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## ADSORPTION COMPLEX OF SOILS ON NON-CARBONATE SUBSTRATE IN FIR AND BEECH-FIR FORESTS OF CROATIA

### ADSORPCIJSKI KOMPLEKS TLA NA NEKARBONATNIM SUPSTRATIMA U JELOVIM I BUKOVO-JELOVIM SASTOJINAMA HRVATSKE

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#### Abstract

The goal of research was to determine the soil adsorption complex properties on the non-carbonate parent substrate in fir and beech-fir forests with regard to the content and relationship of exchangeable base and acid cations. The obtained results were used to establish differences in the adsorption complex in terms of locality and phytocoenosis. The adsorption complex of soils on non-carbonate substrate that mostly gives detritus poor in basic cations is researched. Mentioned main substrate, naturally acid soil and prehumid and humid climate conditions, especially in Gorski Kotar, cause leaching of basic cations from the soil. Degradation processes in dystic cambisol, brunipodzol and podzol lead towards acidification, leaching of basic cations, i.e. nutrients and destruction of clay minerals, thus worsening buffer and physical soil properties. Researches were made in Panonic Croatia region in Forestry Districts of Voćin, Kamenska, Krapina, Zagreb and Faculty's forests on Medvednica, and in Gorski Kotar region in Forestry Districts and Faculty's facilities: Vrbovsko, NPŠO Zalesina, Delnice, Fužine, Lokve, Crni Lug and Tršće.

Selection of the forest stands, in which pedological profiles were open, was based on geological, pedological and vegetation maps, considering main substrate, soil type and phytocoenosis. Pedological researches in the field were done between 8 September and 14 October 1999 and between 5 May and 16 September 2000. Three types of soil were analysed: dystic cambisol (47 profiles), brunipodzol (19 profiles) and podzol (16 profiles). Laboratory analysis of air dry soil samples determined soil texture, soil pH, organic carbon contents, total nitrogen contents, exchangeable acidity and exchangeable cations.

Collected data were processed by statistical methods in Statistica 6.0 program package.

According to the contents of particular cations, especially  $Al^{3+}$  and  $H^+$ , as well as according to the capacity of exchangeable cations two groups related to geographical area were differentiated: Panonic Croatia and Gorski Kotar. Generally, one can say that all soils of researched sites have high to very high contents of acid exchangeable cations, with medium to low contents of basic exchangeable cations, and medium to low base saturation of adsorption complex. Cation exchange capacity is medium to high and considerable positive correlation is determined with the contents of clay texture fraction.

It should be pointed out that the analyses gave very high contents of  $Al^{3+}$  and  $H^+$  ions in adsorption complex of soil at all sites in Gorski Kotar, as well as high contents of  $Al^{3+}$  and  $H^+$  ions in Panonic Croatia. This result is disturbing since numerous authors speak in their researches of toxic effects of  $Al^{3+}$  and  $H^+$  to plants, and of their antagonistic effect to accepting calcium, magnesium and phosphorus.

At all sites, among the base exchangeable cations contents of  $Mg^{2+}$  was the lowest, and this contents is considerably lower at Belevine, Crni Lug and Tršće site.

The most unfavourable rate of acid and basic cations, and the minimal base saturation of the adsorption complex among the sites in Panonic Croatia is found on Medvednica, while such sites in Gorski Kotar are Belevine, Crni Lug and Tršće.

On basis of given results, the sensitivity of researched soils to acidification could be rated as medium to high, and Gorski Kotar region is more sensitive than Panonic Croatia.

Key words: adsorption complex, buffer potential, cation exchange capacity, dystic cambisol, brunipodzol, podzol, fir forests, beech-fir forests

## Sažetak

U radu je istraživana adsorpcijski kompleks tla na nekarbonatnom matičnom supstratu koji uglavnom daje bazama siromašan detritus. Navedeni matični supstrat, prirodno kiselo tlo i uvjeti perhumidne i humidne klime, posebice u Gorskom kotaru, uvjetuju ispiranje baza iz tla. Procesi degradacije kod distričnog kambisola, brunipodzola i podzola idu u smjeru acidifikacije, ispiranja baza, odnosno hraniva i destrukcije minerala gline čime se pogoršavaju puferna i fizikalna svojstva tla.

Istraživanja su obavljena na području panonske Hrvatske u šumarijama Voćin, Kamenska, Krapina, Zagreb i u Fakultetskim šumama na Medvednici, te na području Gorskog kotara u šumarijama i fakultetskim objektima: Vrbovsko, NPŠO Zalesina, Delnice, Fužine, Lokve, Crni Lug i Tršće.

Odabir primjernih objekata šumskih sastojina u kojima su otvoreni pedološki profili napravljen je na temelju geoloških, pedoloških i vegetacijskih karata pri čemu se vodilo računa o matičnom supstratu, tipu tla i fitocenoza. Terenska pedološka istraživanja obavljena su u razdoblju od 08. rujna do 14. listopada 1999. godine i od 05. svibnja do 16. rujna 2000. godine. Obrađena su tri tipa tla: distrični kambisol (47 profila), brunipodzol (19 profila) i podzol (16 profila). Laboratorijskim analizama na zrakovitim uzorcima tla (sitnica tla) određen je mehanički sastav, reakcija tla, sadržaj humusa, sadržaj ukupnog dušika, izmjenjiva kiselost i izmjenjivi kationi.

Prikupljeni podaci obrađeni su statističkim metodama u programskom paketu Statistica 6.0. Prema sadržaju pojedinih kationa, posebno  $Al^{3+}$  i  $H^+$ , kao i prema kapacitetu izmjenjivih kationa izdiferencirale su se dvije grupe koje se slažu s geografskim položajem: panonska Hrvatska i Gorski kotar.

Općenito se može reći da sva tla istraživanih lokaliteta imaju visok do vrlo visok sadržaj kiselih kationa, uz osrednji do nizak sadržaj bazičnih kationa, te osrednju do nisku zasićenost adsorpcijskog kompleksa bazičnim kationima. Kapacitet izmjenjivih kationa je osrednji do visok, a značajna pozitivna korelacija utvrđena je sa sadržajem glinene teksturne frakcije.

Treba istaknuti da je analizama utvrđen vrlo visoki sadržaj  $Al^{3+}$  i  $H^+$  iona u adsorpcijskom kompleksu tla na svim lokalitetima Gorskog kotara, kao i visoki sadržaj  $Al^{3+}$  i  $H^+$  iona u panonskoj Hrvatskoj. Ovaj podatak je zabrinjavajući jer brojni autori u svojim istraživanjima govore o toksičnom utjecaju  $Al^{3+}$  i  $H^+$  na biljke, kao i o njihovom antagonističkom učinku na primanje kalcija, magnezija i fosfora.

Na svim je lokalitetima zabilježen najmanji sadržaj  $Mg^{2+}$  iona među izmjenjivim bazičnim kationima adsorpcijskog kompleksa, a taj je sadržaj značajno manji za lokalitete Belevine, Crni Lug i Tršće.

Najnepovoljniji postotni udio kiselih i bazičnih kationa, te najmanju zasićenost adsorpcijskog kompleksa bazama od lokaliteta panonske Hrvatske ima Medvednica, dok su za Gorski kotar to Belevine, Crni Lug i Tršće.

Na osnovi dobivenih podataka osjetljivost istraživanih tala prema acidifikaciji može se ocijeniti kao osrednja do visoka s time da je područje Gorskog kotara osjetljivije od panonske Hrvatske.

**Ključne riječi:** adsorpcijski kompleks, puferni potencijal, kapacitet izmjenjivih kationa, distrični kambisol, brunipodzol, podzol, jelove sastojine, bukovo-jelove sastojine

## INTRODUCTION

### UVOD

Adsorption is one of the most important physical-chemical processes in the soil. It determines the quantity of plant nutrients, pesticides and other compounds that are bound to the surface of soil particles. For this reason, it is one of the primary processes that play an important role in nutrient transport and soil contamination (Stumm 1996).

Martinović (2003) states that soils with different adsorption complexes represent ecologically highly diverse sites and substrates. This is the reason that the condition of the adsorption complex is an excellent indicator of all kinds of processes, and particularly of degradation changes in the soil.

The condition of the adsorption complex in a soil supplies information on soil quality. According to (Gračanin and Ilijanić. 1977), in relation to the capacity extent, as well as the saturation degree and manner, the soil adsorption complex may have a decisive effect on a multitude of physical, chemical and biological properties, in other words, on soil fertility.

Of physical properties, the adsorption complex significantly affects the soil structure (Weerd et al. 1999). Soils in which the adsorption complex is saturated with calcium show considerably higher stability, a more favourable structural composition and better physiological features than soils in which the adsorption complex is saturated with  $\text{Na}^+$  or  $\text{H}^+$  ions (Gračanin 1947).

Cation adsorption has primary importance for plant nutrition. Cations bound to colloidal soil particles represent reserves of plant nutrients ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{NH}_4^+$ ). This is how soil resists the processes of nutrient leaching via descendent watercourses and retains nutrients in the rhizospheric zone (Steven 1994).

The effect of the adsorption complex on the buffer capacity is important, especially in the current conditions of adverse impacts of anthropogenically-induced soil acidification (Müchenhausen 1975, Ulrich 1982, Alekseev 1990, Glavač 1999). By buffering (neutralizing) acid depositions that reach the soil, stresses on the vegetation, as well as the soil flora and fauna are somewhat lessened.

While acknowledging the synergistic action of adverse factors, a number of authors regard forest soil acidification as the most responsible factor of forest decline in many regions of Europe (Ulrich et al. 1979, Hutchinson et al. 1986, Tamm and Hallbäck 1986, Ulrich 1991, Mayer 1998). Acidification is related to lowered pH values, decreased saturation of the adsorption complex with base cations, and increased  $\text{Al}^{3+}$  ion concentrations in the soil solution.

The adsorption complex content indicates dominant pedogenetic processes in the soil. For example, if the adsorption complex is saturated with acid cations, such as  $\text{H}^+$ ,  $\text{Al}^{3+}$ ,  $\text{Fe}^{2+}$  and  $\text{Mn}^{2+}$ , then the dominant processes in the soil are acidification and eluviation (podzolization).

From the standpoint of plant physiology,  $\text{Al}^{3+}$  and  $\text{H}^+$  ions are definitely the most important. Many experiments have proved the toxic effects of  $\text{Al}^{3+}$  and  $\text{H}^+$  ions on root growth and the antagonistic effects on cation reception (Matsumoto et al. 1976, Foy et al. 1978, Hecht-Buchholz and Foy 1981, Foy 1983, Schier 1985, Sivaguru et al. 2003 and others). Aluminium creates the gravest problems in phosphorus, calcium and magnesium reception. For this reason, the external manifestation of aluminium toxicity generally resembles the signs that characterise lack of phosphorus in nutrition (increased antocyan biosynthesis) (Foy 1984).

This paper explores the soil adsorption complex on non-carbonate substrates in fir and beech-fir stands in Croatia. These stands in Pannonian Croatia cover an area of approximately 14,000 ha (Medvedović 1990). In the area of Delnice, these stands cover 6,489 ha (Management Plan of Delnice Forest Office).

The decomposition of non-carbonate parent substrates, particularly those rich in quartz and acid plagioclases, results in the predominantly sandy textures that are naturally poor in bases. In such substrates in the area of perhumid and humid climates, descendent flows are distinct. This allows the base reserves bound to the adsorption complex to leach easily, thus decreasing the soil buffer capacity against acidification. High saturation with acid cations that have a toxic effect on the roots and an antagonistic effect on the base cation reception (especially  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ ), combined with low pH value, may represent an important negative feature in fir stands exposed to a synergistic action of adverse impacts of biotic (insects, mistletoe) and abiotic (climatic extremes, aerial pollution) factors.

The goal of research was to determine the soil adsorption complex properties on the non-carbonate parent substrate in fir and beech-fir forests with regard to the content and relationship of exchangeable base and acid cations. The obtained results were used to establish differences in the adsorption complex in terms of locality and phytocoenosis. Categories of susceptibility to acidification will be identified for the studied localities.

## METHODOLOGY METODE ISTRAŽIVANJA

### Research sites Područje istraživanja

Field pedological research was conducted in the soils developed on the non-carbonate parent substrate in the range of fir and beech-fir stands in Gorski Kotar and Pannonian Croatia.

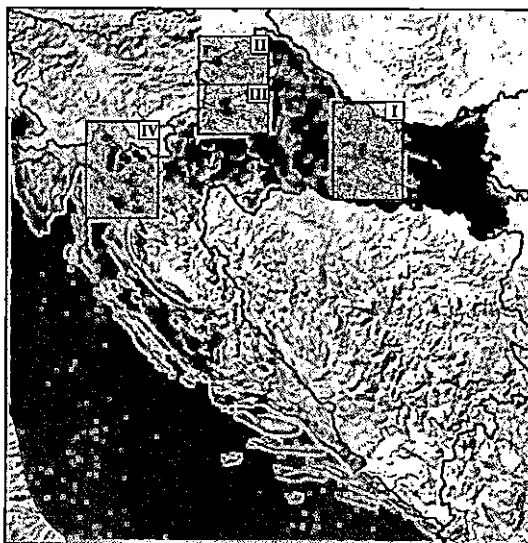


Figure 1 Research area –circles show management units in which pedological sampling was conducted  
Slika 1 Područje istraživanja –krugovi prikazuju gospodarske jedinice u kojima je napravljeno pedološko uzorkovanje

### Selection of sample facilities Izbor primjernih objekata

The localities were selected on the basis of the basic pedological maps M 1:50,000 and their supplements and the detailed pedological maps made during typological forest research. These were compared with the basic geological and vegetation maps. The following criteria were followed:

- Parent substrate: non-carbonate substrate rich in quartz and acid plagioclases conditions the development of acid soils poor in bases;
- Soil acidity as a factor which significantly affects the adsorption complex condition: the most represented acid soils were selected: dystric cambisol, brunipodzol and podzol, while the less common soils, such as ranker, luvisol and colluvium, were excluded;
- Climatic conditions: perhumid and humid climate also favours the genesis of acid soils;
- Phytocoenosis: in the area of Gorski Kotar and a part of Macelj, an edaphically conditioned acidophylic association of fir with hard fern (*Blechno-abietetum*) was selected, while a typical subassociation of Pannonian beech-fir forest (*Abieti-fagetum "panonicum" typicum*), occurring on the silicate base of Macelj, Medvednica and Papuk, was selected in the remaining part of the mountains in Pannonian Croatia (Medvedović 1990).

### Field research *Terenska istraživanja*

Based on the knowledge of pedological parameter variability, the following conditions were set down in order to determine the positions of pedological profiles (Pernar 1996):

- a) Homogeneity of the geological-lithological substrate on the basis of pedological and geological maps and field observations;
- b) Undisturbed micro-relief – any possible excessive pedoturbations in the past caused by natural processes or by anthropogenic actions were excluded;
- c) Extreme positions in the mezorelief – tops and stem bases – were excluded;
- d) Completely closed stand canopy;
- e) Sampling away from the root collar – in the outer third of crown projections of the dominant trees.

Individual samples from pedological profiles were taken by genetic horizons. The position, as well as the bioclimatic and geomorphologic parameters were determined for each profil.

The paper treats three soil types in 11 localities (Table 1): dystric cambisol – 47 profiles, brunipodzol – 19 profiles and podzol – 16 profiles. The field part of the research was conducted during 1999 and 2000.

Table 1 Number of opened pedological profiles by locality and soil type  
*Tablica 1 Broj otvorenih pedoloških profila po lokalitetu i tipu tla*

Locality <i>Lokalitet</i>	Soil type			Number of soil profiles <i>Broj otvorenih pedoloških profila</i>
	Dystric cambisol <i>Distrični kambisol (DS)</i>	Podzol <i>Podzol (P)</i>	Brunipodzol <i>Brunipodzol (BP)</i>	
Pepuk	9	0	1	10
Macelj	4	0	0	4
Medvednica	6	0	0	6
Vrbovsko	4	1	5	10
Belevine	3	5	2	10
Sungerski lug	0	1	2	3
Delnice	7	1	1	9
Fužine	5	2	3	10
Lokve	1	1	0	2
Crni Lug	5	3	0	8
Tršće	3	2	5	10
Number of soil profiles <i>Br. otvorenih pedoloških profila</i>	47	16	19	82

### Laboratory analyses *Laboratorijske analize*

The analyses involved air-dried soil samples, which were dried, ground and sieved through 2 mm - 0.2 mm sieves in the laboratory.

Laboratory soil analyses were conducted with the following procedures:

- a) The mechanical soil composition, was determined with the pipette method after the extraction in 0.1 M  $\text{Na}_4\text{P}_2\text{O}_7$ ;

- b) The soil reaction was measured electrometrically using a combined method in the soil water suspension, that is, in 0.01 M CaCl<sub>2</sub>, with 1:2,5 ratio for surface mineral and argic horizons, and with 1:10 ratio for distinctly humose surface horizons. The laboratory microprocessor pH meter MA 5736, made by Metrel, with an accuracy of ± 0,01 pH was used for measurements;
- c) The humus content was determined with the bichromatic method by Tjurin;
- d) The total nitrogen content was determined with the combustion method according to the Kjeldahl procedure and distillation according to Bremner et al. (1982);
- e) Exchangeable acidity (H<sup>+</sup> i Al<sup>3+</sup>) was determined with the KCl method according to Thomas G.W. (1982).

Exchange cations were determined according to Thomas G. W. (modified) by the extraction with 0.1 M BaCl<sub>2</sub>. The K<sup>+</sup> and Na<sup>+</sup> in the extraction were determined flame-photometrically, and Ca<sup>2+</sup>, Mg<sup>2+</sup>, Fe<sup>2+</sup> and Mn<sup>2+</sup> were read on the atomic absorption spectrophotometer PU 9100X. Laboratory analyses were performed in the pedological laboratory of the Faculty of Forestry, University of Zagreb, and to a smaller extent in the Institute of Plant Nutrition of the Faculty of Agronomy, University of Zagreb.

#### **Statistical data processing** *Statistička obrada podataka*

For purposes of data comparison, pedogenetic horizons were grouped according to depth into the mineral (humus-accumulative Aoh, Aum, A/E and eluvial E) and the argic horizon (cambic (B)v and illuvial Bs) (Vanmechelen et al. 1997). Luvisol was excluded from the analysis due to the small sample. Descriptive statistics was made for all analyzed variables: arithmetic mean, standard deviation, minimum, median, and maximum. The significance level of 5% in all the tests was considered statistically significant. Mutual correlations were made and tested for all the pedological parameters by soil type. Mutual differences for surface mineral and argic horizons among different soil types, as well as different localities were tested with an analysis of variance, on condition that variance homogeneity was satisfied (Bartlett). For variables that did not satisfy variable homogeneity, a nonparametric Kruskal – Wallis test was done (Conover 1980). If the variance analysis showed a statistically significant difference between the horizons, a multiple post hoc test (Duncan) was used to find out which horizons were responsible for the difference. Mutual differences for the horizons of dystic cambisol per phytocoenoses were tested with a t-test provided that variance homogeneity was satisfied (F-test), or with a nonparametric Mann-Whitney U test if variance homogeneity was not satisfied (Sokal and Rohlf 1995). All statistical analyses were performed in the Statistica 6.0 programme package.

### **RESEARCH RESULTS AND DISCUSSION** *REZULTATI ISTRAŽIVANJA I RASPRAVA*

#### **Features of the adsorption complex and other pedological parameters per studied localities** *Značajke adsorpcijskog kompleksa i ostalih pedoloških parametara po tipovima istraživanih tala*

The results of laboratory analyses for the surface mineral and argic soil horizons per studied localities are given in Tables 2 and 3. The differences in the soil adsorption complex content between the investigated localities were best shown with statistical analyses. They cannot be presented in this paper<sup>3</sup> in their full scope for reasons of their size.

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<sup>3</sup> Please contact the authors of the articles for any details related to statistical analyses.

Two groups that correspond to a geographical position have been differentiated according to the individual cation content, especially  $Al^{3+}$  and  $H^+$ , and according to the cation exchange capacity. These groups are Pannonian Croatia and Gorski Kotar. In all the localities in Gorski Kotar, except for Sungerski Lug, the content of changeable  $Al^{3+}$  and  $H^+$  in the soil is considerably higher. As an illustration, (Fig 2), the  $Al^{3+}$  content in the adsorption soil complex in the surface mineral and in the argic horizon was chosen because the differences are the most distinct.

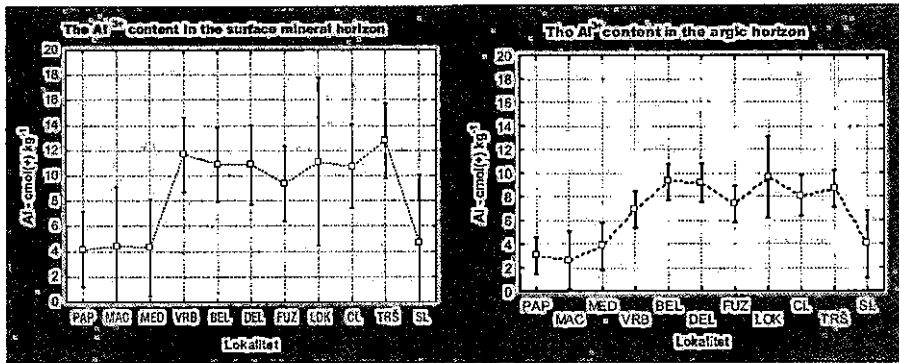


Figure 2 The  $Al^{3+}$  content in the adsorption soil complex in the surface mineral horizon and in the argic horizon of the investigated localities.

Slika 2 Sadržaj  $Al^{3+}$  u adsorpcijskom kompleksu tla u površinskom mineralnom i kambičnom horizontu tla istraživanih lokaliteta.

The reasons should be sought in more intensive processes of eluvial-iluvial migration caused by higher precipitation quantities, which results in basic cation leaching, as well as in immission acidification that additionally burdens the adsorption soil complex. Vukadinović and Lončarić (1998) state that calcium from acid soils is leached when precipitation quantities exceed 600 – 700 mm/year. In all the studied localities, the precipitation quantity is higher than the above and reaches over 2,000 mm/year for Gorski Kotar.

The natural acidification processes, especially in the studied soils – dystric cambisol, brunipodzol and podzol – are intensified with immission acidification. This leads to the impoverishment of the adsorption complex with basic cations and consequently to a decreased buffer potential. A higher content of acid cations, primarily  $Al^{3+}$  and  $H^+$ , in the area of Gorski Kotar, is additionally increased by immission-induced acidification. The fact that immission acidification is the highest in Gorski Kotar, a topic treated by a number of authors (Glavač et al. 1985, Prpić 1987, Komlenović et al. 1988, Komlenović 1989, Bezak et al. 1991, Prpić et al. 1991, Vrbek et al. 1991) coincides with the unfavourable condition of the adsorption complex.

Interestingly, in terms of the adsorption complex the locality of Sungerski Lug, where pedological profiles were opened in brunipodzol and podzol, is grouped with dystric cambisols of the localities Papuk, Macelj and Medvednica. Since Sungerski Lug is situated in equal climatic and vegetational conditions as the other localities of Gorski Kotar, it can be assumed that the parent substrate has significantly affected the condition of the soil adsorption complex. The geological substrate in the area of Sungerski Lug is made up of proluvial-coluvial sediments that are in contact with the limestone dolomite substrate, which is responsible for the specific pedogenesis of these soils. More detailed pedological research in the area of Sungerski Lug should definitely be undertaken.



Table 2<sup>1</sup> Measures of central tendency and variability of the investigated pedological variables for the surface mineral soil horizons per studied localities.

Tablica 2. Mjere centralne tendencije i varijabilneta istraživanih pedoloških varijabli za površinske mineralne horizonte tala po istraživanim lokalitetima.

Variable Varijabla	Units Mjerne jedinice	Papuk - PAP			Macej - MAC			Medvednica - MED			Vrbovsko - VRB			Belešine - BEL			Sungerski lug - SL			Delnice - DEL			Fužine - FUŽ			Lokve - LOK			Cini lug - CL			Tisec - TRŠ			Test	F(H)	p	
		N	Mean	St. dev.	N	Mean	St. dev.	N	Mean	St. dev.	N	Mean	St. dev.	N	Mean	St. dev.	N	Mean	St. dev.	N	Mean	St. dev.	N	Mean	St. dev.	N	Mean	St. dev.	N	Mean	St. dev.							
Inclination Nagib	°	10	24	8,80	4	35	5,25	6	20	3,63	10	17	8,13	10	11	6,45	3	2	2,00	9	13	12,07	10	11	8,34	2	15	6,36	8	18,1	6,06	10	14	12,65	ANOVA	4,5318	0,0001	
Thickness Debljina	cm	10	7	3,01	4	8	1,63	6	10	1,51	10	6	5,15	10	6	4,06	3	5	1,53	9	3	1,00	10	4	3,00	2	6	0,71	8	6	3,42	10	9	5,57	K-W	29,6921	0,0010	
Particle size distribution Tekstura	2,0 - 0,2 mm	mas. %	10	29,0	10,22	4	16,3	12,42	6	19,4	9,07	10	7,6	7,42	10	18,4	9,98	3	21,7	18,85	9	16,3	11,22	10	22,2	18,32	2	13,4	10,39	8	17,0	17,32	10	18,9	14,75	ANOVA	1,5293	0,1470
	0,2 - 0,02 mm	mas. %	10	42,8	8,18	4	57,1	13,08	6	37,7	8,13	10	49,6	5,44	10	43,3	8,99	3	31,4	13,95	9	45,9	7,82	10	42,4	9,24	2	51,6	3,96	8	40,3	11,50	10	44,6	10,62	ANOVA	2,379	0,0171
	0,02 - 0,002 mm	mas. %	10	19,4	6,11	4	16,1	1,27	6	28,3	4,66	10	26,8	5,53	10	25,9	7,25	3	35,1	5,94	9	23,3	6,65	10	23,0	6,34	2	23,8	4,88	8	28,1	6,36	10	22,0	8,23	ANOVA	3,0262	0,0030
	<0,002 mm	mas. %	10	8,8	1,87	4	10,4	1,83	6	14,6	2,29	10	16,1	4,44	10	12,4	4,69	3	11,8	4,42	9	14,5	5,94	10	12,4	4,23	2	11,2	1,56	8	14,7	5,99	10	14,5	6,17	K-W	16,9492	0,0755
pH H <sub>2</sub> O	-	10	4,44	0,27	4	4,02	0,45	6	4,31	0,15	10	4,10	0,28	10	3,95	0,20	3	4,12	0,14	9	4,07	0,26	10	4,09	0,26	2	4,01	0,05	8	3,96	0,16	10	4,18	0,18	ANOVA	3,25	0,0017	
pH CaCl <sub>2</sub>	-	10	3,86	0,24	4	3,41	0,36	6	3,74	0,14	10	3,58	0,29	10	3,32	0,11	3	3,40	0,08	9	3,46	0,24	10	3,45	0,21	2	3,33	0,02	8	3,28	0,16	10	3,52	0,14	K-W	36,9121	0,0001	
Org C	g kg <sup>-1</sup>	10	56,4	19,16	4	106,0	55,20	6	106,3	24,98	10	54,1	43,12	10	67,4	63,07	3	30,9	23,79	9	100,9	71,70	10	89,6	63,78	2	66,2	42,51	8	106,7	64,91	10	60,7	40,35	K-W	19,892	0,0303	
N tot.	g kg <sup>-1</sup>	10	3,7	0,92	4	8,0	2,65	6	6,6	3,14	10	4,4	2,41	10	3,8	3,99	3	1,6	1,10	9	8,6	7,54	10	6,3	3,04	2	8,3	3,61	8	6,1	3,94	10	4,8	2,33	K-W	23,8874	0,0079	
C/N	-	10	15	2,18	4	13	3,75	6	19	9,10	10	12	2,65	10	18	8,39	3	22	11,25	9	13	3,81	10	13	4,93	2	8	1,77	8	18	3,46	10	12	5,07	K-W	23,024	0,0107	
Soil micronutrient complex Ažurnopisni kompleksi dia	Cu	cmol(+) kg <sup>-1</sup>	10	0,87	0,79	4	2,71	0,27	6	1,08	0,86	10	0,53	0,81	10	1,42	1,64	3	0,12	0,02	9	1,86	1,59	10	1,25	1,30	2	0,35	0,09	8	1,25	0,96	10	0,95	1,13	K-W	21,4283	0,0183
	Mg	cmol(+) kg <sup>-1</sup>	10	0,30	0,08	4	0,05	0,00	6	0,05	0,01	10	0,18	0,11	10	0,03	0,02	3	0,01	0,00	9	0,36	0,13	10	0,25	0,16	2	0,25	0,22	8	0,03	0,02	10	0,09	0,08	K-W	59,663	0,0000
	Na	cmol(+) kg <sup>-1</sup>	10	0,32	0,02	4	0,53	0,06	6	0,37	0,07	10	0,34	0,02	10	0,48	0,13	3	0,48	0,04	9	0,36	0,08	10	0,30	0,11	2	0,37	0,05	8	0,39	0,03	10	0,39	0,11	K-W	34,8863	0,0001
	K	cmol(+) kg <sup>-1</sup>	10	0,79	0,15	4	1,20	0,40	6	0,89	0,03	10	0,68	0,09	10	0,80	0,29	3	0,69	0,01	9	0,88	0,27	10	0,71	0,12	2	0,80	0,28	8	0,65	0,06	10	0,80	0,33	K-W	22,5715	0,0124
	Al	cmol(+) kg <sup>-1</sup>	10	4,19	1,91	4	4,39	2,19	6	4,29	1,23	10	11,68	4,85	10	10,89	3,25	3	4,65	2,14	9	10,86	6,07	10	9,37	5,31	2	11,13	2,58	8	10,76	5,54	10	12,76	7,05	K-W	38,8138	0,0000
	H	cmol(+) kg <sup>-1</sup>	10	1,05	0,60	4	2,48	1,41	6	1,77	0,29	10	2,80	1,09	10	3,63	0,72	3	2,00	0,61	9	2,86	1,00	10	2,63	1,32	2	3,78	0,18	8	3,67	1,70	10	2,84	1,32	K-W	33,5268	0,0002
	Fe	cmol(+) kg <sup>-1</sup>	10	0,10	0,09	4	0,29	0,24	6	0,13	0,06	10	0,23	0,19	10	0,56	0,31	3	0,36	0,18	9	0,38	0,23	10	0,36	0,23	2	0,73	0,40	8	0,33	0,13	10	0,31	0,22	K-W	29,9835	0,0009
	Mn	cmol(+) kg <sup>-1</sup>	10	0,11	0,07	4	0,07	0,04	6	0,31	0,11	10	0,08	0,04	10	0,06	0,02	3	0,04	0,01	9	0,06	0,02	10	0,09	0,13	2	0,04	0,01	8	0,11	0,13	10	0,07	0,02	K-W	25,6662	0,0042
	BCE	cmol(+) kg <sup>-1</sup>	10	2,29	0,79	4	4,49	0,62	6	2,39	0,86	10	1,73	0,90	10	2,73	2,00	3	1,29	0,06	9	3,46	1,91	10	3,52	1,48	2	1,77	0,46	8	2,32	1,03	10	2,24	1,41	K-W	18,6131	0,0455
	ACE	cmol(+) kg <sup>-1</sup>	10	5,44	2,50	4	7,23	3,55	6	6,50	1,42	10	14,78	5,59	10	15,13	3,63	3	7,05	2,74	9	14,17	7,05	10	12,43	6,25	2	15,67	3,15	8	14,87	7,14	10	15,97	8,27	K-W	37,6281	0,0000
	CEC	cmol(+) kg <sup>-1</sup>	10	7,72	2,32	4	11,72	4,09	6	8,89	2,13	10	16,51	5,18	10	17,86	4,10	3	8,35	2,78	9	17,63	6,11	10	14,96	6,00	2	17,44	3,61	8	17,19	7,40	10	18,20	8,22	K-W	34,8927	0,0001
	Base saturation	%	10	31,8	13,30	4	41,3	12,51	6	26,6	3,99	10	12,3	9,28	10	14,9	9,24	3	16,5	4,64	9	22,4	14,14	10	19,1	12,50	2	10,1	0,53	8	14,2	5,12	10	14,0	8,99	K-W	29,5675	0,0011

<sup>1</sup> BCE - basic cation exchange; ACE - acid cation exchange; CEC - cation exchange capacity

Table 3 Measures of central tendency and variability of the investigated pedological variables for the agric soil horizons per studied localities.  
Tablica 3. Mjere centraliteta i varijabilneta istraživanih pedoloških varijabli za argiloakumulativne horizonte tala po istraživanim lokalitetima.

Variable Varijabla	Units Mjerne jedinice	Papuk - PAP			Maocli - MAC			Medvednica - MED			Vrhovsko - VRB			Beleivne - BEL			Šumenski hr. - ŠL			Delnice - DEL			Fužine - FUZ			Lokve - LOK			Čma hr. - ČI			Tršće - TRŠ			Test	F(H)	p	
		N	Arit. sr.	St. dev.	N	Arit. sr.	St. dev.	N	Arit. sr.	St. dev.	N	Arit. sr.	St. dev.	N	Arit. sr.	St. dev.	N	Arit. sr.	St. dev.	N	Arit. sr.	St. dev.	N	Arit. sr.	St. dev.	N	Arit. sr.	St. dev.	N	Arit. sr.	St. dev.							
Inclination Nagib	°	10	24	8,80	4	35	5,25	6	20	3,63	10	17	8,13	10	11	6,45	3	2	2,00	9	13	12,07	10	11	8,34	2	15	6,36	8	18	6,06	10	14	12,65	A	4,5318	0,0001	
Thickness Debljina	cm	10	70	14,36	4	56	12,87	6	37	9,99	10	67	15,15	10	48	10,54	3	50	8,39	9	49	16,20	10	58	6,62	2	30	4,95	8	44	13,79	10	62	13,46	A	5,583	0,0000	
Particle size distribution Zakazana	2,0 - 0,2 mm	mas. %	10	34,2	13,70	4	16,4	15,35	6	18,0	6,83	10	10,8	10,39	10	17,9	11,32	3	19,8	17,04	9	13,6	9,32	10	18,3	12,38	2	14,2	9,33	8	13,7	17,02	10	17,1	16,86	A	2,0785	0,0375
	0,2 - 0,02 mm	mas. %	10	31,2	6,72	4	55,6	17,67	6	24,6	6,79	10	40,8	4,54	10	35,3	6,75	3	31,0	17,57	9	32,6	4,43	10	33,9	5,53	2	44,8	1,27	8	30,7	7,25	10	36,7	6,18	K-W	32,3283	0,0004
	0,02 - 0,002 mm	mas. %	10	20,8	5,84	4	15,7	4,75	6	37,8	2,29	10	28,1	6,90	10	26,7	7,85	3	31,6	4,39	9	28,9	8,33	10	28,0	9,42	2	22,4	6,58	8	31,7	8,83	10	26,5	9,59	A	3,2565	0,0016
	<0,002 mm	mas. %	10	13,8	2,60	4	12,4	2,58	6	19,7	3,14	10	20,4	3,74	10	20,0	6,75	3	17,6	1,83	9	24,8	4,62	10	19,7	2,82	2	18,6	4,03	8	23,8	4,44	10	19,7	7,45	K-W	31,1664	0,0006
pH H <sub>2</sub> O	-	10	4,84	0,22	4	4,80	0,42	6	4,76	0,24	10	4,42	0,23	10	4,40	0,19	3	4,50	0,09	9	4,42	0,17	10	4,57	0,18	2	4,48	0,01	8	4,46	0,17	10	4,54	0,20	A	4,49	0,0001	
pH CaCl <sub>2</sub>	-	10	4,18	0,12	4	4,19	0,18	6	4,13	0,12	10	4,07	0,12	10	3,82	0,12	3	3,98	0,13	9	4,00	0,12	10	4,09	0,19	2	3,99	0,04	8	3,88	0,15	10	3,97	0,13	A	5,83	0,0000	
Org C	g kg <sup>-1</sup>	10	12,8	5,17	4	13,8	8,66	6	32,6	16,24	10	20,1	5,83	10	23,1	13,09	3	18,0	5,71	9	32,1	14,89	10	37,5	10,13	2	30,6	5,65	8	29,7	13,14	10	27,1	8,35	A	4,3156	0,0001	
N tot.	g kg <sup>-1</sup>	10	1,5	0,25	4	3,4	2,08	6	2,3	0,87	10	2,0	0,42	10	1,5	0,76	3	1,3	0,51	9	2,8	0,75	10	3,7	0,82	2	3,1	2,47	8	1,8	0,45	10	2,9	0,45	K-W	45,7638	0,0000	
C/N	-	10	8	2,48	4	4	1,09	6	15	6,71	10	10	2,65	10	16	7,44	3	14	5,64	9	11	3,55	10	11	4,68	2	16	14,85	8	19	11,41	10	10	2,60	K-W	26,842	0,0028	
Soil adsorption complex Adsorpcijski kompleks/tla	Ca	cmol(+) kg <sup>-1</sup>	10	0,40	0,33	4	0,59	0,31	6	0,32	0,32	10	0,23	0,29	10	0,53	0,30	3	1,09	0,97	9	0,34	0,43	10	0,38	0,23	2	0,41	0,28	8	0,27	0,33	10	0,42	0,25	A	1,8543	0,0655
	Mg	cmol(+) kg <sup>-1</sup>	10	0,18	0,10	4	0,02	0,02	6	0,01	0,01	10	0,11	0,12	10	0,02	0,01	3	0,01	0,06	9	0,12	0,04	10	0,08	0,02	2	0,19	0,05	8	0,01	0,00	10	0,07	0,08	K-W	60,8735	0,0000
	Na	cmol(+) kg <sup>-1</sup>	10	0,32	0,02	4	0,48	0,04	6	0,36	0,05	10	0,33	0,03	10	0,45	0,14	3	0,02	0,04	9	0,32	0,02	10	0,33	0,02	2	0,33	0,05	8	0,38	0,02	10	0,37	0,09	K-W	39,3043	0,0000
	K	cmol(+) kg <sup>-1</sup>	10	0,84	0,16	4	0,76	0,12	6	0,58	0,07	10	0,57	0,04	10	0,72	0,10	3	0,60	0,01	9	0,64	0,14	10	0,62	0,08	2	0,57	0,06	8	0,58	0,02	10	0,75	0,30	K-W	35,6373	0,0001
	Al	cmol(+) kg <sup>-1</sup>	10	3,00	0,96	4	2,63	0,91	6	3,78	1,18	10	6,89	2,61	10	9,21	2,74	3	3,95	0,54	9	9,14	2,19	10	7,33	2,79	2	9,63	0,74	8	8,08	3,44	10	8,65	3,18	K-W	46,8277	0,0000
	H	cmol(+) kg <sup>-1</sup>	10	0,34	0,24	4	0,59	0,23	6	0,85	0,35	10	0,96	0,39	10	1,59	0,46	3	0,91	0,35	9	0,90	0,69	10	0,93	0,63	2	1,75	0,35	8	1,35	0,75	10	1,36	0,44	A	4,8426	0,0000
	Fe	cmol(+) kg <sup>-1</sup>	10	0,06	0,02	4	0,31	0,30	6	0,08	0,04	10	0,08	0,04	10	0,27	0,19	3	0,15	0,06	9	0,13	0,02	10	0,12	0,07	2	0,24	0,05	8	0,18	0,21	10	0,21	0,15	K-W	35,3451	0,0001
	Mn	cmol(+) kg <sup>-1</sup>	10	0,05	0,01	4	0,05	0,01	6	0,11	0,08	10	0,06	0,01	10	0,08	0,08	3	0,05	0,01	9	0,06	0,02	10	0,05	0,01	2	0,03	0,02	8	0,06	0,01	10	0,05	0,02	K-W	14,558	0,1490
	BCE	cmol(+) kg <sup>-1</sup>	10	1,73	0,38	4	1,84	0,29	6	1,28	0,38	10	1,24	0,45	10	1,72	0,40	3	2,12	0,97	9	1,42	0,45	10	1,41	0,28	2	1,49	0,44	8	1,23	0,31	10	1,61	0,39	A	2,6352	0,0087
	ACE	cmol(+) kg <sup>-1</sup>	10	3,44	0,98	4	3,58	1,26	6	4,81	1,43	10	7,99	2,89	10	11,14	3,04	3	5,05	0,93	9	10,24	2,38	10	8,43	3,37	2	11,64	0,32	8	9,66	4,34	10	10,27	3,60	K-W	47,0231	0,0000
CEC	cmol(+) kg <sup>-1</sup>	10	5,18	1,03	4	5,42	1,54	6	6,09	1,41	10	9,22	2,71	10	12,85	3,07	3	7,17	0,97	9	11,66	2,57	10	9,84	3,38	2	13,14	0,75	8	10,89	4,37	10	11,87	3,67	K-W	46,2373	0,0000	
Base saturation	%	10	34,2	7,91	4	35,4	6,66	6	21,9	7,28	10	14,9	8,52	10	13,9	4,16	3	29,3	11,55	9	12,5	3,20	10	15,9	6,07	2	11,3	2,70	8	12,4	4,39	10	14,9	6,84	A	12,4046	0,0000	

Further discussion dealing with the adsorption complex structure is based on the classification provided by the Forest Soil Coordinating Centre (Vanmechelen et al. 1997) because this classification is the result of the latest research in forest ecosystem soils. All the data, as well as the classification of the adsorption complex of European forest soils are based on the soil samples from central and northern Europe. Some caution should be taken here since there are no data for southern and southeastern Europe.

The average content of basic cation exchange (BCE) ranges from the minimal 1.3  $\text{cmol}(+) \text{kg}^{-1}$  in Sungerski Lug to the maximal 4.5  $\text{cmol}(+) \text{kg}^{-1}$  on Macelj for the surface mineral horizon, and from 1.2  $\text{cmol}(+) \text{kg}^{-1}$  in Crni Lug to 2.1  $\text{cmol}(+) \text{kg}^{-1}$  in Sungerski Lug for the argillic-accumulative horizon (Figure 3).

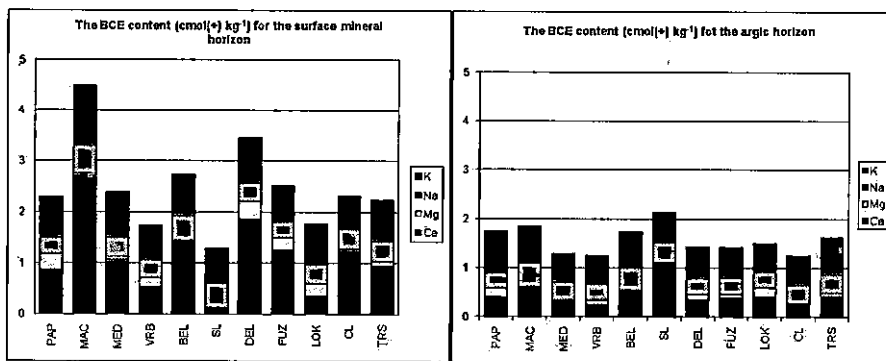


Figure 3 The BCE content for the surface mineral and argillic horizon per localities

Slika 3. Sadržaj IBK u površinskom mineralnom i kambičnom horizontu po lokalitetima

As a comparison, a date was given of the BCE content reaching as much as 100  $\text{cmol}(+) \text{kg}^{-1}$  in clayey soils with a high participation of smectite clay, but in general (in about 90% of the plots) it amounts to less than 20  $\text{cmol}(+) \text{kg}^{-1}$  for the argillic horizon and 25  $\text{cmol}(+) \text{kg}^{-1}$  for the surface mineral horizon. The majority of forest soils are acid. As a result, acid cations prevail in the adsorption complex, so the basic cation exchange content is often very low; for over 50% of the forest soils it amounts to less than 1  $\text{cmol}(+) \text{kg}^{-1}$  in the argillic- horizon (Vanmechelen et al. 1997).

The most common basic cation exchange in the surface mineral horizon of the investigated soils in most of the localities is  $\text{Ca}^{2+}$ , followed by  $\text{K}^+$ , then  $\text{Na}^+$  and finally  $\text{Mg}^{2+}$ , while the argillic horizon is dominated by  $\text{K}^+$  ion in all the localities except in Sungerski Lug. A relatively high participation of  $\text{K}^+$  may be explained by the composition of the parent substrate (the sandstone detritus contains relatively large quantities of muscovite, feldspat, particularly orthoclase and mica).

In terms of basic cation exchange, in all the investigated localities the smallest amount of  $\text{Mg}^{2+}$  was contained in the soil adsorption complex.

Ulrich (1995) states that magnesium deficiency has in the past several decades become a widely recognized phenomenon in acid forest soils exposed to acid deposition, because exchangeable  $\text{Mg}^{2+}$  are leached.

Komlenović and Cestar (1983) also point to inadequate nutrition of spruce with magnesium and to lowered magnesium concentrations in fir needles, measured in the period of 15 years in similar sites.

The average content of acid cation exchange (ACE) ranges from the minimal 5.4 cmol(+) kg<sup>-1</sup> on Papuk to the maximal 16.0 cmol(+) kg<sup>-1</sup> in Tršće for the surface mineral horizon, and from 3.4 cmol(+) kg<sup>-1</sup> on Papuk to 11.6 cmol(+) kg<sup>-1</sup> in Lokve for the argic (Fig. 3). The results for Lokve should be taken with precaution because only two pedological profiles were opened for sampling.

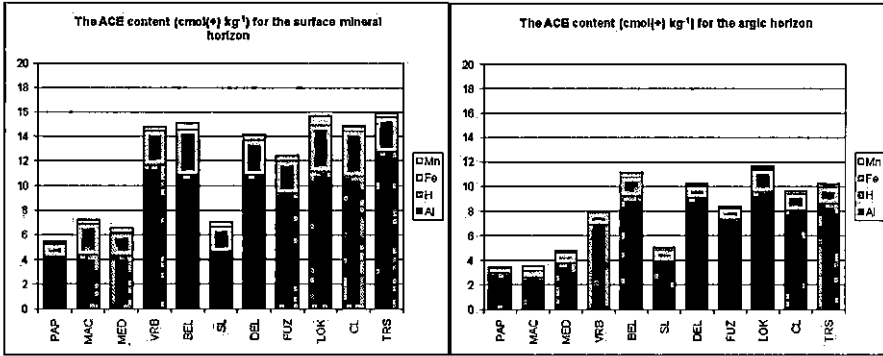


Figure 4 The ACE content for the surface mineral and argic horizon per localities.  
Slika 4 Sadržaj IKK u površinskom mineralnom i kambičnom horizontu po lokalitetima.

The ACE values in the surface mineral horizon obtained by research were higher than those listed for the majority of European forest soils in all the localities. They range from 0.5 to 5 cmol(+) kg<sup>-1</sup> of the soil. However, these values may even exceed 50 cmol(+) kg<sup>-1</sup> of the soil (Vanmechelen et al. 1997).

The average values of the adsorption complex saturation with bases are range from the minimal 10% in Lokve to the maximal 39% on Macelj for the surface mineral horizon, and from 11% in Lokve to 38% on Macelj for the argic horizon.

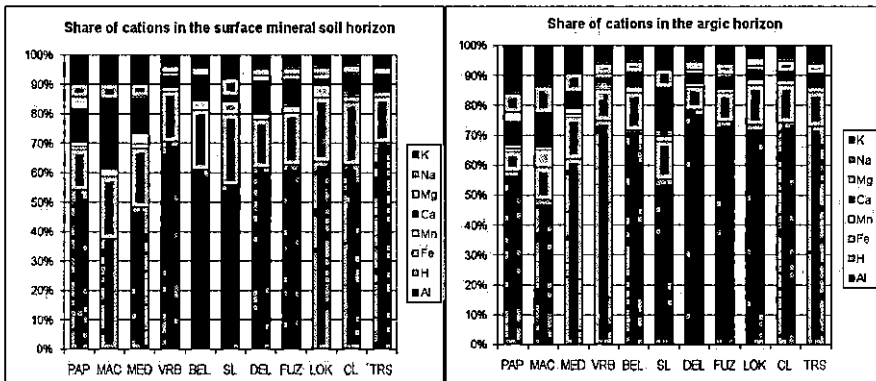


Figure 5 Share of cations in the adsorption complex of the surface mineral and argile soil horizons per localities.  
Slika 5. Udio kationa u adsorpcijskom kompleksu površinskog mineralnog i kambičnog horizonta tla po lokalitetima.

Generally speaking, all the soils in the investigated localities have a high to very high acid cation content, especially  $\text{Al}^{3+}$  and  $\text{H}^+$ , and a medium to low basic cation content, as well as medium to low adsorption complex saturation with basic cations. The cation exchange capacity (CEC) is medium to high.

Based on the obtained results, the sensitivity of the investigated soils to acidification may be estimated as medium to high (Vanmechelen et al. 1997). The soils of fir and beech-fir forests in Pannonian Croatia show less sensitivity to acidification than those in Gorski Kotar. Of all the localities in Pannonian Croatia, Medvednica has the least favourable acid and basic cation ratio percentage, and the lowest adsorption complex saturation with bases.

The  $\text{Mn}^{2+}$  content is interesting in that the surface mineral horizon on Medvednica differs significantly from all the other localities, while the argillic-accumulative horizon shows no differences. This unexpected phenomenon requires further study.

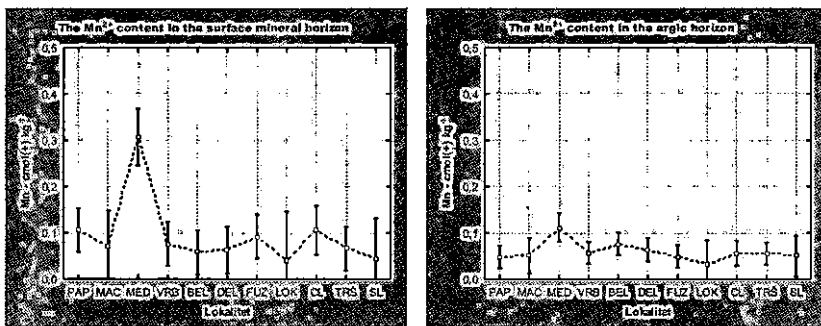


Figure 6 The  $\text{Mn}^{2+}$  content in the adsorption soil complex in the surface mineral horizon and in the argic horizon of the investigated localities.

Slika 6 Sadržaj  $\text{Mn}^{2+}$  u adsorpcijskom kompleksu tla u površinskom mineralnom i kambičnom horizontu tla istraživanih lokaliteta.

Ulrich (1991) states that the increased  $\text{Mn}^{2+}$  content in CEC and in plant organs indicates the initial stage of acidification.

This coincides with research by Komlenović (1989), who claims that the highest forest damage was recorded in the area of Zagreb and Gorski Kotar, and with research by Medvedović et al. (1998), who point to increased input of deposition substances in the forest ecosystem of beech and fir on Medvednica.

Sungerski Lug is an exception, since in terms of the adsorption complex structure it shares similar characteristics with the soils in Pannonian Croatia. However, in terms of climatic and vegetational features it belongs to Gorski Kotar.

For the other localities in Gorski Kotar there are generally no significant differences in the basic and acid exchange cation content and in the adsorption complex saturation with bases. All these localities are consequently equally sensitive or highly sensitive to acidification. With reference to the least favourable BCE and ACE ratio, as well as the pH reaction and base saturation, I would single out the localities of Crni Lug, Belevine, Lokve and Tršće. Interestingly, Belevine, Crni Lug and Tršće have a significantly lower  $\text{Mg}^{2+}$  content in comparison with the other localities in Gorski Kotar.

A very high  $\text{Al}^{3+}$  and  $\text{H}^+$  ion content in all the localities of Gorski Kotar, as well as a high  $\text{Al}^{3+}$  and  $\text{H}^+$  content in Pannonian Croatia arouse considerable concern. This attitude is based

on the results of research that deal with the antagonistic action of Al compounds on the  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  reception, the toxic effect on the bacteria and plant roots, and the inhibitory action on root growth, which leads to increased vulnerability to drought (Foy 1984, Kauppi et al. 1986, Asp et al. 1988, Bengtsson et al. 1988, Kreuzer 1989, Godbold et al. 1991, Boudot et al. 1994, Vanmechelen et al. 1997).

Phosphorus deficiency in acid soils is related to the formation of Fe and Al phosphates, which are insoluble and inaccessible for most plants. Therefore, we may talk of the inhibitory action of Al on P reception (Foy 1984). Additionally, research by Jung (1984) showed that an increase in aluminium content decreases potassium reception.

It ensues from the above that the inhibitory action of aluminium on root growth, which reduces the area with which the young plant receives nutrients and water from the soil, as well as the antagonistic effect on  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{H}_2\text{PO}_4^-$ , and on  $\text{HPO}_4^{2-}$  reception, may affect fir regeneration. This should be verified with further research.

Since fir in Croatia occurs on the southern boundary of its distribution range, adverse climatic changes in the sense of reduced precipitation and increased temperatures and the occurrence of droughts in the vegetation period, coupled with increased aluminium-induced vulnerability to drought, lead to a gradual decrease in vitality and eventually, in combination with other unfavourable abiotic and biotic ecological factors, to tree dieback. Generally, increased temperatures are followed by increased plant sensitivity to pollutants (Guderian 1967, Rist and Davis 1979). Intensive fir dieback in the locality of Fužine, or more precisely MU Brloško, has been the subject of several investigations (Šafar 1969, Komlenović et al. 1991, Matić et al. 1998).

### **Properties of the adsorption complex and other pedological parameters of dystric cambisol in relation to phytocoenoses**

#### *Značajke adsorpcijskog kompleksa i ostalih pedoloških parametara distričnog kambisola prema fitocenozama*

A comparison of differences between the arithmetic means in the two studied phytocoenoses: the Pannonian beech-fir forests (*Abieti-Fagetum "pannonicum"* Rauš 1969) and the fir forest with hard fern (*Blechno-Abietetum* Ht. 1950) that occur on the same soil type – dystric cambisol, but in different ecological conditions, has shown significant differences in the soil texture, soil reaction, Org C and N tot content, as well as in acid cation exchange (ACE) content, cation exchange capacity (CEC) and the adsorption complex saturation with basic cations (Tables 5 and 6). Judging by the soil texture, dystric cambisol in the fir forest with hard fern has a heavier texture with a significantly higher participation of clayey fraction. The soil reaction manifested lower pH values, or higher acidity in the community *Blechno-Abietetum*, which coincides with the acidophilic character of this community. Higher acidity is related to a higher acid cation exchange content. *Blechno-Abietetum* has a significantly higher  $\text{Al}^{3+}$ ,  $\text{H}^+$  and  $\text{Fe}^{2+}$  content in the A horizon, while *Abieti-Fagetum* has a higher  $\text{Mn}^{2+}$  content, which can be related to the initial stage of the acidification process (Ulrich 1991). In the (B)v horizon, *Blechno-Abietetum* has a higher  $\text{Al}^{3+}$ ,  $\text{H}^+$  ion content. *Abieti-Fagetum* has a more favourable condition of the adsorption complex saturation with bases than *Blechno-Abietetum*. This relation is significantly better in the (B)v horizon. In terms of the adsorption complex situation and the soil pH values, it can be said that *Blechno-Abietetum* is more susceptible to acidification effects. The CEC in *Blechno-Abietetum* is higher, which concurs to the significantly higher clayey fraction participation. The accumulation of Org. C and N tot in the A horizon is higher in *Blechno-Abietetum* at a similar C/N ratio.

Table 4 Test of differences in pedological parameters for the A horizon of the Pannonian beech-fir forest (*Abieti-Fagetum* "pannonicum" Rauš 1969) and the fir forest with hard fern (*Blechno-Abietetum* Ht. 1950)  
 Tablica 4. T-test za varijable A horizonta u Panonskoj bukovo-jelovoj šumi (*Abieti-Fagetum* "pannonicum" Rauš 1969) i jelovoj šumi s rebračom (*Blechno-Abietetum* Ht. 1950)

Varijabla	Abi.-Fag. arit. sred.	Ble.-Abi. arit. sred.	Abi.-Fag. std. dev.	Ble.-Abi. std. dev.	t	U	p
Nagib	23	19	8,950	9,725	1,38335	-	0,174045
Debljina	8	6	3,150	4,024	1,93137	-	0,060370
KP	23,4	10,7	10,399	7,807	4,50749	-	0,000054
SP	44,4	49,4	11,341	5,298	-	-1,75828	0,078700
P	21,7	25,8	7,166	5,338	-2,11641	-	0,040426
G	10,5	14,0	3,250	4,138	-2,89962	-	0,005979
pH H <sub>2</sub> O	4,40	4,08	0,285	0,363	2,89986	-	0,005975
pH CaCl <sub>2</sub>	3,80	3,52	0,230	0,369	2,61444	-	0,012446
C org	69,8	115,4	26,511	61,002	-	-2,29341	0,021825
N uk	4,8	8,0	1,854	4,721	-	-2,62468	0,008673
C/N	15	15	3,519	4,194	0,06121	-	0,951491
Ca	1,46	2,13	1,529	1,468	-1,40690	-	0,166992
Mg	0,18	0,25	0,139	0,188	-1,25089	-	0,218066
Na	0,37	0,37	0,076	0,138	-	-0,93011	0,352317
K	0,83	0,83	0,114	0,294	-	0,43320	0,664870
Al	3,81	9,18	1,264	4,562	-	-4,48490	0,000007
H	1,32	2,91	0,666	1,252	-	-3,94977	0,000078
Fe	0,11	0,38	0,092	0,301	-	-3,31271	0,000924
Mn	0,20	0,09	0,176	0,102	-	2,16600	0,030312
BCE	2,83	3,58	1,550	1,538	-1,52735	-	0,134354
ACE	5,44	12,56	1,805	5,493	-	-4,43393	0,000009
AcExc	5,13	12,09	1,768	5,378	-	-4,47215	0,000008
CEC	8,26	16,14	2,252	4,909	-	-4,58682	0,000005
Baze	34,21	25,45	13,968	17,570	1,66553	-	0,103432

Table 5 Test of differences in pedological parameters for the (B)v horizon of the Pannonian beech forest (*Abieti-Fagetum* "pannonicum" Rauš 1969) and the fir forest with hard fern (*Blechno-Abietetum* Ht. 1950)  
 Tablica 5. T-test za varijable (B)v horizonta u Panonskoj bukovo-jelovoj šumi (*Abieti-Fagetum* "pannonicum" Rauš 1969) i jelovoj šumi s rebračom (*Blechno-Abietetum* Ht. 1950)

Varijabla	Abi.-Fag. arit. sred.	Ble.-Abi. arit. sred.	Abi.-Fag. std. dev.	Ble.-Abi. std. dev.	t	U	P
KP	24,8	11,5	12,9250	9,1921	3,90088	-	0,000349
SP	33,4	36,2	14,8414	5,8189	-	-1,83473	0,066547
P	25,7	30,0	9,8922	7,0818	-1,66394	-	0,103750
G	16,2	22,2	5,6499	5,0400	-3,58608	-	0,000885
pH H <sub>2</sub> O	5,00	4,60	0,5913	0,5079	2,32179	-	0,025291
pH CaCl <sub>2</sub>	4,32	4,11	0,5562	0,4623	1,33145	-	0,190396
C org	16,0	27,4	10,2922	12,6824	-3,00760	-	0,004484
N uk	1,8	2,4	0,7092	1,2375	-	-1,37605	0,168808
C/N	9	13	4,6927	8,2313	-	-2,26793	0,023334
Ca	1,01	0,52	2,2985	0,6107	-	0,50965	0,610299
Mg	0,11	0,10	0,1092	0,1213	0,19318	-	0,847772
Na	0,36	0,36	0,0580	0,0637	-0,28494	-	0,777122
K	0,74	0,65	0,1608	0,1973	1,61707	-	0,113534
Al	2,83	7,45	1,2666	2,9872	-	-4,53586	0,000006
H	0,44	1,05	0,3122	0,5335	-	-3,45286	0,000555
Fe	0,08	0,13	0,0502	0,1266	-	-1,98762	0,046854
Mn	0,11	0,05	0,1463	0,0159	-	0,54787	0,583781
BCE	2,22	1,63	2,2792	0,7289	-	1,29960	0,193739
ACE	3,46	8,69	1,3375	3,4791	-	-4,51038	0,000006
AcExc	3,27	8,50	1,4136	3,4206	-	-4,54860	0,000005
CEC	5,68	10,31	1,8670	3,3546	-	-4,25555	0,000021
Baze	36,10	18,43	18,0929	16,0263	3,29483	-	0,002036

## CONCLUSIONS ZAKLJUČCI

A total of 82 profiles were opened in 11 localities for the research. Three soil types were encompassed: dystric cambisol, brunipodzol and podzol. The cation content of the soil adsorption complex is an excellent indicator of dominant pedogenetic processes, nutrient reserves and buffer potential, but unfortunately there are no data for other sites and plant communities in Croatia to be compared with the obtained results. There are no previous measurements in the studied localities, so no conclusions can be made on any changes in the adsorption complex content and other soil parameters in a given time period.

The following conclusions can be drawn on the basis of the obtained results:

The adsorption complex content is a good indicator of variable site conditions. Cluster analysis resulted in two groups that correspond to the geographic position: Pannonian Croatia and Gorski Kotar, with the exception of Sungerski Lug. Further research should show whether the basic reason for this is the parent substrate.

The percentage ratio of basic cation exchange and acid cation exchange for the soils in the studied localities is similar for the surface mineral and argic horizon, while as a rule, absolute values are higher in the surface mineral horizon.

In general, all the soils in the investigated localities have a high to very high acid cation content, especially of  $Al^{3+}$  and  $H^+$ , and a medium to low basic cation content, as well as medium to low adsorption complex saturation with basic cations. The cation exchange capacity (CEC) is medium to high. Based on the obtained data, the sensitivity of the studied localities to acidification can be graded as medium to high. The soils of beech and beech-fir forests in Pannonian Croatia manifest lower sensitivity to acidification than those in Gorski Kotar. Of the localities in Pannonian Croatia, Medvednica has the most unfavourable percentage ratio of acid and basic cations, and the lowest adsorption complex saturation with bases, while in Gorski Kotar this refers to Belevine, Crni Lug and Tršće.

In comparison with all the other localities, that of Medvednica has a significantly higher exchangeable  $Mn^{2+}$  content in the adsorption complex of the surface mineral horizon. The reasons should be further investigated.

In terms of basic cation exchange, the lowest  $Mn^{2+}$  content was recorded in the adsorption complex in all the localities under study. The localities with the highest  $Al^{3+}$  ion content and the least favourable adsorption complex content, which include Belevine, Crni Lug and Tršće, also have a significantly lower  $Mn^{2+}$  content of all the other localities. The negative effects of Mg deficiency are expected to occur in these localities first.

A very high  $Al^{3+}$  and  $H^+$  ion content in all the localities of Gorski Kotar, as well as very high  $Al^{3+}$  and  $H^+$  in Pannonian Croatia arouse concern. This is based on literature findings on the toxic effects of  $Al^{3+}$  and  $H^+$ , as well as on their antagonistic effect on calcium, magnesium and phosphorus reception.

The Pannonian beech-fir forest (*Abieti-Fagetum "pannonicum"* Rauš 1969) and the fir forest with hard fern (*Blechno-Abietetum* Ht. 1950) that occur in the same soil type – dystric cambisol, but in different ecological conditions, have manifested considerable differences in soil texture, soil reaction, the Org. C and N tot content, as well as in the acid cation exchange (ACE) content, the cation exchange capacity (CEC) and the adsorption complex saturation with basic cations. The results for the adsorption complex indicate that the fir forest with hard fern is more sensitive to acidification than the Pannonian beech-fir forest.



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