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HEAVY METAL CONTENTS IN SEDIMENT FROM EXPERIMENTAL WATERSHEDS ON MOUNTAIN GOČ

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Heavy metal contents in the soil and their origin, caused their concentrations in erosion sediment. This paper deals with results of study heavy metal contents (Pb, Cd, Cu, Zn, Ni and Cr) in the sediment from three experimental watersheds on site Ravnine on Mt. Goč. The watersheds are coverd with forest plantines and meadow - pasture vegetation.

Key words: heavy metals, soil, sediment, forest ecosystems, meadow.

INTRODUCTION

Soil erosion and sediment transport are processes of great importance for environmental management. They relate to the quality and quantity of soil resources, and they play an important role in the transfer of nutrients and pollutants from terestrial to aquatic ecosystems.

Heavy metals presence in soil is the result of the natural and the anthropogenic processes. Natural origin of heavy metals is from parent rocks as the result of pedogenetic processes. Anthropogenic origin of heavy metals is different in the case of agroecosystems, but in the case of forest ecosystems and natural meadow

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associations, is exclusively from atmosphere. Harmfull effects of these substances or their toxicity in the surface and ground waters are attributed ionic forms on the suspended particles, i. e. complexing with mineral and organic components.

Heavy metal contents in sediment as the new research goal, are included in the general hydrologic studies in the small watersheds network in Serbia. At the mountain Goč there are three experimental watersheds. The studyng of concentrations of heavy metals has been included into the hydrological research since 1991. yr. The results of investigations were published KADOVIĆ, CVETKOVIĆ (1992), KADOVIĆ, KNEŽEVIĆ, CVETKOVIĆ (1994), and BELANOVIĆ (2000). This paper deals with results of heavy metals (Pb, Cd, Cu, Zn, Ni and Cr) contents in the sediment from three watersheds, during the period 1991 - 1997. yr.

OBJECT OF RESEARCH

At the mountain Goč, within the location Ravnine, three watersheds have been singled out at the elevation 610 - 982 m. asl.: R - I, R - II and R - III, covering 7,60, 6,35, and 8,35 ha respectively. Watershed R - I is under mixed coniferous and deciduous forest plantings, aged 33 yr., R - II is mountainous pasture, and R - III is planting of Austrian pine, aged 23 yr.

The massif of Goč is in the region of temperate - continental climate. As per long - term measurement, average annual precipitation in this part of the massif amounts to 800 mm, with uneven distribution in space and time. Mean annual air temperature is 7,3°C, and relative humidity is 81% (MACAN, 1985).

Based on THORNTHWAITE'S classification, the climates of watersheds are: R - I mild humid (B_1) to more intensely humid climate (B_3); R - II - perhumid (A) to moderattely humide climate (B_2); R - III - mild humid (B1) to moderattely humide climate (B_2).

As for the parent rock, R - I and R - II are serpentinized peridotites undergoing different forms of transformation, and R - III is serpentinite. On this substratum, silicate soils on serpentinite are characterized by different evolution stages of development, from initial to develop brown soils (MACAN, 1985; BELANOVIĆ , 2000.).

Soil diversity is most expressed in the watershed R - I, in part due to the different state and character of forest ecosystems. At the surface of the soil the accumulated organic matter originates from Spruce and Austrian Pine needles. The humus in the organogenous layer 3 - 6 cm deep has the characteristics of the semi-raw form, while in the remaining part of the profile, it has the characteristics to the mild (mull) form.

MATERIAL AND METHOD

Direct measurements and monitoring of hydrologic parameters have been recorded in all experimental watersheds. Within hydrologic research, a cross

measured in compensating reservoars (settling basins). Sediments sampling were taken according square method. The samples of sediment have been analyzed by the AAS method using the Varian AA-10 apparatus in Forestry Faculty laboratory.

The concentrations of heavy metals in sediment, were compared with critical limit values for sediment from some European countries (DE VRIES, *et. al.*, 1998), and with the provisional limit values by OSPAR (1996). Enrichment sediment factor (EF) values by YOUNG (1991), were calculated on the basis of heavy metal concentrations in topsoil.

RESULTS AND DISCUSSION

Heavy metals cycling in forest ecosystems and natural meadow associations is conditioned by numerous factors that, together or individually, can have a decisive significance for their content in the soil. The mechanisms of their transfer pathways depend, on first of all, deposition quantity, type of element, type of soil, and type of vegetation.

Organic substances and microelements were transported in the solution and in the suspension forms. The dominant part of some elements, belong to fixation form with suspended matter. Physical, chemical and and biological processes impact on distribution stable and dissolved compounds. Also, the heavy metals can be presented in the other forms, especialy on the surface of collodial particles, which are larger than substances in real solution, but smaller than particles which are deposited, and they are very important for pollution transport.

Physical properties analyses of the sediment from the experimental watersheds (BELANOVIĆ, 2000), showed the high presence of colloidal particles, which were primary carrier of complexation with the heavy metals. After WHO (1980), colloidal fraction (particles < 0,002 mm) has exceptional significance, because heavy metals of these particles have the strongest links (connections) with that fraction.

Chemical analyses of sediment (KADOVIĆ, 1992; BELANOVIĆ, 2000), show that, sediment has organic origin, because contains 14 - 25% of humus. Higher degree of base saturation and poorly acid to poorly basic soil solution reaction, made possible of the substantial heavy metals adsorption on sediment particles.

During the research period were established that the concentrations of all elements vary in relatively wide ranges. The lead concentrations vary from to 65 - 158,25 $mg.kg^{-1}$ (R - I); copper - 19,2 (R- I) to 49,0 $mg.kg^{-1}$ (R - II); cadmium - 0,31 (R - III) to 3,0 $mg.kg^{-1}$ (R - I); zinc 92,0 (R - II) to 370 $mg.kg^{-1}$ (R - I); the highest concentrations of nickel were measured in the sediment from 1996. (4500 $mg.kg^{-1}$), but vary from 493,7 to 4500 $mg.kg^{-1}$ (R - I); the highest concentrations of chromium were, also, measured in the sediment from 1996. (2100 $mg.kg^{-1}$ - R - I), and the lowest concentration was 97,5 $mg.kg^{-1}$ (R - II). The

Table 1. - Mean annual heavy metal concentrations during the period 1991-97. yr.

Watersheds	Pb	Cd	Cu	Zn	Ni *	Cr*
	Concentrations, $mg.kg^{-1}$					
R I	113,6	0,85	23,13	175,64	1867,7	752,5
R II	114,07	1,54	26,80	179,44	847,14	380,0
R III	104,8	0,79	27,66	228,23	1455,2	960,5

* for period 1992 - 1997. god.

Legislation concerning critical limits of heavy metals in suspended sediment in Serbia does not exist. Official critical limits of heavy metals for sediment are available for several countries in Europe (DE VRIES, *et. al.*, 1998), but the values between some countries are very large. Also, the information on the ecotoxicological basis is mostly not clear. In most cases, values are derived by the equilibrium partition method using MPC (maximum permissible concentration) values for surface water, and related to direct and indirect effects to the living organisms in water - sediment systems. The range in critical limits based of those data, equals 15 - 100 $mg.kg^{-1}$ for Pb; 0,6 - 2,4 $mg.kg^{-1}$ for Cd; 36 - 120 $mg.kg^{-1}$ for Cu; 123 - 1050 $mg.kg^{-1}$ for Zn; 10 - 180 $mg.kg^{-1}$ for Ni; and 37 - 120 $mg.kg^{-1}$ for Cr. This range is slightly higher than the provisional range provided by OSPAR (1996), which equals 5 - 50 $mg.kg^{-1}$ for Pb, Ni and Cu; 0,1 - 1,0 $mg.kg^{-1}$ for Cd; 50 - 500 $mg.kg^{-1}$ for Zn and 10 - 100 $mg.kg^{-1}$ for Cr.

Based on this criteria are established the following:

a) Lead (Pb): The mean concentrations in the all watersheds (113,6 $mg.kg^{-1}$ - R - I; 114,07 $mg.kg^{-1}$ - R - II, and 104,84 $mg.kg^{-1}$ - R - III) are higher than critical limit values according to both of criteria. In case OSPAR (1996) critical limits, the differences are the more significant.

b) Cadmium (Cd): The mean concentrations of Cd (R - I - 0,85 $mg.kg^{-1}$; R - II - 1,54 $mg.kg^{-1}$ and R - III 0,79 $mg.kg^{-1}$) are in the accepted critical limits of European countries (0,6 - 2,4 $mg.kg^{-1}$); OSPAR values (0,1 - 1,0 $mg.kg^{-1}$), concentrations in sediment from R - II watershed is higher. Many authors (KABATA - PENDIAS AND PENDIAS, 1989; WHO, 1980), concluded that Cd which is sorbed in soil mostly immobile at pH 7 - 9. Also, it is known fact that Cd forms stabile compounds with organic matter and than mostly bring out with organic matter.

c) Copper (Cu): Concentrations of Cu in the all watersheds (R - I - 23,13 $mg.kg^{-1}$; R - II - 26,80 $mg.kg^{-1}$; R - III - 27,65 $mg.kg^{-1}$) are under critical limit values in European countries (30 - 120 $mg.kg^{-1}$); but to frame critical (5 - 50 $mg.kg^{-1}$) by OSPAR (1996). In soils formed on serpentinites, Cu and Zn are in the deficiency. Copper, as the most immobile element on soil, was eroded from organic and surface mineral layers, together with stable chelation and mostly complexed with humic acids, and in smaller part with fulvic acids. Great impact on Cu contents in sediment has plant material from Ol layer, which was on part transformed in sediment.

d) Zinc (Zn): Concentrations of Zn from all watersheds (R - I - 175,64 $mg.kg^{-1}$; R - II - 179,44 $mg.kg^{-1}$; R - III - 228,23 $mg.kg^{-1}$), according both of criteria

were in the frame of accepted limits (123 - 1050 $mg.kg^{-1}$ for European countries and 50 - 500 mg.kg-1 from OSPAR). Zinc and copper showed similar trend of accumulation in sediment, although Zn has been eroded from watershed in more higher concentrations. The basic factors which regulated mobility of Zn in soil, are similar as the Cu, although Zn there is, generally, in soluble forms (KABATA - PENDIAS AND PENDIAS, 1989).

e) Nickel (Ni): The mean concentrations of Ni (R - I - 1876,74 $mg.kg^{-1}$; R - II - 847,14 $mg.kg^{-1}$; R - III - 1455,24 $mg.kg^{-1}$), more times are higher than critical limits, according both of criteria. The high concentrations of Ni from R - I watershed are measured, especialy after forest felling. The high concentrations of Ni in sediment, generally, originated from topsoil in which was complexed in the more soluble chelation.

f) Chromium (Cr): The mean concentrations of Cr (R - I - 752,5 $mg.kg^{-1}$; R - II - 380,0 $mg.kg^{-1}$; and R - III - 960,5 $mg.kg^{-1}$), are also, more time higher than the critical limit values after both of criteria (37 - 120 $mg.kg^{-1}$ - European countries and 10 - 100 $mg.kg^{-1}$ - OSPAR), especially in R - I and R - III watersheds. By erosion processes serpentite minerals in which appear in to enter into crystal lattice of layer serpentinite, as dominant minerals in clay and colloidal fractions in soils of the experimental watersheds removed from top soil layers and riched in sediment. Chromium was strong completed with organic matter, first of all, with humic acid, and with clay mineral, building almost insoluble complexes (KABATA - PENDIAS AND PENDIAS, 1989; KEFFER *et. al.*, 1986).

Eroded sediment contains a substantially higher content of organic matter and nutrients / pollutants than topsoil from which it was derived. The difference is called the enrichment factor in eroded sediment (YOUNG 1991). The data about the mean heavy metal contents in 0 - 10 cm of topsoils profile in R - I and R - III watersheds (BELANOVIĆ, 2000) and in 0 - 15 layer in R - II watersheds (KADOVIĆ, *et. al.* 1994), are presented in table 2.

Tables 2. - Heavy metal contents in top soil layers

Watersheds	Cu	Zn	Cd	Pb	Cr	Ni
	Elements $mg.kg^{-1}$					
R I (0 - 10 cm)	15,50	88,52	1,12	62,49	690,0	1240,0
R II (0 - 15 cm)	19,0	62,50	0,18	39,25	685,0	1185,0
R III (0 - 10 cm)	22,51	69,52	1,00	49,52	900,0	1925,0

Enrichment factor (EF) values are presented in table 3 were calculated on the basis of heavy metal contents in the sediment and the topsoil.

Table 3. - Enrichment factor of sediment

Watershed	Elements					
	Cu	Zn	Cd	Pb	Cr	Ni
R I	1,49	1,98	0,89	1,82	1,09	1,51
R II	1,41	2,87	8,56	2,91	0,55	0,71
R III	1,23	3,28	0,79	2,12	1,07	0,76

The concentration differences between sediment and topsoil, may be, first of all, that the upper most few mm of soil are richer in nutrients/microelements than 10 or 15 cm normally bulked for analyses, and secondly, that erosion selectively removes nutrient - rich material; the relative importance of these factors is not known. The high factor value of Cd in R - II watershed, can be explain by the meadow vegetation presence and with smaller organic matter content than in watersheds under forest plantations.

CONCLUSION

Concentrations of heavy metals Pb, Cd, Cu, Zn, Cr and Ni in sediment from three experimental watersheds on Mt. Goč, was analyzed during the period 1991-97. Soils in the experimental watersheds belong humic-silicate on serpentinite and eutric cambsol on serpentinites. The mean concentrations of these heavy metals have the next ranges (mg.kg^{-1}): Pb - 104,8 - 114,07; Cd - 0,79 - 1,54; Cu - 23,13 - 27,66; Zn - 175,64 - 228,23; Cr - 380,0 - 960,5 and Ni - 847,14 - 1867,7.

Based on the accepted criteria, were established that the mean annual concentrations are higher in relate both standards of the critical limit values for Pb, Ni and Cr in all watersheds. The mean concentrations of Cd were in frame of critical values in European countries. In relate to the OSPAR, concentrations were higher in sediment from R - II watershed. The mean content of Cu were under critical limits in relate to the OPSAR. In case of Zn, the mean concentrations were in frame of critical values in relate to the both of standards.

Enrichment factor values of sediment in R - I and R - II watersheds, under decidious plantings, showed that Cu, Zn, Pb and Cr were higher in sediment. The higher concentration of Ni in sediment from R - I watershed lakely was the result of forest felling in relate to the R - II watershed. In case R - III watershed (natural meadow vegetation), the concentrations of Cu, Zn, Cd and Pb were more higher in sediment than in topsoil (0 - 15 cm), and the concentrations of Cr and Ni were higher in topsoil than in the sediments.

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