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HEAVY METAL CONCENTRATIONS IN THE DOMINANT PLANT SPECIES OF PASTURE ON MT. STARA PLANINA

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Stara Planina is one of the centres of plant diversity not only of our country, but also of the Balkan Peninsula, with 1195 plant species in 33 families and 455 genera. Throughout the region, and especially in the mountainous belt, thanks to inadequate utilisation (pasture and mowing), and other anthropogenic impacts, most of the pastures are more or less degraded. Many plant species (cultivated, medicinal, spontaneous native, trees, etc.) are known as the hyper sinks of individual trace elements. The concentrations of some heavy metals (Cu, Zn, Pb, Ni, Cr and Mn) were determined in the (nine) most frequent species of the pastures of Stara Planina, locality Javor, aiming at the identification of the bioaccumulation of these elements.

Key words: heavy metals, mountainous pastures, dominant species

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INTRODUCTION

Stara Planina is our largest mountainous massif, extending from Zaječar in the north to Dimitrovgrad in the south. Its altitude ranges from 300 to 2168 m (MIŠIĆ *et al.*, 1978). It is a centre of plant diversity not only of our country, but also of the Balkan Peninsula, with 1195 plant species in 33 families and 455 genera (RANĐELOVIĆ and RANĐELOVIĆ, 2002; RANĐELOVIĆ *et al.*, 2002). Throughout the region, and especially in the mountainous belt, thanks to inadequate utilisation (pasture and mowing), and numerous other anthropogenic impacts, many pastures are more or less degraded. The degradation proceeds in the direction of reducing the abundance of valuable fodder crop species, and increasing the abundance of valueless (from the aspect of pasturage), thorny and poisonous species. Although this is a global problem, the mechanisms of the processes leading to degradation have not yet been completely elucidated (DE KOVEL *et al.*, 2000).

Many plant species have the capacity of accumulating some biogenic elements and radionucleides above the toxic values (ĐOROVIĆ-MILORADOVIĆ *et al.*, 2002; KELLER *et al.*, 2003). The quantity of heavy metals that can be taken in from the soil depends both on the plant species and the soil properties, first of all the soil pH, and on the properties of the element itself (KASHEM and SINGH, 2002). Also, the root exudates have a significant role in the mobilisation of heavy metals, by creating plant-available complexes with the unavailable forms (TREEBY, 1989). Then, the solubility of e.g. Cd and Zn changes by fertilisation (N and P), they become more mobile and available to plants (KASHEM AND SINGH, 2002). In addition to the indirect uptake of heavy metals from the soil, they can also be available to plants by foliar absorption from the air, although these mechanisms have not yet been explained in detail, as reported by DE VRIES AND BAKKER (1996). KADOVIĆ AND KNEŽEVI? (2002) report that the process of transformation of the migration forms of elements in the ecosystem starts by the deposition of heavy metals on the surface of photosynthetic organs, and this process results in the transformation of a significant share of metals into soluble compounds. Various groups of plants can be good bioaccumulators: cultivated crops, e.g. *Brassica napus* (DJOROVIĆ-MILORADOVIĆ *et al.*, 2002); mushrooms (RADOVANOVIĆ AND MANIĆ, 2002); medicinal species, e.g. *Thymus balcanicus* Borb. (BLAGOJEVIĆ *et al.*, 2002); plants of natural grasslands e.g. *Thlaspi caerulescens* known as hyper-accumulator (MC GRATH *et al.*, 1997; KELLER *et al.*, 2003); some tree species (BLAKE AND GOULDING, 2002), etc.

The aim of this study is to assess whether the dominant species of the natural pastures of Mt. Stara Planina, locality Javor, in natural conditions are bioaccumulators of heavy metals (Cu, Zn, Pb, Ni, Cr and Mn).

MATERIAL AND METHODS

The floristic-phytocoenological records of pasture vegetation at the locality Javor, Management Unit "Široke Luke" (N= 43° 14' 24.7", E= 22° 51' 36.8") were made during the first decade of July, 2003. The height of the

vegetation cover was 95-100 cm, and the general degree of coverage was 100%. The slope of the study locality is 20-25%, exposure - N, altitude 1288 ± 6 m. This area has the montane climate of the Balkan mountainous system, average annual air temperature 6.2°C, the coldest month is January (-4.5°C) and the warmest month is July (15.9°C). On the average, total annual precipitation is 945 mm, the lowest rainfall being in September, and the highest in June.

At this locality, the soils are formed on chlorite - sericite schists, i.e.: dystric humus-siliceous in two varieties lithic and brownised and dystric brown soil (ŠKORIĆ *et al.*, 1985, cit. BELEANOVIĆ *et al.*, 2003).

The quality and quantity representation of plant species was assessed by the combined scale of abundance and coverage, after WESTHOFF AND VAN DER MAAREL (1973). All plants from the study pastures were collected, herbarised, and the species were determined by standard keys for the determination of vascular plants.

The contents of heavy metals (Cu, Zn, Pb, Ni, Cr and Mn) were determined in nine species in the group of very frequent species, which are supposed to be bioaccumulators. They are: *Calamintha vulgaris* (L.) Druce, *Cytisus albus* Hacq., *Galium verum* L., *Hypericum perforatum* L., *Rumex acetosa* L., *Seseli peucedanoides* (M.Bieb.) Kos.-Pol., *Thymus vandasii, Verbascum longifolium* Ten. and *Centaurea phrygia* L. The total heavy metal concentration was determined by the method of atomic absorption spectrophotometry, apparatus Varian AA10. Conservation and preparation of samples was according to UNEP - UN/ECE Method 9107SA (plant material was treated with the mixture of the concentrated HCl, HNO_3 and H_2O_2 , ratio 3:1:2).

RESULTS AND DISCUSSION

Ninety plant species were identified on the pastures of the central zone of Stara Planina (locality Javor). The group of the most frequent plants includes: *Achillea millefolium* L., *Agrostis capillaris* L., *Calamintha vulgaris* (L.)Druce, *Centaurea phrygia* L., *Centaurea scabiosa* L., *Cytisus albus* Hacq., *Festuca pratensis* Huds., *Festuca rubra* L., *Galium verum* L., *Geranium sanguineum* L., *Helianthemum nummularium* (L.) Mill., *Hypericum perforatum* L., *Lathyrus pratensis* L., *Stachys officinalis* (L.) Trev., *Rumex acetosa* L., *Seseli peucedanoides* (M. Bieb.) Kos.-Pol., *Tanacetum vulgare* L., *Thymus vandasii* Vil., *Verbascum longifolium* Ten., *Veronica jacquinni* Baumg. and *Viola tricolor* L. The contents of some heavy metals in the dominant species are presented in Table 1.

Table 1. Heavy metal concentrations in the most frequent species of Javor pastures

No.	Species	Cu mg.kg^{-1}	Zn mg.kg^{-1}	Pb mg.kg^{-1}	Ni mg.kg^{-1}	Cr mg.kg^{-1}	Mn mg.kg^{-1}
1	*Hypericum perforatum* L	14.01	30.02	3.00	1.00	2.00	219.15
2	*Rumex acetosa* L.	4.50	11.50	3.50	1.00	2.00	125.02
3	*Seseli pencedanides* (M.Bieb.)	8.99	25.49	2.50	0.50	1.99	108.95
4	*Calamintha vulgaris* (L.)Druce	11.00	22.00	3.50	0.99	2.50	67.49
5	*Centaurea phrygia L.*	13.99	18.98	2.00	3.00	2.00	105.40
6	*Thymus vandasii* Vil.	12.0	44.99	3.50	5.00	4.50	363.43
7	*Galium verum* L	9.49	36.97	2.50	2.00	1.50	234.31
8	*Verbascum longifolium* Ten.,	12.96	23.43	3.50	1.00	1.49	321.50
9	*Cytisus albus* Hacq.	12.45	32.39	0.99	2.49	1.00	472.32

The chemical composition of plants in general reflects the elementary compositions of the environment in which they grow. The usual concentrations of trace elements (and microelements) in the plants growing in various unpolluted soils are characterised by very wide variations. Heavy metals are toxic if they occur in elevated concentrations, although they are essential (KADOVIĆ AND KNEŽEVIĆ, 2002). The toxic concentrations of heavy metals in plant tissues are very difficult to determine, so that threshold values have a very general and approximate character and can differ significantly for different systems "soil - plant". Heavy metal uptake from the soil can be active and passive. Active uptake develops contrary to the gradient of metal concentration and requires the consumption of energy, while passive uptake is a simple diffusion of ions between the soil solution and the root. Different metals undergo different mechanisms of absorption, for example, Pb is absorbed passively, whereas the uptake of Cu and Zn is an active process (KABATA-PENDIAS AND PENDIAS, 1989). Plants are capable, based on biological selectiveness, of controlling their chemical composition to a certain extent.

The soils of the study locality, after BELANOVIĆ *et al.* (2003), can be considered as good quality soils in productive and ecological senses. Namely, based on the index of acidification status and heavy metal availability, the soils are in the low class. Also, Pb contents in the soil are within the limits after DE VRIES AND BAKKER (1998), and lower than maximal admissible concentrations (MAC) for the area of Serbia after KADOVIĆ AND KNEŽEVIĆ (2002), except in dystric ranker, variety lithic, where the concentration is somewhat higher in the layer 0 - 5. According to the same authors, the contents of Zn are considerably higher than MAC in all soils.

The differences in the uptake of heavy metals between different plant species depends primarily on their genetic characteristics, on the effect of root area and its capacity of ion adsorption, form of root exudates and the rate of evapotranspiration (ALLOWAY, 1995). However, there are also differences in the heavy metal uptake between the plants of the same species, which is first of all, the consequence of climate conditions and moisture regime.

KABATA-PENDIAS AND PENDIAS (1989) report the natural concentrations of elements in the grasses in unpolluted regions, i.e.: Cu - 1-10 mg.kg^{-1} , the values rarely exceed 20 mg.kg^{-1}, Zn - 12-47 mg.kg^{-1}; Pb - 0.1-10 mg.kg^{-1}, Cr - 0.6-3.4

mg.kg^{-1}, Ni - 0.1-1.7 mg.kg^{-1} (in clover 1.2-2.7 mg.kg^{-1}) and Mn - 17-334 mg.kg^{-1}. The average contents in plants after ECCE (1994), for Cu are 2-20 mg.kg^{-1}, Zn - 15-150 mg.kg^{-1}, Pb - 0.1-5 mg.kg^{-1}, Ni - 0.4-4 mg.kg^{-1}, Cr - 0.2-1 mg.kg^{-1}, Mn - 1-700 mg.kg^{-1}. DE VRIES AND BAKKER (1996) calculated the rank of heavy metal contents in the biomass from different land uses (biomass from pastures, agricultural soil, forest) in the zone of temperate climate. According to these authors, the contents of heavy metals in the plants from pastures, whose biomass ranges from 0.5 - 2.0 kg.m^{-2}year^{-1}, range: Cu - 6-12 mg.kg^{-1}, Zn - 30-70 mg.kg^{-1}, Pb - 1-3 mg.kg^{-1} and Cd 0.05 -0.26 mg.kg^{-1}.

The content of Cu in the study species ranges from 4.5 mg.kg^{-1} in *Rumex acetosa* L., to 14.01 mg.kg^{-1} in *Hypericum perforatum* L. The concentration of Cu in the study species of Javor pastures are above the range reported by VRIES AND BAKKER, (1996) and KABATA-PENDIAS AND PENDIAS (1989) in the species *Verbrascum longifolium*, *Cystys albus*, *Centaurea phrygia* and *Hypericum perforatum*, but they are below the average content after ECCE (1994) in all the study plants.

The contents of Zn in all species are below the critical limits after VRIES AND BAKKER, (1996), below the average after ECCE (1994) and KABATA-PENDIAS AND PENDIAS (1989), although the concentrations in the soil are above MAC. The highest concentration was measured in *Thymus vandasii* Vil.- 44,99 mg.kg^{-1}, also BLAGOJEVIĆ *et al.* (2002) measured 98.75 mg.kg^{-1} Zn in the species *Thymus balcanus* Borb. on Mt. Besna Kobila.

The measured concentrations of lead in all species are below the natural concentration in plants after KABATA-PENDIAS AND PENDIAS (1989) and below the average after ECCE (1994), but for the species *Rumex acetosa* L, *Calamintha vulgaris* (L.) Druce, *Thymus vandasii* Vil., *Verbascum longifolium* Ten., they are somewhat above the range for unpolluted areas, after VRIES AND BAKKER, (1996). SIDELICKA (1995, cit. KADOVIĆ AND KNEŽEVIĆ, 2002) reports that the presence of Zn in the soil decreases the uptake of Pb, but the present N and P have a high effect.

In the species *Centaurea phrygia* (3.0 mg.kg^{-1}), *Thymus vandasii* (5.0 mg.kg^{-1}), *Cytisus albus* (2.49 mg.kg^{-1}) the measured concentrations of Ni are higher than the natural concentrations in grasses after KABATA-PENDIAS AND PENDIAS (1989), and the lowest is in the species *Seseli peucedanoides* - 0.5 mg.kg^{-1}. Compared to the contents of Cr measured by KABATA-PENDIAS AND PENDIAS (1989), higher concentrations were measured only in the species *Thymus vandasii*, *i.e.* 4.5 mg.kg^{-1} Cr, while the lowest content was 1.0 mg.kg^{-1} in *Cytisus albus*. After ECCE (1994), the average contents of Ni are higher only in *Thymus vandasii*, while Cr concentration in all species is somewhat higher.

The measured concentrations of Mn are lower than the average, after ECCE (1994), and they are higher than the natural concentration in grasses after KABATA-PENDIAS AND PENDIAS (1989), in the species: *Thymus vandasii* - 363.43 mg.kg^{-1}, *Cytisus albus*, where the highest concentration of 472.32 mg.kg^{-1} was measured. The lowest content of Mn was measured in the species *Calamintha vulgaris* - 67.49 mg.kg^{-1}.

Based to the above preliminary results, it is clear that the species *Thymus vandasii* Vil. is characterised by the highest bioaccumulation of heavy metals, primarily Pb, Ni, Cr and Mn, and then the species *Cytisus albus* Hacq., whose bioaccumulation of Ni and Mn is considerable. However, it is necessary to carry out further research on the system soil - plant on these natural pastures, primarily the study of the adsorption complex, and also to analyse the forms of heavy metal fixation and their origin, as well as the affinity of individual plant species to the specific elements.

CONCLUSION

Bioaccumulation of heavy metals (Cu, Zn, Pb, Ni, Cr and Mn) was assessed in the dominant species of Stara Planina natural pastures, at the locality Javor. The contents of the above elements were measured in the whole plants of the nine most represented species of this pasture. The preliminary results indicate that the contents of the study elements in the majority of species range within the limits of natural concentrations for the areas of unpolluted regions. The highest rank bioaccumulators are the species *Thymus vandasii* Vil., first of all for Pb, Ni, Cr and Mn, and then the species *Cytisus albus* Hacq., whose bioaccumulation of Ni and Mn is considerable.

However, it is necessary to perform further research on the system soil - plant on these natural pastures, primarily the study of the adsorption complex, and also to analyse the forms of heavy metal fixation and their origin, as well as the affinity of individual plant species to the specific elements.

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SADRŽAJ TEŠKIH METALA U DOMINANTNIM VRSTAMA PAŠNJAKA STARE PLANINE

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I z v o d

Stara Planina je jedan od centara florodiverziteta ne samo naše zemlje već i Balkanskog poluostrva na kom egzistira 1195 biljnih vrsta iz 33 familije i 455 rodova. Na čitavom području, a posebno u planinskom pojasu, usled, neadekvatnog iskorištavanja (ispaše i kosidbe), i ostalih antropogenih uticaja većina pašnjaka je u manjoj ili većoj meri degradirana. Mnoge biljne vrste (gajene, lekovite, spontane prirode, drveće itd.) su poznate kao hiperakumulatori pojedinih mikroelemenata. Određivan je sadržaj nekih teških metala (Cu, Zn, Pb, Ni, Cr i Mn) u visokofrekventnim vrstama (devet) pašnjaka na području Stare planine, lokalitet Javor, sa ciljem utvrđivanja bioakumulacije ovih elemenata.

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