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Methods for the determination of the form of aluminium: Pseudogley soils

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Abstract: Exchangeable aluminium (Al_{KCl}) and $CaCl_2$-extractable aluminium (Al_{CaCl_2}) have approximately the same value in the prognosis of detrimental effect on plants. Additional, more in-depth research should show which of the two applied methods of exchangeable Al determination is more suitable (after Sokolov or using aluminon). The contents of total Al and amorphous Al increase with depth and percentage clay. Crystalline Al oxides and $CuCl_2$-extractable aluminium (Al_{CaCl_2}) and EDTA-extractable aluminium (Al_{EDTA}) represent the more mobile reserves of Al and they depend mostly on changes in the acidity parameters of the soil. Exchangeable Al is on average 4.3–4.7 times lower than the contents of Al_{CaCl_2} and Al_{EDTA}, 8 times lower than crystalline Al and 35 times lower than amorphous Al. Some methods are not sufficiently selective, hence further research is required to achieve more favourable methods for the determination of the different forms of Al.

Keywords: exchangeable Al; Al oxalate; Al dithionate; $CuCl_2$ extractable Al; organic Al.

INTRODUCTION

Aluminium is the most represented metal in rocks and soil; on average it accounts for about 7–8 %. In soil, it is found in primary and secondary alumino--silicates, hydrated Al oxides, in the form of compounds with inorganic ligands, bound to organic matter, in allophanes, imogolites, various forms of short-range order materials, exchangeably adsorbed and fixed (in interstratified three-layered minerals), as well as in the soil solution.[1–3]

Knowledge of the total Al and other forms not readily available to plants is significant in order to determine, primarily, the paedogenetic processes and the reserves of mobile aluminium. Paedological research usually deals with the contents of crystalline and amorphous Al oxides (along with Fe oxides). These are

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determined by various methods: Al and Fe organic, most often by the method using pyrophosphate; total non-siliceous using the dithionate method and amorphous oxides by the oxalate method.[4,5] However, the applied methods are less specific to Al than to Fe, hence they often render unreal results.[6] More recent studies include the distinction between non-crystalline and different quasi-crystalline forms of Al in vermiculite interlayers and other non-crystalline forms, as well as the determination of crystalline oxides (sodium citrate–dithionate) and non-crystalline oxides (acid NH_4 oxalate in the dark).[2] Employing the above methods, some authors studied the contents of different forms of Al in several soil types, their correlations and the relation with toxic forms of Al.[7–9]

The content of available Al (exchangeable and in the soil solution) is essential for the evaluation of the risk of plant production on acid soils, in which it can occur in toxic concentrations for plants and micro-organisms.[10] Exchangeable Al (active, mobile) is plant-available Al and it is extracted using non-buffered solutions of neutral salts (mainly 1.0 M KCl). This form is usually determined employing the standard method with titration (Sokolov), but some authors also recommended a colorimetric method with aluminon.[1] In addition to extraction using a highly ionic reagent, such as 1.0 M KCl, phytotoxic Al can be determined by extraction using a 0.010 M solution of $CaCl_2$,[11] which is advantageous because it has an ionic dependence comparable to that of natural soil and is in more direct relation with Al in the soil solution, because it extracts a smaller part of the exchangeable Al.[12]

There have only been a few studies on the different forms of Al and their inter-relationship in Serbian soils. The aim of this study was to determine the content and relations of different forms of Al (available and non-available) in acid soils, type pseudogley (occupying 6 % of the area of Serbia), using some relatively novel chemical methods, taking into account their significance both in paedological research and in the field of soil chemistry and environmental protection.

EXPERIMENTAL

The soil samples were taken at 30 sites under lowland Pseudogleys in Nortwest Serbia (Jabučje, Bajevac, Debrc, Varna, Lipolist, Brankovina, Klašnić), East Serbia (Salaš, Kladovo, Karbulovo) and in the valley of the river Zapadna Morava (Samaila, Čibukovac, Podunavci, Globoder, Kruševac), from three characteristic horizons (Ah, Eg, EBtg and Btg). The basic characteristics of the soil samples were determined by standard methods: pH in H_2O and 1.0 M KCl – potentiometrically; humus – after Kotzman; available P and K–Al method of Egner–Riehm; adsorptive complex of soil (H, T, S) – after Kappen; soil texture – combined method of sieving and the pipette method. Exchangeable Al (Al_{KCl}) was determined by two methods: after Sokolov – extraction with 1.0 M KCl (1:2.5), shaken for 1 h, titration and spectrophotometrically with aluminon[1] – extraction with 1.0 M KCl (1:10), shaken for 30 min and using an aluminon–acetate buffer.

In selected samples phytotoxic Al was also determined – extraction with 0.010 M $CaCl_2$, (1:5), shaken for 1 h using aluminon (Al_{CaCl_2}).[8,11]

At 15 sites, soil samples from three characteristic horizons were taken and in them less available forms of Al were determined with different reagents:

− Na citrate-dithionite solution (Al_{dit}, crystalline oxide): 5.0 g soil was shaken for 1 h with 50 ml of a solution containing 0.15 M Na citrate, 0.050 M citric acid and 2 g dm^{-3} Na dithionite;[7]

− ammonium oxalate solution in the dark (Al_{oxa}, amorphous oxide): 1.0 g soil was shaken in the dark for 4 h with 50 ml of acidified 0.20 M NH_4 oxalate at pH 3.25;[7]

− $CuCl_2$ (Al_{Cu}): 3.0 g soil was shaken for 2 h with 30 ml 0.50 M $CuCl_2$;[13,14]

− EDTA (Al_{EDTA}): 5.0 g soil was shaken for 1 h with 50 ml 0.25 M EDTA (pH 7.0, modification as in the original method 0.50 M EDTA was used).[15]

All the suspensions were centrifuged for 20 min at 2500 relative centrifugal force and filtered (Whatman 42) and the content of Al was determined by AAS with a N_2O–C_2H_2 flame.

The total Al was determined by digestion with HF and perchloric acid and then by AAS.[1]

The results were processed by mathematical–statistical methods of regression analysis and descriptive statistics (program SPSS 10.0.).

RESULTS

The characteristics of pseudogleys are very variable depending on the site and profile depth. Pseudogleys are characterised by lighter soil texture of the eluvial horizons and clay accumulation in the hardly permeable illuvial horizon (Table I). The soils were acidic, except the pseudogleys in Debrc and Kladovo, which were neutral, thanks to the application of liming. Of the total number of samples, 60 % were in the category of very acid soils (pH in KCl ≤ 4.5) and acidity increased slightly with depth. The content of humus in the Ah horizon was below 2 % in about half the samples. The values of cation adsorption capacity (*T*) and of the composition of adsorbed cations (*S* and *H*) varied depending on the pH value, the quantity and composition of organic and mineral colloid particles. Despite their acid reaction, most pseudogleys were rich in base cations, according to other investigations.[16] Only the most acid pseudogleys at two sites in West Serbia (Samaila and Klašnić) were dystric.

The exchangeable Al was determined by two methods. The method with aluminon was preferable because the Al is read directly (not with the total exchangeable acidity) and the uncertainty of detecting the discoloration which occurs in titration was avoided.

The values of exchangeable Al determined by the Sokolov method (non-multiplication with 1.75) ranges from 0–32.4 mg/100g (average 5.93) and by the method with aluminon, the average content Al was 5.26 mg/100g (88.4 % of the values determined by the Sokolov method). Their correlation is high but there are some variations, therefore more in-depth research would show an appropriate method (Fig. 1).

The exchangeable Al increased with depth, especially sharply in the illuvial horizon. The method of simple correlation (quadratic function) shows that the changes of exchangeable Al are maximally affected by the parameters of soil

acidity: pH in H_2O (R = –0.78), pH in KCl (R = –0.86), hydrolytic acidity H (R = 0.85) and V (R = –0.63).

TABLE I. Statistical parameters of the basic characteristics of the pseudogley soils

Horizon	Stat. param.	Total sand	Silt	Clay	pH		Humus %	*H*	*S*	*T*	*V* / %	Al mg/100g	
		%			H_2O	KCl		meq/100g				Sok.	Alum.
Aoh	Min	31.40	17.40	15.50	4.75	3.45	1.17	1.30	4.83	15.42	18.80	0.0	0.0
	Max	67.10	42.20	34.30	7.30	6.80	4.13	20.88	36.52	37.83	96.55	19.80	23.76
	Aver.	41.64	32.80	25.56	5.62	4.63	2.34	8.70	14.91	23.61	62.93	2.05	2.49
	Sd	9.81	7.24	4.48	0.47	0.64	0.79	4.11	5.32	4.35	14.70	4.82	6.27
Eg	Min	26.10	16.50	14.90	4.85	3.60	0.12	2.27	8.04	13.64	31.34	0.09	0.0
	Max	68.60	40.10	43.40	6.40	5.70	3.51	17.62	22.84	34.68	88.22	23.13	19.91
	Aver.	40.38	31.68	27.94	5.54	4.40	1.41	8.59	14.66	23.24	63.48	2.85	2.90
	Sd	9.95	7.00	6.10	0.32	0.45	0.81	3.63	3.75	4.41	12.75	5.21	5.21
EBtg or	Min	24.00	15.20	21.3	4.70	3.20	0.01	2.57	10.05	15.35	38.12	0.0	0.0
Btg	Max	61.40	38.10	49.50	6.40	5.80	1.60	18.92	25.29	36.59	87.28	32.04	26.70
	Aver.	36.44	28.19	35.31	5.57	4.37	0.50	9.35	16.87	26.23	65.28	5.61	4.82
	Sd	9.94	6.31	8.44	0.42	0.68	0.44	4.22	3.57	5.31	11.38	8.80	6.93

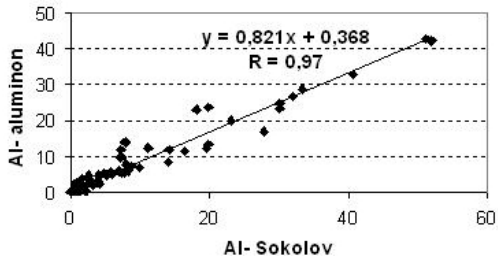

Fig. 1. Exchangeable Al determined by two methods (n = 90).

The release of Al from the reserves commences mainly at pH values ≤ 4.5 in KCl and is well explained by a linear function (Fig. 2).

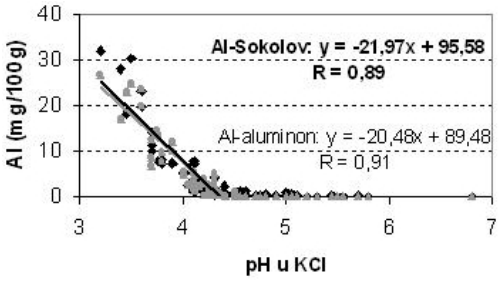

Fig. 2. Relation between pH of the KCl and the exchangeable Al.

The correlation of the exchangeable Al (Al_{KCl}, aluminon) and Al extracted with $CaCl_2$ (Al_{CaCl_2}) is high (Fig. 3). They have approximately the same value in the prognosis of detrimental effect on plants. The average values of the exchangeable Al were about 12 times higher than Al_{CaCl_2}.

The sources of available Al in soil are the less available forms. The content of these forms depends on the composition of the parent rock, the intensity of the leaching processes of clay and other colloids, on the destruction process, the content of organic matter and other soil characteristics.

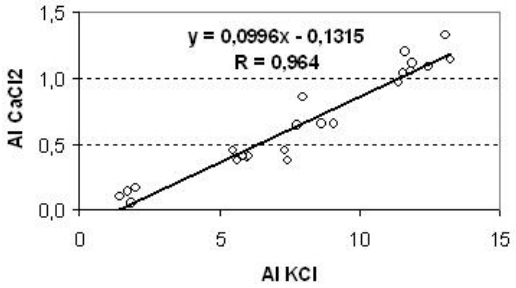

Fig. 3. Relation between Al_{KCl} and Al_{CaCl_2}.

The content of total and amorphous Al increased with depth, which is related to the leaching of colloid particles and Fe and Al oxides in the illuvial horizon (Figs. 4a and 4b). Amorphous Al accounts for on average 1.8 % of the total Al and in the Eg and Btg horizons and a significant, medium correlation between these two forms exists (R = 0.58 and 0.66, respectively).

The concentrations of crystalline Al oxides were less, ranging from 17–51 mg/100 g and had a medium correlation with Al_{oxa} (R = 0.60). The values were changed under the effect of the acidity parameters: pH in H_2O (R = –0.66), pH in KCl (R = –0.53), hydrolytic acidity (R = 0.71) and V (R = –0.54).

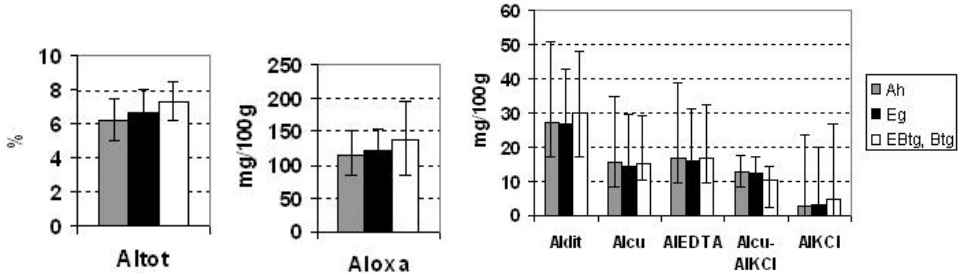

Fig. 4. Content of less available forms of Al per horizon (average, minimum and maximum).

The Al extracted with 0.50 M $CuCl_2$ is Al which forms low and medium stable complexes with organic matter,[13] and this reagent and pyrophosphate are suitable for the determination of organic Al in organic-rich mineral horizons.[9] The aluminium extracted with 0.50 M EDTA is also in good correlation with the organic matter in the soil.[7]

The values of the $CuCl_2$-extractable Al (Al_{Cu}) and EDTA-extractable aluminium (Al_{EDTA}) represent the more mobile reserves of Al and they depend mostly on the changes of the soil acidity parameters.

The average content $CuCl_2$-extractable Al (Al_{Cu}) was 15.02 mg/100g, *i.e.*, 92 % of the Al_{EDTA}, and their correlation is very high (R = 0.96). These forms show good correlation with Al_{dit} and the soil acidity parameters but also not with humus. A better correlation with humus was obtained if the Al_{KCl} was subtracted from Al_{Cu}, according to other authors,[8] and in this manner, the so-called unavailable exchangeable Al is obtained. This correlation was higher in the Ah horizon (values obtained with Al_{KCl} – aluminon, Fig. 5), and also in the Eg horizon (values obtained with Al_{KCl} – Sokolov: R_{ah} = 0.725, R_{Eg} = 0.740 and R_{Btg} = 0.510).

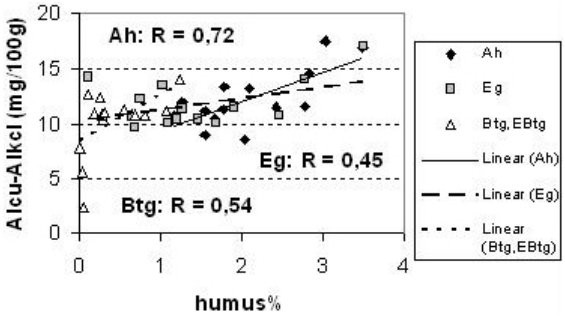

Fig. 5. Relation between humus content, %, and AlCu–AlKCl.

The relation between the available Al and the less available Al forms show that the values of the exchangeable Al are in low correlation with the total and amorphous Al, with Al_{dit} (crystalline) and Al_{EDTA} the correlation is medium (R = 0.71 and 0.73, respectively) and with Al_{Cu} it is high (R = 0.82). The exchangeable Al was on average 4.3–4.7 times lower than the content of Al_{Cu} and Al_{EDTA}, 8 times lower than the crystalline Al and 35 times lower than the amorphous Al. The inclusion also of other soil parameters, using the method of multiple linear regression, did not explain the changes in the exchangeable Al better.

DISCUSSION

The results of this study show that the content of exchangeable Al in pseudogleys is very variable depending on the locality and profile depth and its dynamics depends mostly on the change of the soil pH (active, exchangeable and hydrolytic acidity).

Compared to 1.0 M KCl, on using 0.50 M $CuCl_2$, 6–7 times more Al was on average extracted in the humus horizon, 5 times more in the eluvial horizon and about 3 times more in the illuvial horizon. $CuCl_2$ extracts potentially reactive organic and inorganic Al reserves, because Cu^{2+} is a strong complexation agent, hence it replaces Al from the organic matter and the acidity of the $CuCl_2$ solution can cause depolymerisation of hydroxyl–Al polymers.[13] In this study, it was shown that the value Al_{Cu}−Al_{KCl} in the more humus horizons represents Al bound to organic matter, while in the deeper horizons, $CuCl_2$ probably also extracts the polymerised hydroxyl–Al and the more soluble amorphous Al in the inorganic

phase of the soil, as also reported by the above authors for soil types Ultisol, Oxisol and Histosol.

According to the literature, amorphous Al is a more reactive reserve of Al than crystalline Al.[7,17,18] The present study showed a higher correlation of exchangeable Al with Al_{EDTA} and Al_{Cu} but also with Al_{dit} (crystalline). This could be explained by the fact that exchangeable Al contributes to a considerable extent to the Al reserves, which were shown to be potentially more mobile (especially in the deepest horizon): Al_{dit} on average 7–19 %, Al_{Cu} and Al_{EDTA} 13–37 %. Moreover, as already stated, some amorphous Al forms can also be extracted using EDTA and $CuCl_2$. The issue of selectiveness of the applied methods (also reported by other authors)[14] still remains, which draws attention to the need for further research of methods suitable for individual Al forms.

И З В О Д

МЕТОДЕ ЗА ОДРЕЂИВАЊЕ ОБЛИКА Al: ПСЕУДОГЛЕЈНА ЗЕМЉИШТА

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Размењиви алуминијум (Al_{KCl}) и Al екстрахован са $CaCl_2$ (Al_{CaCl_2}) имају приближно исту вредност у прогнози штетног дејства на биљке. Накнадна детаљнија испитивања треба да покажу која је од две примењене методе за одређивање размењивог Al (по Соколову и алуминоном) погоднија. Садржај укупног и аморфног Al се повећава са дубином и садржајем глине. Кристални Al и Al екстрахован са $CuCl_2$ (Al_{Cu}) и EDTA (Al_{EDTA}) представљају мобилније резерве Al и највише зависе од промена параметара киселости земљишта. Размењиви Al је просечно 4.3–4.7 пута мањи од садржаја Al_{Cu} и Al_{EDTA}, 8 пута мањи од Al кристалног и 35 пута од аморфног. Поједине методе нису довољно селективне, па је потребно даљим истраживањем доћи до погоднијих метода за облике Al.

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