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CATION EXCHANGE PROPERTIES OF SOILS FROM CARBONATE LANDSCAPE IN THE CENTRAL BALKAN NATIONAL PARK

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Abstract

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In the modern landscape ecology it is assumed that the landscape structure consists of discrete 'mosaics' as their diversity to a large extent is created by carbonate rocks. According to some researchers the impact of carbonate rocks is not always confirmed. The cation exchange properties of *Rendzic Leptosols* in grassland landscapes on the territory of the "Central Balkan" National Park were studied as a prerequisite for creating a variety of soil conditions for plant nutrition. The pH, quantities of base cations, exchangeable acidity, cation capacity and base saturation were analysed and assessed. It was determined that the soil-forming process on limestone created a different reaction of the soil solution in the studied sites – neutral, medium acidic and highly acidic. Two contrasting types of cation exchange – hydrolysis-alkaline and hydrolysis-acidic occur in the soils. In the first one, through neutral and slightly alkaline buffer systems, conditions for increased adsorption of base elements from the plants and deficiency of microelements are created in the soil. The second one is characterised by conditions for mobilisation of microelements, gradual loss and possible deficiency of base elements. The conditions for plant nutrition are different. It can be assumed that they are prerequisites for creation of mosaic structure within the boundaries of carbonate rock landscapes. It is recommended to perform the park biodiversity assessment in accordance with cation exchange properties, regardless of the soil type and soil-forming rocks, due to the numerous combinations, created by the soil-forming factors as conditions for plant nutrition.

Key words: national park, limestone, soil, pH, exchangeable cations
Abbreviations: key area (KA), national park (NP), management plan (MP)

Introduction

Various approaches for differentiating the natural and territorial complexes into separate landscape units can be found in the scientific literature. In most of the cases, they seek homogeneity by certain characteristics, which are differentiated by an adopted hierarchical scheme according to the aims of the study (Isachenko, 1953; Neev, 1974). In the modern landscape ecology according to the model of Ewald (2003) it is assumed that the landscape structure consists of discrete 'mosaics', representing sections with irregular shape, and the transition between them is made through 'corridors'. The great variety of 'mosaics' in the landscape to a large extent is created by carbonate rocks (Ewald, 2003; Wohlgemuth, 2003), although this cannot always be demonstrated in practice (Peet et al., 2003). According to some researchers (Löbel et al., 2006), the landscape structure is less important for the variety of 'mosaics' than the soil pH, which explains the diverse response of the biotic component. Some researchers studied the landscape biodiversity indicators and stated that finding the connections is very difficult (Dauber, 2003). At present, the application of Ewald model is very difficult due to the lack of knowledge about the continuum in the spatial heterogeneity of landscapes (McGarigal et al., 2005 pp. 112–119; McGarigal, 2009). It is also difficult to define the landscape elements which distinguish the 'mosaics'. How-

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ever, according to some authors studying the landscape heterogeneity is of fundamental importance and is essential for its preservation (Turner, 2005, p. 319; Atauri et al., 2001). It is estimated that all parameters are significant because of the existing connections in the landscape.

There is no information about the mosaic structure of the landscape on the territory of the "Central Balkan" National Park and the impact of the carbonate soil-forming rocks on it. At present, the landscape variety is assessed on the basis of the regional landscape zoning of Bulgaria (Petrov, 1997), according to which the park territory is in the Balkan landscape area, Central Balkan landscape subarea and Central watershed landscape region. According to the typological classification scheme of the country (Petrov, 1997), the park is a part of class 'Mountain landscape' where 3 types, 6 subtypes and 11 landscape groups are defined. The soils are also poorly studied (Malinova, 2016), which further complicates the assessment of the mosaic structure. In the scientific literature there is information about the cation exchange properties of the soils from the „Central Balkan" National Park, regarding pH, cation capacity, etc., only for the highly acidic soils from the territory of the Boatin reserve (Ganev, 1990a), the regions of Beklemeto (Koynov et al., 1998; Malinova, 2015), Bolovanya, Panitsite and Shopov egrek (Malinova, 2015). The park has a complex geological structure and variety of soil-forming rocks which allow assuming that the analysis of the cation exchange properties of soils would contribute to obtain more comprehensive detail level and reveal the complex mosaic in the landscape structure.

This study presents the results of the pilot testing of cation exchange properties of soils from grassland landscapes with carbonate rocks on the territory of the "Central Balkan" National Park as a prerequisite for creating a variety of soil conditions for plant nutrition. It is considered that the mosaic structure of the landscape can be developed not only on the background of the adjacent landscapes with acidic and carbonate rocks but also within the boundaries of carbonate rocks only.

Materials and Methods

The "Central Balkan" National Park is the second largest national park in Bulgaria, created to preserve the unique wildlife of the Middle Balkan mountain. There are natural forest and high mountain self-regulating ecosystems of exceptional biodiversity.

The structure-forming role in grassland landscape with carbonate rocks on the park territory is performed mostly by limestones (sandy, clayey, organogenic, dolomite, etc.), marls, dolomites, etc. From the information in the park management plans (MP, 2001–2010 pp. 17–18: MP, 2014–2023 pp. 26–27) it can be assumed that its horizontal structure is highly fragmented.

The study is focused on eluvial and transitional parts of the landscape where key sites (KS) were set out. KS 1 is selected in the eluvial part of the landscape – ridge at an altitude of 1581 m, south of the Beklemeto locality. The structure-forming role there is performed by clayey limestone from the Cherniosumska rock formation, consisted of various rocks (sandstones, siltstones, marls, clayey limestones). The selection of KS 1 location is based on the strong influence of the soil-forming rock on the soil properties in the eluvial relief forms.

KS 2 and KS 3 are selected on transitional parts of the landscape. The structure-forming role in the landscape is performed by clayey limestones – in KS 2 from the Cherniosumska rock formation and in Ks 3 from Paradzhiska rock formation (clayey limestones and marls with limestone layers).

KS 2 is located on an eastern slope in the Beklemeto locality at an altitude of 1578 m and KS 3 – on an eastern slope close to Paradzhika locality at an altitude of 1100 m. The selected transitional landscape forms for KS 2 and KS 3 allow analysing the impact of the carbonate soil-forming rock on the soil properties in conditions, different from KS 1.

Morphological descriptions were made and the soil group was determined. The Guidelines for Soil Description (FAO, 2006) were applied for the morphological descriptions and the requirements of IUSS Working Group WRB (2006; 2014) for classifying the soils. Samples for analyses were taken from two layers – sod layer and the layer beneath it. Samples were taken at the end of June 2015.

Cation exchange properties, which are highly informative about the conditions of plant nutrition, were selected for performing the analysis. The following indicators were determined: $pH_{(H_2O)}$ and $pH_{(CaCl_2)}$ (ISO 10390); exchange cations – ISO 11260 & ISO 14254, with reporting of AAS; exchange acidity – ISO 11260 & ISO 14254; cation capacity – the sum of basic cations and exchange acidity. The results were recalculated to absolutely dry mass of the soil.

Results and Discussion

The performed field studies showed some differences in soil cation exchange properties. The soil from the ridge part of the landscape (KS 1) is shallow. The profile is consisted of one soil horizon, about 15 cm. A sod layer of about 5 cm is formed on the surface. The soil is coloured in very dark greyish brown – 10 YR 3/2 (when dry), loam textural class, with developed fine granular structure, and hard consistence.

The coarse fragments content is high, up to 80 % of the soil volume at a depth of 15 cm. The effervescence from a 10% solution impact of HCl is weak on the soil material, which indicates the occurrence of leaching processes.

In KS 2 the profile consists of one soil horizon whose depth is about 15 cm. The grass cover has formed a sod layer with a capacity not greater than 5 cm. The soil is coloured in dark yellowish brown – 10 YR 3/4 (when dry), loam textural class, with developed fine granular structure, and hard consistence. The coarse fragments content is high, up to 40 % of the soil volume at a depth of 15 cm. The effervescence from a 10% solution impact of HCl is only in the *C* horizon, i.e. the leaching process is at a more advanced state, compared with the subject of KS 2.

In KS 3 the soil depth is about 30 cm, followed in depth by the soil-forming rock. The profile is shallow. In the only soil horizon there is a distinct sod layer with a depth of about 10 cm. The soil material is coloured in dark yellowish brown – 7.5 YR 3/4 (when dry), with a fine grained structure. The soil has loam textural class, hard consistence and is leached – the effervescence is observed at the depth of the soil-forming materials.

On the basis of the carbonate soil-forming rock, shallow soil profile, colour and structure, the soil from the three sites is defined as *Rendzic Leptosols*. The presence of diagnostic *Mollic* horizon should be added to the diagnostic features, due to the high base saturation (Table 1).

The results of the performed analyses show significant differences in the cation exchange soil parameters (Table 1). In KS 1 the reaction of the soil solution is in the neutral range, in KS 2 – in the highly acidic range, and in KS 3 – in the medium acidic one. It is well known that the acidic state of soils is determined by the composition and nature of the adsorbed exchange cations which form different acidic, salt-like and buffer adsorption systems on the permanent and variable charges of colloidal surfaces. (Schroeder, 1984, pp. 67–70; Foth, 1984, pp. 192–194; Ganev, 1990 b; Chesworth, 2008, pp. 12–14). Taking into consideration that each equilibrium concentration of hydrogen cations in the soil solution corresponds to a specific acidic and buffer system on the colloidal surfaces, it can be concluded that there is a different mobilization balance of macro- and microelements, as well as different type of cation exchange in the studied soils.

In the soil from KS 1 a cation exchange of hydrolysis-alkaline type occurs through neutral and slightly alkaline buffer systems, which creates conditions for increased adsorption of basic elements from the plants and deficiency of microelements due to their sedimentation as insoluble oxides.

Exchange acidity is present in the leached soils from KS 2 and KS 3, which is measured titrimetrically and by pHCaCl2 (Table 1). The results show thermodynamic instability of the clayey structures. There are amphoteric cations in exchange states in the soils, i.e. the cation exchange is of hydrolysis – acidic type. Ion exchange forms of cations with basic and acidic functions are both present on the permanent charges of the soil adsorbent. The conditions for plant nutrition differ from those in KS 1 due to mobilization of microelements, gradual loss and possible deficiency of basic elements in the leaching processes. Differences between the soils from KS 2 and KS 3 are also determined, due to the advanced soil acidification in KS 2. This process is best observed by assessing the balance of exchange cations in the cation capacity (Table 2). The results show that the lower pH of the soil from KS 2 corresponds to lower content of exchangeable calcium and higher exchange acidity in comparison with the soil from KS 3. Similar conditions for plant nutrition with advanced acidification exist in a number of soils in the country, developed on acid rocks (Malinova, 2014). This indicates that the presence of carbonate rocks in the landscape is not enough to distinguish the 'mosaics', created by their proximity with landscapes in which acid rocks are present.

The soils from the three studied sites are saturated with bases. The presence of exchange acidity in the soils from KS

Table 1
Content of exchangeable cations, cation exchange capacity (T) and base saturation (V) of soils from the Meadow landscapes with carbonate rocks

Key area №	Depth	pH	pH	Exch. Ca	Exch. Mg	Exch. K	Exch. acidity	T	V
	cm	H_2O	$CaCl_2$	cmol(+).kg^{-1}					%
KA 1	0–5	7.2	6.9	32.12	8.51	0.18	0.00	40	100
	5–15	7.3	7.0	23.80	6.47	0.15	0.00	31	100
KA 2	0–5	5.0	4.6	10.76	1.98	0.38	2.40	16	85
	5–15	5.5	4.5	8.43	0.95	0.20	2.00	12	83
KA 3	0–10	5.5	4.6	11.37	1.33	1.51	2.14	16	87
	10–20	5.5	4.6	12.14	1.19	0.78	1.81	16	89

Table 2

Content of exchangeable cations and exchange acidity as a percentage of cation exchange capacity (T) of soils

Key area №	Depth	Exch. Ca	Exch. Mg	Exch. K	Exch. acidity
	cm	% of T			
KA 1	0–5	80.3	21.3	0.5	0.0
	5–15	76.8	20.9	0.5	0.0
KA 2	0–5	67.3	12.4	2.4	15.0
	5–15	70.3	7.9	1.7	16.7
KA 3	0–10	71.1	8.3	9.4	13.4
	10–20	75.9	7.4	4.9	11.3

2 and KS 3 in the conditions of base saturation is an indicator for the high share of permanent charges of the cation capacity (Ganev, 1990b). This can be explained by the nature of the soil-forming process – clay formation in the presence of high carbonate rock – clayey limestone.

The location of the soil profiles is of great importance for the quantities of exchange cations. In KS 1 of the eluvial part of the landscape, the high quantity of exchangeable calcium reflects the strong influence of the soil-forming rock on the described processes. In the transit parts of the landscape – KS 2 and KS 3, the soil-forming process in advanced and the influence of the topography, precipitation and other factors is pronounced by the leaching processes.

Conclusions

Differences in the conditions for plant nutrition in grassland landscapes with carbonate rocks on the territory of the "Central Balkan" National Park were determined by studying the cation exchange soil parameters. It was determined that the presence of carbonate soil-forming rocks is not sufficient to expect a different biological response in comparison with neighbouring landscapes with acid rocks. The study showed presence of neutral, medium acidic and highly acidic reaction of soils, which create two types of cation exchange – hydrolysis-alkaline and hydrolysis-acidic, as the latter one has a different intensity in two of the studied sites. It is assumed that the determined differences in the conditions for plant nutrition are prerequisites for creation of mosaic structure within the boundaries of landscapes with carbonate rocks. The response of the biotic component to the environmental conditions has not been studied in the present report. It is recommended to perform the biodiversity assessment in the park in accordance with cation exchange soil properties, regardless of the soil type and the soil-forming rocks, due to the large number of combinations, created by the soil-forming factors as conditions for plant nutrition.

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