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## TOTAL DEPOSITED DUST AS A REFLECTION OF HEAVY METALS DISTRIBUTION IN AREA WITH INTENSIVELY EXPLOITED COPPER MINERALS

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**A b s t r a c t:** The “Bučim” copper mine environ was monitored for assessing the heavy metals distribution. For that issue characterization of 17 elements content in total deposited dust was performed. The element contents were determinate using atomic emission spectrometry with inductively coupled plasma (ICP-AES). Bučim and Topolnica Villages and the town of Radoviš were chosen as sampling spots. It was determinate that in some period's trough the year large amounts of dust deposits in mine environ. The annual average values of dust deposition in the villages of Bučim and Topolnica are  $489 \text{ mg m}^{-2} \text{ d}^{-1}$  and  $309 \text{ mg m}^{-2} \text{ d}^{-1}$ , respectively. Maximum value for the total deposited dust ( $815 \text{ mg m}^{-2} \text{ d}^{-1}$ ) was obtained at the sampling site in the Bučim village. The close vicinity of the Radoviš town was not exposed on dust deposition ( $97 \text{ mg m}^{-2} \text{ d}^{-1}$ ). Characterization of elements contents showed higher contents of some heavy metals (with emphasis on Cu and Pb) in deposited dust. Maximum value for the content of Cu was obtained in dust from Topolnica village ( $1183 \text{ mg kg}^{-1}$ ) and maximum value for Pb content was obtained in deposited dust from Radoviš.

**Key words:** air pollution; monitoring; heavy metals; total deposited dust; copper mine; Republic of Macedonia

### INTRODUCTION

Emissions of heavy metals into the environment happen through several processes. The emission of heavy metals into the atmosphere is one of the greatest threats to human health. Large amounts of dust are generated during blasts and excavations of mining minerals, whereas they are distributed in the air by the winds. People are directly exposed to the effects of heavy metals through inhalation of airborne micro-particles from atmospheric dust (Jarup, 2003; Godish, 2004). Atmospheric particles affect the human health when they enter into the respiratory system. The polluted air slows down the development of pulmonary functions in children (Gauderman et al., 2000; Gauderman et al., 2004). Senior citizens, especially those with a weakened cardiovascular and respiratory system are a high risk group too. Another risk group is patients with chronic pulmonary emphysema, asthma or cardiovascular diseases (Vallero, 2008).

Heavy metals in the atmosphere originated mainly from dust dispersion from metal refining, fossil fuel combustion, vehicle exhausts, and other human activities and stay in the atmosphere until they are removed by a variety of cleansing processes (Agarwal, 2009). Particular emphasis is given on ore deposits, mining, processing and flotation plants as significant anthropogenic sources of dust. Copper mine with open ore pit type present a potentially emission source of heavy metals in the air. Main processes that allow it are: minerals blasting, drilling and crushing, their loading and transportation to processing and flotation plants. From other hand, large amounts of ore waste and flotation tailings are deposited at open, continuously exposed to air flow and winds caring-out. Heavy metals emitted in the atmosphere by combustion processes usually have relatively high solubility's and reactivity's; especially under low-pH condition (Athar and Vohora, 1995; Hršak et al., 2003; Hou et al.,

2005). They can be carried to places far away from the sources by wind, depending upon whether they are in gaseous form or as particulates. Metallic pollutants are ultimately washed out of the air by rain and deposited on the land.

Total deposited dust is commonly used as monitor for this purpose. These kind of monitoring have been performed as part of a large number of analytical studies for a long time, but their application in recent decades has taken a swing. This is due to the fact that monitoring does not require the use of expensive technical equipment. Analytical results reflect the real situation of heavy metal distribution in the investigated area.

Deposited dust refers to any dust that falls out of suspension in the atmosphere. Solid and liquid particles or dust that falls out of suspension in the atmosphere can get into the environment and lead

to its contamination. Atmospheric total deposition (deposited dust) is very useful mechanism for monitoring the fate of anthropogenic elements introduced into the atmosphere (Čačković et al., 2009). Fine powder with a high content of heavy metals is generated as a result of emissions from the ore processing and metallurgical process and is distributed as a result of wearing the wind. Many investigations have focused on the chemical composition and the content of toxic substances in deposited dust (Morselli et al., 2003; Avila and Rodrigo, 2004; Polkowska et al., 2005; Vike, 2005; Stafilov et al., 2010).

In order to determine the amount of fine dust contained in the air, samples of total deposited matter (deposited dust) were collected at three locations in the area of Bučim copper mine, Republic of Macedonia.

## INVESTIGATED AREA

Investigations were conducted in the eastern part of the Republic of Macedonia (Fig. 1), where the appearance of some metals (Au, Mg, Al, Sc, Ti, V, Cu) in the air is related to the presence of a copper mine and flotation plant, "Bučim", near the town of Radoviš (Barandovski, et al., 2008; Balabanova et al., 2009, 2010, 2011; Stafilov et al., 2010). In this area an influence from the former iron mine, Damjan, has also been determined (Serafimovski et al., 2005). As a result of these anthropogenic activities, distribution of certain heavy metals in air and their deposition in the environs were expected. Moderate continental climate characterized the region of the study area. The altitude varies between 350 and 1000 m. The average annual temperature is around 10°C. The average annual rainfall amounts to 563 mm with large variations from year to year. The most frequent winds in the region are those from the west with a frequency of 199 ‰ and speed of 2.7 m s<sup>-1</sup>, and winds from the east with a frequency of 124 ‰ and speed of 2.0 m s<sup>-1</sup> (Lazarevski, 1993).

The "Bučim" mine and the ore processing plant have been functioning since 1979 and it is assumed that the mine has about 40 million tons of ore reserves. Ore tailings are dropped out by the dampers from the open ore pit at open site near the mine. The ore tailings deposit occupies a surface of 0.80 km<sup>2</sup>, located southwest of the open ore pit, near the regional road Štip–Strumica. The ore tailings deposit has about 130 million tons of ore tail-

ings. Exposure of this great mass of ore tailings to constant air flow and wind, leads to the distribution of large amounts of dust in the air. The flotation plant produces 4,000,000 tons of copper ore annually. In the process of flotation of copper minerals, the average annual amount of flotation tailings created is approximately 3.95 million tons. These tailings are drained and disposed of on a dump near the mine (2.2 km).

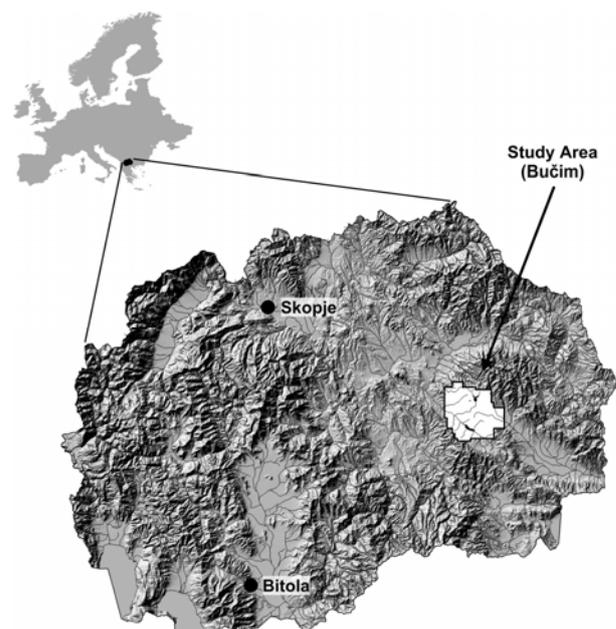


Fig. 1. Location of study area

### Geological description

At the study area the following main geotectonic structural units have been identified: (1) the Kriva Lakavica basin, the Smrdeš–Gabreš syncline, the Radoviš basin, the Radoviš anticline divided to the Štip Block and the Bučim Block (Hristov et al., 1965; Stefanova et al., 2004; Stafilov et al., 2010). The Radoviš anticline represents the eastern boundary of the Vardar zone towards the Serbian–Macedonian mass. These two large structural units are separated by a deep NW-SE fault

(Hristov et al., 1965). The Bučim–Damjan–Borov Dol area is divided into two tectonic blocks. The Bučim 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 in the 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 mineralizations. The Bučim copper-porphyry deposit with additional gold mineralization is found in the northern block (Stefanova et al., 2004).

## EXPERIMENTAL

### Sampling and sampling preparation

In order to determine daily amount of deposited dust, samples of total deposited matter (deposited dust) were collected. The town of Radoviš and the Bučim and Topolnica villages (Fig. 2) were the three monitoring spots around Bučim copper mine. The total quantity of the deposited dust was monitored monthly in 2009. Samples of total deposited

matter (wet and dry deposition) were collected using the dust deposition gauges. This method measures dust deposition rate and involves the passive deposition and capture of dust within a funnel and plastic container. Data is usually collected over monthly periods and results are expressed  $\text{mg m}^{-2} \text{d}^{-1}$  (i.e. the mass of dust deposited per  $\text{m}^2$  per day). This method enables determination of the relative ‘dustiness’ of sampling locations.

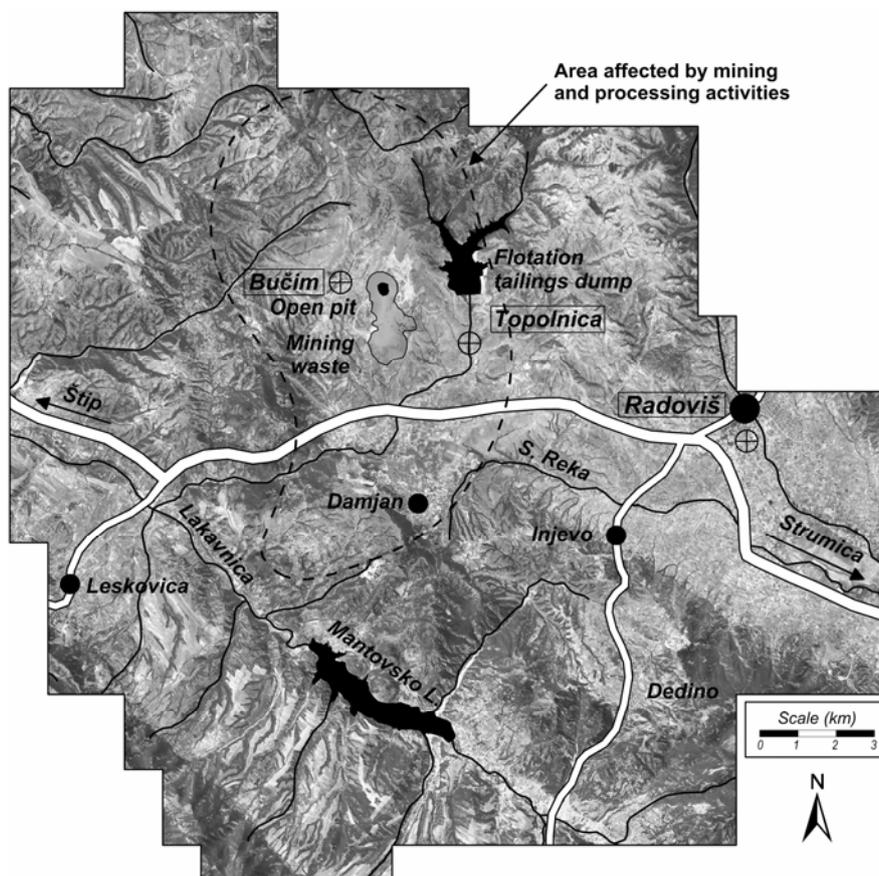


Fig. 2. Location of the sampling points for deposited dust

A deposit gauge, which comprises a  $28 \pm 1$  cm diameter funnel inserted into a plastic container (at least 5–10 liters in size) through a rubber stopper. Stand approximately 2 m tall and a canister which holds the plastic container to protect it from sunlight. The plastic container may also collect rainwater and other material such as bugs and leaf litter, etc. This does not contaminate the sample and should not be removed in the field. After  $30 \pm 2$  days, any deposited matter in the funnel was washed into the plastic container using distilled water. The aliquot of each sample was evaporated near dryness and then 3–5 ml of nitric acid, *p.a.* (MERCK, Germany) was added and collected into the 25 ml volumetric flasks.

### Chemical analysis

Seventeen elements (Al, B, Ca, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, Pb, Sr, V and Zn) were determined by using atomic emission spectrometer with inductively coupled plasma, ICP-AES (Varian 715-ES). The optimal instrumental parameters for this technique were previously given (Stafilov et al., 2010). For ICP-AES instrument calibration and quantitative determination of each element in deposited dust, a commercial standard mix solution

(11355-ICP Multi Element Standard IV, Merck) was used. The correlation coefficient of calibration curve for each element was 0.999. In order to check for possible background contamination, blank samples were used and processed simultaneously with field samples. The method detection limit was calculated based on average measuring of the blank sample. For all laboratory samples and standard solutions, treated ultra pure water was used. The QC of the applied technique was performed by standard addition method, and it was found that the recovery for the investigated elements ranges between 98.5–101.2 %.

### Data processing

For the statistical analysis of data parametric and nonparametric statistical methods were used (Hollander and Wolfe, 1999). The obtained values for the contents of the investigated elements were statistically processed using basic descriptive statistics. Data distribution was examined with the application of normality tests. Line and bar/colon plots were used for better visibility of elements content and trends of dust deposition through the year.

## RESULTS AND DISCUSSION

The amount of total deposited dust that is spread in the air is presented in Fig. 3. It is evident that a large amount of deposited dust were recorded in the close vicinity of the mine (Bučim and Topolnica villages) in some periods in the year where the values are above the maximum permitted amount of dust powder ( $300 \text{ mg m}^{-2} \text{ d}^{-1}$ ). Maximum value for the total deposited dust ( $815 \text{ mg m}^{-2} \text{ d}^{-1}$ ) was obtained in August in the Bučim village. This is the highest value for the amount of total deposited dust compared to the other two places. The annual average for the total deposited dust in the vicinity of the Bučim village is  $489 \text{ mg m}^{-2} \text{ d}^{-1}$ , for Topolnica is  $309 \text{ mg m}^{-2} \text{ d}^{-1}$  and accounted for Radoviš is  $97 \text{ mg m}^{-2} \text{ d}^{-1}$ . A lower value was obtained for the amount of the total deposited dust in Topolnica village environ, while for Radoviš was obtained a much lower value (Fig. 3).

The obtained values for 17 elements content were proceed using descriptive statistics (Table 1). As it can be seen, median values for the copper in deposited dust samples taken from the studied area is  $158 \text{ mg kg}^{-1}$  and the min/max range of values

shows much higher content of this element in the samples from the mining area (ranges from 52 to  $1182 \text{ mg kg}^{-1}$ ). Similar results were obtained for the distribution of Fe, Pb and Zn thereby the median value and the min/max range for these elements indicate their increased content.

Because of high ore content of Cu (0.3 %) and large amount of copper in flotation tailing (Serafimovski et al., 2005) it was expected this element to have significantly higher content in samples of deposited dust compared to the other elements. As it can be seen from the data presented in Table 2, the median values for Cu in samples of deposited dust taken from the Radoviš area is  $396 \text{ mg kg}^{-1}$  and the ranges (from 94.8 to  $1171 \text{ mg kg}^{-1}$ ) for the Topolnica village the median values in samples of deposited dust is  $150 \text{ mg kg}^{-1}$  with ranges (from 52.5 to  $1183 \text{ mg kg}^{-1}$ ) and for the Bučim village the median values in deposited dust samples is  $145 \text{ mg kg}^{-1}$  and the ranges from 85.3 to  $317 \text{ mg kg}^{-1}$ . The maximum value for the content of Cu was obtained from Topolnica village (settlement near by the flotation tailings landfill) (Fig. 4). Even the amounts of deposited dust was

not above the maximum permitted level in the town of Radoviš higher contents of Cu were found at the beginning of the year (max. value was obtained in May), with descending trend to the end of the year. These high contents of Cu are not only due to mining works, but also the town works, the

traffic and industry. The developed technological processes allow emission of higher contents of Cu in the air and its deposition in Radoviš environs. In general, villages are less affected with these potentially emission sources of copper.

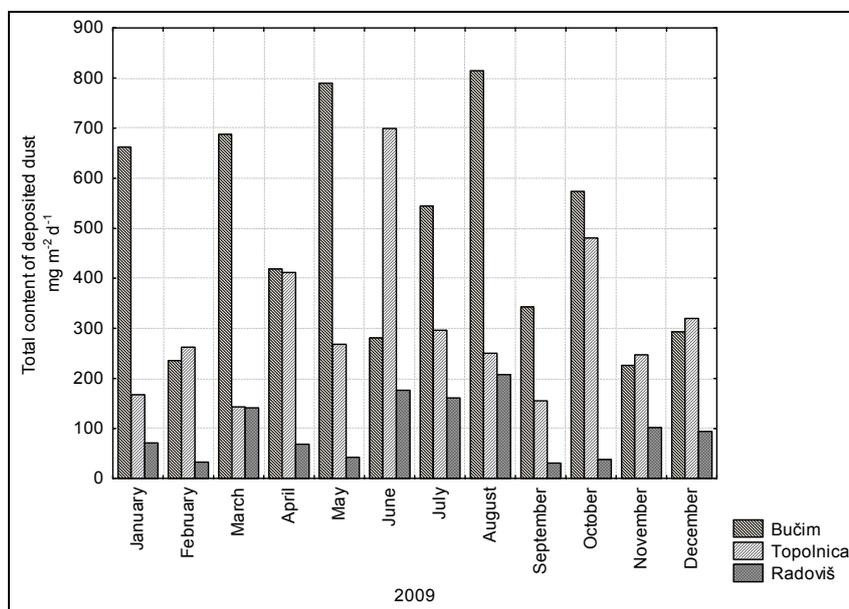


Fig. 3. The total content of deposited dust

Table 1

*Descriptive statistics of measurements (N = 36, 17 elements)*  
*Values of Al, Ca, Fe, K, Mg and Na are in %, remaining elements in mg kg<sup>-1</sup>*

Element	N	X	X <sub>g</sub>	Md	Min	Max	P <sub>10</sub>	P <sub>90</sub>	s	A	E
Al	36	0.2	0.16	0,17	0.02	0.57	0.07	0.3	0.13	1.51	2.16
Ca	36	6.20	4.01	4.17	0.52	21.9	1.01	14.6	5.65	1.30	1.19
Fe	36	0.32	0.26	0.27	0.05	1.00	0.14	0.66	0.20	1.59	2.77
K	36	1.21	0.84	0.77	0.12	6.21	0.28	2.20	1.23	2.62	7.14
Mg	36	0.48	0.44	0.44	0.15	1.36	0.24	0.81	0.24	1.56	3.71
Na	36	0.51	0.35	0.35	0.06	2.42	0.08	1.06	0.48	2.06	5.71
B	36	443	195	188	8.91	3085	38.3	1427	654	2.52	7.02
Cr	36	8.61	6.60	6.69	0.96	41.2	3.17	17.8	7.36	2.75	10.4
Cu	36	310	210	158	52.5	1182	84.1	861	313	1.70	1.95
Li	36	3.70	1.99	2.06	0.27	60.3	0.95	3.83	9.77	5.89	35.1
Mn	36	183	162	151	50.8	459	95.7	362	98.9	1.37	1.53
Mo	36	4.25	2.73	3.59	0.50	15.7	0.50	9.57	3.70	1.37	1.91
Ni	36	21.7	13.5	12.9	1.78	148	5.39	35.3	28.8	3.24	11.5
Pb	36	49.3	35.1	28.6	7.19	189	14.6	122	47.3	1.83	2.61
Sr	36	212	128	132	16.9	887	34.0	572	223	1.59	1.79
V	36	9.35	8.01	7.24	2.31	27.1	4.34	16.8	5.47	1.27	1.76
Zn	36	259	176	149	38.9	1045	72.7	665	275	2.04	3.29

N – number of samples, X – arithmetical mean, X<sub>g</sub> – geometrical mean, Md – median, Min – minimum, Max – maximum, P<sub>10</sub> – 10 percentile, P<sub>90</sub> – 90 percentile, s – standard deviation, A – skewness, E – kurtosis

Table 2

Statistical parameters for annual average of the content of chemical elements in samples of deposited dust (Values of Al, Ca, Fe, K, Mg and Na are in %, remaining elements in mg kg<sup>-1</sup>)

Element	N*	Sampling site					
		Bučim village.		Topolnica village		Radoviš	
		Median	Range	Median	Range	Median	Range
Al	12	0.13	0.02–0.19	0.15	0.07–0.58	0.25	0.16–0.56
Ca	12	9.12	1.74–2.19	1.32	0.53–4.74	7.25	1.56–20.9
Fe	12	0.23	0.05–0.34	0.27	0.10–1.02	0.36	0.14–0.77
K	12	0.76	0.12–4.71	0.86	0.28–6.21	0.69	0.23–2.12
Mg	12	0.43	0.15–0.84	0.34	0.21–0.84	0.48	0.19–1.36
Na	12	0.16	0.06–0.92	0.31	0.08–0.87	0.77	0.24–2.41
B	12	203	8.91–1427	93.4	34.7–305	454	101–3085
Cr	12	4.22	0.96–7.78	6.32	1.74–20.1	12.6	6.42–41.2
<b>Cu</b>	<b>12</b>	<b>145</b>	<b>85.3–317</b>	<b>150</b>	<b>52.5–1183</b>	<b>396</b>	<b>94.8–1171</b>
Li	12	1.17	0.27–2.11	2.13	1.20–5.16	2.79	0.95–60.3
Mn	12	128	50.8–459	148	69.8–411	197	98.4–419
Mo	12	3.53	0.50–6.91	2.51	0.50–12.3	4.18	0.50–15.7
Ni	12	6.94	2.81–14.1	13.5	6.49–27.8	26.9	1.79–148
<b>Pb</b>	<b>12</b>	<b>25.7</b>	<b>12.1–56.6</b>	<b>26.8</b>	<b>7.20–184</b>	<b>69.5</b>	<b>20.1–189</b>
Sr	12	303	70.7–888	46.4	16.9–269	170	34.1–572
V	12	5.49	2.31–8.23	8.63	4.34–27.1	13.1	5.23–18.5
Zn	12	217	92.5–1045	89.0	38.9–240	176	86.6–665

\*N – number of samples

Similar results were obtained for the content of Pb. With previously investigations in the same study area, Cu and Pb were separated as anthropogenic introduced elements in the Bučim mine environment (Balabanova et al., 2009, 2010, 2011; Stafilov et al, 2010). Maximum value was obtained from the town of Radoviš (189 mg kg<sup>-1</sup> in February) and varies during the whole year (Fig. 5). This discontinuity of the monthly values for lead contents in deposited dust, indicates that to Pb emissions contribute town characteristic factors (special emphasis is given on traffic and industry). Despite the large amounts of total deposited dust from Bučim village, lead contents were insignificant. Maximum

value (184 mg kg<sup>-1</sup>) for the lead content in deposited dust from the Topolnica village was obtained in March, when starts' decreasing of lead content and the trend is retained until the end of the year (Fig. 5).

The ultimate effect is that despite large amounts of deposited dust, population in Bučim and Topolnica villages is not affected with high content of anthropogenic introduced metals (Cu and Pb) due to copper mining works. Deposited dust collected in the town of Radoviš, despite small amounts of deposited dust, has higher content of Cu and Pb.

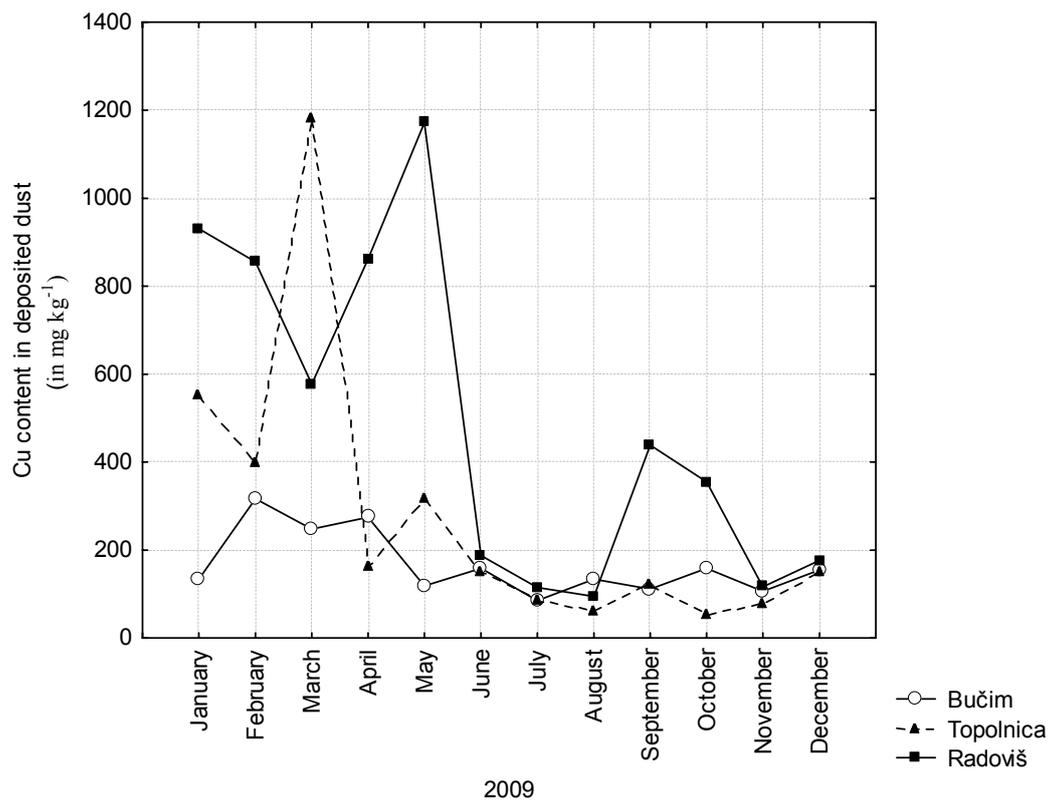


Fig. 4. Trends of copper content in deposited dust through the whole year

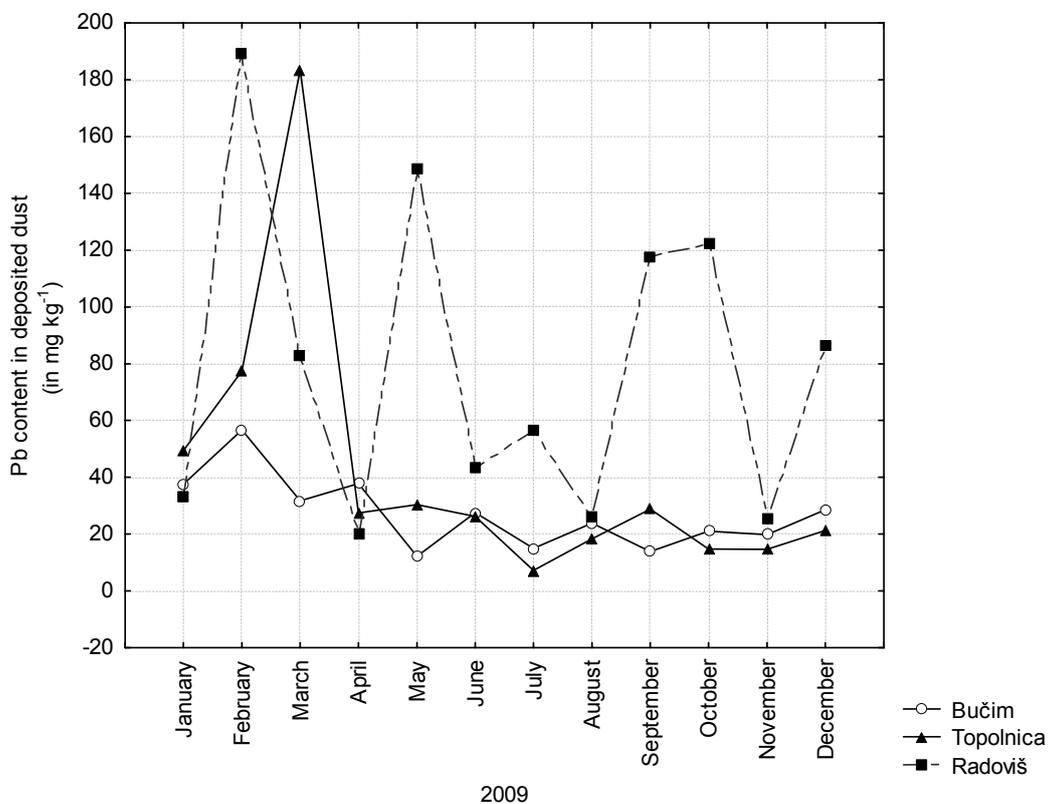


Fig. 5. Trends of lead content in deposited dust through the whole year

## CONCLUSION

Total deposited dust has proved to be very effective environmental media sample for monitoring present distribution of heavy metals in area with intensively exploited of copper minerals. In this investigation, obtained data about element contents showed that copper mine contribute to dust distribution in it's environ. Conducted monitoring with deposited dust samples showed that anthropogenic introduced elements (with emphasis on Cu and Pb) deposit in higher content in close vicinity of their hot spots (open ore pit, ore waste and flotation tailings landfill). In the copper mine environ, there were some values above the maximum permitted amount of dust powder ( $300 \text{ mg m}^{-2} \text{ d}^{-1}$ ). Annual average for the total deposited dust in the

vicinity of the Bučim village was  $489 \text{ mg m}^{-2} \text{ d}^{-1}$ , for Topolnica  $309 \text{ mg m}^{-2} \text{ d}^{-1}$  and for Radoviš  $97 \text{ mg m}^{-2} \text{ d}^{-1}$ . Maximum value for the Cu content was obtained from Topolnica village (settlement near by the flotation tailings landfill). In the town of Radoviš deposited dust was not above the maximum permitted amount for dust powder, but higher content of Cu and Pb contents were found (max. values  $1171 \text{ mg kg}^{-1}$  and  $189 \text{ mg kg}^{-1}$ , respectively). The higher contents of Cu and Pb are not only due to mining works, but also the town works, the traffic, industry and developed technological processes allow emission of higher amounts of these heavy metals in air.

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## Резиме

## СЕДИМЕНТЕН ПРАВ КАКО РЕФЛЕКСИЈА НА ДИСТРИБУЦИЈАТА НА ТЕШКИ МЕТАЛИ ВО ОБЛАСТ СО ИНТЕНЗИВНО ИСКОРИСТУВАЊЕ НА БАКАРНИ МИНЕРАЛИ

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trajcest@pmf.ukim.mk**Клучни зборови:** загадување на воздухот; тешки метали; седиментна прашина; рудник за бакар; Република Македонија

Во околината на рудникот за бакар „Бучим“ беше спроведен мониторинг за да се утврди дистрибуцијата на тешки метали. Во примероците на седиментен прав беше утврдена содржина на 17 елементи. Анализата на содржината на елементите беше направена со примена на атомска емисиона спектрометрија со индуктивно спрегната плазма (ИСП-АЕС). Како мерни места беа избрани селата Бучим и Тополница и градот Радовиш. Беше утврдено дека во одредени периоди од годината во околината на рудникот „Бучим“ доаѓа до депозиција на релативно големи количества прав. Просечните вредности на седиментниот прав во селата Бучим и Тополница изнесуваат  $489 \text{ mg m}^{-2} \text{ d}^{-1}$

и  $309 \text{ mg m}^{-2} \text{ d}^{-1}$ , соодветно. Максимална вредност за вкупен седиментен прав е добиена од мерното место с. Бучим. Блиската околина на градот Радовиш не е изложена на дистрибуцијата на прав од рудникот (средна вредност од  $97 \text{ mg m}^{-2} \text{ d}^{-1}$ ). Карактеризацијата на содржината на елементите покажа повисока содржина на бакар и олово во седиментниот прав. Максималната вредност за содржината на Cu е добиена од примероците на седиментен прав од селото Тополница ( $1183 \text{ mg kg}^{-1}$ ), а максималната вредност за содржината на олово е добиена во седиментен прав од градот Радовиш.