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CONTENT OF METALS AND METALLOIDS IN SOIL SAMPLED IN BOR AND ITS SURROUNDINGS (EASTERN SERBIA)

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ABSTRACT
In the municipality of Bor (Eastern Serbia), which is known for its production of copper from sulphide ores, soil was sampled in urban, rural and background area. The content of metals (Pb, Cu, Cd, Zn, Ni, Cr) and metalloids (As, Sb, Se, Te) in the soil was determined. The highest concentrations of the analyzed elements and frequent exceedance of the limit values were observed in soil samples from the urban-industrial area closest to the copper smelter. However, Cr and Ni concentrations were above the allowed values only in the background area. Strong correlations between elements (Pb, Cu, Cd, Zn, As, Sb, Se and Te), obtained by the Pearson's matrix, indicate their anthropogenic origin. Correlation coefficient for Ni and Cr amounting to 0.940, and their negative correlation with the other studied elements, indicate that their origin is mainly from natural soil composition.
Keywords: soil pollution, metals, metalloids, copper smelter

1. INTRODUCTION

Soil is a very specific component of the biosphere and has very important and complex functions as a filter, buffer, storage, and transformation system, thus protecting the ecosystem against the effects of pollution. Pollution occurs when an element or a substance is present in a greater quantity than background concentrations, as a result of human activities, which has a negative effect on the environment [1]. Sources of metals and metalloids in soils are mainly of natural and anthropogenic origin [2]. Anthropogenic sources of soil contamination include mining and smelting of non-ferrous metal ores and metallurgical industries, urban and industrial waste disposal, agricultural activities such as fertilizers and pesticides application, waste incineration, vehicle exhausts, etc. [2,3,4]. results Contamination of soil by Cu compounds results from utilisation of Cu-containing materials, such as fertilizers, sprays, and agricultural or municipal wastes, as well as from industrial emissions. The anthropogenic sources of Zn are the non-ferrous metal industry and agricultural activity. Pb is a hazardous metal to people and animals because it can enter the food chain or can be inhaled as a part of soil dust. Soil contamination with Cd is believed to be the most serious health risk. The concentration of Cd in topsoil is reported to be very high in the vicinities of Pb and Zn mines and smelters. Sewage sludges and phosphate fertilizers are also known as important sources of Cd. The terrestrial abundance of Ni and Cr indicates its association mainly with rocks. Ni recently has become a serious pollutant emitted from metal processing operations and from increasing combustion of fossil fuels. The Cr content in surface soil is known to be increasing due to pollution from various sources (industrial wastes, electroplating sludges, pigments, etc). Arsenic is highly associated with ore deposits and it is also frequently found combined with S, Se, and Te. Numerous oxide minerals of As are a

result of the oxidation of sulfide deposits (arsenates and arsenites). Se, Te and Sb are often associated with S minerals and sulfide ore deposits [1].
The aim of this paper was to determine the content of metals (Pb, Cu, Cd, Zn, Ni, Cr) and metalloids (As, Sb, Se, Te) in soil sampled in Bor and its surroundings, and the impact assessment of emissions from copper production on soil pollution.

2. THE STUDY AREA AND SAMPLING SITES

The territory of Bor and its surroundings is located in the central part of Eastern Serbia on the Balkan Peninsula. Mining and pyrometallurgical production of copper from sulphide ores are the main industrial activities in the study area. The copper smelter, which is a part of the Mining and Metallurgical Complex, is the biggest source of SO_2 and particulate matter emissions in Serbia. Open pits and flotation tailing ponds also represent environmental pollution sources [5,6,7].
Soil sampling sites were selected in relation to the position of the dominant sources of pollution and prevailing wind directions. The urban-industrial area (UI) includes the sampling sites in Bor, which were located at a distance of 0.5-1 km from the Mining and Metallurgical Complex, where winds of ENE and ESE directions bring the pollution from the smelter. Rural area (R) includes the sampling sites in rural settlements Slatina and Ostrelj, located about 4.5 km and 6.5 km from the pollution sources in the WNW and NW wind directions, respectively. Rural settlement Zlot (the Lazar's Canyon) is located about 13 km from the pollution sources, in the NE wind direction, and can be considered as a background area (B) [7].

3. EXPERIMENTAL

About 0.5 kg of soil at a depth of 5-20 cm was sampled from the each area (UI, R, B). Soil samples were air-dried for 10 days, and then in a dryer (CER, VLS-60) for 24 h at 50°C. The soil samples were sieved using a 0.883 mm stainless steel sieve (Impact Test Equipment Ltd.) and then ground in laboratory mill (SIEBTECHNIK) into fine powder, as in the paper Serbula et al. [7].
Content of metals and metalloids (Pb, Cu, Cd, Zn, Ni, Cr, As, Sb, Te, Se) in soil was determined by the portable XRF analyzer NITONXL3t 900. The results of the elemental analysis of the soil samples are given in ppm units.

4. RESULTS AND DISCUSSION

The maximum allowable concentrations (MAC) of metals/metalloids in soil are defined by the Regulation of the Republic of Serbia. The MACs for Cu, Zn, Pb, Cd, Ni, Cr and As are amounting to 100 ppm, 300 ppm, 100 ppm, 3 ppm, 50 ppm, 100 ppm and 25 ppm, respectively [8].
Figure 1 shows the average concentrations of the examined elements in soil at four sampling sites (UI, R, B). The results of the analysed soil show that Cu concentrations were increased in all the samples. The highest Cu concentration was found in the samples from the urban-industrial area, being 15 times higher than the MAC. The minimum exceedance was detected in the sample from the background area which is furthest from the pollution source. Zn concentrations were within the allowable values at all the sampling sites. Pb concentration in soil was above the MAC only at the sampling site Bor, which is closest to the industrial area with high traffic frequency. Exceedance of the MAC for Cd was multiple in all the soil samples. The content of Ni and Cr was within the allowable concentrations in the urban-industrial and rural area, whereas the exceedance of the MAC was found in the samples from the background area. This kind of distribution of Ni and Cr concentrations can be a consequence of the soil composition in the background area. Metalloid As can often be found in concentrations above the limit value (LV) in the air of Bor [5]. As concentrations in the soil were above the MAC at the sampling sites Bor, Ostrelj and Slatina, whereas the As concentrations in the soil from the background area were within the allowable values. The Regulation of the RS document does not determine the MAC for metalloids Sb, Te i Se. However, the highest concentrations of these elements were observed in the urban-industrial area, and the lowest in the background area which is furthest from the Mining and Metallurgical Complex.

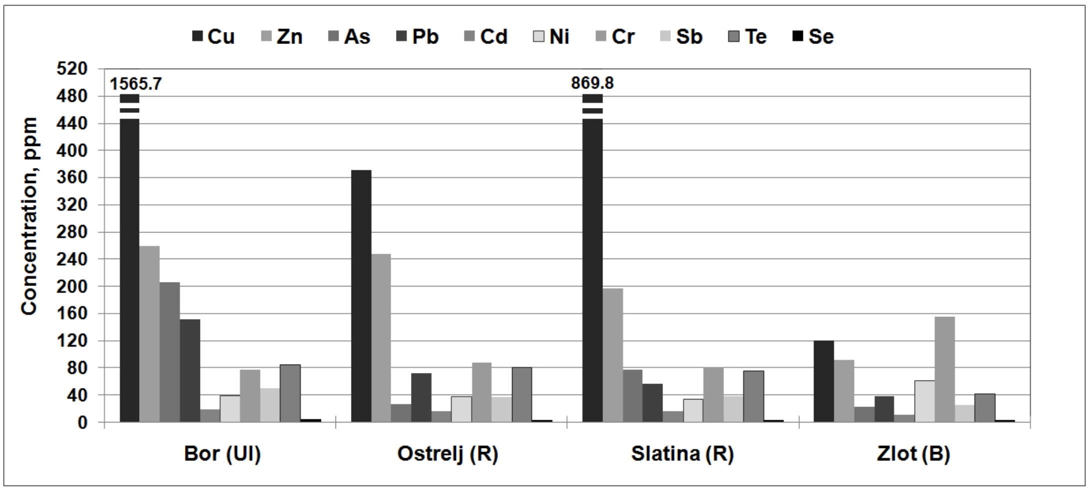

Figure 1. Concetration of elements in soils from four sampling sites

The results on the Cu, Pb and Zn concentrations in the soil, analyzed in 1997, were from the same sampling sites as the ones in this paper (urban-industrial and rural area). Soil pollution in the period of more than ten years has considerably increased up to several times [9]. Concentrations of the studied elements indicate that soil pollution is greatly influenced by the emission from the copper smelter at the closest sampling sites [7].

Many authors have studied soil in industrial areas. Cui et al. [2], showed that soils from the villages in close vicinity of the smelter (1,500 m and 500 m) were heavily contaminated with Cd and Pb, compared to a village situated 50 km from the smelter. Soils in the area of Pb-Zn mine are severely contaminated with As, Cd, Zn, Pb and Cu, according to Liu et al. [4]. Concentrations of Pb, Cd, Zn and Cu in soil from the industrial areas are often several times above the background values [10].

Table 1 shows the correlation matrix among the examined elements at all the sampling sites. Strong correlations with statistical significance of p=0.01 and p=0.05, which can be observed among Pb, As, Se, Zn, Cu, Cd, Sb and Te, show the same anthropogenic origin of these elements in the soil. The values of Pearson's coefficient (r) of 0.940 between Ni and Cr indicate a strong correlation of these two metals. Ni and Cr are in negative correlations with all the other elements, which can be attributed to the soil composition at this area which is probably naturally richer in these metals.

Table 1. Pearson's correlation matrix among metals and metalloids in soil

	Pb	Se	As	Zn	Cu	Ni	Cr	Sb	Cd	Te
Pb	1									
Se	.905**	1								
As	.904**	.885**	1							
Zn	.694**	.537**	.569**	1						
Cu	.851**	.761**	.872**	.630**	1					
Ni	-.218	-.161	-.165	-.319	-.331	1				
Cr	-.209	-.179	-.192	-.271	-.292	.940**	1			
Sb	.549**	.446*	.597**	.462*	.709**	-.473*	-.545**	1		
Cd	.440*	.377	.468*	.379	.510*	-.528**	-.631**	.869**	1	
Te	.266	.174	.340	.224	.448*	-.451*	-.486*	.871**	.761**	1

* p=0.05; ** p=0.01

Figure 2, shows the biplot diagram of Principal Component Analysis (PCA) for Cu, Zn, As, Pb, Cd, Ni, Cr, Sb, Te and Se concentrations in soil at the sampling sites in the urban-industrial, rural and background area. Two principal components (PC) were extracted, which explains more than 78% of the total variance. Principal component 1 (PC1) accounts for more than 56% and the Principal component 2 (PC2) approximately accounts for about 22% of the total variance. Ni and Cr form separate group, which is in accordance with the results of the correlation analysis. Different behaviour of these two metals indicates their natural origin. The remaining elements are also naturally found in the soil, but their higher concentrations suggest its anthropogenic origin.

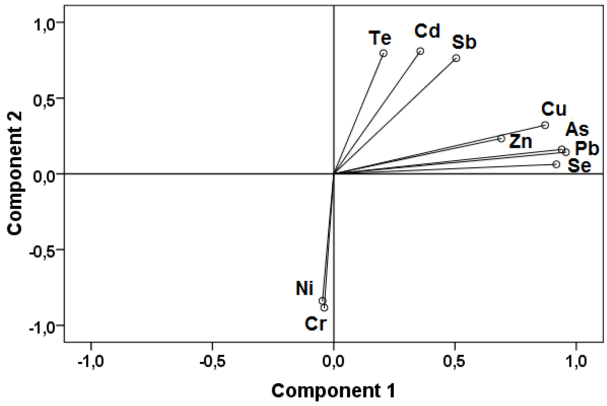

Figure 2. Biplots based on the first two components identified by PCA for elements content in soil

5. CONCLUSION

The highest concentrations of the analyzed elements (except Cr and Ni) were observed in the soil samples from the urban-industrial area which is closest to the copper smelter. High correlation coefficients and a great statistical significance (p=0.01; p=0.05) among the analyzed elements indicate its anthropogenic origin. However, exceedances of the MAC for Ni and Cr were observed in the soil of the background area, which is farthest from the industrial complex. High concentrations of Ni and Cr in soil from this area may be due to the composition of rocks and soils. A high correlation coefficient of 0.940 between Ni and Cr, as well as their negative correlation with the other elements, indicate that their origin is mainly from the natural soil composition.

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