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SOIL METAL POLLUTION RELATED TO ACTIVE BUCHIM COPPER MINE, REPUBLIC OF MACEDONIA

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Abstract

Within this study a total content of 20 elements was determined in 25 soil samples taken from the vicinity of the "Buchim" mine, Republic of Macedonia, covering an area of 14.2 km^2. The results have been compared to new Dutchlist and NOAA standards and it was concluded that the content of As, Cd, Cu, Pb and Zn in most of the samples is over the corresponding optimal or action values probably due to the anthropogenic activities. Thus As values ranged 13.1-225 mg kg^{-1} with 20 above the optimum (29 mg kg^{-1}) and 7 above action value (55 mg kg^{-1}), Cd values ranged 0.67-17.9 mg kg^{-1} with 17 above optimum (0.8 mg kg^{-1}) and 1 over the action value (12 mg kg^{-1}), Cu with range 17.8-1734 mg kg^{-1} with 16 over optimal (36 mg kg^{-1}) and 3 above action value (190 mg kg^{-1}), Pb with range 46-3456 mg kg^{-1} with 19 over optimal (85 mg kg^{-1}) and 1 above action value (530 mg kg^{-1}), and Zn with range 88-3438 mg kg^{-1} with 12 over optimal (140 mg kg^{-1}) and 1 above action value (720 mg kg^{-1}). The multivariate statistical method (R-mode factor analysis) was applied and three geochemical associations of elements were obtained. Factor 1 (Al-Ca-Fe-K-Mg-Co-Cr-Mn-Ni-Sr-V) was estimated as geogenic factor related primarily to the Pleistocene sediments and Precambrian gneises. Factor 2 (As-Cd-Pb-Zn) associates anthropogenic elements related to dusting from ore and flotation tailing dump sites. The occurrence of Factor 3 (Na-Ba-Cu-Sr) is related primarily to the decomposition of rocks (Proterozoic gneises and amphibolites).

Keywords: arsenic, Buchim mine, contamination, copper, pollution, soil

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1. Introduction

It is well known that mining and metallurgical activities lead to enormous soil contamination with heavy metals (Aliu et al., 2009, 2010; Aryal et al., 2006; Cappuyns et al., 2006; Cemek and Kizilkaya 2006; Kabata-Pendias and Pendias, 2001; Li et al., 2005, 2006; Paiu et al., 2017; Pruvot et al., 2006; Stafilov et al., 2010a, 2010b; Tembo et al., 2006; Wilson et al., 2005). Mining and flotation processing plants are also significant anthropogenic sources of heavy metals. Namely, the large amounts of ore waste and flotation tailings usually are deposited at open, continuously exposited to air flow and winds caring-out (Athar and Vohora, 1995; Hou et al., 2005; Hršak et al., 2003; Shahhosseini et al., 2016; Stafilov et al., 2010c). Solid and liquid particles or dust that falls out of suspension in the atmosphere can get into the environment and lead to its contamination. (Balabanova et al., 2011b; Čačković et al., 2009). Therefore, it is necessary to take measures to protect the environment from pollution with heavy metals from when it comes from such processes. This is especially important for the proper waste management. There are several the most important approaches to minimize the environmental impact, i.e. more sustainable mining operations, like proper deposition, monitoring, reusing, bioremediation etc. (Astel et al., 2016; Dold, 2008).

For the last four decades the Buchim Mine, located in the eastern part of country, is the major copper producer, but it is one of the major emission

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sources of particular heavy metals in the area too. Within this paper we introduce our findings of the 2010 study, which took place in the aforementioned Buchim Mine area (Fig. 1).

The mine and the ore processing plant have been functioning since 1979 and process 4 million tons of ore annually. It is assumed that the mine at the moment have about 40 million tons of ore reserves. Porphyry copper type mineralization within the Buchim deposit is related directly to the Tertiary andesite and latite sub-volcanic intrusions into the gneiss and amphibolite rocks of the Pre-Cambrian age (Serafimovski et al., 1995). Exposure of the ore particles to the free atmosphere was provided due to an opened ore body with an approximate volume of 0.05 km^3. The content of copper in ore is at on the average of 0.3 % Cu. Characteristic metallic minerals are chalcopyrite, pyrite, and bornite, with small amounts of galena, sphalerite, magnetite, hematite, and cubanite (Alderton et al., 2005; Serafimovski et al., 1996).

Open pit mine processing results in a fact that waste material is disposed in the open waste dump in the vicinity of the mine facilities. Copper ore is processed within the flotation facility and while copper concentrate is sent abroad for smelting, the flotation tailings are deposited on flotation dam in the vicinity of the Topolnica village (Fig. 1). After four decades of uninterrupted copper production from the mine, around it was deposited more than 150 Mt of material within the waste dump and more than 140 Mt of material at the tailing dam. That enormous piles of material were left at open under constant action of air flow and winds resulting in irregular distribution of fine contaminated dusty material in the area (Barandovski et al., 2008, 2012; Balabanova et al., 2010).

2. Material and methods

2.1. Geological features of the area of consideration

In the geological composition of the studied area, in general dominate, Precambrian metamorphic rocks (Ivanov, 1982), there are two different types of gneiss, mica-schist, amphibolites (Čifliganec, 1993) and series of Paleozoic schist with marble intercalations (Ivanov, 1982). This Precambrian complex (Fig. 2) with two structural levels (Hristov et al., 1973) pierced by multistage Tertiary magmatism (Ivanov, 1982; Serafimovski, 1990; Stojanov and Serafimovski, 1990), which has been represented by latite, andesite, trachyte and rhyolite (Boev and Yanev, 2001), with absolute age of 24-27.5 Ma (Čifliganec, 1993; Lehman et al., 2013; Serafimovski, 1993).

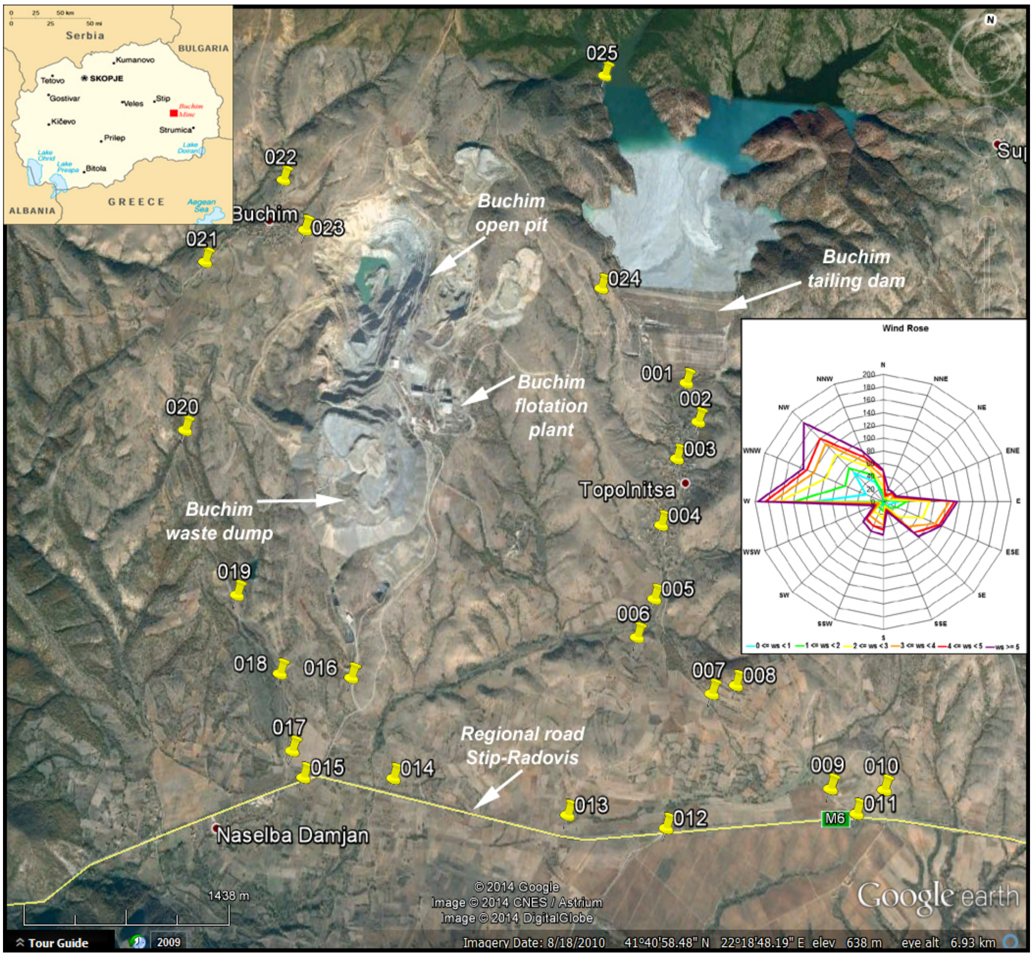


Fig. 1. Location of the soil samples around the Buchim copper mine, with the position of the mine and wind rose as insets

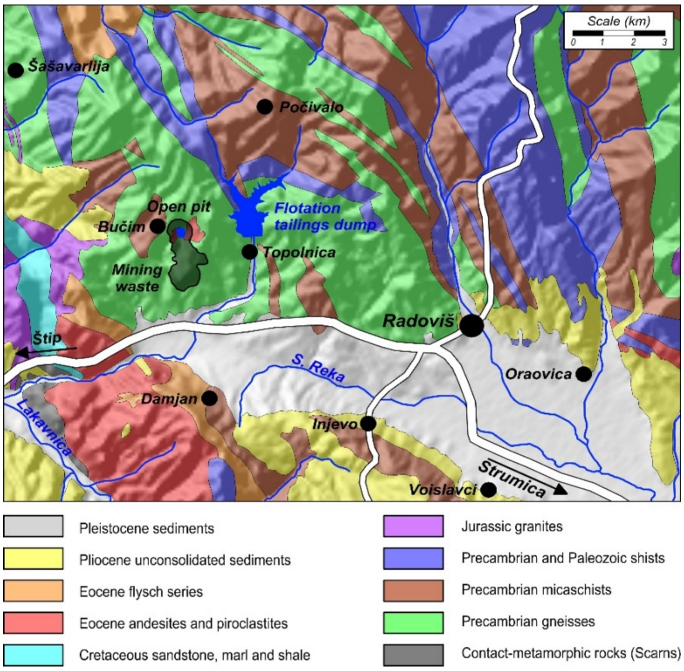


Fig. 2. Geological map of the Buchim mine area (Balabanova et al., 2013)

The main copper mineralization within the Buchim mine has been localized around the volcanic breakthrough while spatially is laid in gneiss, which represent the most common rocks in the studied area. Up to date systematic studies, mostly of the Central part ore body, have identified the following minerals within the Buchim deposit: pyrite, chalcopyrite, magnetite, rutile, sphene, titano-magnetite, ilmenite, hematite, specularite, pyrrhotite, valerite, cubanite, sphalerite, galena, bismuthinite, bornite, enargite, native gold, chalcocite etc. (Serafimovski, 1990).

From numerous performed analyses of pyrite it was confirmed that it shows the usual composition with around 52–53 % S and 47 % Fe. Only in few samples was determined presence of nickel (0.09-1.42% Ni) and cobalt (0.27-1.64% Co) which substitute the iron in the mineral structure. Opposite to them were determined increased concentrations of arsenic in pyrites from 0.15-0.22% As (Serafimovski et al., 2008), as well as zinc, 0.22-0.37% Zn (Serafimovski et al., 2013). Opposite to the pyrite composition above, the composition of chalcopyrite is highly pure. Its composition is in conformity with those given by Criddle and Stanley (1986), while the structural formula calculations have shown that the chalcopyrite formula could be written as $Cu_{(0.99–1.06)}$ $Fe_{(0.99–1.03)}$ $S_{(1.91–2.02)}$, which is equal with the idealized one $CuFeS_2$. However, there was determined some arsenic presence (0.002-0.108% As) as well as zinc (0.35-0.44% Zn), vanadium (0.22-0.45% V), nickel (0.33-0.48% Ni) etc. (Serafimovski et al., 2013).

Tailing dam material have shown that it has its own specifics such are some of the heavy metal contents. Some them were as follows: 3-10 mg kg^{-1} Cd, 119-382 mg kg^{-1} As, 19-64 mg kg^{-1} Co, 57-89 mg kg^{-1} Cr, 8-60 mg kg^{-1} Ni, 33-225 mg kg^{-1} Pb, 34-96 mg kg^{-1} Zn and 260-8187 mg kg^{-1} Cu (Gjorgiev, 2012).

2.2. Soil sampling and analysis

Sampling was carried out at the beginning of February 2010. Soil surface samples (0 cm to 5 cm depth) were collected in around the Buchim Mine and its surrounding region (Fig. 1). The samples were taken from 0-5 cm depths because pollutants are coming usually as result of the wind rose that of direction NW-SE and bring pollutants from waste dump and tailing dam. Also, the major part of the area of consideration is built of Precambrian rocks where it is hard to enter deeper in the rock, more than 5-7 cm. We have sampled and analyzed 25 samples from 25 locations around the famous copper producing Buchim copper Mine area of 14.2 km^2.

Sampling was done according to the method described by Serafimovski et al. (2015) applying Global Positioning System and topographic maps at scale of 1:25,000. The composite material of each sample (about 0.5 kg) was placed into plastic self-closing bags and brought to the Faculty of Natural and Technical Sciences, University “Goce Delcev” Stip, Republic of Macedonia, where they were prepared for the analysis.

All of the collected soil samples were then shipped to the Institute of Chemistry at the Faculty of Science, Ss. Cyril and Methodius University, Skopje, R. Macedonia. Atomic emission spectrometry with inductively coupled plasma (ICP-AES) after total digestion with HNO_3, HF, $HClO_4$ and HCl was used for the analysis of the samples from the area of interest. To avoid any laboratory bias, drift or miscon-duct, samples were distributed to the laboratory in a random order (25 samples, 3 replicates as well as 4 standards/blank probes). Precision estimate was performed by eleven samples selected in random order, also. The precision was less than 5%.

2.3. Statistical 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.

3. Results and discussions

3.1. Descriptive statistics

The latest study of soils around the Buchim mine complex was performed on 25 locations and for each sampling point samples were analyzed for a geochemical package of 20 elements (Table 1). Elements such are iron, manganese, chromium, vanadium, nickel, cobalt, which display slightly elevated concentrations, but without any significant impact, as well as elements such are Al, Ca, Na, Ba, Sr, etc. being direct product of geological setting and without any anthropogenetic enrichment (Table 1). These results are in agreement with those obtained by Balabanova et al. (2013) from the study of soil pollution in the wider region of Radoviš and its environ where As, Cu, Pb, V and Zn were determined as anthropogenetic elements due to the mining and ore processing activities in Buchim plant.

These areas are especially pronounced in the main polluted area around flotation on the east and south western parts of the area. The high contents of Cu and Pb are not only due to mining works, but also the town works, traffic, industry and developed technological processes which aloud emission of higher amounts of these metals in air (Balabanova et al., 2009, 2010, 2011a, 2011b, 2013; Stafilov et al., 2010c).

As it can be seen from the results given in Table 1, there were analyzed 20 elements and their minimal, maximal, average and referent values according to the New Dutchlist (http://www.contaminated-land.co.uk/std-guid/dutch-l.htm), are given.

3.2. Correlation analysis

Data from geochemical analyzes were statistically processed in regular Excel calculations procedure going through the Data menu choosing Data analysis option with an array of Analysis tools continuing with Correlation and selected data range for that particular type of data analysis. The results of correlation analysis are displayed in Table 2.

Table 1. Elemental concentration and statistical data from the soil samples around the Buchim copper mine compared with the optimal and intervention values according to the Dutch list

Sample	Fe	Mg	As	Ba	Cd	Co	Cr	Cu	Li	Mn	Ni	Pb	Sr	V	Zn
P-1	4.14	1.45	180	194	3.57	18.5	127	46.3	0.13	717	34.2	659	88.7	134	746
P-2	4.68	1.97	53.0	131	1.52	22.3	171	39.5	0.15	832	45.6	229	104	144	307
P-3	3.36	1.15	51.1	317	1.87	12.9	50.0	33.9	0.16	599	24.4	208	90.6	83.5	279
P-4	3.35	1.28	13.1	283	0.75	14.4	78.8	38.3	0.13	649	29.6	101	106	81.7	157
P-5	3.68	1.28	225	370	4.72	13.6	86.8	41.3	0.19	670	32.6	104	110	92.4	170
P-6	4.27	1.51	44.6	242	2.41	14.6	114	39.9	0.25	683	24.8	111	92.5	141	162
P-7	3.28	0.58	39.7	256	2.96	11.6	82.4	32.5	0.09	533	23.7	370	35.3	72.6	472
P-8	3.64	0.67	44.6	355	0.70	12.9	96.0	36.8	0.13	528	31.9	76.0	31.7	86.7	132
P-9	1.62	0.31	39.7	257	2.34	11.1	55.8	19.7	0.13	315	17.1	144	26.1	42.7	162
P-10	0.73	0.12	135	168	17.9	3.62	30.1	41.5	0.08	206	9.8	3465	17.6	14.0	3438
P-11	1.46	0.37	49.5	235	1.07	9.98	45.4	33.6	0.13	375	20.2	141	30.4	39.3	197
P-12	1.74	0.30	39.9	271	1.84	7.18	57.4	28.6	0.13	165	14.9	186	27.3	42.5	218
P-13	2.00	0.52	37.6	308	1.87	11.8	65.1	23.9	0.14	442	21.4	155	51.3	48.7	199
P-14	3.28	1.17	34.3	240	1.52	11.3	80.4	33.6	0.10	551	25.4	69	78.9	99.9	110
P-15	2.94	0.93	54.4	472	1.14	10.2	63.2	1734	0.11	605	30.4	116	116	76.5	122
P-16	2.16	0.41	127	388	0.76	8.95	33.8	63.0	0.08	484	17.4	175	43.6	36.3	88
P-17	3.06	0.77	82.8	485	1.61	11.5	48.5	276	0.07	549	22.6	103	128	79.5	91
P-18	3.15	0.89	67.4	459	0.75	12.9	49.5	261	0.09	789	26.1	115	132	76.6	93
P-19	2.59	0.83	70.7	370	0.99	9.45	56.6	76.1	0.09	378	21.1	158	92.5	58.9	139
P-20	2.53	0.63	20.9	377	0.88	9.80	68.3	65.2	0.15	242	33.3	108	47.3	69.1	136
P-21	4.53	1.45	68.8	198	0.67	14.3	108	49.5	0.10	773	43.1	55.1	83.1	133	123
P-22	5.02	1.92	25.8	252	0.69	16.3	159	51.1	0.07	998	69.4	61.5	117	126	111
P-23	4.64	1.16	47.3	352	0.84	17.5	76.2	109	0.08	779	44.0	169	80.1	109	118
P-24	2.42	0.80	19.1	444	0.73	9.03	48.8	17.8	0.15	338	25.3	46.0	77.5	61.4	94.8
P-25	4.43	1.80	26.3	193	0.67	14.0	165	34.5	0.23	618	50.4	81.7	87.6	141	132
Min	0.73	0.12	13.1	131	0.67	3.62	30.1	17.8	0.07	165	9.8	46	17.6	14	88
Max	5.02	1.97	225	485	17.9	22.3	171	1734	0.25	998	69.4	3465	132	144	3438
Average	3.15	0.97	63.9	305	2.19	12.4	80.7	129	0.13	552	29.5	288	75.8	83.6	320
Optimal	1.8	-	29	160	0.8	9	100	366	-	33	35	85	-	42	140
Action	-	-	55	625	12	240	380	190	-	-	210	530	-	250	720
Above optimal	21	0	20	24	17	22	6	16	0	25	5	19	0	22	12
Above action	0	0	7	0	1	0	0	3	0	0	0	1	0	0	1

Note: All data for elemental concentration (except for Fe and Mg, %) are given as mg kg^{-1}

Table 2. Matrix of correlation coefficients in soil samples (n=25) around the Buchim copper mine

Al	1.00																		
Ca	0.93*	1.00																	
Fe	0.82*	0.76*	1.00																
K	-0.74*	-0.76*	-0.87*	1.00															
Mg	0.94*	0.93*	0.91*	-0.86*	1.00														
Na	0.30	0.22	-0.04	0.08	0.20	1.00													
As	0.20	0.08	-0.04	0.20	-0.03	0.18	1.00												
Ba	-0.32	-0.49**	-0.17	0.40**	-0.31	0.06	0.00	1.00											
Cd	-0.14	-0.15	-0.42	0.41**	-0.32	0.18	0.47**	-0.32	1.00										
Co	0.77*	0.78*	0.85*	-0.75*	0.82*	-0.04	0.00	-0.29	-0.42**	1.00									
Cr	0.77*	0.85*	0.81*	-0.83*	0.86*	-0.14	-0.09	-0.55*	-0.23	0.77	1.00								
Cu	-0.07	-0.08	-0.02	0.14	-0.02	0.19	-0.02	0.45**	-0.08	-0.11	-0.13	1.00							
Li	0.34	0.43**	0.20	-0.20	0.34	-0.03	-0.04	-0.24	-0.11	0.21	0.38	-0.15	1.00						
Mn	0.83*	0.71*	0.88*	-0.73*	0.83*	0.16	0.08	-0.11	-0.33	0.83*	0.66*	0.10	-0.01	1.00					
Ni	0.69*	0.66*	0.84*	-0.75*	0.82*	0.04	-0.16	-0.21	-0.37	0.71*	0.82*	0.01	0.08	0.76*	1.00				
Pb	-0.19	-0.15	-0.42**	0.39	-0.33	0.17	0.36	-0.34	0.97*	-0.42**	-0.23	-0.07	-0.22	-0.33	-0.33	1.00			
Sr	0.73*	0.58*	0.63*	-0.47**	0.70*	0.49**	0.09	0.31	-0.33	0.53*	0.35	0.33	0.04	0.72*	0.49**	-0.36	1.00		
V	0.86*	0.85*	0.95*	-0.88*	0.94*	0.01	-0.04	-0.33	-0.35	0.84*	0.87*	-0.04	0.37	0.80*	0.77*	-0.36	0.59*	1.00	
Zn	-0.17	-0.12	-0.40**	0.36	-0.31	0.15	0.36	-0.37	0.97*	-0.39	-0.20	-0.08	-0.19	-0.32	-0.31	1.00*	-0.36	-0.34	1.00
		Ca	Fe	K	Mg	Na	As	Ba	Cd	Co	Cr	Cu	Li	Mn	Ni	Pb	Sr	V	Zn

** Marked correlations are significant at p <0 .01000 N=25*
Marked correlations are significant at p <0 .05000 N=25

From Table 2 it can be seen that 13 were included elements in the whole correlation calculation, which pointed out two correlation elemental suites (Fig. 3). The first elemental association, Cd-Pb-Zn, was characterized by the following correlation coefficients: Cd-Pb of 0.967, Zn-Pb of 0.998 and Zn-Cd of 0.970. Such high correlation coefficients, especially for Zn and Cd, can be attributed to their primary sources. The second elemental association, Ni-Co-Cr, was characterized by the following correlation coefficients: Ni-Co of 0.708, Ni-Cr of 0.821 and Co-Cr of 0.773, which are in the upper range of positive correlation values, also. This was confirmed by Serafimovski et al. (2015), also. All these correlation coefficients are relatively high and reflect the clear geochemical relationship of these elements, which basically belong to ultramafites or they are metals that are representative of primary mantle (oceanic crust).

However, here we are dealing with their anthropogenic input in soils around the Buchim mine, which clearly indicates their connection with the processing of copper ore from the mine, which in turn seems a fact that copper is the metal of oceanic crust.

3.3. Factor analysis

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. With factor analysis the distribution was reduced to three synthetic variables, which showed linkage in terms of geochemical similarities, and which included 74.9% of the variability of analyzed elements. The factor analysis singled out three geochemical associations of elements. The values of factor loadings are presented in Table 3.

Geochemical association (Al-Ca-Fe-K-Mg-Co-Cr-Mn -Ni-Sr-V) interpreted as Factor 1 is a geogenic factor. Their origins are related primarily to the dusting of sediments and gneises formations (Pleistocene sediments, Precambrian gneises). A similar situation had been previously determined for the territories of Macedonia and Kosovo (Stafilov et al., 2010b, 2010c, 2014; Stafilov and Šajn, 2016; Šajn et al., 2013).

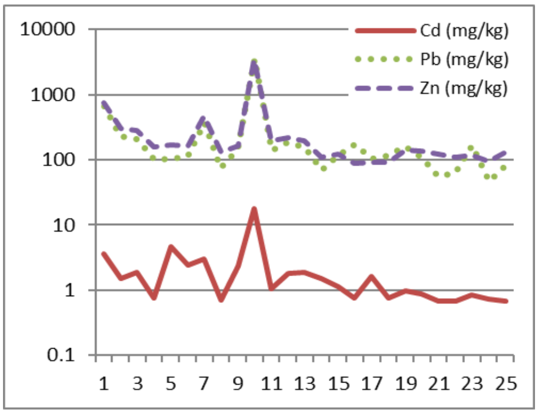
Geochemical association (As-Cd-Pb-Zn) or Factor 2 associates anthropogenetic elements. This factor group accounts for 19.2% of total data variability. Higher values, as in the case of F1, are related to dusting. Arsenic is also included in this association although F2 score is only -0.45. because the tailing dam material have already shown high As contents (119-382 mg kg^{-1}).

Factor 3 (Na-Ba -Cu-Sr) and is least expressed natural factors (9.5% of the total variability of the data). Their occurrence is related primarily to the enrichment of the deeper horizon (B – clay accumulated). Empirically, these elements could be related to the decomposition of rocks, especially Proterozoic gneises and amfibolites.

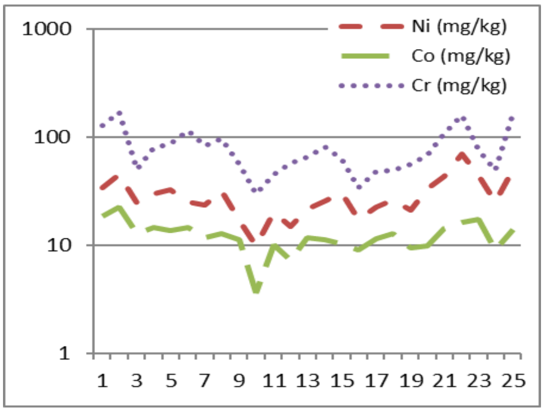
3.4. Distribution of particular anthropogenic elements

Distribution of particular anthropogenically introduced elements is given as follows:

Arsenic (As). Natural occurrence of arsenic is due to its participation within sulfides (arsenopyrite-FeAsS, realgar-As_4S_4, orpiment-As_2S_3). Ingestion of As could lead to severe exposure, which may result in medical problems of digestive and nervous systems, heart activity as well as several types of cancers (lung, skin or liver (Goyer, 1996; Frumkin and Gerberding, 2007). Natural and anthropogenic As contamination has been reported in numerous areas around the World and had been accepted as global environmental issue. Numerous authors pointed out that major sources of anthropogenic As contamination are lead-zinc, gold and other types of mining, As processing and smelting of base metals (Bačeva et al., 2014; Stafilov et al., 2010a, 2010d). The average amount of As in the world's soils is 5 mg kg^{-1} (Bowen, 1979), and in the European topsoil is 12 mg kg^{-1} (Salminen et al., 2005).



(a)



(b)

Fig. 3. Correlation diagrams for the geochemical suite one Cd-Pb-Zn (a) and suite two Ni-Co-Cr (b) from the soil analytical data around the Buchim copper mine

Table 3. Matrix of dominant rotated factor loadings

	F1	***F2***	***F3***
Al	0.945262	-0.052745	0.211686
Ca	0.939539	-0.068074	0.006680
Fe	0.905926	0.282814	0.059554
K	-0.860982	-0.256987	0.178701
Mg	0.971518	0.131635	0.109750
Na	0.123675	-0.256551	0.558617
As	0.047949	-0.456336	0.263480
Ba	-0.423471	0.407507	0.568237
Cd	-0.190078	-0.965342	-0.020534
Co	0.850811	0.247638	-0.026307
Cr	0.898249	0.081522	-0.297139
Cu	-0.098954	0.121779	0.523626
Li	0.301404	0.074968	-0.247080
Mn	0.834708	0.171962	0.318453
Ni	0.799595	0.229941	0.016715
Pb	-0.202406	-0.960176	-0.043735
Sr	0.585824	0.214038	0.684939
V	0.943862	0.191386	-0.033584
Zn	-0.172873	-0.966037	-0.076606
Expl.Var	8.787521	3.651249	1.801129
Prp.Totl	0.462501	0.192171	0.094796

The average amount of As in the topsoil for the entire study area is 63.9 mg kg^{-1}, with a range of 13.1-225 mg kg^{-1} (Table 1, Fig. 4). This is 2.8 times higher than the larger area of the same locality (Balabanova et al., 2013).

As it is presented on Fig. 4 arsenic concentrations at particular sampling points were higher than optimal as well as over the action values according the New Dutchlist. Due to its natural and anthropogenic presence arsenic showed high values around the waste dump and flotation dam of which both are left open to atmospheric factors. As a direct consequence to that fact an arsenic contamination, especially in the vicinity of tailing dam, strongly reflects the influence of the wind rose. Outflow from the flotation dam and dry riverbed draining the Buchim Mine were detected as highly arsenic contaminated with 51-225 mg kg^{-1}As and 67.4-82.8 mg kg^{-1}As, respectively. This very similar to the findings of Serafimovski et al. (2015). According to this data, it is evident that the source of high arsenic in this region is directly related with processing of copper ores in the Buchim mine. In the mineral association of the Buchim deposit it was determined one phase of low-temperature pyrites, which in its chemical composition have up to 2.5% As (Serafimovski et al., 2008). During the processing of ore, probably one part of that arsenic has been released and distributed into the adjacent environment.

Cadmium (Cd) is a heavy metal that is dispersed throughout the modern environment mainly as a result of pollution from a variety of sources (Bhattacharyya et al., 2000; Järup et al., 1998). Cadmium is produced mainly as a by-product from mining, smelting, and refining sulphide ores of zinc, and to a lesser degree, lead and copper. The metal has no known beneficial biological function and prolonged exposure to this element has been linked to toxic effects in both humans and animals (Zadorozhnaja et al., 2000). Cadmium and cadmium compounds are, compared to other heavy metals, relatively water soluble. They are therefore also more mobile in e.g. soil, generally more bioavailable and tend to bioaccumulate.

The average amount of Cd in soils in the world is 0.35 mg kg^{-1} (Bowen, 1979), in the European topsoil is 0.12 mg kg^{-1} (Salminen et al., 2005). The average amount of Cd in the topsoil for the entire study area is 2.19 mg kg^{-1}, with a range of 0.67-17.9 mg kg^{-1} (Table 1). In the main polluted area, the average content of Cd is more than 18-times higher than the European Cd average and up to 6.3 times more than average in non-polluted areas in Macedonia (Stafilov et al., 2010a, 2010b). It is evident from the obtained results (Table 1, Fig. 5) that the content of cadmium is very high in topsoils from the areas of the copper mine facilities, as well as in the topsoils from the flotation tailings dam vicinity.

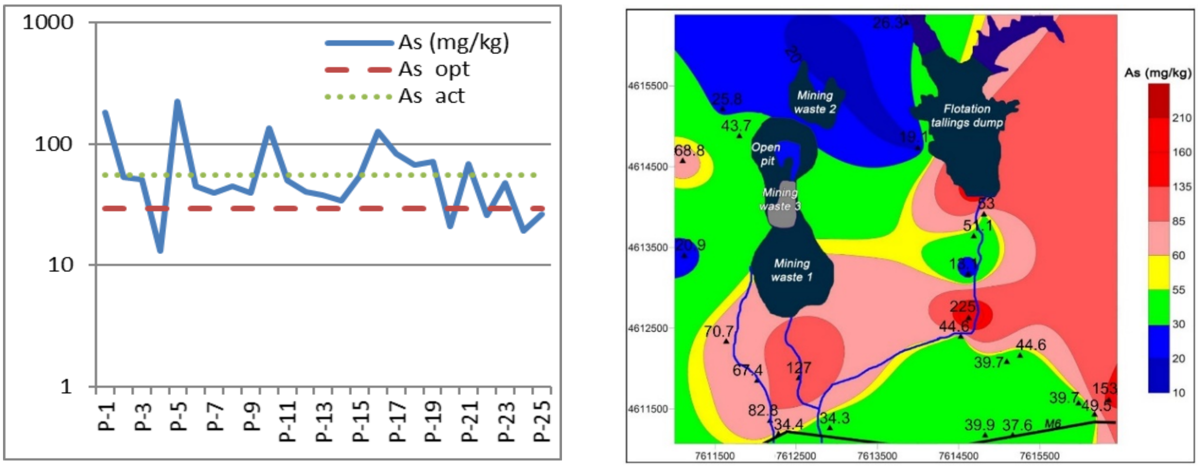
In the investigated region several topsoil samples with extremely high content of cadmium are present. It should be noted that the content in sample No. 10 of 17.9 mg kg^{-1} is 150-times higher than the European topsoil average of 0.12 mg kg^{-1}. These higher contents of cadmium in soil samples are the result of anthropogenic origin where cadmium inputs from mine industrial complexes as it was confirmed elsewhere (Šajn et al., 2011).

***Copper (Cu)*.** The most important statement on Cu contamination of soils is the great affinity of surface soils to accumulate this metal. Soil contamination by Cu compounds, which has been the subject of detailed studies for several decades confirmed several significant sources: fertilizers, sewage sludge, manures, agrochemicals, industrial by-product wastes etc., that have contributed to increased Cu levels. However, the highest increased levels of Cu are observed in soils surrounding Cu mines and smelters (Kabata-Pendias and Pendias, 2001). As Cu is only slightly mobile under most soil conditions elevated contents may persist for a long time. The average amount of Cu in the world's soils is 30 mg kg^{-1} (Bowen, 1979), in the European topsoil is 17 mg kg^{-1} (Salminen et al., 2005), in Macedonia is 32 mg kg^{-1} (Stafilov and Šajn, 2016) and in wide area of Radoviš is 59 mg kg^{-1} (Balabanova et al., 2013). The average amount of Cu in the topsoil for the entire study area is 129 mg kg^{-1}, with a range of 17.8-1734 mg kg^{-1} (Table 1, Fig. 6).

As can be seen, we found that there is not significant difference in copper concentrations from analyzed mine and flotation areas (Table 1; Fig. 6) excluding three sites (sample 15, 17 and 18 positions) located in the open pit draining system (dry riverbed). An average copper concentration within the most polluted area surpasses European average values by 15.3 times and Macedonian average by 8.2 times.

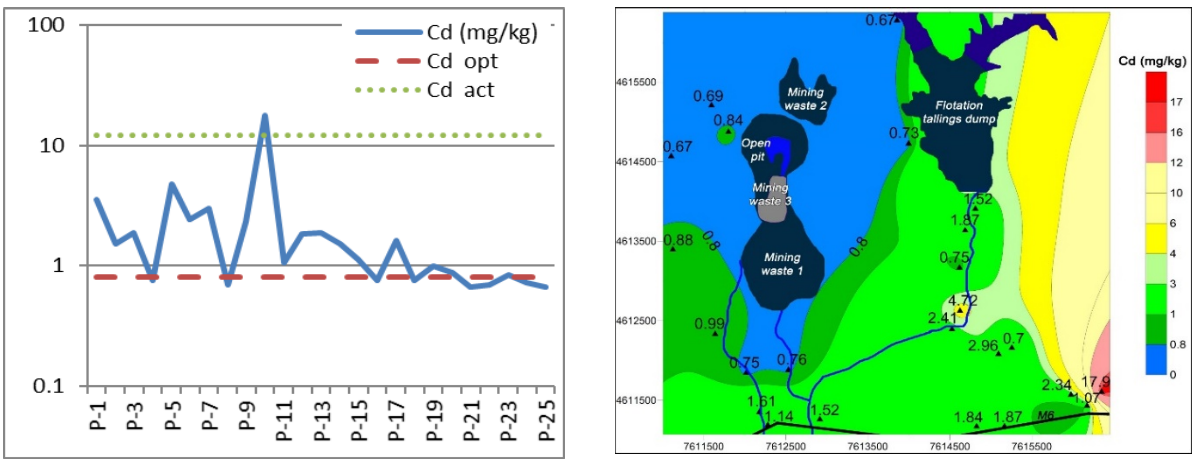
We would like to stress out that the most copper contaminated areas are those within the dry riverbed in the adjacent vicinity of the Buchim mine.

Lead (Pb). In mining areas, Pb may be dispersed due to the erosion and chemical weathering of tailings. The severity of these processes depends on chemical characteristics, and the minerals present in the tailings (Kabata-Pendias and Pendias, 2001). In general, several observations of Pb balance in various ecosystems show that the input of this metal greatly exceeds its output. The strong Pb adsorption in soils may mean that Pb additions to soil are permanent and irreversible. The average amount of Pb in the world's soils is 35 mg kg^{-1} (Bowen, 1979), in the European topsoil is 33 mg kg^{-1} (Salminen et al., 2005), in Macedonia is 95 mg kg^{-1} (Stafilov and Šajn, 2016) and in wide area of Radoviš is 30 mg kg^{-1} (Balabanova et al., 2013). The average amount in the topsoil for the entire study area is 288 mg kg^{-1}, with a range of 46–3465 mg kg^{-1} (Table 1). Similarly to cadmium distribution, the differences between the content of lead in the studied areas are very significant (Table 1, Fig. 7).



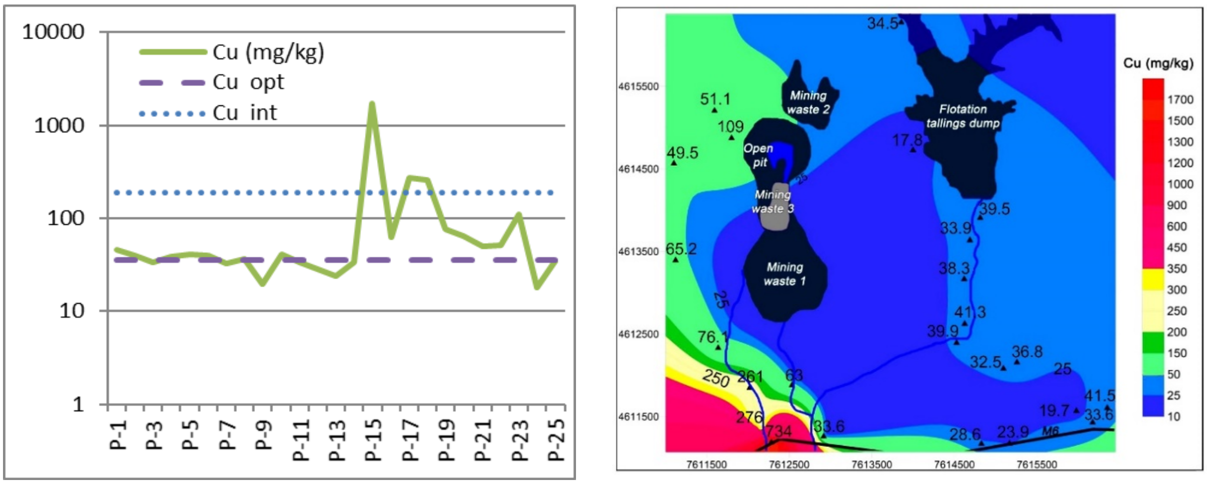
(a) (b)

Fig. 4. (a) Diagram of arsenic distribution in the soil compared with optimal (opt) and action values (act); (b) spatial distribution map of arsenic in soil



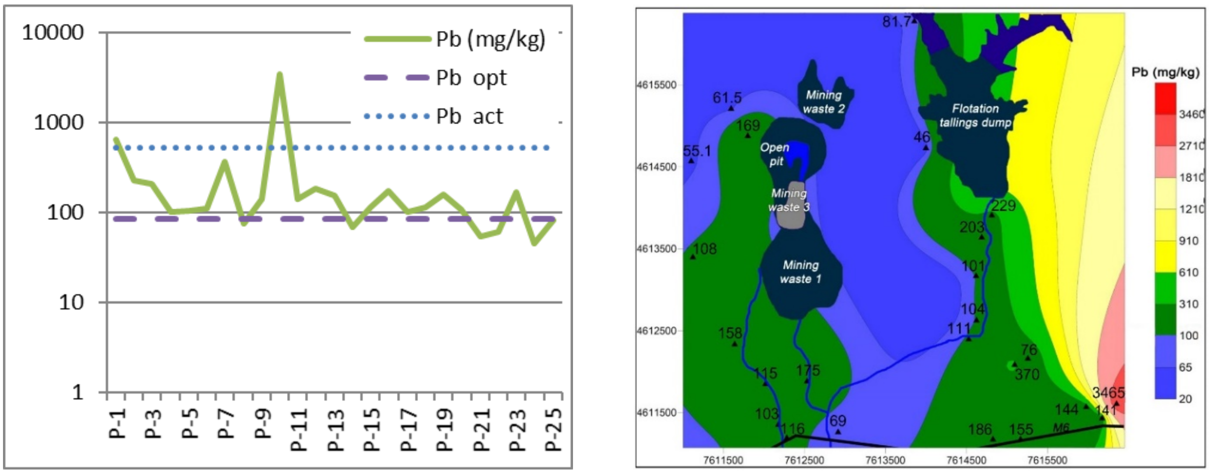
(a) (b)

Fig. 5. (a) Diagram of cadmium distribution in the soil compared with optimal (opt) and action values (act); (b) spatial distribution map of cadmium in soil



(a) (b)

Fig. 6. (a) Diagram of Cu distribution in the soil compared with optimal (opt) and action (act) values; (b) spatial distribution map of copper in soil

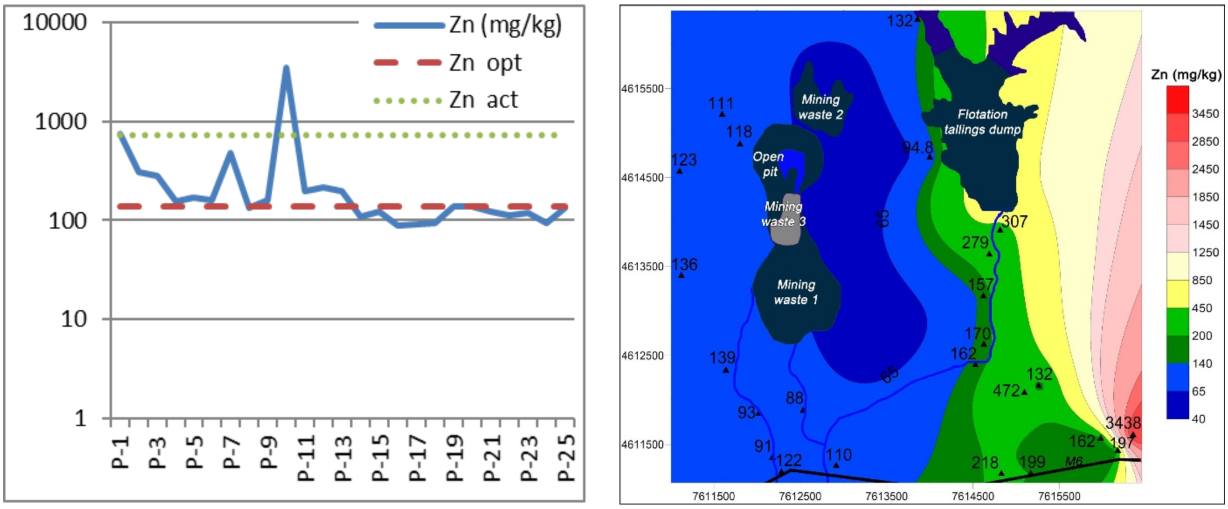


(a) (b)

Fig. 7. (a) Diagram of lead distribution in the soil compared with optimal and action values; (b) spatial distribution map of lead in soil

In the main polluted area, the average concentration of Pb is 8.7-times higher than the European Pb average and Macedonian average for 6.5-times. Although the average content of lead in the topsoil for the entire study area was found to be about 288 mg kg^{-1}, there are areas with very high contamination, as it was for example, for the main polluted area (sample 10) with content of 3465 mg kg^{-1} (Table 1). The highest values for Pb content were established in the topsoils in the eastern and south-western part of an area.

Zinc (Zn). The most important anthropogenic sources of Zn are the metallurgy industry, burning of fossil fuels, mines and Zn ore processing (Aliu et al., 2010). Zn is an essential element for most living organism (plants, animals and humans) with important role in enzymes processes and cellular metabolism, in immune function, protein synthesis, DNA synthesis, and cell division and daily intake of zinc is required to maintain a steady state because the body has no specialized zinc storage system (Rink and Gabriel, 2000). Even the toxicity of Zn is relatively low, there are cases when poisoning with Zn can occur in both acute and chronic forms (Prasad, 1995). The average amount of Zn in the world's soils is 90 mg kg^{-1} (Bowen, 1979), in the European topsoil is 68 mg kg^{-1} (Salminen et al., 2005), in Macedonia is 140 mg kg^{-1} (Stafilov and Šajn, 2016) and in Radovis area (including Buchim mine area) is from 59 to 70 mg kg^{-1} (Balabanoska et al., 2013; Jordanoska et al., 2018). The average Zn amount in the topsoil for the entire study area is 320 mg kg^{-1}, with a range of 88-3438 mg kg^{-1} (Table 1). For the main polluted area, the average concentration of Zn is 4.7-times higher than the European Zn average and Macedonian average for 10.1-times. Similarly, to the findings for lead, although the average content of zinc in the topsoil for the entire study area was found to be about 320 mg kg^{-1}, there are areas with very high level of contamination (Table 1, Fig. 8).



(a) (b)

Fig. 8. (a) Diagram of zinc distribution in the soil compared with optimal and action values; (b) spatial distribution map of zinc in soil

4. Conclusions

Summarizing the obtained findings within this study we may conclude that around the Buchim Mine there are two areas contaminated with heavy metals. One of them, characterized by increased values of Pb, Zn, Cd and Co, addresses soils around the tailing dam. The second one, characterized by increased values of Cu, As, Cr and V, addresses soils around the waste dump.

These contaminations coincide with the so-called rose of winds in the Buchim mine area and display reflection through increased concentrations of above mentioned metals in soil, air and water.

Two basic geochemical elemental suites were determined, Pb-Zn-Cd and Ni-Co-Cr. Those groups were characterized by correlation coefficients Cd-Pb 0.967, Zn-Pb 0.998 and Zn-Cd 0.970 for the first one, as well as Ni-Co 0.708, Ni-Cr 0.821 and Co-Cr 0.773 for the second one. Although expected, we did not find that copper makes any geochemical pair with some other elements with elevated concentrations. Nevertheless, it constantly showed increased concentrations, which undoubtedly can be related to the porphyry copper ore from the Buchim Mine and its processing in that area for a longer period, while metal deposition in soil the most frequently comes through the airborne contamination.

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