5th International Symposium

MINING AND ENVIRONMENTAL PROTECTION

10 - 13 June 2015., Vrdnik, Serbia

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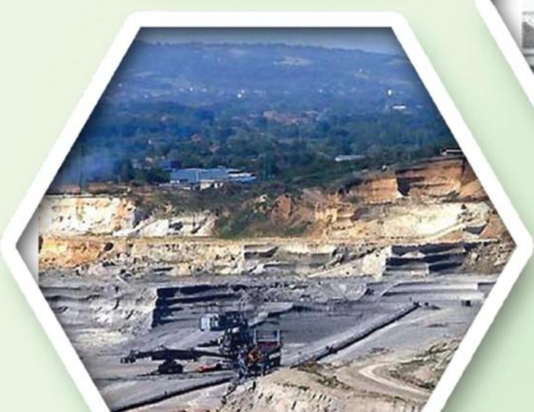
PROCEEDINGS



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Editor
Prof. dr Ivica Ristovic

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C O N T E N T S:

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SOIL METAL POLLUTION RELATED TO ACTIVE ZLETOVO Pb-Zn MINE, REPUBLIC OF MACEDONIA

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University "Goce Delčev", Faculty of Natural and Technical Sciences, Stip, Republic of Macedonia

Abstract: *Within this study a total content of 20 elements was determined in 24 soil samples taken from the vicinity of the "Zletovo" mine, Republic of Macedonia, covering an area of 24.5 km^2. However, in this paper we present four elements significant from anthropogenic point of view. In that manner, in soils of the "Zletovo" mine area Fe values ranged 19.3-76.9 g kg^{-1} with 24 above the optimum (18 g kg^{-1}) and 1 above action value (72 g kg^{-1}), Mn values ranged 643-28000 mg kg^{-1} with 24 above optimum (33 mg kg^{-1}) as well as 24 over the action value (330 mg kg^{-1}), Pb with range of 42.3-529.66 mg kg^{-1} with 23 over optimal (85 mg kg^{-1}) and none above action value (530 mg kg^{-1}), and Zn with range 138-3240 mg kg^{-1} with 23 over optimal (140 mg kg^{-1}) and 14 above action value (720 mg kg^{-1}).*

Keywords: *Zletovo Mine, Waste, Heavy Metals, Pollution, Soil*

1. INTRODUCTION

Mine wastes represent the greatest proportion of waste produced by industrial activity. It is well known that mining and metallurgical activities lead to enormous soil contamination with heavy metals [1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13]. In fact, the quantity of solid mine waste and the quantity of Earth's materials moved by fundamental global geological processes are of the same order of magnitude or approximately several thousand million tonnes per year [14, 15]. Opposite to the fundamental global geological processes such as oceanic crust formation, soil erosion, sediment discharge to the oceans, and mountain building, which naturally move Earth's materials around the Earth's crust and shape our planet, the human extracts material from the Earth during mining and discards most of the extracted crust as waste. Although the modern mining industry is of considerable importance to the world economy as it provides a great diversity of mineral products for industrial and household consumers. 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. [16]. Increased environmental awareness about the anthropogenic input around the industrial facilities around the world induced the study of Zletovo Mine's influence to the adjacent environ. Here we are showing our work and analytical data of 2011 study of concentration of different chemical elements in surface soil around one of the oldest Macedonian mines (Zletovo Mine) and determination of its environmental impact to the adjacent vicinity (Fig. 1).

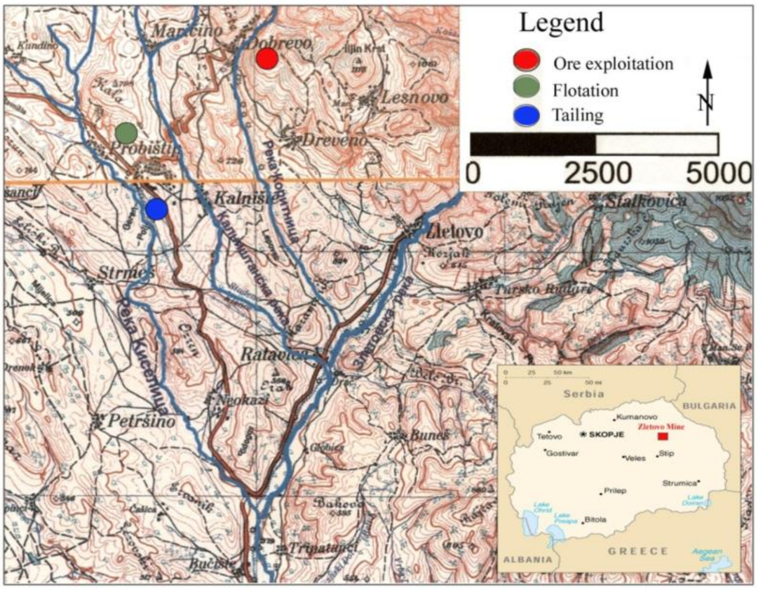

Figure 1 *Main sources of heavy metals pollution induced by work of Zletovo Mine, Macedonia*

2. THE ZLETOVO Pb-Zn DEPOSIT SHORT FACTS

The Zletovo mine is located in the vicinity of the city of Probistip, Macedonia. The mine started operation in 1940 and its production lasts until today with certain short-term interruptions. As it is well known the mineralization is related to Tertiary calcalkaline magmatic rocks, mostly dacites and andesites. Mineralization is found in a dacitic volcano-sedimentary suite that has been altered to clays and micas [17, 18]. Detailed information about the mineral parageneses and geochemical features of major minerals in ore veins is provided in extensive literature [19, 20]. The main ore mineral association is composed of galena and sphalerite, followed by tetrahedrite, pyrrhotite, magnetite, chalcopyrite, pyrite, and Mn oxides are also common. Production during certain periods have reached 300000 t of ore per annum, with ore grades higher than 9% Pb and 2% Zn, and variable concentrations of Ag, Bi, Cd, and Cu. Ore was concentrated by flotation at Probistip and tailings were disposed of in two impoundments situated in adjacent river and stream valleys. One of them, the river Kiselica, drains the flotation plant at Probistip while the Koritnica River drains the area containing the main workings of the Zletovo mine (Figure 1). Both of them join the River Zletovska, which flows down into the River Bregalnica.

3. SAMPLING AREA AND METHODS

Sampling was carried out at the beginning of May 2011. Soil surface samples (0 cm to 5 cm depth) were collected in around the Zletovo Mine and its surrounding region (Fig. 1). The main locations that have been sampled were at the drainage systems of Zletovo, Koritnica River, Globica, Kiselica, Strmos, Buciste, Ziganci and Ularci as well as sites around these streams-rivers. Soil samples were collected at several locations, but in general perpendicular to the stream-river flows. In total, 24 samples were collected from 24 locations, over an area of 24.5 km^2. Samples were located using the Global Positioning System (GPS) and topographic maps at scale of 1:25 000. Each sample represented the composite material collected at the central sampling point itself together with at least four points collected around a central one with a radius of 1 m towards N, E, S and W directions. 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. Hot (80°C) concentrated nitric acid digest was used to leach elements from the soil. Solutions were analysed by ICP-AES or ICP-MS, depending on concentrations. The precision was less than 5%. A large number of analytes were determined but only those that are likely mining related and environmentally significant are presented and discussed here. The concentrations were compared to reference guidelines to assess their significance.

4. RESULTS AND DISCUSSION

Studying results and statistically processing them it was determined that representative are elements such are lead, zinc, iron and manganese and they are given in more details within this paper while there are elements such are chromium, vanadium, nickel, cobalt, have not displayed elevated concentrations and being without any significant impact as direct product of geological setting and anthropogenetic activity (Table 1).

Table 1. *Concentrations of particular heavy metals in soil samples from the vicinity of the Zletovo Mine, Macedonia*

Sample	Pb (mg kg^{-1})	Zn (mg kg^{-1})	Fe (g kg^{-1})	Mn (mg kg^{-1})
ZN-1	42.3	138	19.3	643
ZN-2	102	283	29.66	1980
ZN-3	153	163	31.66	8680
ZN-4	529.66	2300	44.5	8553
ZN-5	389	1800	29.45	5920
ZN-6	201	300	31.23	1842
ZN-7	116.3	298	29.36	2016
ZN-8	192	420	42.36	2090
ZN-9	209	265	37.89	2312
ZN-10	493.8	2333	61	28000
ZN-11	435	2400	61.12	5440
ZN-12	333	1390	37.45	8666
ZN-13	480	2320	76.9	4350
ZN-14	358	3007	63.32	21560
ZN-15	443	3240	55.22	18960
ZN-16	211	444	29.45	3320
ZN-17	198	489	31.22	5550
ZN-18	211	611	29.33	2750
ZN-19	283	1230	33.71	2630
ZN-20	233	1120	30.16	2610
ZN-21	229	1326	31.78	2590
ZN-22	190	745	34.23	6870
ZN-23	165	796	29.97	7540
ZN-24	200	910	28.63	6110
min	42.3	138	19.3	643
max	529.66	3240	76.9	28000
average	284.36	1303.54	40.67	7791.75
Dutch list (Optimum)	85	140	18	33
Dutch list (Action)	530	720	72	330
Above optimum	23	23	24	24
Above action	0	14	1	24

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 [6]. 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} [21], in the European topsoil is 33 mg kg^{-1} [6], in Macedonia (studied part) is 26 mg kg^{-1} [22]. As it is obvious from the table above (Table 1), we would like to stress out that lead values ranged from the 42.30÷529.66 mg·kg^{-1} Pb, while the lowest values were determined near the Zletovo village the highest ones were determined in samples from localities Koritnica, Kiselica and Strmos. Calculated enrichment factor and index of geo-accumulation were 16.66 and 0.327, respectively. In the main polluted area the average concentration of Pb is 8.6-times higher than the European Pb average and Macedonian average for 10.9-times. Although the average content of lead in the topsoil for the entire study area was found to be about

284.36 mg kg^{-1}, there are areas with increased concentration up to 529.66 mg kg^{-1}, although even such values were not above action values by the Dutch list (Table 1; Figure 2).

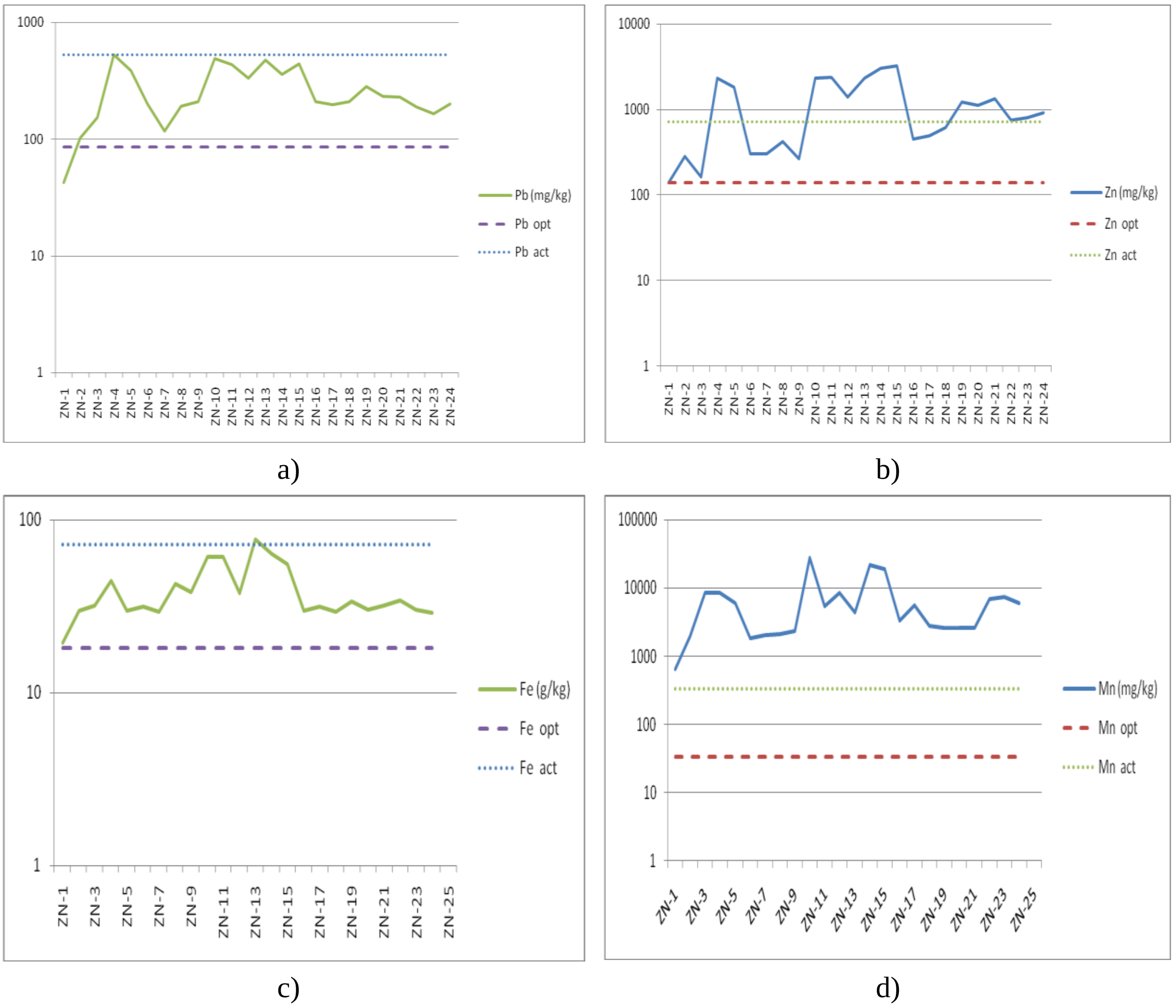

Figure 2 *Measured concentrations of some heavy metals (Pb, Zn, Fe, Mn) vs. Dutch standard in soils around the Zletovo Mine, Macedonia. (Note: all plots have logarithmic vertical scale)*

Zinc (Zn). The most important anthropogenic sources of Zn are the metallurgy industry, burning of fossil fuels, mines and Zn ore processing [1]. 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 [23]. Even the toxicity of Zn is relatively low, there are cases when poisoning with Zn can occur in both acute and chronic forms [24]. The average amount of Zn in the world's soils is 90 mg kg^{-1} [21], in the European topsoil is 68 mg kg^{-1} [25], in Macedonia (studied part) is 55 mg kg^{-1} [22]. The highest concentrations of zinc were determined near the Koritnica, Kiselica and Ziganci while the whole range was quite wide starting from 138 mg·kg^{-1} Zn and ending up to 3240 mg·kg^{-1}Zn with enrichment factor of 24.60 and index of geo-accumulation of 0.135. For the main polluted area, the average concentration of Zn is 19.2-times higher than the European Zn average and Macedonian average for 23.7-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 1303.5 mg kg^{-1}, there are areas with very high level of contamination (Table 1; Figure 2).

Iron (Fe). Since about 3 000 years BC iron has been the most commonly used metal in all civilizations. The common range of Fe contents in soils is between 0.1 and 10% (in forms of oxides and hydroxides, as amorphous compounds and small particles) and its distribution in soil profiles is variable and controlled by several soil parameters (ex. soil texture etc.). However, Fe plays a special role in the behavior of several trace elements and is in the intermediate position between macro and micronutrients in plants, animals and humans. As a very chemically reactive metal, Fe tarnishes rapidly in air or water. Effects of corrosion processes, on a global scale, are a serious source of this metal in different environmental compartments [26]. Contents of Fe in soils are both inherited from parent materials and/or resulted from soil processes that are controlled by climatic factors. Must to mention fact in regards to iron is that it is an excellent metallic material for environmental remediation because it is a strong and nontoxic reducer, effective in coprecipitating and sorbing inorganic pollutants [27]. The average amount of Fe in the world's soils is 35 g kg^{-1} [21], in the European topsoil is 21.7 g kg^{-1} [25], in Macedonia in the considered area is 33 g kg^{-1} [22]. As it is obvious from the table above (Table 1), we would like to stress out that iron values ranged from the 19.3÷76.9 g·kg^{-1} Fe. Either the iron haven't shown significantly increased values, the highest ones were recorded for the locations such as Kiselica, Koritnica and Strmos. Also, for iron were calculated enrichment factor of 2.15 and index of geo-accumulation of 0.193. In the main polluted area the average concentration of Fe is 1.9-times higher than the European Fe average and Macedonian average for 1.2-times. Although the average content of iron in the topsoil for the entire study area was found to be about 40.67 g kg^{-1}, there are areas with increased concentration up to 76.9 g kg^{-1}, although only one value was above action value by the Dutch list (Table 1; Figure 2).

Manganese (Mn). The major anthropogenic sources of Mn are: municipal wastewaters, sewage sludge, and metal smelting processes. The combustion of fuel additives (MMT) is of a lesser importance. In soils irrigated with water affected by acid mine drainage the soluble Mn fraction increases due to reductive dissolution of Mn oxides [28]. Manganese has not been considered to be a polluting metal in soils; however, the MAC value for this metal in agricultural soils is estimated at the range 1500–3000 mg kg^{-1}. Manganese is a member of the iron family and both elements are closely associated in geochemical processes (Mn cycles follow Fe cycles in various terrestrial environments). The behavior of Mn in surfacial deposits is very complex and is governed by different environmental factors, of which Eh–pH conditions are the most important. There the negatively charged $Mn(OH)_4$ and MnO_2 are responsible for the high degree of association of Mn concretions with some trace metals, in particular with Co, Ni, Cu, Zn, Pb, Ba, Tl, W, and Mo. In addition, the oxidation of As, Cr, V, Se, Hg, and Pu by Mn oxides is likely to control the redox behavior of these elements in soils. On the world scale, the range of Mn average contents was calculated at 488 mg kg^{-1}, while for the U.S. soils the calculation is 495 mg/kg [24] while in the European topsoil is 382 mg kg^{-1} [25], and in Macedonia in the considered area is averaging 650 mg kg^{-1} [22]. Manganese analyses around the Zletovo mine area have shown the highest concentrations among analyzed elements, ranging from 643 up to 28000 mg kg^{-1} Mn. Calculated enrichment factor was of respectable 203.3 while the index of geo-accumulation was 0.0246. In the main polluted area the average concentration of Mn is 14.9-times higher than the European Pb average and Macedonian average for 11.9-times. Although the average content of manganese in the topsoil for the entire study area was found to be about 7791.75 mg kg^{-1}, there are areas with increased concentration up to 28000 mg kg^{-1}, however all the measured values were above action value by the Dutch list (Table 1). Data from geochemical analyzes were statistically processed in regular Excel calculations procedure going through the Data menu where we chose Data analysis option with an array of Analysis tools where we continued with Correlation and selected data range for that particular type of data analysis. Summarizing results and findings of this process, we have found that there are strong correlations between the aforementioned elements (Table 2) and appropriate correlation plot (Figure 3).

Table 2 *Correlation of Pb, Zn, Fe and Mn in soil samples from the vicinity of the Zletovo Mine, Macedonia*

	Pb (mg kg^{-1})	*Zn (mg kg^{-1})*	*Fe (g kg^{-1})*	*Mn (mg kg^{-1})*
Pb (mg kg^{-1})	1			
Zn (mg kg^{-1})	0,890744195	1		
Fe (g kg^{-1})	0,786717042	0,791725219	1	
Mn (mg kg^{-1})	0,587304633	0,693057484	0,585819281	1

The first suite encloses Pb-Zn with correlation coefficient of 0.89, Fe-Pb of 0.78 and Fe-Zn of 0.79. These values indicate a high elemental correlation for this suite where lead and zinc have "historical" roots of their high correlation even in their primary sources. The second elemental suite consists of Mn-Pb-Zn-Fe with correlation coefficient for Mn-Pb of 0.58, Mn-Zn of 0.69 and Mn-Fe of 0.58. All these correlation coefficients are relatively high and reflect the and the clear geochemical relationship of these elements, which basically belong to their geochemical nature.

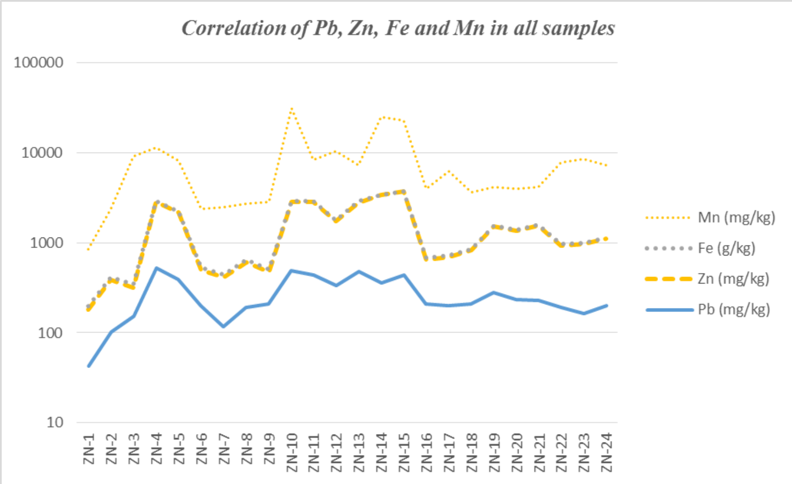

Figure 3 *Correlation of Pb, Zn, Fe and Mn) in soils from the vicinity of the Zletovo Mine, Macedonia (Note: all plots have logarithmic vertical scale)*

However, here we are dealing with their anthropogenic input in soils around the Zletovo mine, which clearly indicates their connection with the processing of lead-zinc ore from the mine.

5. CONCLUSION

Analytical data of the soil study around the Zletovo mine displayed contamination with heavy metals where have been determined increased concentrations of Pb, Zn, Fe and Mn. These contaminations coincide with the active exploitation of the mine and respective material discharges from the mining processes. Our study confirmed that in soils of the “Zletovo” mine area Fe values ranged 19.3-76.9 g kg^{-1}, Mn values ranged 643-28000 mg kg^{-1}, Pb with range of 42.3-529.66 mg kg^{-1} and Zn with range 138-3240 mg kg^{-1}, as well as determined several geochemical pairs have shown correlation coefficients: Pb-Zn with correlation coefficient 0.89, Fe-Pb of 0.78, Fe-Zn of 0.79, Mn-Pb of 0.58, Mn-Zn of 0.69 and Mn-Fe of 0.58. Increased concentration of almost all analyzed metals in soil around the Zletovo mine implies direct correlation to the processing of lead-zinc ore in the mine, while metal deposition in soil the most frequently comes through the several medias (water, waste leachates and air).

REFERENCES

[1] Aliu M., Šajn R., Stafilov T.: Distribution of zinc in surface soils in K. Mitrovica Region, Kosovo, *International Journal of Pure & Applied Chemistry*, 5; (2010), pp. 351-357.

[2] Aliu M., Šajn R., Stafilov T.: Distribution of cadmium in surface soils in K. Mitrovica Region, Kosovo, *Geologica Macedonica*, **23**, (2013), pp. 27–34.

[3] Aryal R. K., Murakami M., Furumai H., Nakajima F., JinadasaH. K. P. K.: Prolonged deposition of heavy metals in infiltration facilities and its possible threat to groundwater contamination, *Water Science and Technology*, **54**, (2006), pp. 205–212.

[4] Cappuyns V., Swennen R. Vandamme A., Niclaes M.: Environmental impact of the former Pb-Zn mining and smelting in East Belgium, *J Geochemical Exploration*, **88**, (2006), pp. 6–9.

[5] Cemek B., Kizilkaya R.: Spatial variability and monitoring of Pb contamination of farming soils affected by industry, *Environmental Monitoring and Assessment*, **117**, (2006), pp. 357-375

[6] Kabata-Pendias A., Pendias H.: *Trace Elements in Soil and Plants.* 5th ed.; CRC Press: Boca Raton, FL, (2011), pp 505.

[7] Li J., Xie Z. M., Zhu Y. G., Naidu R.: Risk assessment of heavy metal contaminated soil in the vicinity of a lead/zinc mine, *J. Environmental Science China*, **17**, (2005), pp. 881–885

[8] Li Y., Wang Y. B., Gou X., Su Y., Wang G.: Risk assessment of heavy metals in soils and vegetables around non-ferrous metals mining and smelting sites, Baiyin, China, *Journal of Environmental Science China*, **18**, (2006), pp. 1124–1134.

[9] Pruvot C., Douay F., Herve F., Waterlot C.: Heavy metals in soil, crops and grass as a source of human exposure in the former mining areas, *Journal of Soils and Sediments*, **6**, (2006), pp. 215–220.

[10] Stafilov T., Šajn R., Pančevski Z., Boev B., Frontasyeva V. M., Strelkova P. L.: Heavy metal contamination of topsoils around a lead and zinc smelter in the Republic of Macedonia. *Journal of Hazardous Materials*, **175**, (2010a), pp. 896–914.

[11] Stafilov T., Šajn R., Boev B., Cvetković J., Mukaetov D., Andreevski M., Lepitkova S.: Distribution of some elements in surface soil over the Kavadarci Region, Republic of Macedonia, *Environmental Earth Sciences*, **61**, (2010b), pp. 1515-1530.

[12] Tembo B. D., Sichilongo K., Cernak J.: Distribution of copper, lead, cadmium and zinc concentrations in soils around Kabwe town in Zambia, *Chemosphere*, **63**, (2006), pp. 497-501.

[13] Wilson B., Lang B., Pyatt F.B.: The dispersion of heavy metals in the vicinity of Britannia Mine, British Columbia, Canada. *Ecotoxicology and Environmental Safety*, **60**, (2005), pp. 269–276.

[14] Fyfe W. S.: The environmental crisis: quantifying geosphere interactions. *Science* 213, (1981), pp. 105–110.

[15] Förstner U.: Introduction. In: Azcue JM (ed) Environmental impacts of mining activities: emphasison mitigation and remedial measures. Springer, (1999), - pp 1–3.

[16] Dold, B.: Sustainability in Metal Mining: From Exploration, Over Processing to Mine Waste Management. *ReViews in Environmental Science and Biotechnology*, 8, (2008), pp. 275-285.

[17] Serafimovski T. and Aleksandrov M.: Lead-zinc deposits and occurrences in the Republic of Macedonia. Faculty of Mining and Geology *Special issue no. 4*, Stip, (1995), - pp 387 (in Macedonian)

[18] Serafimovski T. and Boev B.: Metallogeny of the Kratovo-Zletovo volcano-intrusive complex. In: Knezevic V, Krstic B [Eds] Terranes of Serbia, Proc. UNESCO-IGCP project no. 356, *Plate Tectonics of the Alpine metallogeny in the Carpatho-Balkan region, Belgrade*, (1996), pp. 347-352

[19] Mudrinic, C, Serafimovski T.: Geochemical and geochronological examinations by isotopes in Zletovo ore field. *Geologica Macedonica,* T 5, Nr.1, (1991), pp. 105-120.

[20] Serafimovski T, Tasev G.: The Zletovo Subvolcanic Hydrothermal Pb-Zn Mineral Deposit in the Republic of Macedonia. Geodynamics and Ore Deposit Evolution of the Alpine-Balkan-Carpathian-Dinaride Province. *Final GEODE-ABCD Workshop. Programme and Abstracts.* Seggauberg, Austria, 22-24 March, (2003), 50-51.

[21] Bowen H. M.: *Environmental Chemistry of the Elements.* Academic Press, New York, (1979), - pp. 333.

[22] Stafilov, T., Balabanova, B. and Šajn, R.: *Geochemical atlas of the region of the Bregalnica River basin*. Faculty of Natural Sciences and Mathematics-Skopje, (2014), - pp. 172

[23] Rink L, Gabriel P.: Zinc and the Immune System. *Proc Nutr Soc* **59**, (2000), pp. 541-552.

[24] Prasad A. S.: Zinc: An Overview. *Nutrition*, 11, (1995), pp. 93-99.

[25] Salminen, R., Batista, M.J., Bidovec, M., Demetriades, A., De Vivo, B., De Vos, W., Duris, M., Gilucis, A., Gregorauskiene, V., Halamic, J., Heitzmann, P., Jordan, G., Klaver, G., Klein, P., Lis, J., Locutura, J., Marsina, K., Mazreku, A., O'Connor, P.J., Olsson, S. A., Ottesen, R.T., Petersell, V., Plant, J.A., Reeder, S., Salpeteur, I., Sandstrom, H., Siewers, U., Steenfelt, A. and Tarvainen T.: *Geochemical Atlas of Europe. Part 1, Background information, methodology and maps*. Geological Survey of Finland, Espoo, (2005), - pp. 526.

[26] Kabata-Pendias A., Pendias H.: *Biogeochemistry of trace elements*, 2nd ed.; Wyd Nauk PWN, Warszaw (in Polish), (1999), - pp. 363.

[27] Kaplan, D.I., Knox, A.S., Myers, J.: Mercury geochemistry in wetland and its implications for in situ remediation. *J. Environ. Eng.* -ASCE 128, (2002), pp. 723–732.

[28] Green C.H., Heil D.M., Cardon G.E., et al.: Solubility of manganese and trace metals in soils affected by acid mine runoff. *J. Environ. Qual.* 32, (2003), pp. 1323–1334.