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Accumulation of Heavy Metals as Related to Cation Exchange in Some Forest and Pasture Soils of Stara Planina (Serbia)

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Abstract

Heavy metal accumulation in the components of terrestrial ecosystems is conditioned by the deposition intensity, soil characteristics, mineral composition, and vegetation type. The exchangeable ionic reactions between the adsorptive complex and the soil solution are important sources of nutrients and also a significant mechanism for heavy metal retardation in the soil. The aim of this study is to determine the effect of cation exchange capacity on heavy metal accumulation in the soils under different vegetation (forest and pasture). The differences in the behaviour of individual elements depending on CEC in forest and pasture soils result primarily from different ratios of base and acid cations in the soil adsorptive complex and their reactions with heavy metals.

Keywords: Heavy metal, cation exchange capacity, forest soil, pasture soil

1. Introduction

Heavy metal accumulation in the components of terrestrial ecosystems is conditioned by the deposition intensity, soil characteristics, mineral composition, and vegetation type. Soil, as a natural resource, has the main ecological and production function in the terrestrial ecosystems. It is significant for the retention of heavy metals, primarily thanks to its buffer and filter role. In the soil adsorptive complex, base and acid cations in different ratios are in dynamic balance with the corresponding cations in the soil solution. The exchangeable ionic reactions between the adsorptive complex and

the soil solution are important sources of nutrients and also a significant mechanism for heavy metal retardation in the soil.

The distribution of exchangeable cations in the soil profiles of the same soil type depends on the type of vegetation (pasture, forest), as well as on the properties of the element and its cycling in the ecosystem (Jobbágy and Jackson, 2004). This research is especially significant in hilly and mountainous areas, where forest and agroecosystems are combined. The study of soil properties in the conditions of different vegetation covers points to the potentials of the sustainable use of this strategic resource in different silvopastoral systems.

The research of the soil chemical properties under different land uses is especially significant for the organisation of the territory in the aim of sustainable management. Ruark and Schoeneberger (2003) report that the cultivation of woody plants and other crops together (silvopastorally) improves the soil properties. The same authors report that the research during the past two decades emphasised three main indirect processes of soil property improvement: 1) increased N input through biological nitrogen fixation by nitrogen-fixing trees, 2) enhanced availability of nutrients resulting from decomposition of tree biomass, 3) greater uptake of nutrients from deeper layers by the roots of tree species.

The content of mineral nutrients in the soil solution is defined by soil type, climate and vegetation type, i.e., nutrient cycling in the ecosystem. Different processes and chemical reactions in the soil, especially the transformation of organic matter, affect the cation release from the adsorptive complex. Thus, according to Jobbágy and Jackson (2004), in base saturated soils (75 – 100%), surface layers contain higher concentrations of Ca, Mg and Na under forest, while the content K ions is higher under pasture. However, according to Krishnaswamy and Richter (2002), the content of base cations is in direct relation with soil acidity. The above authors claim that base cation content in the top 30 cm of soils is 73.9 % under pasture and 22.8 % under forest, where the observed soil pH-value was lower. According to the same authors, carbon content is higher in forest soils, whereas the lower content in pasture soils is attributed to the low quantity of organic residue and frequent wildfires. Under such conditions, with small losses of carbon quantity, pH-value and the content of exchangeable cations increase, and Al ions are exchanged by Ca²⁺ ions.

Based on the previous research in this area and based on the literature, higher contents of base cations can be expected in pasture soils, and of aluminium in forest soils. The differences in base cation contents in the adsorptive complex will have a significant impact on the heavy metal accumulation in the soils.

The aim of this study is to determine the effect of cation exchange capacity on heavy metal accumulation in the soils under different vegetation (forest and pasture).

2. Material and Method

The study area is Stara Planina, the localities Babin Zub - N= 43°22'35.7'' E= 022°37'38.3'' altitude 1547 ± 4m, Široke Luke - N= 43°14'24.7'' E= 022° 51'36.8''

altitude $1288 \pm 6\text{m}$, and Prelesje - N= $43^{\circ}10'42.5''$ E= $022^{\circ}56'20.0''$ altitude $1287 \pm 7\text{m}$.

As for the climate, Stara Planina region is the transition zone between temperate-continental climate in the north and montane climate of the Balkan mountainous system in the southeast. Annual temperature amplitude declines from the north towards the south and southeast, so the difference in air temperature between Zaječar and Dimitrovgrad is more than 2°C . The distribution of annual precipitation sum is different in the area of Stara Planina, in the Timok valley annual precipitation is 700 mm, while in Pirotska Dolina (valley), it is often below 600 mm. Based on Popović's (2007) study and the analyses of meteorological data for the area of Stara Planina (Đorđević-Milošević, 1996), it can be concluded that the change in the direction of arid climate is underway.

Stara Planina vegetation, in general, is characterised by a considerable diversity of forest, shrub, meadow, pasture and peat bog communities and, as such, it is one of the centres of flora diversity of the Balkan Peninsula, with 147 identified threatened and endemic species (Mišić et al., 1978; Randelović, Randelović, 2002).

Pasture areas of the study sites are occupied by plant community *Agrostietum vulgaris (capillaris)* Z. Pavlović 1955. Meadows of *Agrostietum vulgaris* are of secondary anthropogenic origin, as they are the result of two anthropogenic factors: reduced area under forest on the one hand, and mowing, on the other hand. The association *Agrostietum vulgaris* covers a huge area in the hilly region. On Stara Planina, this community is the dominant meadow type and it is widely distributed. In this area, it develops on quite different sites.

During the plant community research in beech forest ecosystems, the community of subalpine beech forest (*Fagetum moesiacaе subalpinum* Greb. 1950) was identified at the site Babin Zub: canopy 0.6, diameter of mean stand tree $d_s - 36\text{cm}$, height 25.4 m and age 110 years.

The community of montane beech forest (*Fagetum moesiacaе montanum* B. Jov. 1976, subassociation *typicum facies asperulosum*) was identified in beech forest ecosystems at the site Javor: canopy 0.6 – 0.8, diameter of mean stand tree $d_s - 34\text{cm}$, height 24.0 m and age 130 years.

The community of montane beech forest (*Fagetum moesiacaе montanum* B. Jov. 1976, subassociation *typicum facies nudum*) was identified in beech forest ecosystems at the site Prelesje: canopy 0.7, diameter of mean stand tree $d_s - 19\text{cm}$, height 17.3 m and age 65 years.

Four soil profiles were opened in each of the pasture areas. Based on morphological and basic physico-chemical soil characteristics after FAO (1985) classification, two types of pasture soils were determined:

Babin Zub:

Dystric leptosol on sandstone

Javor:

Dystric leptosol on chlorite schist

Dystric cambisol on chlorite schist

Prelesje:

Eutric cambisol on sandstone

Dystric leptosol on sandstone.

Four soil profiles were opened in each of the forest areas. Based on morphological and basic physico-chemical soil characteristics after FAO (1988) classification, two types of pasture soils were determined:

Babin Zub:

Dystric cambisol on sandstone

Javor:

Dystric cambisol on chlorite schist and phyllite

Prelesje:

Dystric cambisol on sandstone

Eutric Cambisol on sandstone.

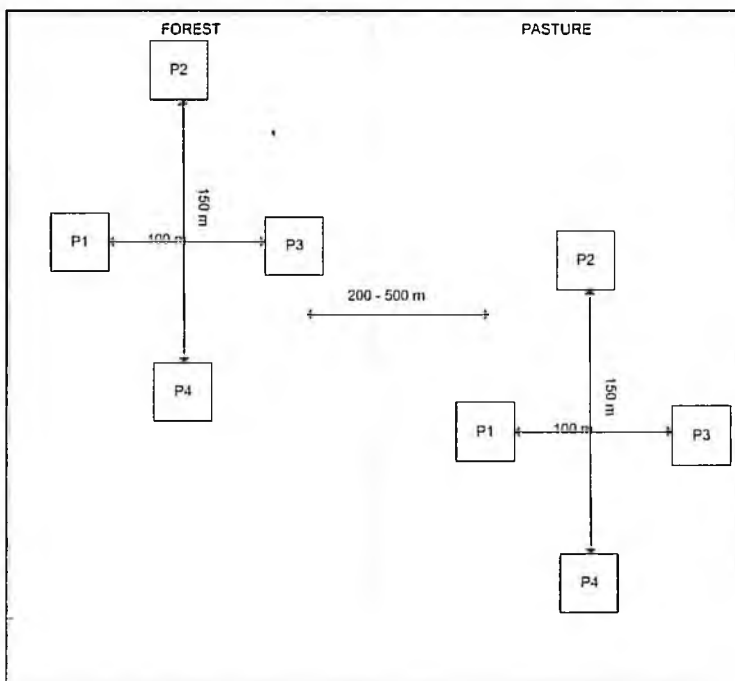


Figure 1. Profile opening scheme in pasture and forest areas

The soils were sampled at the depth of: 0-5, 5-10, 10-20 and 20-40 cm. The main physical and chemical soil characteristics were determined by ICP Methodology (IPC Forest Manual, Part III, Soil Sampling and Analysis, Hamburg, updated 2006). Total heavy metal content was determined by atomic adsorption spectrophotometer (AAS), and the conservation and preparation of samples by the extraction with HCl, HNO₃ and H₂O₂ (3:1:2). Cation exchange capacity was calculated as the sum of acid (Al, H, Fe and Mn) and base (Ca, Mg, K, and Na) cations. Exchangeable cations were extracted with

0.1M BaCl₂, and measured (ISO11260 & ISO 14254). The significance of differences between total heavy metal contents, as well as other characteristics of forest soil and pasture soil, was tested by the analysis of variance. Indicator values of heavy metal sorption were calculated according to equation:

$$I_{SO} = I_{Ad} / RI_1 \text{ (range 0- 5)}$$

I_{Ad} – Indicator value of adsorption

The retardation indicator (*Helhveg*, 2000) serves for the classification of heavy metal mobility in soils. The retardation indicator is determined in function of the pH value and supplements (clay content, organic content, Fe-oxide), and calculated according to equation:

$$RI_1 = RI_{pH} + RI_{Organic\ content} + RI_{clay\ content}$$

Indicator values of heavy metal adsorption (*Belanovič*, 2006), were calculated according to equation:

$$I_{Ad} = \sum_i^0 \left[\left(\frac{TM}{Ca + Mg + K} \right)_c \times \omega_i \right]; i - \text{layer (0-5; 5-10 and 10-20)}$$

I_{Ad} – indicator of adsorption (rank 0 - 10); $(TM/(Ca+Mg+K))_c$ – class of indicator of adsorption (class 1-5),

TM – content of heavy metals (Zn, Cu, Pb and Cd); (Ca+Mg+K) exchangeable ionic Ca+Mg+K;

3. Results and Discussion

Cation exchange capacity is higher in forest soils than in pasture soils. Forest ecosystems are characterised by a higher degree of heavy metal retardation than grass ecosystems or aquatic ecosystems, thanks to their larger relative area and greater roughness. The processes such as dry and wet deposition, washing down from the surface of plant photosynthetic organs, canopy drop and stem flow and the deposition in forest litter on the soil surface, as a rule, result in the increase in heavy metal content on the soil surface (*Vanmechelen et al.*, 1997).

The results of the analysis of variance (F-test) (Table 1) show that there are no statistically significant differences between total concentrations of Zn, Pb, Cd in forest soils and pasture soils at the significance level 95%.

Table 1. Results of the analysis of variance

LSD 95%															
	Cu ²⁺	Zn ²⁺	Pb ²⁺	Cd ²⁺	orgC	Humus	totalN	CEC	Al ⁺⁺⁺	Ca ²⁺	Al/ (Ca+Mg)	Al/Ca	AxE	Fe	Mn
F calculate	7.90	0.01	0.67	1.46	5.78	5.55	7.30	10.0	6.64	0.08	7.29	6.86	7.03	2.69	16.89
F table	3.84	3.84	3.84	3.84	3.94	3.94	3.84	3.96	3.96	3.96	3.96	3.96	3.96	3.96	3.96
Average value Forest	24.21	66.22	26.07	0.81	3.55	6.19	0.39	30.19	22.52	5.78	8.67	10.66	23.14	0.016	0.41
Average value Pasture	31.52	66.65	24.62	0.69	5.22	8.97	0.51	21.92	14.61	5.53	3.82	4.65	15.02	0.009	0.22
Group homogene	a b	a a	a a	a a	a b	a b	a b	a b	a b	a a	a b	a b	a b	a b	a b

The results of the analysis of variance (F-test) show that there are statistically significant differences, at the significance level 95%, between the contents of total Cu, organic C, humus, total N, exchangeable cations, contents of exchangeable Al, Fe and Mn, Al/Ca ratio, total acid cations (AxEc), in forest soils and pasture soils. According to LSD test, at the significance threshold 5%, two groups of factors separate according to the significance of the contents of total Cu, organic C, humus, total N, exchangeable cations, contents of exchangeable Al, Fe and Mn, Al/Ca ratio, total acid cations (AxEc).

Heavy metals occur in the soil as exchangeable - adsorbed on soil colloids, specifically-adsorbed, bound in various chemical compounds (oxides, carbonates, phosphates, sulphides) and structurally bound in the silicates (primary and secondary minerals) (Adriano, 1986). Different factors affect the bonding of heavy metals to the soil, and the main problem is the estimation of the heavy metal load in the soil. The load of heavy metals in the soil can be indicated to some extent by the monitoring of their content in the soil.

The assessment of the soil sorptive capacity renders significant information on the soil susceptibility to heavy metal loads (Sastre et al., 2006). According to Sastre et al. (2006) the concentration Ca+Mg in the soil solution increases with the increase in heavy metal concentration, which points to the cation exchange process between these macroelements and heavy metals. By the increase in heavy metal content, the cation exchange process increases and leads to the release of Ca, Mg and K from the soil adsorptive complex. It is a fact that cation exchange is the leading force in metal sorption.

Sparling et al., (2001) conclude that soil pH is related to land use. According to Krishnaswamy and Richter (2002), the content of base cations is in direct correlation with soil acidity. They report that base cation content in the study conditions, in the top 30 cm under pasture was considerably higher than in forest soils where the observed soil pH-value was lower.

Soil acidification has a significant impact on the soil chemical and biological processes. Higher acidification of forests and pastures by atmospheric deposition causes an irreversible decline of cation exchange capacity (CEC) and the mobilisation of potentially toxic elements Al, Fe and Mn (Blake and Goulding, 2002). Soil acidification reduces the number of plant species in natural pastures.

Soil characteristics positively correlated with cadmium retention were pH, organic matter content and cation exchange capacity (CEC), specific surface area, while free iron oxides were negatively correlated (De Matos, et al., 2001). The buffer characteristics of the soil solid phase are conditioned by the quantity of colloids and the type of adsorbed cations. A high significance is assigned to the energy of hydrogen ion adsorption by the colloids and the degree of colloid dissociation. The soil organic matter mainly consists of weak acids so, accordingly, hydrogen ions are weakly dissociated, and for this reason organic matter increases the buffering capacity of the soil. Adsorption, surface deposition and polymerisation are the examples of sorption, the basic term for the retention mechanism on the soil surface. The sorption of metal cations depends primarily on pH value, and it is characterised by a narrow pH rank when adsorption increases up to almost 100%. De Matos et al. (2000) showed the strong influence of the cation exchange phenomenon on the retardation and mobility of Zn and Cd. Zinc retention was positively correlated with pH, CEC and specific surface area (de

Matos, et al., 2001). Copper retention has positive correlation with pH, sum of bases or exchangeable calcium, organic matter content and to CEC (De Matos et al., 2001). Lead retention was better correlated to clay content, pH and SB or exchangeable Ca (De Matos, et al., 2001).

Table 2 presents the relation between heavy metals and cation exchange of the adsorptive complex. Zn and Pb concentrations increase with the CEC increase in forest and pasture soils. In forest and pasture soils, Cu contents decrease with the increase of CEC. Cd concentration increases with the CEC increase in forest soil, while Cd contents decrease with CEC increase in pasture soils. The differences in the behaviour of individual elements depending on CEC in forest and pasture soils result primarily from different ratios of base and acid cations in the soil adsorptive complex and their reactions with heavy metals.

The heavy metal solubility is mainly caused by relatively constant soil characteristics, such as the contents of organic matter and clay, pH value, but also the parameters such as the concentration of available Ca and the concentration of soluble organic carbon (De Vries and Bakker, 1998). The assessment of pollutant sorption in the soil is based on the solid – liquid distribution coefficient, which is the relation between the quantity of heavy metals sorbed on the solid phase and the total concentration in the solution in contact with the soil (Sparks, 1995; Sastre et al., 2006).

Some authors suggest the ratios of elements as the criterion for the soil chemical status from the aspect of root development, i.e. Ca/Al, Mg/Al, base cations/Al (Rehefuess and Prietzel, 1998; Alveteg, 1998; Shaodong and Min, 2004). Al/BCE ratio in pasture soils is on the average lower than in forest soils in the area of Stara Planina (Belanović and Košanin, 2004). Al/Ca ratio does not define the critical values from the aspect of root growth (Kulhavy, 1998), but the wide ratio of Al/Ca results in the low seed development of some mountainous plants (Van der Berg et al., 2003). Also, the ratio Al/base cations indicates the changes in critical loads occurring due to the increased or decreased deposition (Posch and Hettelingh, 2001). Several studies report the unfavourable ratio Mg/Al in the soil solution as the main problem of increment in European forests (Joki-Heiskala et al., 2003). Rehefuess and Prietzel (1998) claim that tree vitality and increment depend on the supply of nutrients Mg, K and Ca in the soil solution and their interaction with Al. Soil acidification has a direct or indirect effect on the increase of heavy metal concentration in the soil solution.

The sorption indicator (Table 3) represents the retardation capacity of the soil for heavy metals, and is obtained from the ratio of adsorption indicators and retardation indicators. The adsorption indicator points to the equilibrium state between macro elements Ca, Mg and K and heavy metal contents. If the sorption indicator is higher, the soil capacity of accumulating and retaining heavy metals is lower, and this increases the potential pollution of surface and ground waters and the environmental quality in general.

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Table 2. Results of regression analysis of total heavy metal contents and CEC

Element	Regression equation	R	R ² (%)	P-value	F	F -tab	t _a p- value	t _b p- value
FOREST								
	$Zn = \frac{1}{(0,0086 + 0,183 \cdot CEC^{-1})}$	0.55	30.20	0.0001	19.90	4.04	4.554 0.000	4.461 0.0001
	$Cu = 33,565 \cdot CEC^{0,109}$	-0.15	2.18	0.3215	1.00	4.06	9.78 0.000	-1.002 0.3215
	$Pb = \frac{1}{(0,0269 + 0,3888 \cdot CEC^{-1})}$	0.43	18.51	0.0023	10.45	4.04	4.855 0.000	3.232 0.0023
	$Cd = 1,1133 - \frac{7,441}{CEC}$	-0.24	5.95	0.0947	2.91	4.04	5.549 0.0000	-1.706 0.0947
PASTURE								
	$Zn = \frac{1}{(-0,00299 + 0,4487 \cdot CEC^{-1})}$	0.69	48.14	0.0000	39.91	4.07	-0.786 0.4360	6.317 0.000
	$Cu = 3,1169 + 586,779 \cdot CEC^{-1}$	0.59	34.79	0.000	22.94	4.07	0.475 0.6370	4.789 0.000
	$Pb = -27,58 + 16,96 \cdot \ln(CEC)$	0.59	34.61	0.000	22.76	4.07	-2.54 0.0148	4.771 0.000
	$Cd = 0,981 - 0,015 \cdot CEC$	-0.19	3.62	0.2104	1.62	4.07	3.709 0.0006	-1.271 0.2104

Function parameters: S_r - standard error of regression; t_a - t - test; t_b - t - test; p - confidence level; F - calculated; F value; F₁ - F value from tables of F distribution; R² - determination coefficient F (0.05; k-1 and N-k); R - correlation coefficient

Table 3. The indicator value for heavy metal sorption in studied soils

Locality	Profile	Is Zn	Is Cu	Is Pb	Is Cd
		FOREST			
Javor	9	4.24	2.22	1.40	0.95
	10	4.17	2.27	1.69	4.55
	11	3.10	1.53	1.16	3.06
	12	2.63	1.72	1.32	2.78
Babin Zub	17	4.35	2.28	1.79	4.06
	18	4.91	2.46	1.89	4.91
	19	3.89	1.97	1.58	3.94
	20	4.67	1.83	1.58	4.00
Prelesje	26	1.52	1.09	0.80	1.52
	27	4.33	2.17	1.70	4.00
	28	1.67	1.28	0.97	1.84
	29	2.62	1.67	1.16	3.06
		PASTURE			
Javor	1	2.22	1.31	0.91	0.71
	2	2.80	1.70	1.11	3.33
	3	3.46	1.99	1.29	3.08
	4	2.76	1.50	0.94	2.72
Babin Zub	13	2.35	1.24	1.16	0.63
	14	3.33	2.00	1.67	3.20
	15	3.70	1.99	1.61	3.08
	16	3.70	2.13	1.61	3.33
Prelesje	22	2.86	2.08	1.16	3.33
	23	2.62	1.67	1.27	3.33
	24	2.56	2.03	1.20	2.90
	25	3.33	2.17	1.42	1.74

The indicators of heavy metal adsorption are in relation with their accumulation in individual layers of the above soils and range within the classes of very low to very high for Cd and medium to very high for Zn, Cu and Pb. The sorption indicator ranges between 0-5, depending on I_{Ab} and R_1 , i.e. heavy metal load and retention capacity for heavy metals in the study soils. The differences are conditioned by the state of nutrient elements in the soil, edaphic conditions, and type of vegetation.

4. Conclusion

This research deals with forest soils and pasture soils on Mt. Stara Planina. Heavy metal accumulation in the components of the terrestrial ecosystems is conditioned by the deposition intensity, soil characteristics, mineral composition of the substrate, and vegetation type. In the soil adsorptive complex, base and acid cations in different ratios are in dynamic balance with the corresponding cations in the soil solution. The exchangeable ionic reactions between the adsorptive complex and soil solution are important sources of nutrients and also a significant mechanism for heavy metal retardation in the soil.

Zn and Pb concentrations increase with the CEC increase in forest and pasture soils. In forest and pasture soils, Cu contents decrease with the CEC increase. Cd concentration increases with the CEC increase in forest soil, while Cd contents decrease with the CEC increase in pasture soils. The differences in the behaviour of individual elements depending on CEC in forest and pasture soils result primarily from different ratios of base and acid cations in the soil adsorptive complex and their reactions with heavy metals.

The assessment of the soil sorptive capacity renders significant information on the soil susceptibility to heavy metal loads. The sorption indicator represents the soil retardation capacity for heavy metals. The adsorption indicator points to the equilibrium state between macrolelements Ca, Mg and K and the content of heavy metals. If the sorption indicator is higher, the soil capacity of accumulating and retaining heavy metals is lower, and this increases the potential pollution of surface and ground waters and environmental quality in general.

The indicators of heavy metal adsorption are in relation with their accumulation in individual layers of the above soils and range within the classes of very low to very high for Cd and medium to very high for Zn, Cu and Pb. The differences are conditioned by the state of nutrient elements in the soil, edaphic conditions, and type of vegetation.

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