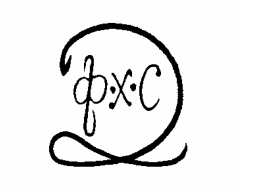

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ASSESSMENT OF HEAVY METAL CONTENT IN SOILS OF SOME URBAN AND RURAL ENVIRONMENTS IN SERBIA

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ABSTRACT

This study deals with the assessment of heavy metals contents in soil of Serbia in urban and rural environment. Analysed heavy metals (Cd, Co, Cr, Cu, Mn, Ni, Pb, Zn) were determined using an atomic absorption spectrometry. Concentrations of Co, Cu, Ni and Zn at some sampling sites of urban environment exceeded the limit values, which are still far from the remediation values established by Legislation of the Republic of Serbia.

INTRODUCTION

The soil is the main repository of heavy metals in terrestrial ecosystems. These metals reach the soil environment through both pedogenic and anthropogenic processes. The major sources of heavy metals enrichment in soils are anthropogenic activities, associated with industrial processes. The spatial distribution and source identification of heavy metals in soil is important in order to reveal the areas of pollution and assess the potential sources. Health authorities in many parts of the world are becoming increasingly concerned about the effects of heavy metals on environmental and human health. Different statistical tools, such as correlation analysis (principal component analysis, cluster analysis) and geostatistical analysis (GIS-based spatial mapping) are applied in environmental studies to highlight pollutant sources and to study spatial distribution patterns [1-4]. In this study heavy metals contents in soils of Serbia were assessedin the three urban areas: surroundings of the coal fired power plant (CFPP) in Obrenovac, Belgrade; surroundings of the steel production facility (CPF) in Smederevo; the city zone of Subotica; and a rural area of Pčinja and South Morava River Basin, southeastern Serbia.

EXPERIMENTAL

Soil samples were collected up to 10 cm depth. Applying the 'systematic random sampling' procedure, a total of 60 samples were collected, 15 from each investigated area [5]. Soil samples for metal content determination were

digested according to USEPA procedure [6]. Total metal content (Cd, Co, Cr, Cu, Mn, Ni, Pb, Zn) was determined by using atomic absorption spectrometer Shimadzu AA7000. Standards used in the analysis were AccuStandard solutions obtained from Carlo Erba Reagenti. The quality assurance checks were performed using the certified reference material SRM 2711 (National Institute of Standards and Technology). The overall uncertainty of the analytical procedure was below 10%.

RESULTS AND DISCUSSION

The concentrations of analysed heavy metals were summarized in Table 1. Concentrations of Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn at some sampling sites were higher than the concentrations for uncontaminated European soils, i.e. 0.145 mg kg^{-1}, 7.78 mg kg^{-1}, 60mg kg^{-1}, 13mg kg^{-1}, 650 mg kg^{-1}, 18 mg kg^{-1}, 22.6 mg kg^{-1} and 52 mg kg^{-1} for these elements, respectively [7]. Concentrations of Co, Cu, Ni and Zn at some sampling sites exceeded the limits values (9 mg kg^{-1} for Co, 36 mg kg^{-1} for Cu, 35 mg kg^{-1} for Ni and 140 mg kg^{-1} for Zn) established by Serbian regulations for land use [8]. Detailed explanation about elevated concentrations around CFPP and CFP could be found elsewhere [1, 3]. In the investigated areas of this study, only the average values of Co slightly exceeded the limit values of 9 mg kg^{-1}, which is far from the remediation value of 240 mg kg^{-1}[8]. At four and at two sites in Smederevo and Subotica, respectively, elevated concentrations for Cu, higher than limit value of 36mg kg^{-1}were determined. At one location in Subotica extremely high value for Cu of 3660 mg kg^{-1}, greater from the remediation value of 190 mg $kg^{-1}$was determined and this value was excluded from statistical analysis presented in Table 1. Further analysis is required in order to distinguish pollution source of Cu in this site. Increased concentrations of investigated heavy metals in urban areas of this study are associated with pollution sources. The highest average value for Mn was revealed in rural area in southeastern Serbia. It could be associated with its natural origin, but detailed geochemical analysis is needed to confirm this finding. In area surrounding CFPP elevated concentrations of Mn at some sampling locations were attributed to its leaching during and after transport of the coal ash. Elevated concentrations for Ni in Belgrade and Smederevo are both natural and anthropogenic local sources of contamination. There is still no need for remediation actions on these sites, as values are lower than 210 mg kg^{-1} for Ni [8]. At two locations in each urban areas of Serbia investigated here, the values higher than limit value of 140 mg $kg^{-1}$for Zn were determined, but these values are still far from the remediation value of 720 mg kg^{-1} [8].

Table 1. Average (min-max) values of heavy metal concentrations in analyzed soils(mg kg^{-1}).

	Study areas of Serbia			
Element	Belgrade	Smederevo	Subotica	Southeastern Serbia
Cd	0.26 (0.04-1.05)	3.33 (2.31-4.61)	1.10 (0.38-5.95)	0.17 (0.10-0.25)
Co	10.5 (6.2-13.4)	28.2 (13.9-41.3)	13.9 (5.5-19.1)	9.5 (3.8-13.8)
Cr	29.7 (11.7-45.4)	55.7 (34.1-97.9)	21.5 (12.5-40.4)	25.6 (10.7-41.2)
Cu	19.3 (12.4-26.9)	39.1 (13.3-148.4)	29.6 (1.4-61.4)	19.3 (12.4-26.9)
Mn	620 (195-1270)	730 (400-860)	400 (340-530)	830 (360-1050)
Ni	62.6 (24.3-106)	78.2 (47.4-148)	23.5 (7.7-64.8)	15.9 (6.7-26.1)
Pb	26.4 (17.4-70.2)	33.0 (20.2-64.6)	52.8 (17.4-81.1)	14.1 (7.1-20.8)
Zn	89.2 (48.5-207)	98.9 (71.2-152)	30.5 (3.9-170)	48.6 (28.8-70.1)

Applying geostatistical analysis based on ordinary kriging method Ćujić et al. (2016) and Dragović et al. (2014) found the highest concentrations of heavy metals at sites in predominant wind directions in areas surrounding CFPP in Obrenovac and SPF in Smederevo. The distribution of heavy metals in soils around the point source (e.g. CFPP, CFP) is highly needed for the assessment of perturbations of geochemicalcycles of heavy metals in the environment and their effects on environmental and human health as well as for development of appropriate remediation strategies.

CONCLUSION

This study was performed in order to assess environmental consequence of anthropogenic activities in urban and rural areas in Serbia, with regard of heavy metals in soil. The assessment study revealed some hot spots for: Cd, Co, Mn and Ni in the study area of Belgrade, as a consequence of CFPP

operation; Cd, Co, Cu Ni, Pb and Zn in the study area of Smederevo, as a consequence of SPF operation; Cu and Pb in Subotica, as a consequence of traffic. In general, operations of CFPP and SPF have no significant negative impact on the surrounding environment with regard to the content of investigated heavy metals. In the rural area of southeastern Serbia anthropogenic activities were not significant in the terms of heavy metals in soil; the higher Mn concentrations could be attributed to natural sources.

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