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## Soil acidity and mobile aluminum status in pseudogley soils in the Čačak–Kraljevo Basin

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**Abstract:** Soil acidity and aluminum toxicity are considered the most damaging soil conditions affecting the growth of most crops. This paper reviews the results of tests of pH, exchangeable acidity and the mobile aluminum (Al) concentration in profiles of pseudogley soils from the Čačak–Kraljevo Basin. For these purposes, 102 soil pits were dug in 2009 in several sites around the Čačak–Kraljevo Basin. The tests encompassed 54 field, 28 meadow, and 20 forest soil samples. Samples of soil in a disturbed state were taken from the Ah and Eg horizons (102 samples), from the B<sub>1</sub>tg horizon in 39 field, 24 meadow and 15 forest pits (a total of 78 samples) and from the B<sub>2</sub>tg horizon in 14 field, 11 meadow, and 4 forest pits (a total of 29 samples). The mean pH values (1 M KCl) of the tested soil profiles were 4.28, 3.90 and 3.80 for the Ah, Eg and B<sub>1</sub>tg horizons, respectively. The soil pH of the forest samples was lower than those in the meadow and arable land samples (mean values of 4.06, 3.97 and 3.85 for arable land, meadow and forest samples, respectively). The soil acidification was especially intensive in the deep horizons; thus, 27 (Ah), 77 (Eg) and 87 % (B<sub>1</sub>tg) of the soil samples had a pH value below 4.0. The mean values of the total exchangeable acidity (TEA) were 1.55, 2.33 and 3.40 meq (100 g)<sup>-1</sup> for the Ah, Eg and B<sub>1</sub>tg horizons, respectively. The TEA values in the forest soils were considerably higher (3.39 meq (100 g)<sup>-1</sup>) than those in the arable and meadow soils (1.96 and 1.93 meq (100 g)<sup>-1</sup>, respectively). The mean mobile Al contents of the tested soil samples were 11.02, 19.58 and 28.33 mg Al (100 g)<sup>-1</sup> for the Ah, Eg and B<sub>1</sub>tg horizons, respectively. According to the pH and TEA values, mobile Al was considerably higher in the forest soils (a mean value of 26.08 mg Al (100 g)<sup>-1</sup>) than in the arable and meadow soils (mean values of 16.85 and 16.00 mg Al (100 g)<sup>-1</sup>, respectively). The Eg and B<sub>1</sub>tg horizons of the forest soil had

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especially high mobile Al contents (mean values of 28.50 and 32.95 mg Al (100 g)<sup>-1</sup>, respectively). High levels of mobile Al were especially frequent in the forest soils, with 35 (Ah), 85.0 (Eg) and 93.3 % (B<sub>1</sub>tg) of the tested samples ranging above 10 mg Al (100 g)<sup>-1</sup>.

*Keywords:* soil; acidity; aluminum; pseudogley.

## INTRODUCTION

Soil acidity limits crop production on 30–40 % of the world's arable land and up to 60 % of the world's potentially arable land. There are several estimates of the extent of acid soils in the world. Van Wambeke<sup>1</sup> reported acid soils covering 1,455 million ha, or about 11 % of the total global land surface, while Von Uexkull and Mutert<sup>2</sup> estimated that acid soils (defined as soils with pH < 5.5 in the top layer) covered 3,950 million ha, or around 30 % of global arable land, with a growing trend. These results are in agreement with those of Eswaran *et al.*<sup>3</sup>, who estimated that globally around 26 % of the total ice-free land is constrained for crop production by soil acidity. Acid soils occur mainly in two global belts: the northern belt, with a cold, humid temperate climate, and the southern tropical belt, with warm and humid conditions.<sup>2</sup>

In Serbia, acid soils are widespread, accounting for over 60 % of the total arable land. These are mostly lowland or hillside types of pseudogley or their leached variants, acid vertisols, podzolic eutric cambisols, diluvial, brown or leached brown soils of mountainous regions, which are rather poor in bases, medium to heavily acid, with very poor texture and low organic content. These soils are more or less ill suited for the cultivation of most cereal crops.<sup>4,5</sup> Most acid soils are located in Central Serbia and in Kosovo and Metohija. With the exception of soils in major river valleys (formed on alluvial deposits) and soils formed on calcareous, marine and lake sediments and limestones, nearly all regions of Central Serbia have soils that are acid to some degree.<sup>6</sup>

The acidity of these soils, their high contents of H<sup>+</sup> and low contents of essential plant nutrients, primarily P and Ca, are limiting factors for high and stable yields of cultivated cereal crops. Apart from acidity, these soils are also often characterized by high contents of toxic forms of Al, Fe and Mn, and by deficits caused by leaching or decreased availability of P, Ca, Mg and some other micro-nutrients, especially Mo, Zn and B.<sup>6–8</sup>

Aluminum (Al) toxicity is the primary factor that limits crop production on strongly acidic soils. At soil pH values at or below 5, toxic forms of Al dissolve into the soil solution, inhibiting root growth and function and thus reducing crop yield. Mineral soils contain large amounts of Al, most of which is locked in aluminosilicates or Al oxides of the clay fraction and does not pose a toxicity hazard. Upon soil acidification, a fraction of this Al becomes soluble and potentially toxic to plants. Thus, acidic mineral soils are practically synonymous with

Al toxicity. Intensification of the process of solubilization of Al compounds is connected with the degree of soil acidification caused by the washing out of alkaline metals ions ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ ) from the soil and a decrease in the pH of the soil solutions. The determination of the content of available Al (exchangeable and in the soil solution) is essential for an evaluation of the risk of plant production on acid soils, in which it can occur in concentrations toxic for plants and microorganisms.<sup>9</sup>

The objective of this study was to test the pH value, exchangeable acidity and mobile aluminum (Al) status in the profiles of pseudogley soils of the Čačak–Kraljevo Basin.

## EXPERIMENTAL

### *General characteristics of the Čačak–Kraljevo Basin*

Čačak–Kraljevo Basin is located in western Serbia. It is a narrow belt approximately 70 km long in the NW–SE direction and 5 to 18 km wide. The Kablar, Ovčar, Troglav, Stolovi, Goč, Suvobor, Vujno and Kotlenik Mountains border the basin in the SW and NE directions. The pseudogley soils of this area (approximately 32,000 hectares situated mainly between 180 and 200 m above sea level) were formed on the diluvial–Holocene terrace of the Western Morava River and its tributaries. The low productivity of these soils is, to a smaller or a greater extent, the result of unfavorable physical and chemical properties over all the observed parameters of these properties, starting from physiological depth, over texture, structure, porosity to the air and water regime, *i.e.*, from the amount of easily mobile Al ions and exchangeable adsorbed base cations to the degree of base and H-ions saturation. It is characterized with a basic profile structure of the A–Eg–Btg type, and with conditions that create a transition horizon Eg/Btg, buried beneath the Btg (fossil) humus horizon of meadow soil.<sup>10</sup> Based on the development of the physical and chemical properties in the pseudogley, eluvial (Ah, Ahp and Eg) and alluvial (Btg) horizons could be distinguished. In addition, there are significant differences between the varieties of forest, meadow and field pseudogley, especially in the humus horizon.

### *Sampling and chemical analysis*

A total of 102 soil pits were dug in 2009 at several locations around the Čačak–Kraljevo Basin. The tests encompassed 54 field, 28 meadow, and 20 forest soil profiles. Samples of soil in the disturbed state were taken from the humus and Eg horizons (102 samples), from the B<sub>1</sub>tg horizon in 39 field, 24 meadow and 15 forest soil profiles (a total of 78 samples) and from the B<sub>2</sub>tg horizon in 14 field, 11 meadow, and 4 forest soil profiles (a total of 29 samples). In the laboratory, the exchangeable acidity was determined in a 1 M KCl soil solution (pH 6.0) using a potentiometer with a glass electrode, as well as by the Sokolov Method, in which the content of Al ions in the extract is determined in addition to the total exchangeable acidity ( $\text{H}^+ + \text{Al}^{3+}$ ). Exchangeable Al ( $\text{Al}_{\text{KCl}}$ ) and exchangeable acidity ( $\text{meq (100 g}^{-1}\text{)}$ ) were determined by extraction with 1 M KCl (1:2.5), shaken for 1 h and titration (the Sokolov Method).<sup>11</sup> For the evaluation of the  $\text{Al}^{3+}$  in the extracts of 1 mol L<sup>-1</sup> KCl solution, 1:10 (v/v) soil/solution ratio, the following procedures were used: titrimetric method (standard method). Primarily, the exchangeable acidity ( $\text{Al}^{3+} + \text{H}^+_{\text{tit}}$ ) was determined by titrations of 25 mL KCl extract with 0.025 mol L<sup>-1</sup> NaOH, using 1.0 g L<sup>-1</sup> phenolphthalein as an indicator (titration from colorless to pink). Then, the concentration of mobile  $\text{Al}^{3+}$  was obtained by back-titration

of the same KCl extract, previously used, after the acidification with a drop of HCl and addition of 40 g L<sup>-1</sup> NaF, with 0.025 mol L<sup>-1</sup> HCl (titration from pink to colorless).<sup>11</sup>

#### RESULTS AND DISCUSSION

Aluminum (Al) toxicity is considered as the main growth- and yield-limiting factor on soils with pH below 5.0.<sup>12</sup> Soil acidity is a serious agricultural problem in many parts of the world, affecting as much as 40 % of the world's arable land.<sup>13</sup>

Al toxicity is affected by many factors, such as pH, concentration of Al, temperature, and concentrations of cations and anions in the culture solution. The critical soil pH at which sufficient Al becomes soluble to be toxic is difficult to predict because it depends on many other factors, including clay mineralogy, organic matter, other cations and anions and total salts.<sup>14,15</sup> In general, Al starts to dissolve when the pH<sub>Ca</sub> is lower than 5.5, while below 4.5, there is a marked increase in the extractable Al. The content of soluble Al ions in soils ranges from 1–33 ppm, but seldom exceeds 4 ppm. Increased concentrations of aluminum (for many plant species as low as 1–2 ppm) inhibit root cell division and elongation, resulting in poor root development, reduction of water and nutrient uptake, drought susceptibility, and subsequently in a significant decrease in yield.<sup>16,17</sup> Al interferes with the uptake, transport and utilization of essential nutrients, including Ca, Mg, K, P, Cu, Fe, Mn and Zn.<sup>18,19</sup>

The results of this study showed that the content of exchangeable Al in pseudogleys is highly variable, depending on the locality and profile depth. Its dynamics depends mostly on the soil pH (active, exchangeable or hydrolytic acidity). The mean pH (1 mol L<sup>-1</sup> KCl) of the tested soil profiles were 4.28, 3.90 and 3.80, for Ah, Eg and B<sub>1</sub>tg horizons, respectively. In addition, the pH of the forest soil profiles was lower in comparison with the meadow and arable land profiles (mean values of 4.06, 3.97 and 3.85, for arable land, meadow soil and forest soil, respectively). Soil acidification was especially intensive in deep soil horizons since 27 (Ah), 77 (Eg) and 87 % (B<sub>1</sub>tg) of the soil profiles had a pH below 4.0 (Table I; Fig. 1).

Soil reaction is one of the best parameters for an estimation of the exchangeable Al content. Al solubility increases at active soil acidities below 5.5. In addition to soil reaction, Al dynamics is also affected by other factors, especially the soil organic matter content and composition. Acid cations in complexes or chelates with organic matter are not readily exchangeable by normal exchange reactions.<sup>20,21</sup>

The mean values of the total exchangeable acidity (TEA) in the tested soil profiles were 1.55, 2.33 and 3.40 meq (100 g)<sup>-1</sup>, for the Ah, Eg and B<sub>1</sub>tg horizons, respectively. However, it was considerably higher in the forest soils (mean 3.39 meq (100 g)<sup>-1</sup>) than in the arable and meadow soils (means 1.96 and 1.93, respectively). The deep horizons (Eg and B<sub>1</sub>tg) of the meadow and forest soil pro-

files had especially high *TEA* values. Especially high frequencies of high *TEA* values (over 3.0 meq (100 g)<sup>-1</sup>) were found in the forest soil profiles (Table I; Fig. 2).

TABLE I. Distribution of pH (1 M KCl, in % of total), total exchangeable acidity (*TEA* as sum of H<sup>+</sup> and Al<sup>3+</sup>, in % of total) and mobile aluminum in soil profiles (in % of total); a = arable land; m = meadow; f = forest

Horizon	n	pH (1 M KCl)				<i>TEA</i>				Mobile Al			
		pH Range				pH Range							
		< 4.0	4.1–4.5	4.6–5.1	> 5	< 1.0	1–2	2–3	> 3.0	< 3.0	3–6	6–10	> 10
Ah (a)	54	18.5	57.5	22.2	1.8	86.8	13.2	0.0	0.0	63.0	18.5	11.1	7.4
Ah (m)	28	20.8	75.0	4.2	0.0	85.2	14.8	0.0	0.0	64.4	17.8	7.1	10.7
Ah (f)	20	55.0	30.0	5.0	10.0	55.0	20.0	5.0	20.0	40.0	10.0	15.0	35.0
Ah (total)	102	26.5	56.1	14.3	3.1	80.0	15.0	1.0	4.0	58.8	16.3	10.8	14.1
Eg (a)	54	64.8	27.8	7.4	0.0	35.8	37.8	22.6	3.8	20.4	13.0	12.9	53.7
Eg (m)	28	91.7	8.3	0.0	0.0	18.5	63.0	11.1	7.4	10.7	7.1	21.4	60.8
Eg (f)	20	90.0	10.0	0.0	0.0	10.0	20.0	30.0	40.0	0.0	15.0	0.0	85.0
Eg (total)	102	76.5	19.4	4.1	0.0	26.0	41.0	21.0	12.0	13.7	11.8	12.8	61.7
B <sub>1</sub> tg (a)	39	76.9	20.5	2.6	0.0	24.3	18.9	24.3	32.5	12.8	12.8	7.7	66.7
B <sub>1</sub> tg (m)	24	95.0	5.0	0.0	0.0	8.7	21.7	39.2	30.4	0.0	8.3	12.5	79.2
B <sub>1</sub> tg (f)	15	100	0.0	0.0	0.0	0.0	21.4	28.6	50.0	0.0	0.0	6.7	93.3
B <sub>1</sub> tg (total)	78	86.9	11.8	1.3	0.0	14.8	20.3	29.6	35.3	6.4	9.0	8.9	75.7
B <sub>2</sub> tg (total)	29	90.2	6.6	3.2	0.0	14.8	27.6	36.5	21.1	0.0	14.2	13.5	72.3

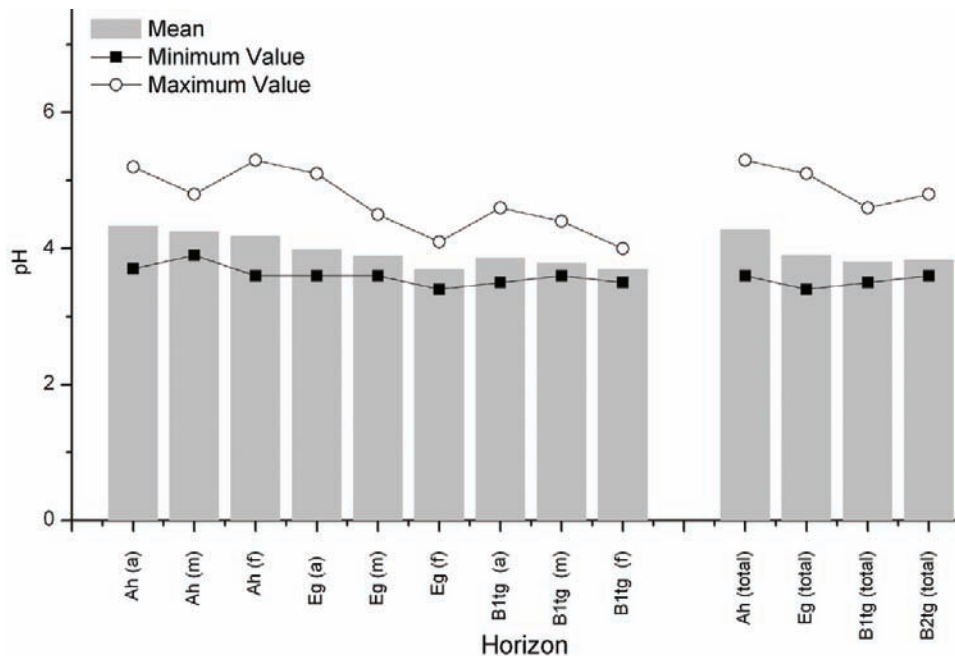


Fig. 1. Distribution of pH (1 M KCl) in the soil profiles.

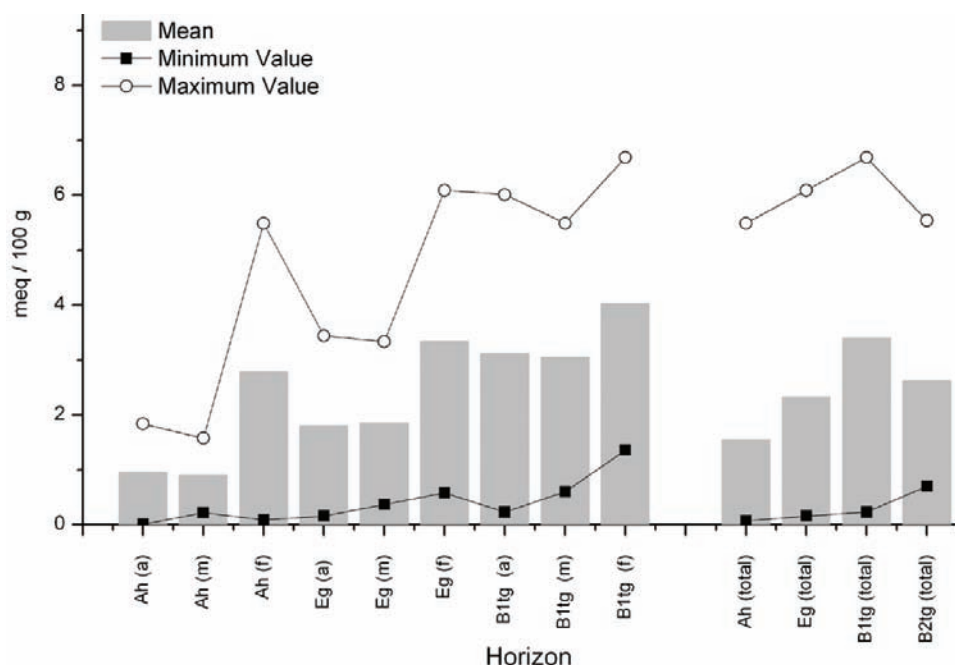


Fig. 2. Distribution of total exchangeable acidity (*TEA*) (sum of  $H^+$  and  $Al^{3+}$ ) in the soil profiles ( $meq (100 g)^{-1}$  soil).

The mean mobile Al contents in the tested soil profiles were 11.02, 19.58 and 28.33  $mg Al (100 g)^{-1}$  for the Ah, Eg and B<sub>1</sub>tg horizons, respectively. In accordance with soil pH and *TEA*, the mobile Al in the forest soils was considerably higher (mean 26.08  $mg Al (100 g)^{-1}$ ) than in arable and meadows soils (means 16.85 and 16.00  $mg Al (100 g)^{-1}$ , respectively). The Eg and B<sub>1</sub>tg horizons of the forest soil profiles had especially high mobile Al contents (means 28.50 and 32.95  $mg Al (100 g)^{-1}$ , respectively). The frequency of high levels of mobile Al was especially high in the forest soils since 35 (Ah), 85.0 (Eg) and 93.3 % (B<sub>1</sub>tg) of the tested profiles were in the range above 10  $mg Al (100 g)^{-1}$  (Table I, Fig. 3).

High contents of mobile aluminum in pseudogley soil were also observed by Osaki *et al.*,<sup>22</sup> Abreu *et al.*<sup>23</sup> and Mládková *et al.*<sup>24</sup>

Increased *TEA* values are characteristic for soils in which acidification processes are rather far advanced, the reaction of their soil solutions being fairly acidic, with pH values lower than 5.0. This is typical of the pseudogley in the Čačak–Kraljevo Basin, the most widely distributed soil type in the location. As, for the same *TEA* value, an increased concentration of Al ions is much more dangerous for plants than  $H^+$  at the same concentration, plants increasingly suffer if a high share of Al ions is present in the soil. Already at 6–10  $mg (100 g)^{-1}$  of read-



ily mobile Al in the soil, plant growth is retarded to a greater or lesser extent depending on the crop in question.<sup>25</sup> High TEA values created predominantly by Al ions is one of the most important causes for the low productivity of the pseudogley in the studied basin, where average yields of cultivated plants, despite the application of fertilizers and different agrotechnical measures, are low and vary greatly in dependence on the weather conditions of the year.

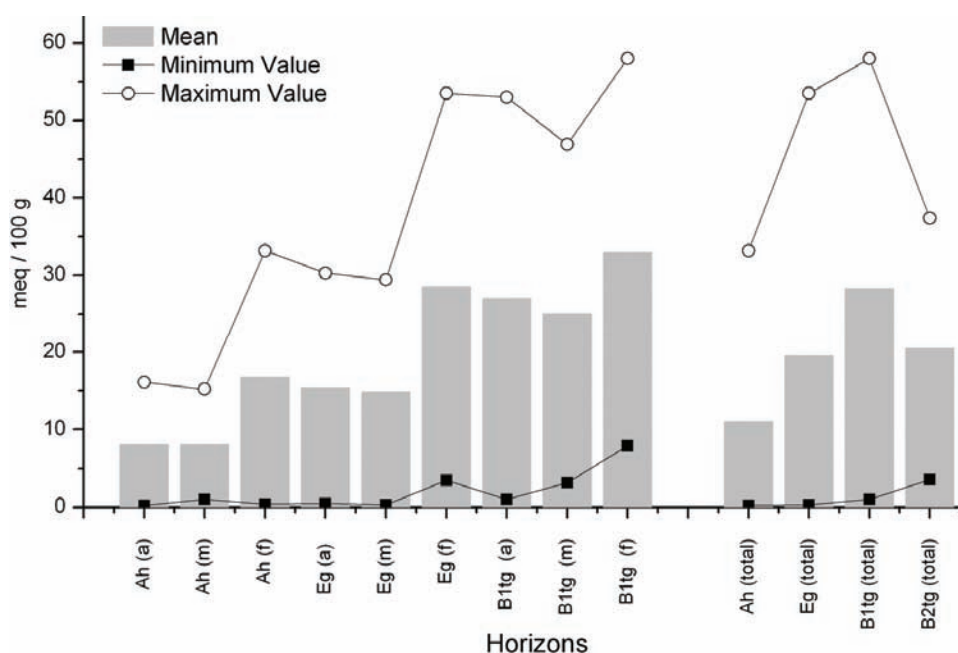


Fig. 3. Distribution of mobile aluminum in the soil profiles (meq (100 g)<sup>-1</sup> soil).

The sources of the available Al (in the soil solution and exchangeable Al) are the aluminum contained in aluminosilicates, amorphous and crystalline Al oxides, organically bound Al, Al in interlayers of three-layered minerals, *etc.* The content of these forms in stagnosols depends on the parent rock composition, the intensity of the processes of clay leaching and other colloids, the weathering process, organic matter content and other soil characteristics.<sup>26</sup>

In studies of different soil types, many researchers concluded that the content of Al oxides is not proportional to the content of exchangeable Al.<sup>27,28</sup> The form of the Al plays a decisive role in its potential bioavailability and toxicity. The toxicity of aluminum to plants qualitatively decreases in the order: Al<sub>13</sub> (not in the form of phosphates or silicates), Al<sup>3+</sup>, Al(OH)<sup>2+</sup> and Al(OH)<sub>2</sub><sup>+</sup>. Aluminum bound in fluoride or organic complexes and Al(OH)<sub>3</sub> are supposed to be non-toxic.<sup>29</sup> The complexation of Al by natural organic substances is of considerable significance in regulating the concentrations of the highly toxic Al<sup>3+</sup> in acid soils

and natural waters.<sup>30</sup> The distribution of toxic  $\text{Al}^{3+}$  is particularly affected by the contents of humic and fulvic acids in the surface soil horizons. Aluminum complexes with both types of acids decrease the toxic impact of  $\text{Al}^{3+}$  by decreasing its bioavailability and activity in the soil solution.<sup>31,32</sup>

The investigations of stagnosols from Serbia showed that the content of exchangeable Al increased significantly with increasing contents of less available Al forms,  $\text{Al}_{\text{Cu}}$ ,  $\text{Al}_{\text{EDTA}}$  and  $\text{Al}_{\text{dit}}$ , but the correlation with amorphous Al was low.<sup>26</sup> These findings were explained with possibility of EDTA and  $\text{CuCl}_2$  to extract the organic Al, Al in interlayers of three-layered minerals and other Al forms comprised in the amorphous Al. The results of the present study indicate that further research on the mobility of Al reserves in different types of acid soils is required.

Lime is widely known as the most effective means for correcting soil acidity. The direct effect of soil amendment through lime is a change in the soil pH. Its application usually results in significant reduction of exchangeable Al, allowing for a more efficient uptake of N and P.<sup>33</sup> Osei<sup>34</sup> studied the effects of different lime application rates and time of application on some chemical properties of an acid soil. Significant increase in pH (> 28 %) was obtained at all soil sampling depths. Available P also increased significantly (> 90 %). Exchangeable Al was completely eliminated when most of the soil samples had pH > 5.0. The results clearly indicated that liming as a management practice, could be used to alleviate or prevent acidification of pseudogley soil.

Strategies to overcome the negative effects of Al on plant growth in these soils include the application of lime to raise the soil pH and lower the soil exchangeable Al, and the use of crop species that are resistant to Al-toxic soils. The incorporation of lime fertilizers alleviates soil acidity, provides calcium to plants, increases the amount of plant available phosphorus, provides mineralization of organic and harvest residues, and decreases the amount of toxic substances and heavy metals in the soil. Chemical amendment (melioration) of acid soils (soil adaptation to the plant) and the breeding and selection of tolerant genotypes (plant adaptation to the soil) are two complementary possibilities to alleviate the problems related to increasing the productivity of acid soils.<sup>35</sup>

#### CONCLUSIONS

Aluminum (Al) toxicity is considered as the main growth- and yield-limiting factor on soils with pH below 5.0. The obtained results showed variability of the soil properties among the examined sites, and the deeper soil horizons have higher contents of mobile Al. The mean mobile Al contents of the tested soil samples were 11.02, 19.58 and 28.33 mg Al  $100 \text{ g}^{-1}$  for the Ah, Eg and B<sub>1</sub>tg horizons, respectively. It was found that increasing *TEA* and lower pH significantly contributed to an increase in Al toxicity. The mobile Al was significantly higher in the pseudogley of forest soils (26.08 mg Al  $(100 \text{ g})^{-1}$ ) than in the arable and



meadow soils (16.85 and 16.00 mg Al (100 g)<sup>-1</sup>, respectively). To explain fully the role and toxicity of Al in soil productivity, the TEA, pH, Ca and soil organic matter must be controlled. Finally, to prevent manifestation of Al toxicity on plants growing in pseudogley and similar acid soils, it is necessary to conduct preliminary soil analyses, particularly of the deeper soil horizons. Chemical amendment (melioration) of acid soils (soil adaptation to the plant) and the breeding and selection of tolerant genotypes (plant adaptation to the soil) are two complementary possibilities for solving the problems related to increasing the productivity of acid soils.

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#### ИЗВОД

#### КИСЕЛОСТ И САДРЖАЈ ПОКРЕТЉИВОГ АЛУМИНИЈУМА У ПСЕУДОГЛЕЈНИМ ЗЕМЉИШТИМА ЧАЧАНСКО-КРАЉЕВАЧКЕ КОТЛИНЕ

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Киселост земљишта и токсичност алуминијума се сматрају најважнијим факторима који ограничавају раст биљака на киселим земљиштима. У овом раду су испитивани рН вредност земљишта и садржај покретљивог алуминијума (Al) у профилима земљишта псеудоглеја Чачанско-краљевачке котлине. Укупно 102 земљишна профила су отворена током 2009. године на појединим локалитетима Чачанско-краљевачке котлине. Истраживањима је обухваћено 54 узорка са ораница, 28 са ливада и 20 узорака из профила који су отворени под шумском вегетацијом. Из отворених профила, узети су узорци земљишта у поремећеном стању из Ah и Eg хоризонта (102 профила), а затим из B<sub>1</sub>tg хоризонта са 39 ораница, 24 ливаде и 15 шумских профила (укупно 78) и из B<sub>2</sub>tg хоризонта 14 ораница, 11 ливада и 4 шумска профила (укупно 29). Просечна рН вредност (1 М KCl) испитиваних земљишних профила је 4,28, 3,90 и 3,80, за Ah, Eg и B<sub>1</sub>tg хоризонте. Такође, рН вредност земљишта шумских профила је нижа у поређењу са ливадама и обрадивим земљиштем (4,06, 3,97 и 3,85, за обрадиво земљиште, ливаде и шуме). Земљишна киселост је посебно изражена у дубљим хоризонтима, јер 27 (Ah), 77 (Eg) и 87 % (B<sub>1</sub>tg) земљишних профила имају рН вредност нижу од 4,0. Средња укупна разменљива киселост (TEA) испитиваних земљишних профила је 1,55, 2,33 и 3,40 meq (100 g)<sup>-1</sup>, у Ah, Eg и B<sub>1</sub>tg хоризонтима. Међутим, код шумским земљиштима TEA је знатно виша (просечно 3,39 meq (100 g)<sup>-1</sup>) него код обрадивог земљишта и ливада (1,96 и 1,93). Просечан садржај покретљивог Al у испитиваним земљиштима је 11,02, 19,58 и 28,33 mg Al (100 g)<sup>-1</sup>, у Ah, Eg и B<sub>1</sub>tg хоризонтима. Услед разлика у рН и TEA вредностима његов садржај у шумским земљиштима је знатно виши (просечно 26,08 mg Al (100 g)<sup>-1</sup>) него код обрадивог земљишта и ливада (16,85 и 16,00 Al (100 g)<sup>-1</sup>). Eg и B<sub>1</sub>tg хоризонти шумског земљишта имају посебно висок садржај покретљивог Al (28,50 и 32,95 mg Al (100 g)<sup>-1</sup>). Учесталост високог нивоа покретљивог Al у шумским земљиштима постоји због тога што 35 (Ah), 85,0 (Eg) и 93,3 % (B<sub>1</sub>tg) испитиваних профила поседују више од 10 mg Al (100 g)<sup>-1</sup>.

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