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MACRO AND MICROELEMENT CONTENTS IN SOIL OF SOME GRASSLAND LANDSCAPE IN „CENTRAL BALKAN" NATIONAL PARK

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Abstract

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The present study aims to analyze and assess the content of some macro- and microelements in soils from high mountainous grassland landscapes on the territory of the "Central Balkan" National Park, where grazing takes place. Soils were studied and classified as *Umbrisols*. The humus quantity is very high – 13–25%. The coefficients of its decrease with depth – between the layers 0–10 cm and 10–20 cm, which represent the entire depth of the profiles, are within the range 1.0–1.2 and can be assessed as very low. They are accepted as the proof of predominantly grassland soil-forming process which is an indication of the conservative structure of the landscapes in these territories. The heavy metals Zn, Cu, Pb, As and Cd were studied and exceedances of the maximum permissible limit for soils in grasslands were determined only for cadmium (2.1–4.0 $mg.kg^{-1}$). It can be assumed that the soils are not contaminated by anthropogenic sources. The analysis indicates that the increased concentrations are due to the geochemical background and biogenic accumulation of cadmium in soils, rich in organic matter. It is recommended to carry out analysis of the cadmium content in other components of the grassland landscapes, as well as environmental risk assessment.

Key words: landscape, national park, cadmium, lead, pasture, soil

Abbreviations: KS – key sites, AAS – atomic absorption spectrophotometer, ICP – inductively coupled plasma spectrometer

Introduction

The proximity of the "Central Balkan" National Park to the metallurgical plant near the town of Pirdop is a prerequisite for pollution of the different landscape components on the park territory. The information about the heavy metal contents in the soils of the park territory is very limited. In the forest area, Bezlova et al. (2001) reported contamination of *Cambisols* with copper, zinc and arsenic near the western boundary of the park. Regarding the *Umbrisols* from grassland landscapes, information about the content of copper, zinc, nickel, cobalt, lead and manganese can be found in the Bulgarian Soil Atlas (1998) and in the Reference database of soils in Bulgaria (Teoharov et al., 2009), as the cited data do not show contamination with these elements.

In their study, Mihova et al. (1995) determined increased geochemical background in separate parts of the park. As a result the content of zinc, cadmium, copper and arsenic in soils from the alpine areas above the tree line, where grazing takes place, is increased. According to the authors, the heavy metals have reached the dairy products through the food chain and as a result these dairy products did not meet the food safety requirements. Data about the soil contamination in different parts of the park is presented in the project for Management Plan of the "Central Balkan" National Park (MP, 2014–2023), but a definitive assessment for the remote from the metallurgical plant territories, has not been made. The influence of soil-forming rocks is assumed. These contradictory results suggest the need to expand the studies of heavy metals and arsenic

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content in grassland landscapes, as well as to define their origin – natural or anthropogenic.

The present study aims to analyze and assess the content of some macro- and microelements in soils from high mountainous grassland landscapes on the territory of the "Central Balkan" National Park, where grazing takes place.

Materials and Methods

Subject and Sampling Sites

Soils from grassland landscapes in the high mountainous territory of the "Central Balkan" National Park were studied. The region of the Bolovaniya locality, Beklemeto locality and the junction for Tazha hut below the Botev peak were selected as sites with permanent grazing. The study was concentrated on the eluvial parts of the landscape, where weathering products are formed, which allows to determine the influence of soil-forming rocks on the chemical composition of soils more clearly. Flattened ridge parts were selected for setting out key sites (KS). KS 1 is located at an altitude of 1536 m in the area of the Bolovanya locality; the soil-forming rocks are amphibole and amphibole-biotite granodiorites. KS 2 and KS 3 were selected in the Beklemeto locality at an altitude of 1529 m and 1635 m; the soil-forming rocks are argillites. KS 4 is located at an altitude of 1877 m where the soil-forming rocks are weathering materials from South Bulgarian granite.

Four soil profiles were set out, of which morphological description was made and the soil type was classified. Samples were taken from two layers – 0–10 cm and 10–20 cm. The sampling points were coordinated with GPS. The samples were taken at the end of June 2015.

Analytical Methods

The content of org. C was determined using the modified method of Turin (120°C, 45 min, catalyst Ag_2S_{O4}) and the method of Kononova – Belchikova (Kononova, 1963; Filcheva and Tsadilas, 2002); total nitrogen by the Kjeldahl method using KJELTEC AUTO 1030; macro- and microelements – P, Zn, Cu, Pb and Cd – ISO 11466 (extraction with aqua regia) and subsequent measurements with Lambda 5 UV/VIS spectrophotometer Perkin Elmer and AAS Perkin Elmer 5000. Pressurized microwave closed system with acids ($HCl+HNO_3$, ratio 3:1) was used for determination of As and ICP was used for carrying out the testing. The coarse fragments content was determined by weight. The results were recalculated to absolutely dry mass of the soil.

Results and Discussion

The studied soils are characterized by shallow soil profile. The only soil horizon is divided into 2 parts – „A_{sod}" and „A". The first part has a depth of about 10 cm and consists of densely interwoven undecomposed dead grass residues, living plan parts and mineral soil particles. The second part (depth of about 10 cm) is predominated by mineral components. The colour of the soil in the profiles is very dark (10YR 2/1 when dry). The soil material has soft consistence, loam textural class and very fine structure. The abundance of coarse fragments of „A_{sod}" varies between 2% and 10% and of „A" between 18% and 31%. The soils are classified as *Umbrisols* due to the compliance with the requirements of the World Reference Base for Soil (WRBSR, 2014) regarding the depth of the profile, colour, structure and humus content (Table 1).

Table 1
Content of macro- and microelements in soils from grassland landscapes of the „Central Balkan" National Park

Sampling site	Depth	pH	Organic C	Total N	C/N	Total P	Zn	Cu	Pb	As	Cd
	cm	H_2O	$g.kg^{-1}$			$mg.kg^{-1}$					
KS 1	0–10	4.6	75.3	5.77	13	825	75	18	45	5.51	1.04
(Bolovanya locality)	10–20	5.1	63.0	5.41	12	758	87	38	55	5.98	1.77
KS 2	0–10	4.8	143.2	13.43	11	1583	85	36	61	8.00	4.01
(Beklemeto locality)	10–20	4.8	134.9	11.60	12	1477	68	34	57	7.92	1.72
KS 3	0–10	4.4	144.2	11.06	13	1766	81	41	63	8.99	2.13
(Beklemeto locality)	10–20	4.7	138.1	13.52	10	1683	78	36	47	6.81	1.67
KS 4	0–10	4.6	137.9	11.43	12	1370	53	14	42	3.68	1.12
(junction for Tazha hut)	10–20	4.9	122.0	9.94	12	1193	51	12	41	11.46	1.44

The selected altitudes for the key sites – between 1529 m and 1877 m, define harsh high mountainous climate, intensive leaching and very high soil acidity (Table 1), therefore organic matter accumulation processes occur in the soils. The humus quantity is very high throughout the profiles (13% - 25%). The coefficients of its decrease between the two parts of the humus-accumulative horizon (A_{sod} and A) are within the range 1.0 – 1.2. Taking into consideration that due to various reasons the upper forest boundary is not permanent, these very low coefficients allow to reject the prolonged impact of the forest soil forming process in the past. The results are an indicator of the conservative structure of the landscapes in these territories.

The ratios organic C/N show high soil richness in nitrogen (according to the criteria of Artinova, 2014) due to their low values. The quantity of the total phosphorus is high in the soil from KS 1 and very high in all other sites, which is also due to the accumulation of organic matter.

The content of zinc, copper and arsenic in the studied soils correspond to the background concentrations in the country – 88 mg.kg^{-1} for zinc, 34 mg.kg^{-1} for copper and 10 mg.kg^{-1} for arsenic (Regulation no. 3 of 2008) or lower.

Regarding the lead content, higher concentrations than the background concentration limit (26 mg.kg^{-1}) and precautionary concentration limit (40 mg.kg^{-1}) are determined. The maximum permissible value is not exceeded.

All results for the cadmium content in soils are higher than the background and precautionary concentration limits – 0.4 mg.kg^{-1} and 0.6 mg.kg^{-1}, respectively. In KS 2 the cadmium content exceeds the maximum permissible concentration (2 mg.kg^{-1}) for soils from permanent grasslands with pH < 6.0 (Regulation no. 3 of 2008) 2 times, and in KS 3 is slightly higher. The cadmium content in depth of the two profiles is high, which accounts for a natural process of soil enrichment with this element of the soil forming rocks, i. e. the soils are not contaminated by anthropogenic sources. This can be explained by the normal behavior of cadmium to actively bond with the organic matter in soils (Petrov, 1984; Pendias et al, 1989; Sheila, 1994). In fact, there are no industrial emission sources on the territory of the "Central Balkan" National Park and the distant transfer of such emissions would contaminate relatively evenly the entire park territory, and there is no such information.

The results are indicative for another process – increased accumulation of cadmium by plants due to its high mobility. According to some authors this process could pose a risk to the environment and human health due to the easy movement through the food chain (Yüzbaşı, 2003; García et al., 2006; Maas, 2011). At this stage it is recommended to expand the studies of the grassland landscapes. A prerequisite for contamination of different components are the high soil acidity and mobility of cadmium, which account for transformation of soil into source of pollution.

Conclusions

The studied soils from grassland landscapes on the territory of the "Central Balkan" National Park are defined as *Umbrisols*. Their characteristics are used to evaluate the conservativeness in the structure of grassland landscapes.

Regarding the studied heavy metals, exceedances of the maximum permissible norm for soils in grasslands were determined only for cadmium, but it is assumed that the soils are not contaminated by anthropogenic sources. The analysis shows that the observed processes are due to increased geochemical background, high soil acidity and biogenic accumulation of cadmium in soils, rich in organic matter. It is recommended to perform analysis of cadmium content in other landscape components and environmental risk assessment.

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