.5	34.4	50
	Min	0.5	15.6	9.35	11.2	10.9	16.8	22.5
	Max	50.7	53.5	1200	28.5	49	163	116
Cultivated soil	Median	11.2	68.1	26.1	39.5	33.4	64.6	63.6
	Min	0.5	24.1	9.35	16.2	7.01	0.3	38.9
	Max	113	285	58.9	189	130	171	105
Uncultivated soil	Median	22.7	63.2	25.1	28.8	18.9	71.4	73.3
	Min	0.5	35.8	18.6	19.2	5.07	36.2	34
	Max	157	180	39	40.7	29.3	159	108
Urban soil	Median	5.8	45.4	22	23.5	21.6	40.2	78.8
	Min	0.5	35.3	20.9	13.8	6.72	28	60
	Max	119	65.5	49.4	39.8	32.4	137	113

Fig. 5 Distribution of potentially toxic elements in TS/SS soil samples (values are given in mg kg^{-1})

Principal component analysis was applied for the grouping of separate statistically significant associations. Copper content did not show significant correlation with any of the other elements.

With factor analysis the distribution was reduced to four synthetic variables, which showed linkage in terms of geochemical similarities, and which included 77% of the variability of analyzed elements. The factor analysis singled out four geochemical associations of elements. The values of factor loadings are presented in Table 3. For multivariate analysis, three elements (Cu, Na and V) were eliminated for further analysis because they had low share in communality, low values of factor loadings and low tendency to form an independent factor.

TABLE 3 MATRIX OF DOMINANT ROTATED FACTOR LOADINGS (F > 0.50)

Element	F1	F2	F3	F4	Comm
Mg	0.92	0.03	0.09	0.14	86.7
Cr	0.85	0.20	-0.24	0.09	82.0
Al	0.83	0.14	0.09	0.11	73.8
Fe	0.81	0.05	0.04	0.50	91.6
Ca	0.73	0.46	0.16	-0.07	77.1
Pb	0.06	0.87	0.08	0.05	76.3
Ni	0.50	0.84	0.05	0.04	95.4
Li	0.15	0.80	0.11	0.23	73.1
Mn	0.59	0.63	0.20	0.14	79.8
Ba	-0.02	0.04	0.94	0.17	91.8
Sr	0.16	0.06	0.86	-0.17	80.3
K	-0.06	0.32	0.60	0.38	61.0
Zn	0.25	0.28	0.05	0.76	72.3
Ga	0.24	-0.08	0.20	0.76	67.5
As	-0.09	0.40	-0.28	0.50	49.5
Var	28.2	20.8	15.2	13.4	77.2

F1, F2, F3 F4– factor loading; Var – variance (%); Comm – communality (%)

Geochemical association (Mg-Cr-Al-Fe-Ca-Mn-Ni) interpreted as Factor 1 is a geogenic factor. Their origins are related primarily to the dusting of Pliocene sediments and flysch formations (Pliocene unconsolidated sediments, Eocene flysch series). This occurrence was proofed, obtaining higher values for the contents of elements from topsoil against subsoil samples. A similar situation had been previously determined for the territories of Macedonia and Kosovo [16, 23, 24].

Geochemical association (Pb-Ni-Li-Mn) or Factor 2 associates geogenic elements. This factor group is associated with lithogenesis and accounts for 20.8% of total data variability. Elements of F2 are related to volcanism E (Eocene andesite and piroclastite). Higher values, as in the case of F1, are related to dusting.

Factor 3 (Ba-Sr-K) and Factor 4 (Zn-Ga-As-Fe) are least expressed natural factors (15.2% and 13.4% of the total variability of the data). Their occurrence is related primarily to the enrichment of the deeper horizon (B – clay accumulated) which is particularly valid for the elements in the group F4. Empirically, these elements could be related to the decomposition of rocks, especially Proterozoic micashist and schist (Precambrian and Paleozoic shists, Precambrian micaschists).

For better visualization, an individual map of copper's spatial distribution, a main anthropogenic element, is provided (Fig. 6). Comparative analysis was performed to narrow down the areas with higher content of copper, from the TS/SS distribution as suggested by Reference [25]. The spatial distribution maps showed that copper has a naturally occurrence in the region, but anthropogenic deposition of higher contents ($>47 \text{ mg kg}^{-1}$) affects the Bucim-Topolnica-Damjan topsoil.

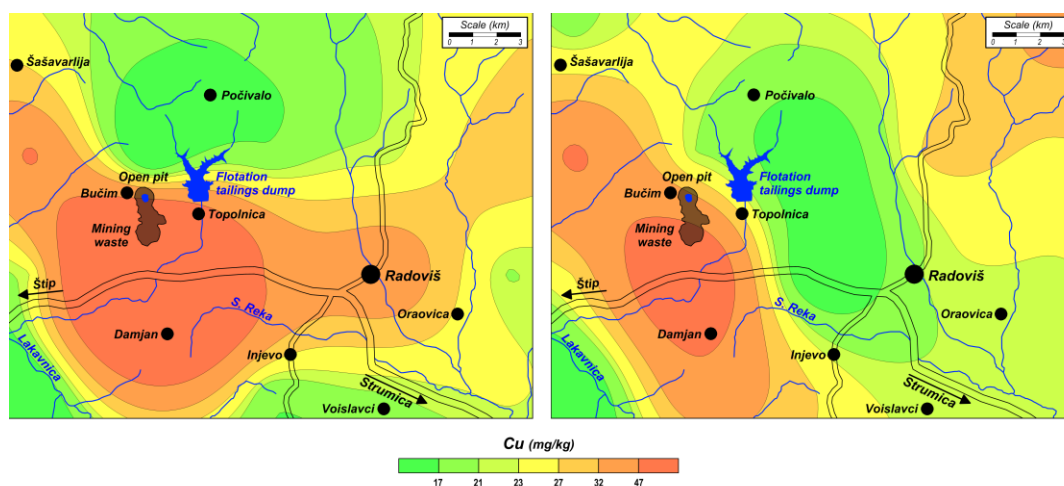


Fig. 6 Spatial distribution of Cu in topsoil (left) and subsoil (right)

The spatial distribution of F1, F2, F3 and F4 (top and subsoil), is characterized by natural distribution. Because of that, distribution was able to be compared by elements in topsoil and subsoil (Figs. 7-10). There was no pollution effect in the vertical variability brought by the anthropogenic influence from copper mine, which confirms that this anthropogenic process does not cause any significant land degradation. Anthropogenic pollution is transported by fine dust, which only leads to topsoil pollution.

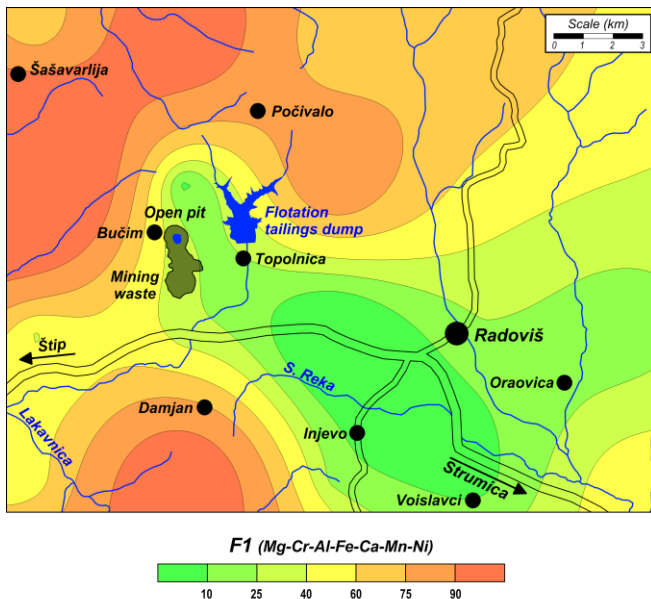


Fig. 7 Spatial distribution of Factor 1 scores (Mg-Cr-Al-Fe-Ca-Mn-Ni) in topsoil (above) and subsoil (below)

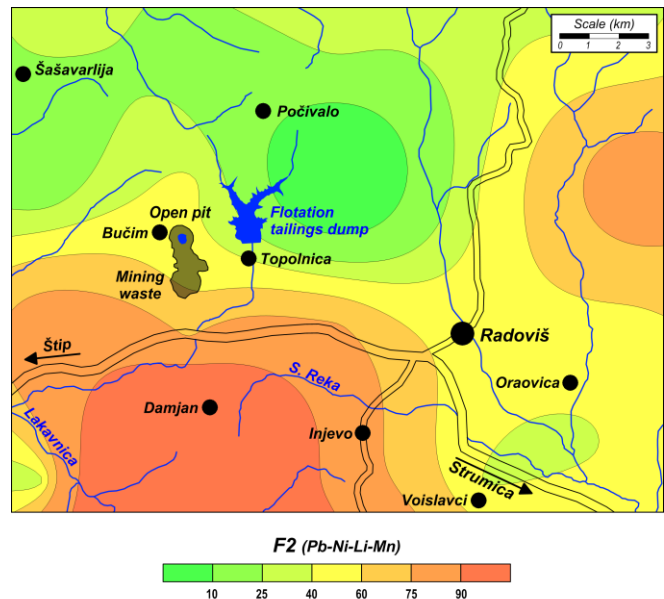


Fig. 8 Spatial distribution of Factor 2 scores (Pb-Ni-Li-Mn) in topsoil (above) and subsoil (below)

V. CONCLUSION

Distribution of potentially risk elements occurs in the emission source environs, where higher contents of Cu with enrichment factor of TS/SS ratio for 10 times, and a maximum value for copper of 1200 mg kg^{-1} were found. Anthropogenic source affects cultivated area, presenting a potential risk to human health. These anthropogenic activities contribute higher contents of potentially risk elements like As, Cr, Ni, Pb, V and Zn (max. values: 160 mg kg^{-1} , 290 mg kg^{-1} , 190 mg kg^{-1} , 130 mg kg^{-1} , 170 mg kg^{-1} and 120 mg kg^{-1} , respectively).

With respect of land use, maximum values for Cr, Ni and Pb were found in cultivated areas (290 mg kg^{-1} , 190 mg kg^{-1} and 130 mg kg^{-1} , respectively). Uses of multivariate factor analysis provide a simplified overview of the distribution of the analysed elements. Contents of all analysed elements were correlated, in order for separation of certain geochemical associations: F1 (Al-Ca-Cr-Fe-Mg-Mo), F2 (Li-Mn-Na-Ni-Pb) and F3 (Ba-Sr). Spatial distribution was applied in this study using the comparative model for TS/SS relation. Spatial distribution of analysed elements shows that only the close vicinity of the mine area was affected by high contents of $\text{Zn} < \text{Pb} < \text{As} < \text{V} < \text{Ni} < \text{Cr} < \text{Cu}$. According to the results obtained from this study, the comparative method of monitoring TS/SS enrichments (natural and anthropogenic) can be recommended for future studies along with multivariate factor or PCA, for easier monitoring for multi-elements distribution in potentially contaminated soils.

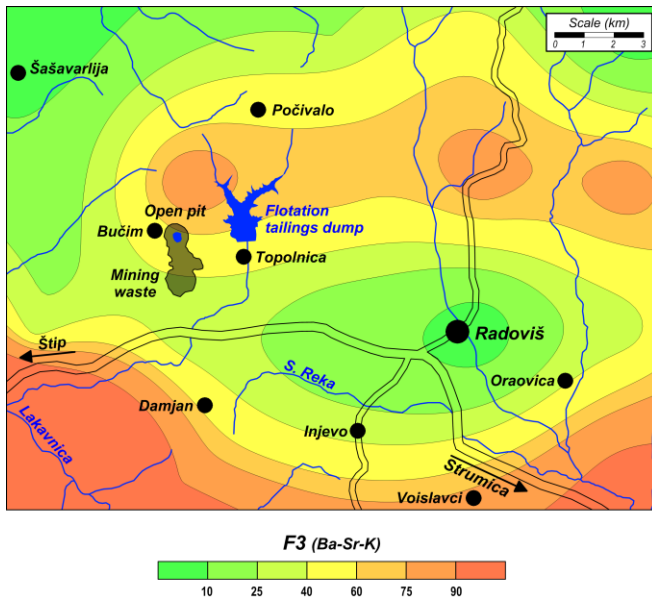


Fig. 9 Spatial distribution of Factor 3 scores (Ba-Sr-K) in topsoil (above) and subsoil (below)

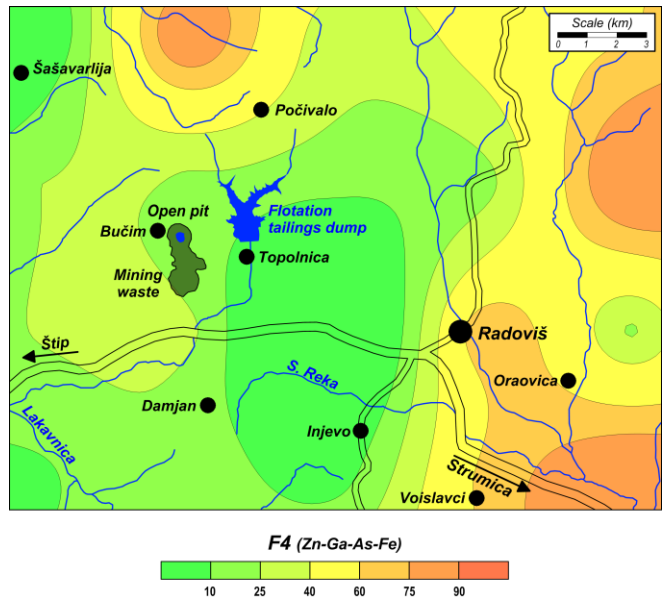


Fig. 10 Spatial distribution of Factor 4 scores (Zn-Ga-As-Fe) in topsoil (above) and subsoil (below)

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