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SERIJA A

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CONTENT OF HEAVY METALS IN THE FOREST OF BEACH ON THE

CONTENT OF HEAVY METALS IN THE FOREST OF BEACH ON THE MT CRNI VRH AND IN THE FOREST OF SESSILE OAK ON THE MT. FRUŠKA GORA

Milan KNEŽEVIĆ, Snežana BELANOVIĆ, Olivera KOŠANIN,
Batkо KADОVIĆ

Faculty of Forestry, Belgrade, Yugoslavia

Knežević Milan, Snežana Belanović, Olivera Košanin, Ratko Kadović (2000): *Content of heavy metals in the forest of beach on the Mt Crni Vrh and in the forest of sessile oak on the Mt. Fruška Gora - Zemljiste i biljika* Vol. 49, No. 1, 19 - 28, Beograd.

The cycling of heavy metals in forest ecosystems is conditioned by type of element, type of soil and type of vegetation that, together or individually, can have a decisive significance for their input in the particular parts of ecosystems.

This paper presents the results of the research of heavy metal (Cu, Pb, Cd and Zn), in the two forest ecosystems:

on the mountain Crni Vrh in the forest of beech (*Fagetum moesiaceae montanum*) on podzolic acid brown soil; and

on the mountain Fruška Gora in the forest of beech and sessile oak (*Querco-fagetum*) on acid brown soil.

The samples of the soil and the preparations of samples were taken according to UNEP-UN/ECE (1994) technique. Major physical and chemical properties of soil were researched by standard methods recognized by JDPZ. The contents of total lead, copper, cadmium and zinc in forest soil and plant material were determined by AAS method on the PYE Unicorn SP9 apparatus.

Key words: forest ecosystem, heavy metals, forest soils, edificators.

INTRODUCTION

Anthropogenic impacts destroy the laws of natural balance and cause degradation and destruction of forest ecosystems.

Forest ecosystems, both those adjacent to industrial centers and those situated in relatively unpolluted regions, are exposed to the effects of hazardous pollutants.

Air pollution occurs as the predisposition factor before the occurrence of pests and diseases, it causes forest damage as well as forest dying (SMITH, 1990).

This paper presents the results of the study heavy metals (Pb, Cd, Cu and Zn) content in the soil and in the main vegetative organs of edificators in the two most important forest ecosystems in Serbia.

OBJECTS OF STUDY

The following two sites were studied:

- Crni Vrh, mountain in East Serbia near the mining and metallurgical basin Bor. The study was carried out in one of the most important forest communities of Serbia, community of montane beech (*Fagetum moesiaca montanum*), on podzolized acid brown soil over gneiss, altitude 740m, north exposure, slope 15°.

- Fruška Gora is in the north part of Srem. It is actually a low mountainous arc, which connects the mountains in Slavonia and Šumadija. The study was carried out in the forest of sessile oak (*Quercetum montanum*), on acid brown soil over limestone, altitude 507m, Southwest exposure, slope 5-8°.

METHOD

The main physical-chemical characteristics of the soil were analyzed by standard methods accepted by JDPZ (Methods for the research of soil physical characteristics, Book 5, 1971; Chemical methods of soil research, Book 1, 1966). The samples of soil and plant material for the determination of the contents of biogeneous elements and heavy metals were analyzed by methods UNEP-UN/ECE (1994). Heavy metals in the soil and plant material were determined by atomic absorption spectro-photometry. Exchangeable cations (acid and base) were determined by UNEP-UN/ECE (1994).

RESULTS

Forest species differ in their capacities of accumulating air-borne substances. Air pollution can have a direct and an indirect impact on plants. The direct impact affects the leaves (1) and results in reduced photosynthesis and shortened growth period. Broadleaf species are especially endangered by hazardous gas emissions because of the larger assimilation area during the growth season, which can result in premature leaf falling.

Indirect impact of heavy metals is realized through the soil. Heavy metals, in addition to their twofold effect on the soil, are also toxic to microorganisms and root hairs.

Terrain and laboratory analysis of the soil shows that in the study location at Crni Vrh in the forest community of montane beech, podzolized acid brown soil occurs.

Morphological structure of podzolized acid brown soil at Crni Vrh is Olf - Oh - A - (B) - C. Study soil is characterized by sandy-loamy texture (Table 1).

Chemical characteristics (Table 2) range within the scope of described characteristics of podzolized acid brown soil (JOVIĆ and KNEŽEVIĆ, 1990, AVDALOVIĆ, 1972).

Soil reaction is strongly acid. Humus percentage at the depth of 0-5cm is 6.19%, and at the depth of 5-10cm, it is 3.36%. With further increase of the depth, humus content drops below 2%. Humus substances have the characteristics semi-raw humus.

Adsorptive complex is characterized by a high capacity of cation adsorption (27.99-20.80mg ekv/100g soil). The value decreases with the depth of soil profile. The study soil has an especially high capacity of adsorption of acid cations and hydrolytic acidity. The content of adsorbed bases is very low and, regarding the degree of base saturation (V%), the soil is base-unsaturated.

The soil is intermediate to rich in total nitrogen. The content of readily available K₂O is somewhat higher than that of P₂O₅. Actually, the content of assimilative forms of potassium and phosphorus in the soil is low, and slowly decreases with depth.

A very acid reaction of these soils is explained by the intensive pollution and by the close vicinity of mining and metallurgical basin Bor.

The soil in the sessile oak community (*Quercetum montanum*) on Fruška Gora has the characteristics of acid brown soil on limestone, with the following morpho-genetic structure: Olf - A - (B) - C. The results of particle size analysis (Table 1) show that study soil is a sandy loam.

Table 1. - Physical properties of the soil

Site	Profile	Depth cm	Hygroscopic moisture %	Particle size composition in %				Total clay+silt				
				2.0- 0.2mm	0.2- 0.06mm	0.06- 0.006mm	<0.002mm					
FRUŠKA GORΑ	1 / 96	Olf	-	3.67	3.90	30.80	21.70	27.30	7.80	8.50	56.40	43.60
		5 - 10	2.65	5.11	36.89	14.80	23.30	9.50	10.40	56.80	43.20	
		10 - 20	2.03	7.39	36.11	14.50	20.30	9.40	12.30	58.00	42.00	
	20 - 40	1.80	6.58	36.92	13.70	19.50	10.10	13.20	57.20	42.80		
		Olf	-	-	-	-	-	-	-	-	-	
		Oh	-	-	-	-	-	-	-	-	-	
CRNI VRH	3 / 96	0 - 5	1.68	29.08	17.32	12.40	18.70	11.30	11.20	58.80	41.20	
		5 - 10	1.28	30.46	17.54	11.70	18.40	9.60	12.30	59.70	40.30	
	(B)	10 - 20	1.13	26.83	19.97	11.00	18.40	8.10	15.70	57.80	42.20	
		20 - 40	1.16	23.49	21.01	12.30	17.50	9.30	16.40	56.80	43.20	

M. KNEŽEVIĆ *et al.* CONTENT OF HEAVY METALS*Table 2. - Chemical properties of the soil*

Profile N°	Depth	Horizon	pH H ₂ O	Y, cm 0.1 M NaOH (T-S)	Adsorptive complex mg equiv/100 g soil S	FRUSKA GORA T	V %	Humus %	C %	N %	C/N	Readily available P ₂ O ₅ in mg/100 g soil K ₂ O
1 / 96	0 - 3	Olf	6.22	5.76	-	-	-	51.13	29.66	1.79	16.6	>40.0
	0 - 5	A	6.58	5.74	7.16	4.66	21.40	82.12	6.52	3.78	0.38	8.0
	5 - 10	A	5.58	4.52	14.33	9.31	12.00	21.31	56.31	3.50	2.03	>40.0
	10 - 20	(B)	5.32	3.80	16.72	10.87	7.20	18.07	39.85	1.94	0.25	3.6
	20 - 40	(B)	5.20	3.70	16.72	10.87	2.80	13.67	20.48	1.34	0.16	18.6
	Olf	4.40	3.27	-	-	-	-	-	-	-	0.85	7.6
3 / 96	0 - 5	Oh	3.92	2.97	-	-	-	27.99	5.72	6.19	3.59	12.8
	5 - 10	A	3.86	2.90	40.59	26.39	1.60	-	-	0.28	0.40	8.60
	10 - 20	(B)	3.92	3.02	32.47	21.11	1.00	22.11	4.52	3.36	0.20	9.7
	20 - 40	(B)	3.96	3.03	32.95	21.42	0.20	21.62	0.93	1.95	0.11	0.50
	Olf	3.95	3.20	32.00	20.80	0.00	20.80	0.00	1.43	0.83	-	6.80

In the Olf layer, we observed a great accumulation of humus (51.13%), but also simultaneously a wide C:N ratio (16.6). The content of readily available P_2O_5 and K_2O in the Olf layer is very high, which indicates an intensive biogeochemical accumulation. The reaction is weak acid. The surface layer of A horizon (0-5cm) is characterized by weak acid reaction and a high degree of base saturation. Humus content decreases with depth (6.52-1.34%), but also the C:N ratio approaches the normal magnitude. The soil is well-supplied and even rich in nitrogen. The content of readily available forms of phosphorus and potassium in study soil is low and decreases with depth. Other chemical characteristics of the soil (Table 2) correspond to acid brown soil.

HEAVY METAL CONTENT IN THE SOIL

The presence of heavy metals in the soil is the result of both natural and anthropogenic effects. In the former case, heavy metals originate from parent rocks as the result of pedogenetic processes. Anthropogenic origin in forest ecosystems is mainly from the atmosphere. Heavy metals accumulate in the humus layer as the result of high adsorptive capacity of humus acids.

The aim of the study of heavy metal contents in the soil (Table 3) was to determine the degree to which the soil is loaded with heavy metals (Pb, Cu, Cd and Zn) at the sites Crni Vrh and Fruška Gora, as the consequence of air pollution. The results were compared to the permissible content in the soil, according to the Regulation (Official Gazette of Serbia, No.11/1990).

Lead content in the organogenic horizon of the podzolized acid brown soil on Crni Vrh, exceeds the allowed limit of $100\text{mg} \cdot \text{kg}^{-1}$. This refers especially to Olf layer, where the value of $475\text{mg} \cdot \text{kg}^{-1}$ was recorded. In the soil layer 0-40cm, lead content ranges from 31 to $35\text{mg} \cdot \text{kg}^{-1}$. These relatively low values, compared to the organogenic horizon, can be explained by low mobility of lead in the soil. The recorded values are still higher than the usual quantities of lead originating from parent rock.

Cadmium content in the Olf layer exceeds the allowed value of $2\text{mg} \cdot \text{kg}^{-1}$, and amounts to $3\text{mg} \cdot \text{kg}^{-1}$. In Oh layer, Cd content is still high $1.5\text{mg} \cdot \text{kg}^{-1}$, but it is within the allowed limits. In the soil layer 0-40cm, Cd content is $0.4\text{mg} \cdot \text{kg}^{-1}$, and it is within the allowed limits, which is explained by cadmium not being subject to leaching.

The content of Zn in the organogenic Olf and Oh layers is within the allowed limits. In the soil layer up to 40cm, the values approximate $20\text{mg} \cdot \text{kg}^{-1}$ i.e. significantly below the allowed $300\text{mg} \cdot \text{kg}^{-1}$. From the above it can be seen that there is no danger from the hazardous effect of Zn.

In the Olf layer, the content of Cu is $1375\text{mg} \cdot \text{kg}^{-1}$ and in the Oh layer it is $725\text{mg} \cdot \text{kg}^{-1}$, which means that the allowed limit of $100\text{mg} \cdot \text{kg}^{-1}$ is highly exceeded.

From the above analysis it can be concluded that the study soil, in the forest community of montane beech on Crni Vrh, is under a strong effect of atmospheric pollutants. Especially high concentrations of Cu, Pb and Cd in the organogenic horizon are explained by the high adsorption capacity.

Lead content in the Olf layer on Fruška Gora is $35\text{mg} \cdot \text{kg}^{-1}$. The highest value occurs in the layer 0-10cm ($45\text{mg} \cdot \text{kg}^{-1}$). The concentration of Pb is lower than the allowed value $100\text{mg} \cdot \text{kg}^{-1}$ throughout the soil profile.

Cd content in the Olf layer is $2.5\text{mg} \cdot \text{kg}^{-1}$. It is higher than the allowed value, which does not occur in other parts of the profile.

The content of Zn is similar to the situation with Pb. Actually, in the surface layer, the content of Zn is $99\text{mg} \cdot \text{kg}^{-1}$, and in the organomineral part it is $47\text{mg} \cdot \text{kg}^{-1}$.

The content of Cu in the Olf layer is $27\text{mg} \cdot \text{kg}^{-1}$, and the value decreases mildly with depth. The assessed values are within the allowed limits for Cu.

Based on the above, it can be concluded that the study acid brown soil in the community *Quercetum montanum* on Fruška Gora contains an increased concentration of heavy metals, but the concentration is below the maximal allowed value.

HEAVY METAL CONTENT IN PLANT MATERIAL

Heavy metal content in plant parts depends on the presence in the air and in the soil, on soil pH-value, presence of organic substances, clay and humus, as well as on the method of absorption and plant species.

The presence of heavy metals (Pb and Cd, Cu and Zn) in the main vegetative parts of edificators on Fruška Gora and Crni Vrh is shown in Table 3. The comparison was made to the average concentrations according to Element Concentration Cadasters in Ecosystems (1994).

Table 3. - Heavy metal content in plant parts

Sample	Zn $\text{mg} \cdot \text{kg}^{-1}$	Cu $\text{mg} \cdot \text{kg}^{-1}$	Pb $\text{mg} \cdot \text{kg}^{-1}$	Cd $\text{mg} \cdot \text{kg}^{-1}$
FRUŠKA GORA				
sessile oak bark	17.00	17.00	10.00	1.50
beech bark	16.50	19.00	6.00	1.50
CRNI VRH				
sessile oak leaves	30.00	12.50	0.00	0.80
beech leaves	56.00	15.50	0.00	0.80
beech root	55.00	20.00	1.25	0.00
beech bark	19.00	10.00	2.25	0.00
beech leaves	40.50	18.00	2.00	0.00

Zinc is almost exclusively absorbed from the soil. Zn mobility in the plants is average and the distribution is specific, it is accumulated mostly in the root and in juvenile leaves. In the study localities the content of Zn ranges within the average limits after ECCE (1994), 15 - 150 mg.kg⁻¹, with clearly expressed accumulation in the beech root on Crni Vrh, as well as in oak and beech leaves in both localities. The uptake of individual elements from the soil by the plant is frequently inhibited by the presence of another element, and thus Zn uptake is in antagonistic reaction with the absorption of Cd and Cu (LUO, RIMMER, 1995).

Cd uptake, after MILER *et al.*, 1976, (cit. KASTORI, PETROVIĆ, 1993), depends on numerous external and internal factors. Cd uptake by the root system depends on pH - value in the soil, i.e. the lower the pH-value the more intensive the absorption. In higher concentrations, it is toxic for plants. According to ECCE, average concentration of Cd in plant material is 0.03 - 0.5 mg.kg⁻¹, which is significantly below that determined in plant organs on Fruška Gora. However, in beech bark and leaves on Crni Vrh, Cd concentration is below the detection limit

Average concentration of Cu after ECCE (1994) is 2 - 20 mg.kg⁻¹. Cu ions are very intensively absorbed by above-ground organs, which explains Cu concentration in sessile oak and beech leaves 12.50 - 17.0 mg.kg⁻¹ on Fruška Gora, and in beech leaves 18 mg.kg⁻¹ on Crni Vrh. Cu mobility is intermediate. It is a component of enzymes and in this way it affects the metabolism of nitrogen compounds and carbohydrates (KASTORI, 1990).

Compared to Cu, Cd and Zn, lead is more intensively absorbed by the root system. It is absorbed in the form of ions or organic compounds, though the mechanism of absorption has not yet been sufficiently elucidated. Pb accumulation is more intensive in the root than in the aboveground parts, but organic compounds of lead are readily absorbed and transferred to aboveground parts. In the study samples of sessile oak and beech on Fruška Gora, the concentration in the bark is significantly higher than the average after ECCE, while the presence of in the leaves was not recorded. Average concentration of Pb after ECCE (1994) is 0,1 - 5 mg.kg⁻¹, which is significantly below the determined concentration in plant parts on Crni Vrh.

CONCLUSIONS

It can be concluded that the degree of contamination of forest litter and forest soil by the analyzed heavy metals depends on site conditions, soil properties and the effect of air pollution and deposition of these elements.

This paper deals with the total content of lead, copper, cadmium and zinc in two different forest sites in Serbia. The degree of contamination with individual elements in forest litter, soil and vegetation was assessed.

In forest litter, the maximal allowed content is exceeded by lead and copper on Crni Vrh, and by cadmium in both study localities.

In the semi-decomposed litter on Crni Vrh, the exceptionally high maximal values of copper (1375mg.kg⁻¹) and lead (475mg.kg⁻¹) are the consequence of the vicinity of the mining and metallurgical basin Bor.

In the soil, heavy metal content (Pb, Cd, Cu and Zn) ranges within the allowed limits, according to the Regulation (Official Gazette of Serbia, No.11/1990).

In the main plant parts, the presence of Zn and Cu is within the limits of average concentrations after ECCE (1994) in both localities.

On Mt. Fruška Gora, we recorded the higher contents of Pb and Cd, i.e. Cd in the bark and leaves of sessile oak and beech, and Pb in the beech bark. These elements on Mt. Crni Vrh are within the average limits after ECCE (1994).

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SADRŽAJ TEŠKIH METALA U ŠUMI BUKVE NA CRNOM VRHU I KITNJAKA NA FRUŠKOJ GORI

Milan KNEŽEVIĆ, Snežana BELANOVIĆ, Olivera KOŠANIN,
Ratko KADOVIĆ
Šumarski fakultet, Beograd, Jugoslavija

I z v o d

Kruženje teških metala u šumskim ekosistemima uslovljeno je pre svega, vrstom elementa, tipom zemljišta i tipom vegetacije koji pojedinačno ili zajedno imaju presudan uticaj za njihovo položenje u pojedinim delovima ekosistema.

U ovom radu su prikazani rezultati proučavanja sadržaja teških metala (Cu, Pb, Cd, i Zn), u zemljištu i u glavnim vegetativnim delovima edifikatora u dva šumska ekosistema:

na Crnom Vrhu u šumi bukve (*Fagetum montanum*) na opodzoljenom kiselom smeđem zemljištu; i

na Fruškoj Gori u šumi bukve i hrasta kitnjaka (*Quercetum - Fagetum*) na kiselom smeđem zemljištu.

Uzorkovanje i priprema uzoraka zemljišta i biljnog materijala je obavljena prema metodici UNEP-UN/ECE (1994). Proučavanja osnovnih fizičkih i hemijskih osobina zemljišta vršena su po standardnim metodama koje je prihvatio JDPZ. Sadržaj ukupnog olova, bakra, kadmijuma i cinka u zemljištu i biljnog materijalu određen je metodom AAS na aparatu tipa PYE Unicam SP9.

Na osnovu izvršenih proučavanja može se zaključiti da stepen zagađenosti šumske prostirke i zemljišta istraživanim teškim metalima zavisi od stanišnih uslova, osobina zemljišta i uticaja zagađenosti vazduha i depozicije ovih elemenata.

U ovom radu istraživan je ukupan sadržaj olova, bakra, kadmijuma i cinka u dva različita šumska staništa Srbije. Utvrđen je stepen opterećenosti prostirke, zemljišta i vegetacije pojedinačnim elementima.

U šumskoj prostirci konstatovano je da maksimalno dozvoljen sadržaj prelaze: olovo i bakar na Crnom Vrhu, a kadmijum na oba ispitivana lokaliteta.

U poluzloženoj prostirci na Crnom Vrhu utvrđena je izuzetno visoka maksimalna vrednost bakra (1375mg.kg⁻¹) i olova (475mg.kg⁻¹), što je posledica blizine rudarsko-topioničarskog basena Bor.

U samom zemljištu sadržaj teških metala (Pb, Cd, Cu i Zn) nalazi se u dozvoljenim granicama prema Pravilniku (Sl. glasnik Srbije, br.11/1990).

U glavnim biljnim delovima prisustvo Zn i Cu je u granicama prosečnih koncentracija po ECCE(1994) na oba lokaliteta.

Na Fruškoj Gori u povišenom sadržaju zastupljeni su Pb i Cd, i to Cd u kori i lišcu kitnjaka i bukve, a Pb u kori bukve. Ovi elementi na Crnom Vrhu su u granicama prosečnim po ECCE-u (1994).