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EXCHANGEABLE PROPERTIES OF FOREST SOILS UNDER BEECH ECOSYSTEMS IN CENTRAL BALKAN AND OSOGOVO

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Abstract

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For forest soils, which are naturally acidic, there is only a limited number of reports, concerning their cation exchange capacity (CEC) controlling mechanisms and on the possible impacts of acidic deposition, climate change and increasing harvesting pressure for biofuels. Therefore, the aim of this investigation was to characterise the cation exchange capacity of forest soils (Dystric and Eutric Cambisols) under beech stands (*Fagus sylvatica* L.) from the Central range of the Balkan mountain and from the Osogovo Mountain. The cationexchange properties have been analyzed following the methodology of Ganev and Arsova (1980). The cation exchange capacity ($T_{8.2}$) in the surface horizons of soil samples from the Balkan mountain vary within a wide range of 10.6 cmol.kg^{-1} to 20.9 cmol.kg^{-1}. For the soil from the Osogovo Mountain, the total cationexchange capacity was higher ranging from 18.4 cmol.kg^{-1} - 34.4 cmol.kg^{-1}. The concentrations of negatively charged strongly acid exchangeable sites (T_{CA}) were from 6.0 to 15.5 cmol.kg^{-1}, for the soil from the Balkan mountain, while for the Osogovo Mountain - they were about two times higher - from 12.0 cmol.kg^{-1} to 27.1 cmol.kg^{-1}. A similar trend for the exchangeable aluminium (Al_e) values for the surface horizons of the Balkan mountain soil (from 1.0 cmol.kg^{-1} to 2.5 cmol.kg^{-1}) and of the Osogovo Mountain, soil (from 1.6 cmol.kg^{-1}, to 5.9 cmol.kg^{-1}) was established. The slight increase in the content of Al_e in the soil from Osogovo Mountain suggests a stronger destruction of Al-bearing minerals, most probably due to isomorphic substitutions. It was found that podzolization was occurring more pronouncedly in the soils of the Balkan mountain. The base saturation (*BS*) in the studied soils varies from 33.0 to 75.0% of the total cation exchange capacity. For all studied sampling sites, the negative charges of soil colloids which behave as strong acids (T_{CA}) exceed the *BS* values, due to the additional proportion of H^+ and Al^{3+} acidic cations.

Key words: cation exchange capacity, beech stand, cambisols, podzolization

Introduction

The ion exchange processes in soils play important role in their nutrient retention capacity. The cation exchange capacity (CEC) of soils is an important parameter for estimating the degree of cation retention or loss from soils. Most previous studies of soil chemistry have so far concentrated on agricultural soils. The growth of forests is a long-term process, during which nutrients are cycled from plant to soil through litterfall and root turnover. The stem-flow and rainfalls are other ways for dissolved nutrients input to the soil surface. Thus, the availability of nutrients in forest soils is a long-term concern, which is related to the physicochemical and biological processes occurring over the years. Moreover, a species tree differences also play a role in generating differences in the through-fall volume and, respectively, the soil nutrient concentrations (Crozier and Boerner, 1986; Van Breemen et al., 1997). Many investigations show that organic matter (Johnson et al., 1997, Vesterdal, 1999) and clay minerals (Martel et al., 1978; Manrique et al., 1991) are the main sources of negatively charged sites able to retain exchangeable cations. For forest soils, there are only a few reports, dealing with the issue of cation exchange capacity (CEC) (Ganev and Milchev, 1971; Doichinova and Zhiyanski, 2008; Velizarova, 2011). These soils are generally acidic and contain high amounts of organic carbon. Their CEC may be primarily, or exclusively, associated with functional groups of organic matter (OM) (Ross et al., 1991; Skyllberg et al.,

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2001; Johnson, 2002). In addition, it is important to get an insight into the retention and immobilization of potentially toxic cations such as Al and Mn, and storage of major nutrient cations, especially Ca, Mg and K (Ganev and Milchev, 1971). Thus, it is important to understand better the cation exchange mechanism(s) in forest soils, because of the potential impacts of acidic deposition, nitrogen deposition, climate change and increasing harvesting pressure for biofuels (Ignatova et al., 2008).

Therefore, the purpose of the present investigation was to characterise the cation exchange capacities of forest soils under beech stands from the Central range of the Balkan mountain and from the Osogovo Mountain.

Materials and Methods

Soil samples were taken from mineral soil horizons of the investigated areas and were analyzed for CEC, organic carbon contents and soil pH. Sampling sites in the Central range of Balkan mountain were assigned as B1, B2, B3 and B4 and those in the Osogovo Mountain – Os5, Os6, Os7, respectively. The prevailing type of forest is European beech (*Fagus sylvatica* L.). The age of beech stands of sampling sites of the Balkan mountain vary from 50 to 80 years, whereas that from the Osogovo Mountain from 130 to140 years. In spite of the fact that the sampling sites are located at different altitudes, the soils are Cambisols (Dystric Cambisols - B2, B3, Os5, Os6 and Eutric Cambisols - B1, B4 and Os7) according to WRBSR (2006) (Table 1). At each sampling site, 3 soil profiles have been established and soil patterns have been collected from genetically formed soil horizons. Cation exchange properties have been analyzed following the methodology of Ganev and Arsova (1980). Total soil organic carbon content and pH in H_2O were determined according to Donov et al. (1971) protocols. All values represent the average of three replications of the determined indexes. Velizarova and Velichkov (2005) and Velizarova (2010) gave a detailed description of the studied regions.

Results and Discussion

In Table 2, the results of the cation exchange properties of soils are presented in cmol. kg^{-1}, and for soil organic carbon (SOC) the contents are in g.kg^{-1}. The dependencies of the components of the cation exchange capacity (CEC) – total exchange capacity ($T_{8.2}$), charges on the positions, which behave as strongly acid (TCA), weakly acid (TA), soil pH and on SOC contents, are presented in Figures 1 and 2, respectively. Figure 3 presents data about the share (in %) of the exchangeable soil positions from the total soil exchange capacity.

The results for pH of the studied soils show variation from 4.7 to 5.8 in the surface horizons. According to the established values for sampling sites B1, B2, B3, B4, Os5, Os6, the soils are acidic, whereas those from Os7 are slightly acidic. Ross et al. (2008) suggest that for forest soils, which are acidic, a critical, but often overlooked, point is that lower pH does not necessarily result from greater inputs of strong acidity, but from input of weak (organic) acidity and less buffering from weatherable minerals. The results for soil organic carbon (SOC) content in the surface horizons were in the range of values, which are typical for Cambisols – from 21.6 g.kg^{-1} to 49.7 g.kg^{-1}. The soils from sampling sites in the Osogovo Mountain, demonstrate higher SOC in the surface mineral horizons from 31.0 g.kg^{-1} to 49.7 g.kg^{-1} (Table 2) and a higher carbon stock (Velizarova and Velichkov, 2005). These sampling sites are located at higher altitudes, where the specific climate conditions contribute to a decreased rate of humification and mineralization processes of the organic matter as compared to the sampling sites in the Balkan mountain. Various studies indicate that in mountainous terrains, SOC stocks increases with altitude (Conant et al., 1998; Jenny, 1994; Townsend et al., 1995). The differentiation of SOC content in the horizons along the depth of the soil profile showed distinctly higher values in surface horizons A (31.0 – 49.7 g·kg^{-1}) than those in the B (13.0 – 25.5 g·kg^{-1}) and BC (3.1 – 5.5 g·kg^{-1}) for the soils from the Osogovo Mountain. However, in the soil profiles from the sampling sites in the Balkan mountain, the

Table 1
Characteristic of sampling sites of Balkan Mountain (B) and Osogovo Mountain (Os)

№ ES	Studied region	Altitude, m	Exposure	Age, years	Stand quality
1 B1	Botevgrad	520	North, N	68	I
2 B2	Teteven	600	Northwest,NW	48	I
3 B3	Troian	650	Northeast, NE	71	I
6 B4	Omurtag	650	Northeast, NE	80	I
3 Os5	Osogovo	1400	Northeast, NE	140	I
6 Os6	Osogovo	1550	Southwest, SW	140	I
7 Os7	Osogovo	1500	EastSoutheast, ESE	130	I

SOC content was similar and varied in a narrow range along the depth of the soil profiles.

The results show that the total cation exchange capacity ($T_{8.2}$) in the surface horizons of the soil from the Balkan mountain vary in a wide range from 10.6 cmol.kg^{-1} to 20.9 cmol.kg^{-1} (Table 2). The soil from the Osogovo Mountain is characterized by a higher total cation exchange capacity i. e., from 18.4 cmol.kg^{-1} to 34.4 cmol.kg^{-1}. The values of the negatively charged exchangeable positions, which behave as strong acid (T_{CA}), according to the conceptual and methodological approach of Ganev (1990), for the soil from the Balkan mountain were from 6.0 to 15.5 cmol.kg^{-1}, while they were about two times higher in the soil from sampling sites, situated in the Osogovo Mountain - from 12.0 cmol.kg^{-1} to 27.1 cmol.kg^{-1}. Those types of charges, by definition, are permanent and not pH-dependent, which is confirmed by our results, presented on Figure 1B and most likely are due to the different mineralogy of the soils analysed as well as the different contents of the strongly acidic groups in the soil organic matter. Alternatively, a clear positive dependence between pH and $T_{8.2}$ and T_A was found (Figure 1A and 1C). The main chemical mechanism resulting in the formation of those types of charges is clay minerals destruction and transformation of the H-saturated clays into *Al*-saturated (Harwood and Coleman, 1954; Low, 1955; Ganev, 1990). Due to these processes, additional exchangeable aluminium (Al_e) at the expense of the base cations (Ca^{2+} and Mg^{2+}) appears in the soil solution.

As can be seen, that Al_e in the soil from the Balkan mountain varies in the surface horizons from 1.0 cmol.kg^{-1} to 2.5 cmol.kg^{-1}, which is much lower, than that in the soil from the Osogovo Mountain from 1.6 cmol.kg^{-1} to 5.9 cmol.kg^{-1}. As it was already mentioned, the soils from the Osogovo are characterized by a high SOC content. Martin and Reeve (1958), Schnitzer and Skinner (1963) and Schnitzer (2000) emphasized the importance of Al complexed by soil organic matter (OM). An increase in organically complexed *Al* suggests that the $H_{8.2}$ decrease resulted from changes in the extractability of *Al* and enhances sorption to the mineral surfaces the higher *Al* values may be due to, either high exchangeable *Al* or labile organic *Al*-complexes in the soil solution. The increased concentrations of Al_e in the soil from the Osogovo

Table 2
Cation exchange properties of the soil

Sampling sites	Genetic horizon	Soil depth, cm	pH	C, g.kg^{-1}	$T_{8.2}$	T_{CA}	T_A	$H_{8.2}^+$	Al	Ca	Mg	T_{CA}	T_A	$H_{8.2}^+$	Al	Ca	Mg	V, %
					in cmol.kg^{-1}							in % of $T_{8.2}$						
Central range of Balkan mountain																		
B1	A	0-14	5.30	32.7	20.9	15.5	5.4	6.4	1.0	5.6	9.0	74.4	25.6	30.6	5.0	26.6	42.8	69.4
	B	14-45	5.10	31.8	16.2	9.4	6.8	7.8	0.9	2.4	6.0	57.9	42.1	47.9	5.8	15.0	37.1	52.1
B2	A	0-10	4.90	33.6	10.6	7.2	3.4	4.5	1.0	2.1	4.1	67.7	32.3	42.1	9.8	19.4	38.5	57.9
	B	10-50	4.80	28.3	13.2	8.3	4.9	7.0	2.1	2.8	3.5	62.7	37.3	53.1	15.7	20.9	26.1	46.9
B3	A	0-13	4.70	27.3	14.9	7.0	7.9	10.0	2.1	2.6	2.3	47.0	53.0	67.0	14.0	17.7	15.3	33.0
	B	13-42	4.40	26.4	10.3	5.9	4.4	6.6	2.2	1.9	1.8	57.4	42.6	64.2	21.6	18.5	17.3	35.8
B4	A	0-11	5.10	21.6	13.6	9.0	4.6	7.1	2.5	2.8	3.7	66.3	33.7	52.1	18.4	20.6	27.4	47.9
		11-45	4.5	16.2	7.8	6.5	1.3	3.6	2.3	1.9	2.3	83.5	16.5	46.2	29.6	24.5	29.4	53.8
Osogovo mountain																		
Os5	A	0-27	4.97	49.7	34.4	27.1	7.2	13.1	5.9	4.5	16.8	78.9	21.1	38.1	17.0	13.0	48.9	61.9
	B	27-78	5.30	25.5	14.8	10.6	4.2	9.5	5.2	0.7	4.7	71.5	28.5	63.7	35.2	4.4	31.9	36.3
	C	78-120	5.49	3.1	15.2	11.8	3.4	6.9	3.5	1.6	6.7	77.8	22.2	45.3	23.1	10.7	44.0	54.7
Os6	A	0-27	4.81	31.0	18.4	12.0	6.4	12.2	5.8	4.3	1.9	65.3	34.7	66.3	31.6	23.2	10.5	33.7
	B	27-69	5.70	13.1	15.9	14.0	1.9	4.6	2.7	2.4	8.9	88.1	11.9	29.0	17.1	14.9	56.2	71.0
	C	69-87	5.84	1.5	15.0	13.4	1.6	3.7	2.1	6.1	5.1	89.4	10.6	24.9	14.3	40.6	34.4	75.0
Os7	A	0-26	5.79	40.3	27.7	13.3	14.4	16.9	2.5	1.1	9.7	47.9	52.1	61.1	9.0	3.8	35.0	38.9
	B	26-80	5.53	15.8	15.1	11.0	4.1	7.9	3.8	4.3	2.9	73.1	26.9	52.4	25.5	28.7	19.0	47.6
	C	80-97	5.81	5.5	21.2	10.7	10.5	12.1	1.6	3.1	6.0	50.6	49.4	57.1	7.6	14.5	28.4	42.9

Mountain may have potentially harmful effects on the forest vegetation (Minocha et al., 1997; Shortle and Smith, 1988), and soil quality (Lawrence et al., 1995; Mulder et al., 1989). The increased quantity of Al_e is related to the soil clay transformation. Charge development on the silicate clays is mainly due to isomorphous substitution of Al^{3+} for Si^{4+} or Mg^{2+} for Al^{3+}. The results about distribution of Al_e along the soil profile show its downward migration and accumulation in deeper located horizons for almost all sampling sites (Figure 3). The percentage of exchangeable Al_e from$H_{8.2}$ on the soil colloids, reaches maximum of 30.0 % in B-horizon of the soil from the B4 sampling site ((Figure 3 - B4) and 35.2 % in B-horizon for the Os 5 (Figure 3 – Os 5). The process of downward migration of Al^{3+}, together with organic matter, from the surface areas and their accumulation in the profile's deeper areas, known as podsolization, obviously occurs in the studied soils. The data obtained for the share of the total soil acidity $H_{8.2}$ to the $T_{8.2}$ show high values – from 25.0 % to 66.0 % and exceed those for T_A. Obviously, H^+ ions are adsorbed both - on the negatively charged positions, which behave as weakly and strongly acidic sites. Part of the adsorbed H^+ ions produce increasing amounts of exchangeable Al_e (Figure 4). The slight increase of Al_e in the soil from the Osogovo Mountain suggests a stronger destruction of Al- bearing minerals in these sites.

The base saturation (*BS*) in the studied soil varies from 33.0 % to 75.0% of the total cation exchange capacity. For all studied sampling sites, the negative charges of soil colloids, which behave as a strong acid (TCA), exceed the *BS* values (Figures 3 and 4). Hence, the proportion of exchangeable positions of the soil colloids are occupied not only by "base" cations, but also by acid cations - H^+ and Al^{3+} as confirmed by results obtained for total acidity and exchangeable aluminium ($H_{8.2}$ and Al_e). The decreasing trends of *BS*, observed for

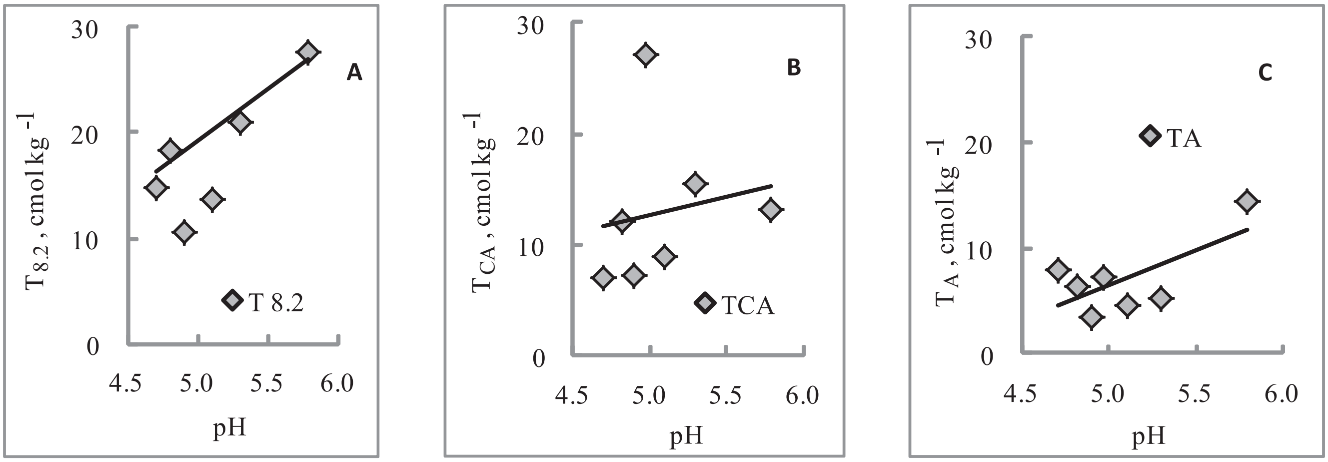

Fig. 1. The relationships between $T_{8.2}$ (A), T_{CA} (B) , T_A (C) and soil pH

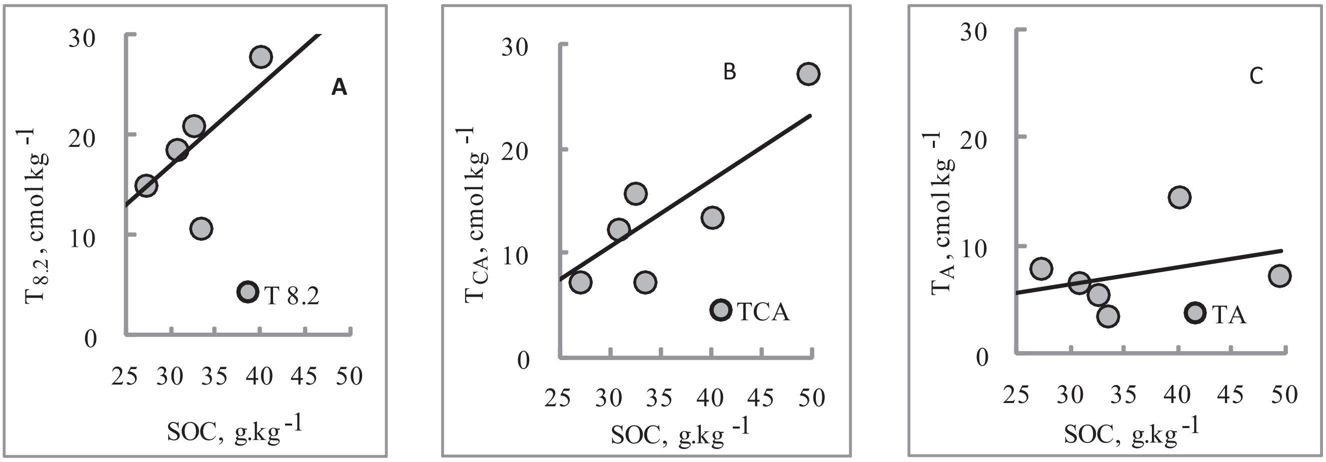

Fig. 2. The relationships between $T_{8.2}$ (A), T_{CA} (B), T_A (C) and SOC content

the soil from the Balkan Mountain suppose accelerated processes of soil acidification. However, the pH of the soil from these sampling sites is about 5.0. Bloom and Grigal (1985) and Reuss et al. (1990) found that at pH of about 4.5–5.0, the positive relationship between pH and *BS* breaks down. Most probably, the lower pH results from an input of weak organic

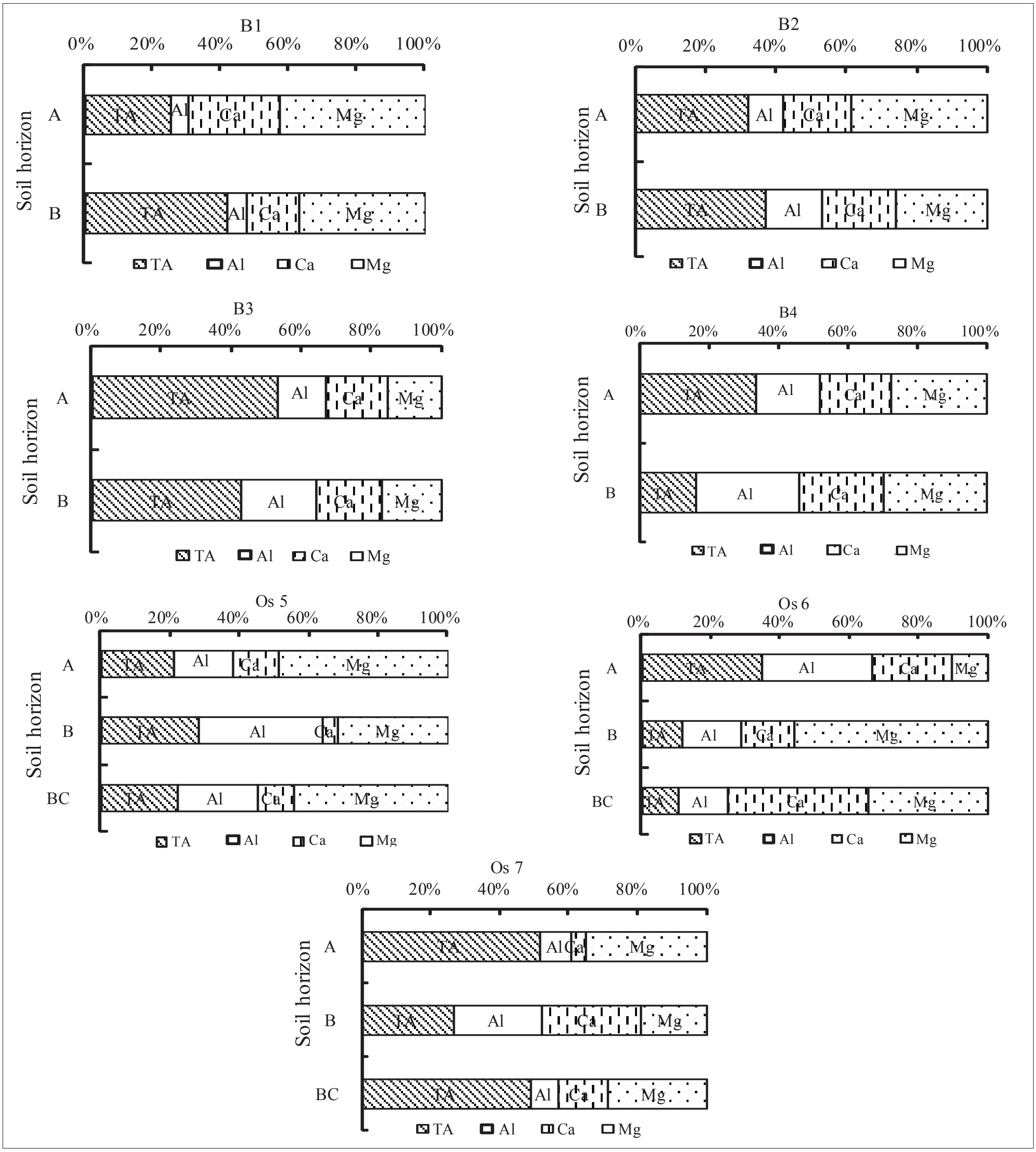

Fig. 3. Share (in %) of the T_A, Al_e, Ca, Mg from the $T_{8.2}$

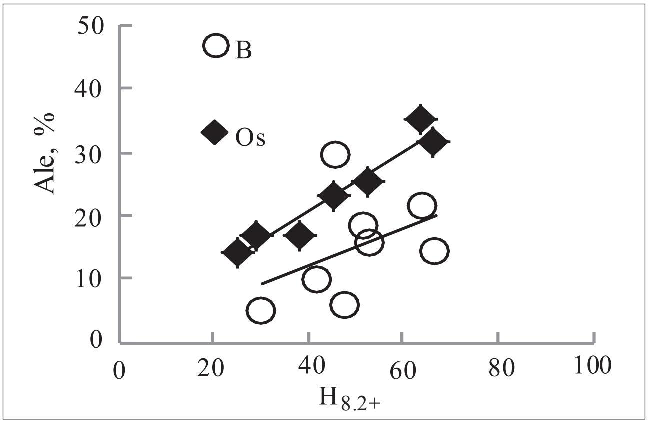

Fig. 4. Dependence between Al_e and $H_{8.2}$

acidity like fulvic acids, prevailing in Cambisols, and less buffering from weatherable minerals (Ross et al., 2008).

Conclusions

Our studies on the physico-chemical characteristics of surface and sub-surface horizons of forest soils show that pH varies from 4.7 to 5.8 in the surface horizons. According to the established values for pH, the studied soils are slightly acidic or acidic. The soil organic carbon (SOC) contents found were within the range of values typical for Cambisols from 21.6 g.kg^{-1} to 49.7 g.kg^{-1}. The soil from the Osogovo Mountain, demonstrate higher SOC in the surface mineral horizons from 31.0 g.kg^{-1} to 49.7 g.kg^{-1}. The differentiation of SOC contents in the horizons along the depth of the soil profile showed distinctly higher values in the surface A horizons in the soils from the Osogovo mountain, whereas in the soils from the Balkan mountain the SOC content varies in a narrow range along the depth. Cation exchange capacity ($T_{8.2}$) in the surface horizons of the soil from the Balkan mountain varies in a wide range from 10.6 mol.kg^{-1} to 20.9 cmol.kg^{-1}. In the soil from the Osogovo Mountain, total cation exchange capacity was higher from 18.4 cmol.kg^{-1} to 34.4 cmol.kg^{-1}. The values of the negatively charged exchangeable positions were from 6.0 to 15.5 cmol.kg^{-1} for the soil from the Balkan Mountain, while for the Osogovo Mountain they were about twice higher from 12.0 cmol.kg^{-1} to 27.1 cmol.kg^{-1}. A similar trend for the exchangeable aluminium (Al_e) values was established for the surface horizons in the soil from the Balkan mountain from 1.0 cmol.kg^{-1} to 2.5 cmol.kg^{-1} and twice higher for that from the Osogovo Mountain – 1.6 cmol.kg^{-1} to 5.9 cmol.kg^{-1}.The slight increase in the content of Al_e in the soil from the Osogovo Mountain confirms a stronger destruction of Al- bearing minerals, most probably due to isomorphous substitutions or higher values of organically complexed sluble Al due to the higher organic matter content in this soil. A downward migration of Al^{3+}, together with organic matter, from the surface horizons and their accumulation in the profile's deeper zones, obviously occurs in the studied soils and is more pronounced in the soil from the Balkan mountain.

The base saturation (*BS*) in the studied soils varies between 33.0 % and 75.0% of the total cation exchange capacity. For all studied sampling sites, the negative charges of the soil colloids which behave as strong acid (T_{CA}) exceed the *BS* values, due to the additional proportion of the H^+ and Al^{3+} cations.

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