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HEAVY METALS IN SOIL IN SREM (VOJVODINA): CONTAMINATION LEVEL AND MOBILITY

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ABSTRACT

Potentially harmful trace elements pollution in soils is a worldwide environmental problem that has received increasing attention over the last few decades because of its adverse effects. Metals in soils are present in different chemical forms which affect their ability to transfer. The objective of this body of work was to assessment of contamination degree of elements Cu, Hg, Ni, Cr, Co, Zn, Pb, Cd As and B in agricultural and grazing soils surrounding the industrial objects, in order to quantify their real influence and real health risk by using investigated soils as croplands. Combination of different methods was applied for estimation of the environmental status of soils and to determine the potential risk of ecological damage. Obtained results indicate that heavy metal contamination should be taken into account during development of management strategies to protect the soil in the Serbia.

Key words: heavy metals, B, soils, contamination level, mobility factor.

INTRODUCTION

Detailed investigation of heavy metals soil contamination as potentially toxic elements is particularly important, since Serbia has involved recently in systematic examination and assessment of the potential risk and contamination level. This assessment in the area such as Srem and Vojvodina is important considering that the most part is used for agricultural activities. However, in the last century, many industrial objects (especially food industry) were built in this area, reducing the surface of the agricultural area and increasing contamination level. Industrial pollution typically contaminate shallow layers of soil(0-40 cm), and in the case of natural enrichment contamination is present in deeper layers as well (6) The accumulation of heavy metals in soils is a potential risk to human health, firstly because of elements transfer in an aqueous medium, and secondly their adoption by the plant and entering in the food chain.

Many authors studied heavy metals concentrations in [illegible] nonagricultural soils of Vojvodina, and concluded that the value of ele[illegible] Ni, As, Cd, Cu, Cr mostly were below the maximum allowed conc[illegible] However, in the vineyard soils have been identified presence of higher [illegible] result of usage Cu-compounds based fungicides (10). Furthermore, higher [illegible] (of geochemical origin) was detected (2,3). In some parts less terraces [illegible] values of Ni, Cr, Pb above the MAC in top soils presented as anthropoge[illegible] soil as natural (5). Not many authors determined bioavailability of the stu[illegible] was found as slightly mobile in some parts of Srem (3). Also, Maksim[illegible] determined low mobility in case of Ni, As, Cu, but in mobile forms are Cd [illegible]

In this paper, the main goal is assessment of contamination deg[illegible] Cu, Hg, Ni, Cr, Co, Zn, Pb, Cd As and B in agricultural and grazing soils [illegible] industrial objects, in order to quantify their real influence and real health [illegible] investigated soils as croplands. Additionally, it is very important to dete[illegible] percents of the measured concentrations are really bioavailable and can [illegible] cycle. Thus is possible to evaluate the potential use of the soils in this [illegible] future.

MATERIAL AND METHOD OF WORK

Investigated area included 8 towns and different industrial obj[illegible] - samples labeled as S1-S5 (metal cutting and boiler factory-S1, printing [illegible] pesticide factory-S4,S5);2. Pećinci, S6-S8 (sugar factory); 3.Stara Paz[illegible] S14 (salt processing plant-S9, printing shop-S10,solid metal waste [illegible] processing plant (abandoned)-S11-S14); 4.Inđija- S15-S20 (tobacco [illegible] paint and varnish factory and battery factory-S17, S18, pet food [illegible] factory- S19;sample S20 islocated between these factories); 5. Ruma-[illegible] industry S21, S22 and tire factory S23- S26); 6.Sremska Mitrovica- [illegible] (wood, cellulose and paper factory S27, S28; S29 is placed further, [illegible] sugar mill plant S30-S32);7. Šid samples S33-S41(paint and [illegible] S35,insulation material factory S36, S37 and S38 between this factory [illegible] S41, print shop- S39, S40);8. Beočin –samples S42-S45 (cement factory)

Soil samples were collected in October 2010 at 45 localities [illegible] industrial objects. T he samples were collected with stainless steel [illegible] depths: 10-30 cm and 30-50 cm or 0-10 cm and 10-50 cm depending [illegible] agricultural or grazing. Sampling methodology defined in the GE[illegible] (Geological Mapping of Agricultural and Grazing Soils).

In order to determine distribution – geochemical affinity of [illegible] bioavailability modified Tessier sequential extraction (14) were used [illegible] phases: F1-exchangeable (1MNH_4CH_3COO); F2-metal bound to carb[illegible] reducible species (0.01M HCl and 0.1M NH_2OH HCl); F3-metal bound [illegible] reducible phases or Fe-oxides fraction (0.2M $H_2C_2O_4$ and 0.2M $(NH_4)_2C_2O_4$[illegible] matter and sulfides (30% H_2O_2 adjusted to pH 2 with HNO_3/ followed [illegible] 3.2M $CH_3COO(NH_4)$; F5-Residual fraction (6M HCl).

Determination of concentrations Cu, Cd, Pb, Cr, Cu, Co, Ni, Pb, B, As, were performed by ICP/AES –(inductively coupled plasma atomic emission spectrometry-iCAP-6500 Duo, Thermo Scientific, UK). Hg were detected by hydride generation system AAS atomic apsorption spectrometry (PERKINELMER 6500, MHS-15).

The X-ray powder diffraction (XRPD) studies were performed by automatically diffractometer for powder "PHILIPS", model PW-1710. There was used long-focus (LFF) Cu-anode (U = 40 kV and I = 30 mA), with the monochromatic $K\alpha_1$ radiation (wave-length $\lambda = 1.54051$Å) and Xe proportional counter.

Descriptive statistics, Kolmogorov-Smirnov test for the normality of distribution, Wilcoxon Signed-Rank test were performed using the demo version of NCSS statistical software.

RESULTS AND DISCUSSION

XRD analyses of fraction <0,063 mm showed mineralogical composition: the most dominant mineral is quartz as a primal mineral (with exception of the sample S41, where is dominant calcite),feldspar and clay minerals type illite, sericite, chlorite and montmorillonite. Carbonates - calcite and dolomite are present in different concentration range. In bottom soils, these minerals in some samples are detected in higher percents than feldspar or clays. amphiboles and hematite are detected in soils as well. The results of heavy metal concentrations as mean, maximum, minimum as well as standard deviations (st. d), are given in Table 1.

Table 1. Descriptive statistic of heavy metal concentrations (mg/kg)

	As	B#	Cd	Cr	Cu	Ni	Pb	Co	Zn	Hg
[illegible]	6.55	8.50	0.36	49.3	27.9	51.6	21.6	10.7	65.9	0.37
[illegible]	3.78	4.44	0.17	39.0	15.5	40.4	13.9	3.99	36.7	0.27
[illegible]	6.52	8.03	0.33	36.8	22.8	39.9	18.6	9.97	51.29	0.25
[illegible]	1.09	1.43	0.21	21.1	13.6	23.5	6.42	5.31	33.4	0.07
[illegible]	21.4	24.5	1.27	247	94.4	230	67.7	24.1	192	0.95
[illegible]	6.48	6.32	0.28	44.8	37.0	49.7	18.2	10.1	55.6	0.23
[illegible]	3.16	2.74	0.10	29.1	79.6	44.8	15.6	3.55	24.0	0.12
[illegible]	6.77	6.01	0.28	36.9	22.0	36.4	13.5	9.45	52.5	0.22
[illegible]	0.40	0.78	0.16	20.1	14.2	21.7	5.34	5.44	27.4	0.05
[illegible]	12.6	12.8	0.68	152	553	273	95.4	20.2	154	0.57
[illegible]	20	50	0.6	64	22	17	61.6	4	78	0.15
[illegible]	37	-	8.4	242	116	101	384	104	400	7.67

*maximum allowed concentration of elements (modified) (Official Gazette of the Republic Serbia, 88/2010) and B# (Official Gazette of Serbia 23, 1994)
**intervention values (modified)

The main contamination assessment criteria - maximum allowed concentrations (MAC) and intervention values (IV) of metals in soils defined in standard Official Gazette of the Republic Serbia, 88/2010) and for boron- Official Gazette of Serbia 23, 1994, Table 1) are used. As proposition of standard MAC and IV need to be modified regardless quantity of clay (%) and organic matter (%).The mean of clay and organic matter in the investigated soils are 6,84% and 4,78%, respectively.

Using Wilcoxon's test was found that the contents of B, Cd, Ni, Pb, Zn and Hg are higher in the top soils, i.e.more concentrated in the surface layer. In contrast, copper is more concentrated in the bottom soils.

In accordance with the fact that the distribution of the result does not belong to the normal Gauss distribution, median value compared with the standard values (Table 1). It can be concluded that median values of Ni, Co and Hg exceeds the standard values in both depths and the value of Cu at the surface exceeds but in the subsurface is equivalent to the standard value. Median of concentrations of the other elements do not exceed the MAC (Table 1).

Range of concentrations of nickel indicates that all values in the examined area are above value of 17 mg/kg. The maximum value is registered in both depths of samples taken away 400 m from the cement factory in urban area of Beočin (S43) and nearby the cement factory S42-top soil (106 mg/kg). High values were also detected at the locality S22 (167 mg/kg , top soil), 250 m away from the leather factory and S21 (158 and [illegible] mg/kg), nearby the factory, in urban area of Ruma town. The range values of chromium content in the investigated area are both below and above limited. The peaks were observed in samples S21 (top soil) and S43 (bottom soil). As mentioned above, some authors concluded that the main origin of Ni in soils and sediments of Vojvodina is geochemical (3,14). The minerals chlorite and amphibole, both detected in these samples can be one of the main source of Ni and Cr (14).These minerals also may be significant sources of Ni and Cr in presented samples as well. The other might be cement factory because of cement- arrived fugitive dust or combustion of fossil fuel. Fugitive dust can be the source of Pb, Zn, Cd, Hg and Cu as well (1,6). In the leather industry are used chromium salts, so it can be one of the sources in this sample (4).On the other hand, combustion of fossil fuel (coil) can be the source of fly ash rich with As, Cd, Pb, Cu, Ni, Co, Mn, Fe, Zn, Cr, B, Hg (6,9) The values of cobalt content are above MAC in the whole researched area, and the maximum value was observed in samples S42 (top soil)and S12 (bottom soil), placed near metal processing plant. According to the concentration range of copper, it can be concluded that there are soils with copper content below and above MAC. The maximum values were recorded again 400m from cement factory (S43) and the extremely high value of copper detected in sample [illegible] 250 m away from the leather factory, in an abandoned orchard and probably originated from the usage of copper-based fungicides Bordeaux mixture type, used earlier, [illegible] before the sampling. Here should be noted that these fungicides can contain lead and zinc as well (11). The value range of content Hg, indicates variety of concentration distribution in the soil around the industrial facilities. The highest values are registered in the sample (both top soil): S21 and S27-sample of agricultural soil, taken nearby cellulose factory and S7 (bottom soil), taken 400 m away from the sugar factory in Pećinci town. Most probably presence of Hg in soils is a consequence of fossil fuel combustion and agrochemicals usage. Concentration of Pb in soils around industrial facilities are below the MAC according to given standards. The exceptions are the [illegible] value in the sample S42 (top soil, Table 1). Also, higher value are registered in the sample S29 (65.3 and 95.4 mg/kg) in an urban area of Sremska Mitrovica town, [illegible]

250m away from the wood and cellulose factory and sample S-28 (54,6mg/kg topsoil), 400m further. The origin of lead thus could be usage of fertilizers, pesticides, fuel combustion or cement fugitive dust and urban area activities. Popović et al (13) explained unexpected value of lead in the soil placed further from heavy traffic as mixture of influences: cement factory in Beočin and traffic. Maximum values of zinc detected in samples S21 and S12 (top soil and bottom soil, respectively). Metal processing factory can be a source of metal Cr, Ni, Fe, Zn, and Cu (12), Values of Cd content in the soils of studied area are both higher and lower than the limited value. The highest concentration was detected at locality labeled S4-sample of agricultural soil, placed between pesticides factory and building material factory in Šimanovci town, as well as in the sample S42 (topsoil (0.63mg/kg).The origin of Cd can be agricultural activities, and fossil fuel combustion, since that presence of Cd, and Pb detected in fertilizers which have been used in Serbia (15). Arsenic content in all samples is below MAC, except sample S41, where is registered the maximum value (Table 1). The contents of boron in all samples are below the MAC of 50 mg/kg. The maximum was recorded in the sample S-11(agricultural soil) next to solid metal waste in Stara Pazova town, probably as the result of using fertilizers.

As summary, the most contaminated samples are: S12 contaminated with Ni, Co, Cr, Zn, Cu; S21- Ni, Cr, Hg, Cu, Zn; S 22- Ni, Cu ,Cr, Hg, Zn; S29- Pb, Zn,Ni, Cu, Cr,Hg; S42-Ni, Cu,Zn,Hg; S43-Ni, Cu, Cr,Hg. Obviously, the greatest influence on investigated area soils can have factories: cement and leather factory, metal processing factory and besides that urban activities and usage of agrochemicals.

Geochemical affinity and distribution of the elements between phases F1-F5 is present in Diagram (Figure 1).The elements: Zn, As, Pb, Cr, Ni, Co, B, and Cu are mostly concentrated in residual fraction (F5). The exception is Cd in top soils (dominant presence in carbonate phase -F2), and Hg (dominant presence in exchangeable phase -F1). This distribution of the elements suggest both, the natural and anthropogenic origin. In order to assess the potential mobility and bioavailability of metals, as well as environmental and health risk, the distribution of element concentration between phases is used to calculate mobility factor (MF). MF is calculated as a ratio of soluble, exchangeable and carbonate-bound fraction (in our case F1 and F2), and sum for all fractions (%)(7)

The results of mobility factor (MF) for both depths, (presented in Diagram - Figure 2), pointed the most higher values in case of B (52.82 and 56.73%), Hg (56.64 and 45,17%) and Cd (42.19 and 34.12%). MF values of the other elements decreases: As>Co>Pb>Ni>Zn>Cu>Cr in top soils and Co>As>Pb>Ni>Cu>Zn>Cr in bottom soil. The obtained results indicate that if there was changing in pH value or increasing the ion activity/concentration in soil solution, it would change balance and the elements become mobile in specified percentages.

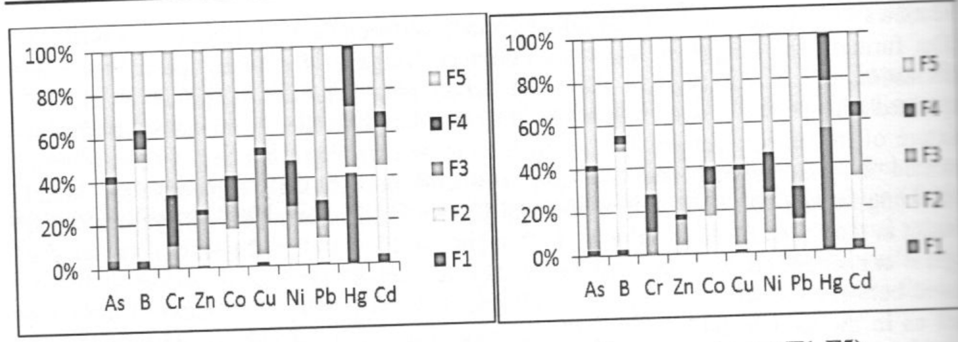

Figure 1. Diagrams of distribution elements between phases (F1-F5) in top soil and bottom soil

Furthermore, MF factor indicates that in case of Cr there is no risk to become mobile and bioavailable (Cr<1%), since it is mostly distributed in low-mobility fractions. There is low risk for Cu, Ni, Zn (1-10%), medium risk for Pb, Co and As (10-30%), high risk for Cd and Hg (top soil), and very high risk for B and Hg(bottom soil, above 50%).

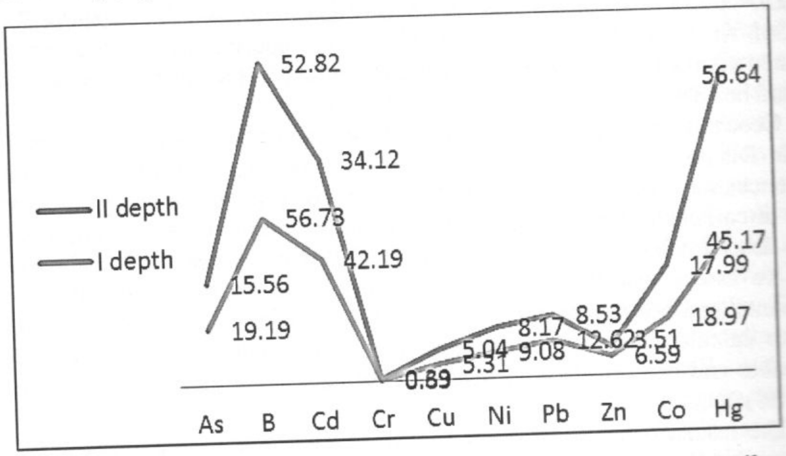

Figure 2. Mobility factor (%) of the elements in top and bottom soils

Accordingly discussion above, it is possible to conclude for the group of elements which mean values or median (Table 1) exceeds MAC, such as Ni and Co, do not have significant environmental influence to, since they are distributed mostly in less mobile forms. This indicates their dominate geochemical origin. In contrast, mean values and median of cadmium and boron are below the limit, but in the soils of research area of Srem, this element can easily become mobile, since bounded in carbonate/slightly reducible phase. Hg is toxic element of very high potential risk, and it indicates anthropogenic influence.

CONCLUSION

Comparing the median values of toxic elements of soils surrounding the industrial objects to the defined standard is obvious that concentrations of Ni, Co, Hg, and Cu in the top and bottom soils are higher, but below the intervention values. Also, B, Cd, Ni, Pb, Zn and Hg, are more concentrate in top soils, and Cu in bottom soils.

Accordingly these criteria, the most contaminated area is Beočin, because of the increased content of Cr, Ni, Cu, and Co which can be influenced firstly of geological matrix (the presence of ultramafic and mafic rocks) and secondly presence of cement factory which could attribut increasing of As, Pb and Cd. Higher values of toxic elements in the investigated area could be consequence of presence of the other industrial objects and combustion of fossil fuel in industrial processes, usage of fertilizers and pesticides, fungicides and activity in urban area .Hg, Cd and B are the most mobile elements in studied sediments and Cr is the least bioavailable, which suggests it's geochemical origin.

The results of this investigation suggest existence of localities with high level content of toxic metals, but there is evidence of lower level of mobility and bioavailability, except Hg in some localities. Thus, some parts of investigated area can be used as agricultural, but with constant monitoring of contamination level.

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