The forms of aluminium in Stagnosols in Serbia

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ABSTRACT

The interactive relations of Al forms and the most important characteristics of Stagnosols were researched to diagnose which factors are the best to control the content of phytotoxic Al forms. The values of exchangeable Al (Al_{KCl}) range from 0.0 to 560.7 mg/kg and increase with depth. The variation of exchangeable Al is high and it depends on the changes of all forms of soil acidity and the degree of base cation saturation. Their relation is best described by a non-linear function. The contents of total Al and Al extracted by ammonium oxalate in dark (Al amorphous, Al_{oxa}) increase with depth, together with the increase of the content of clay particles. The values of Al extracted by sodium citrate/dithionite (Al crystalline, Al_{dit}), 0.5M $CuCl_2$ (Al_{Cu}) and 0.25M EDTA (Al_{EDTA}) are in good correlation and they predominantly depend on the parameters of soil acidity. The value of Al_{Cu}-Al_{KCl} (in eluvial horizons) is best represented by organically bound Al. Effects of the reserves of aluminium Al_{dit}, Al_{Cu} and Al_{EDTA} on the changes of exchangeable Al are higher (medium and high correlation), while the effects of the total Al and Al_{oxa} are lower.

Keywords: Stagnosol; soil; exchangeable Al; Al amorphous; Al crystalline; organic Al

Stagnosols (FAO 2006) cover about 538 000 ha, or 6%, from the area of Serbia. One of the most important chemical characteristics of Stagnosols is that they are more or less leached, acid soils, and therefore one of the major problems is the elevated content of mobile aluminium, which can be toxic for plants and other parts of the environment.

The study of Al regime in Stagnosols of Serbia was reported by several researchers (Nikodijević 1972, Jakovljević et al. 2001, Dugalić et al. 2002). They found that the content of exchangeable Al was variable per sites and profile depths and that the interaction of pH and Al was high. It is concluded that liming is very efficacious for Al decrease, and that fertilizing with phosphorus, humification, and deep tillage have positive effects.

Soil reaction is one of the best parameters for estimation of exchangeable Al content. Al solubility increases at the active soil acidity below 5.5. In addition to soil reaction, Al dynamics is also affected by other factors, especially soil organic matter content and composition. Acid cations in the complexes or the chelates with organic matter are not readily exchangeable by normal exchange reactions (McLean 1965, Dijksta and Fitzhugh

2003). Bouman et al. (1995) also reported that the low content of exchangeable Al in acid prairie soils can be the consequence of organically bound Al, as well as of the inhibition of acid decomposition of minerals, the effect of high concentrations of soluble Mg^{2+} and H_4SiO_4 on the stabilisation of clay minerals, climate conditions – soil freezing and melting.

A significant issue that has not been sufficiently investigated in Stagnosols is the content and the dynamics of less readily available Al forms and their effect on available Al. According to Nikodijević (1972), in some Stagnosol profiles in West Serbia total Al varies from 5.8–7.9% in the topsoil horizon, 9–10.6% in Btg, and amorphous Al_2O_3 (Tamm method) in Ah horizon from 3200 to 4310 mg/kg, Btg horizon from 4040 to 5750 mg/kg (it accounts for 2–4% of the total Al). The correlation between exchangeable Al, total Al and amorphous Al is weak.

In the studies of different types of soil, many researchers conclude that the content of Al oxides is not proportional to the content of exchangeable Al (Alvarez et al. 2002, Garcia-Rodeja et al. 2004). McLaughlin et al. (1990) reported that in grassland soils in Australia, the values of Al amor-

phous oxides (extracted by NH_4-oxalate) range from 470 to 2160 mg/kg; Al crystalline oxides (extracted by Na citrate-dithionite) range from 206 to 1110 mg/kg; Al extracted by $CuCl_2$ from 221 to 1050 mg/kg. These less available fractions are in good correlation, but these forms and the content of toxic Al forms (extracted by KCl and $CaCl_2$) are in low correlation. Similar relations are also reported by Jarvis (1986).

On the other hand, it is considered that Al solubility is controlled by the amorphous forms of $Al(OH)_3$ rather than by its crystalline forms (Juo and Kamprath 1979). Jarvis (1986) reports that Al in the forms which are not well crystallised represents more labile reserves: exchangeable Al, electro-statically bound to negatively charged clays or organic colloids; Al present in organic complexes, or as non-crystalline coatings on soil particles, and Al present as the microcrystalline phase of hydroxy-polymer components which occupy the clay mineral interlayers.

It is evident that, in accordance with Bertsch and Bloom (1996), the methods of Al determination are not always selective for specific phases, although there are some relations between operationally defined, less available Al and the selective extractants.

This study deals with the contents of different forms of Al (by depth, sites), their interdependence, and their relation with Stagnosol characteristics. The aim of the study is to determine the most suitable factors to control the content of Al phytotoxic form.

MATERIAL AND METHODS

Al dynamics was assessed at 15 sites of lowland Stagnosols in the Northwest and East Serbia and in the valley of the Zapadna Morava river. Lowland Stagnosols in Serbia occur in temperate continental climate conditions, at the altitude of 100–350 m, on flat or mildly sloped lake, diluvial and river terraces. Closer data about the study area are presented in Table 1.

The samples were taken at each site from farmland and meadow lands, from three characteristic horizons (Ah, Eg, EBtg or Btg) (90 samples). The basic characteristics of soil samples were determined by standard methods: pH of the soil solution in water suspension (pH_{H_2O}) and in 1M KCl suspension (pH_{KCl}) – potentiometrically; humus – by oxidation with solution $KMnO_4$ (according to Kotzman); available P and K – extraction with AL solution (method by Egner-Riehm), and P was determined by colorimetry with molybdate, and K by flame photometry; hydrolytic acidity (H meq/100 g) – after Kappen (extraction by CH_3COONa, titration with 0.1M NaOH); the sum of exchangeable basis (S) – after Kappen (extraction by 0.1M HCl, titration with 0.1M NaOH); total capacity of cation adsorption (T) and degree of base saturation (*V*%) – was calculated; soil texture – combined method of sieving and pipette method. Exchangeable Al (Al_{KCl}) and exchangeable acidity (meq/100 g) were determined by extraction with 1M KCl and titration (Sokolov's method).

The less available Al forms were determined at the selected sites (45 samples). Total Al was determined by digestion with HF and perchloric acid, on AAS with N_2O-C_2H_2 flame (Barnhisel and Bertsch 1982).

Less available forms were also determined on AAS after the application of the procedure described by Jarvis (1986) and McLaughlin et al. (1990): Al crystalline (Al_{dit}) – Na citrate-dithionite solution (5 g soil were shaken for 1 h with 50 ml solution containing 0.15M Na citrate, 0.05M citric acid and 2 g/l Na dithionite); Al amorphous (Al_{oxa}) – ammonium oxalate solution in the dark (1 g soil was shaken in the dark for 4 h with 50 ml of acidified 0.2M NH_4 oxalate at pH 3.25); Al extracted by $CuCl_2$ (Al_{Cu}) – 3 g soil was shaken for 2 h with 30 ml 0.5M $CuCl_2$; Al extracted by EDTA (Al_{EDTA}) – 5 g soil was shaken for 1 h with 50 ml 0.25M EDTA [modification, the original method by Farmer et al. (1980) applies 0.5M EDTA]. All the suspensions were centrifuged for 20 min at 2500 relative centrifugal force and filtered (Whatman 42) before analysis.

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

RESULTS AND DISCUSSION

Stagnosol characteristics and the content of exchangeable Al

Different factors of soil formation bring about different Stagnosol characteristics. The structure of the profiles to the analysed depth is Aoh-Eg-Btg; Aoh-Eg-EBtg; Aoh-EBtg-Btg. The thickness of the humus – accumulation horizon is most often 15–20 cm, the impermeable horizon is mainly at 40–60 cm.

Table 1. Basic characteristics of the study area

Area	Mean annual temperature (°C)	Annual precipitation (mm)	Sites of Stagnosol formation	Parent rock
Northwest Serbia	11–12	650–850	abrasion terraces and hillocks of the Pannonian Sea	aeolian sediments covering the Pleistocene sandy loams and clays
Valley of the Zapadna Morava river	10–11	710–750	older river terraces	sandy-loessoid Pleistocene clays and loams below which are older sediments of heavier composition
East Serbia	10–11	610–690	Karbulovo	mixture of clay and sands of indefinite age
			diluvial terrace-Salaš	fluvial andesite gravel, covering clay sediments of the Sarmatian
			IV Danube terrace-Kladovo	more acid sediments deposited in the already existing substrate

Stagnosols are characterised by textural variability per profile depth, which is manifested in the lighter soil texture of the eluvial horizons and in clay accumulation in the hardly permeable illuvial horizon (Table 2). Stagnosols in West Serbia and in the valley of the Zapadna Morava river have a heavier soil texture (the texture of Aoh horizon is mainly loam, eluvial Eg horizon is loam and clay loam, Btg horizon is clay and clay loam) than Stagnosols in East Serbia, which have a higher percentage of coarse sand (on average about 4–5 times) and less silt (on average 1.7 times). Eluvial horizons are sandy loam and sandy clay loam, and the deepest horizons are mainly clay loam and sandy clay loam.

Stagnosols show mainly acid reaction, except Stagnosols in Debrc and Kladovo (under farmland), which have neutral reaction, thanks to the

Table 2. Statistical parameters of Stagnosol basic characteristics

Horizons	Statistical parameters	Sand	Silt	Clay	pH		Humus	H	S	T	V%	Al
		(%)			H$_2$O	KCl	(%)	(meq/100 g)				(mg/kg)
Aoh	min	31.40	17.40	15.50	4.75	3.45	1.17	1.30	4.83	15.42	18.80	0.00
	max	67.10	42.20	34.30	7.30	6.80	4.13	20.88	36.52	37.83	96.55	346.5
	mean	41.64	32.80	25.56	5.62	4.63	2.34	8.70	14.91	23.61	62.93	35.8
	SD	9.81	7.24	4.48	0.47	0.64	0.79	4.11	5.32	4.35	14.70	84.4
Eg	min	26.10	16.50	14.90	4.85	3.60	0.12	2.27	8.04	13.64	31.34	1.6
	max	68.60	40.10	43.40	6.40	5.70	3.51	17.62	22.84	34.68	88.22	404.8
	mean	40.38	31.68	27.94	5.54	4.40	1.41	8.59	14.66	23.24	63.48	49.9
	SD	9.95	7.00	6.10	0.32	0.45	0.81	3.63	3.75	4.41	12.75	91.2
EBtg; Btg	min	24.00	15.20	21.3	4.70	3.20	0.01	2.57	10.05	15.35	38.12	0.00
	max	61.40	38.10	49.50	6.40	5.80	1.60	18.92	25.29	36.59	87.28	560.7
	mean	36.44	28.19	35.31	5.57	4.37	0.50	9.35	16.87	26.23	65.28	98.1
	SD	9.94	6.31	8.44	0.42	0.68	0.44	4.22	3.57	5.31	11.38	154.1

SD – standard deviation, H – hydrolytic acidity, S – sum of exchangeable basis, T – total capacity of cation adsorption

Table 3. Coefficient of correlation between exchangeable Al and other soil parameters

Parameters	Function	All	Ah	Eg	Btg
pH_{H_2O}	LIN	−0.62**	−0.54**	−0.71**	−0.71**
	QUA	−0.78**	−0.76**	−0.80**	−0.90**
pH_{KCl}	LIN	−0.65**	−0.58**	−0.71**	−0.68**
	QUA	−0.86**	−0.82**	−0.89**	−0.94**
Humus (%)	LIN	−0.33**	−0.18	−0.30	−0.41*
Exchangeable acidity (meq/100 g)	LIN	0.997**	0.990**	0.998**	0.998**
H (meq/100 g)	LIN	0.70**	0.71**	0.64**	0.79**
	QUA	0.85**	0.94**	0.77**	0.93**
S (meq /100 g)	LIN	−0.19	−0.40*	−0.54**	0.01
T (meq /100 g)	LIN	0.41**	0.18	0.06	0.63**
$V\%$	LIN	−0.55**	−0.62**	−0.70**	−0.59**
	QUA	−0.63**	−0.84**	−0.84**	−0.66**
Fine sand (%)	LIN	−0.45**	−0.35	−0.37*	−0.47**
Clay (%)	LIN	0.30*	−0.17	0.002	0.41*

H – hydrolytic acidity, S – sum of exchangeable basis, T – total capacity of cation adsorption, $V\%$ – degree of base saturation

applied calcisation (Table 2). In many profiles acidity increases mildly with depth. Of the total number of samples, 60% are in the category of very acid soils ($pH_{KCl} \leq 4.5$); in Aoh horizon, 49% of samples have very acid reaction, in Eg 60%, and in the transient, i.e. illuvial horizon 76.7%.

The content of humus in Aoh horizon is below 2% in 47% samples, the content of readily available phosphorus is low in 73% of topsoil samples (≤ 80 mg/kg), and about half of the samples have low contents of K_2O (≤ 120 mg/kg).

The values of cation adsorption capacity and of the composition of adsorbed cations vary depending on pH values, the quantity and composition of organic and mineral colloid particles. Despite their acid reaction, most Stagnosols are rich in base cations. Only the most acid Stagnosols at two sites in West Serbia (Samaila and Klašnić) are dystric.

Exchangeable Al in the studied Stagnosols ranges from 0 to 560.70 mg/kg (Table 2). It increases with depth, especially sharply in the illuvial horizon, with the greatest spatial variation in the surface horizon (coeff. var. = 236%), and less in deeper horizons (coeff. var. Eg = 183%, coeff. var. Btg = 157%).

The method of simple correlation shows that the changes of exchangeable Al are maximally affected by the parameters of soil acidity: active, exchangeable and hydrolytic acidity and by the degree of saturation with base cations (Table 3).

Exchangeable Al has a high negative non-linear correlation with soil pH values (Figure 1). The Al release from the reserves starts mainly at the values of active acidity below 5.5, i.e. exchangeable below 4.5, which agrees with the above-mentioned data from literature. At $pH_{KCl} < 4.0$, the values of Al range from 85.8 to 560.7 mg/kg, and at pH 4–4.5, from 4.7 to 85.8 mg/kg. Evidently, at the values of exchangeable acidity lower than 4.0, Al concentrations are above 100 mg/kg, which is a potential risk for the crops grown on Stagnosol and degraded Cambisol in Serbia (Jakovljević et al. 2001).

For practical purposes, exchangeable Al in Stagnosol can be fairly reliably ($R_{LIN} = -0.894^{**}$) estimated based on pH_{KCl}, taking into account only the very acid soil samples ($pH_{KCl} < 4.5$), by linear equation ($y = 1672.7 − 384.5x$), and better by polynomial equation ($R_{QUE} = -0.952^{**}$; $y = 401.29x^2 − 3561.6x + 7913.5$) (Figure 1). Other soil characteristics have low correlation with the changes of exchangeable Al (Table 2).

To investigate whether the changes of exchangeable Al are better explained by several parameters together, we analysed the mutual effect of pH_{KCl} (x_1), humus (x_2) and % clay (x_3) on exchangeable Al, by the method of multiple linear regression. For all samples, the function is: $y = 516.2 − 11.42x_1^{**} − 0.925x_2 + 0.231x_3^* (R = 0.675^{**})$. Only for very acid samples, the equation is $y = 1634.0 − 37.42x_1^{**} − 0.986x_2 − 0.027x_3 (R = 0.898^{**})$. It can be concluded that the mutual effect of the
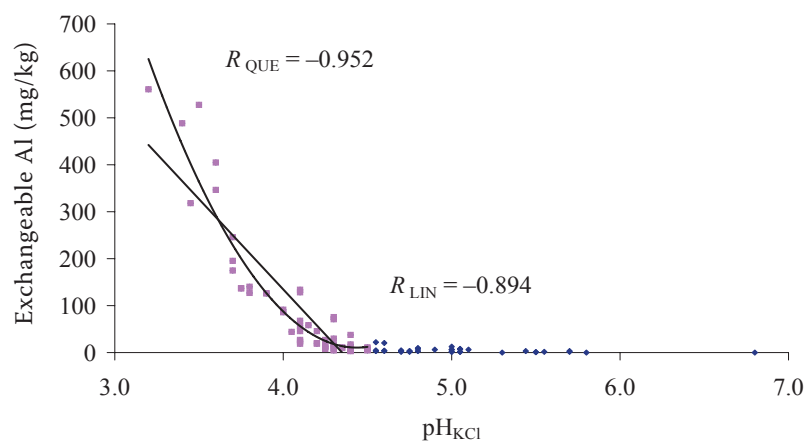
Figure 1. Relation between pH_{KCl} and exchange-able Al

Content of total Al and less available forms of Al and their effect on exchangeable Al

The source of available Al (in the soil solution and exchangeable Al) is Al which is in the composition of aluminosilicate, 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, intensity of the processes of leaching of clay and other colloids, on the destruction process, organic matter content and other soil characteristics.

Total content of Al in Stagnosols ranges from 5.0 to 8.5% (Table 4). Al concentration in most profiles increases with depth, parallel with the increase of clay content. The spatial variation of the values of total Al is relatively low (coeff. var. = 14%), it is somewhat higher in the top horizon.

The concentration of amorphous non-siliceous Al oxides (Al_{oxa}) in Stagnosols varies from 850 to 1950 mg/kg. The content has an increasing trend with depth, which is related to leaching and accumulation of colloid particles. The correlation with clay fraction is medium ($R = 0.56–0.71^{**}$). In the eluvial horizons (Ah and Eg), the values are spatially more uniform, compared to the deeper horizons (coeff. var. = 21%). Amorphous Al accounts for average 1.8% of the total Al and between these two forms in Eg and Btg horizons there is a significant, medium correlation ($R = 0.58^*; 0.66^{**}$). The level of amorphous Al in Stagnosol is within the limits occurring in the soil under pastures in Southeast Australia (470–2160 mg/kg) (McLaughlin et al. 1990), and it is higher than that reported by Jarvis (1986) in different grassland soils in Great Britain (117–742 mg/kg), using the same method.

The values of crystalline Al oxides (Al_{dit}) are relatively low, about two times lower than those in Australian soils (McLaughlin et al. 1990), similar to the values found by Jarvis (1986) in alluvial soil and in the soils on Eocene clay.

As opposed to the previous forms, the values of crystalline Al are changed under the effect of the parameters of acidity: pH_{H_2O} ($R = -0.66^{**}$), pH_{KCl} ($R = -0.53^{**}$), hydrolytic acidity ($R = 0.71^{**}$),

Table 4. Content of total Al, less available forms and exchangeable Al (mg/kg) per horizons (range, mean and standard deviation)

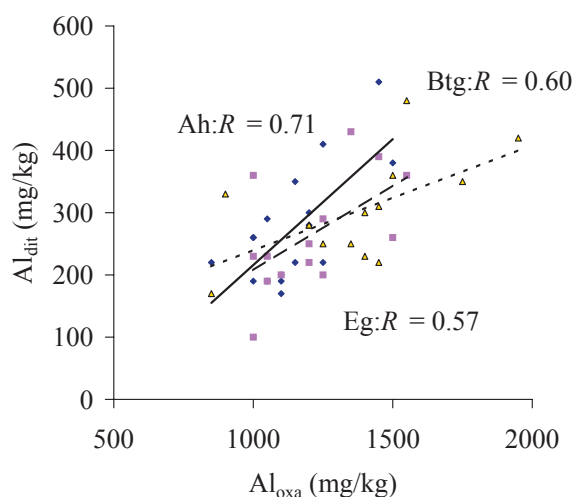| Horizons	Total Al (%)	Al_{oxa} (amorph)	Al_{dit} (crystalline)	Al_{Cu}	Al_{EDTA}	Al_{Cu}-Al_{KCl}	Exchange-able Al_{KCl}
Aoh	5.0–7.5 6.2 ± 0.90	850–1500 1141 ± 16.2	170–510 273 ± 9.3	85–350 154.4 ± 6.39	96–388 166.8 ± 8.12	31.8–176.9 114.5 ± 3.76	0.9–318.2 33.2 ± 8.24
Eg	5.6–8.0 6.7 ± 0.78	1000–1550 1211 ± 19.1	100–430 265 ± 9.09	101–295 143.6 ± 5.57	96–310 156.4 ± 6.58	0.0–172.4 96.2 ± 4.60	3.2–404.8 58.6 ± 11.92
EBtg; Btg	6.2–8.5 7.3 ± 0.72	850–1950 1371 ± 29.2	170–480 302 ± 8.2	102–291 151.7 ± 4.89	97–323 165.8 ± 60.2	0.0–132 80.2 ± 4.54	0.9–560.7 90.8 ± 14.57

Figure 2. Relation between Al_{dit} and Al_{oxa}

◆ Ah
□ Eg
△ Btg
−− Linear (Ah)
— Linear (Eg)
--- Linear (Btg)

$V\%$ ($R = -0.54^{**}$). For this reason, the content of this Al form is more variable per sites in all horizons, and especially in the eluvial horizon (average coeff. var. = 32%).

Average value of crystalline Al is significantly lower than Al_{oxa} (23%) and the correlation is medium (Figure 2). Crystalline Al accounts for 0.4% of the total Al (the percentage is low, especially in Eg horizon), with a very low correlation.

Al extracted with 0.5M $CuCl_2$ after Juo and Kamprath (1979) is Al that forms low and medium stable complexes with organic matter, and according to Jarvis (1986), Al extracted with 0.5M EDTA is in good correlation with organic matter in the soil.

In this research, compared to the extraction with 0.25M EDTA (average content of the determined Al 163 mg/kg), by the extraction with 0.5M $CuCl_2$, the average Al quantity is lower – 150.2 mg/kg, i.e. 92% of Al_{EDTA}, and their correlation is very high ($R = 0.96^{**}$).

The variation of Al values determined by these methods per sites is fairly high (average coeff. var. = 37–42%) and Al concentracion shows good correlation with soil acidity parameters, but not with humus (low correlation).

Al_{Cu} and Al_{EDTA} account for average 12–13% of amorphous Al, the correlation is medium only in topsoil horizon ($R = 0.68^{**}$ and 0.61^{**}), while it is low in deeper horizons. Al obtained by these methods is lower than Al_{dit} (about 50%) and the values show high correlation (average $R = 0.89^{**}$ and 0.94^{**}).

According to McLaughlin et al. (1990), a better parameter for the determination of organic Al is the value obtained if Al_{KCl} is subtracted from Al_{Cu}; that is so-called non-readily exchangeable Al. This is also confirmed in this research, because the correlation between Al_{Cu}-Al_{KCl} and humus is higher, especially in Ah horizon ($R = 0.73$, $y = 38.6x + 33.1$) and eluvial ($R = 0.74$, $y = 36.7x + 42.0$) (Figure 3). The values of Al_{Cu}-Al_{KCl} decrease with
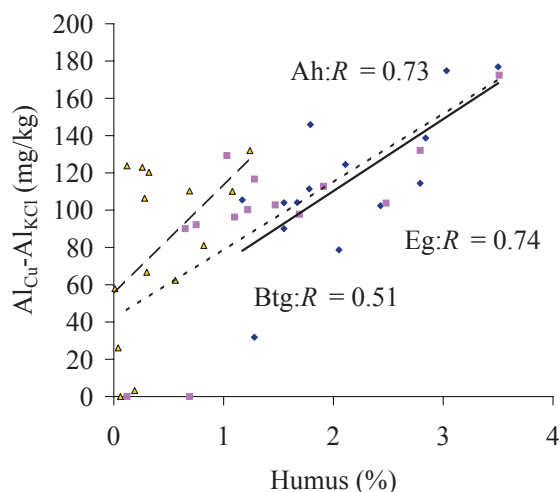
◆ Ah
□ Eg
△ EBtg, Btg
−− Linear (EBtg, Btg)
— Linear (Ah)
--- Linear (Eg)

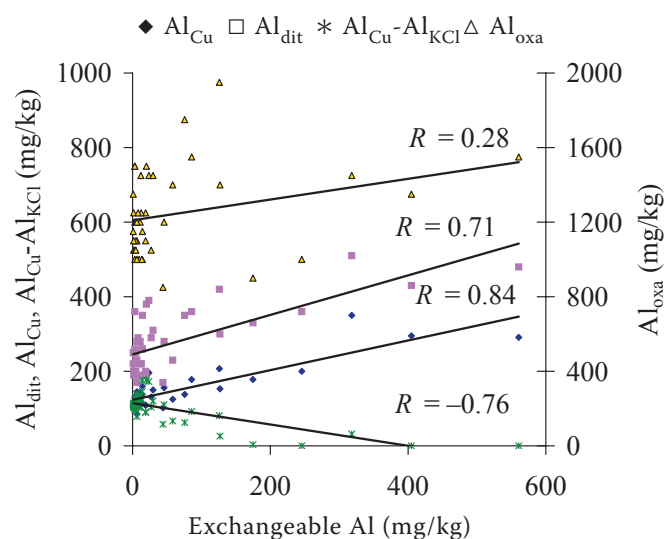Figure 3. Relation between humus and Al_{Cu}-Al_{KCl}

Figure 4. Correlation of exchangeable Al and other Al forms

depth, as the consequence of the decrease of humus (Table 4).

The relation between available Al and less available Al forms is a significant issue, which has not been sufficiently studied. In this research, the values of exchangeable Al are in low correlation with total Al ($R = 0.17$) and amorphous Al ($R = 0.28$) (Figure 4). Alternatively, the correlation with Al_{dit} (crystalline) is medium ($R = 0.71$, $y = 0.53x + 245.1$),

as well as Al_{EDTA} ($R = 0.73$, $y = 0.43x + 134.3$), and the correlation with Al_{Cu} is high ($R = 0.82$, $y = 0.40x + 123.5$). Exchangeable Al is on average 2.5–2.7 times lower than the content of Al_{Cu} and Al_{EDTA}, 4.6 times lower than crystalline Al, and 20 times lower than amorphous Al.

The mutual effect of pH_{KCl} and various forms of Al on the changes of exchangeable Al (Table 5) is calculated by the method of multiple linear regression. Compared to the individual effect of pH_{KCl} ($R = -0.68$), by the inclusion of Al forms, the changes of exchangeable Al are somewhat better described, but the differences are low. Under the constant values of pH, with the increase of Al reserves, the available Al increases (significantly and very significantly, except for Al_{oxa}) – total Al affects the changes of exchangeable Al by 11%, Al_{oxa} by about 6%, Al_{dit} by 31%, Al_{EDTA} by 30% and Al_{Cu} by 49%.

The content of total Al depends on the content of clay and on the mineralogical composition. It is evident that amorphous Al accounts for a small part of the total Al (below 2%). Between these two forms there is a lower correlation in the top horizon than in the deeper horizon, probably because organic Al is a part of amorphous Al in this horizon (also reported by McLaughlin et al. 1990).

Al extracted with 0.5M $CuCl_2$ and 0.25M EDTA shows a low correlation with humus content, in contrast to the results of Juo and Kamprath (1979) and Garcia-Rodeja et al. (2004). The values obtained by the subtraction of Al_{KCl} from Al_{Cu} are more suitable (also reported by McLaughlin et al. 1990), although medium correlation ($R = 0.72$) shows that 0.5M $CuCl_2$ can extract, in addition to exchangeable Al and organic Al, also the other

Table 5. Multiple linear regression (Al exchangeable = dependent variable)

Parameters	Partial regression coefficient	Partial correlation coefficient	Coefficient multiple correlation R
Constant	479.21		0.718**
pH_{KCl}	−144.31	−0.707**	
Al total	32.39	0.326*	
Constant	543.58		0.700**
pH_{KCl}	−134.34	−0.668**	
Al_{oxa}	8.94E-02	0.239	
Constant	270.19		0.791**
pH_{KCl}	−87.54	−0.507**	
Al_{dit}	0.641	0.557**	
Constant	243.08		0.790**
pH_{KCl}	−73.44	−0.413**	
Al_{EDTA}	0.887	0.552**	
Constant	20.70		0.849**
pH_{KCl}	−40.40	−0.261	
Al_{Cu}	1.481	0.697**	

Al forms (such as some hydroxy-Al polymers and interlayered Al); it was also reported by Juo and Kamprath (1979).

The study results show that the content of exchangeable Al in Stagnosols is very variable per sites and profile depths and that its changes are affected predominantly by all forms of soil acidity and V%. Likewise, the content of exchangeable Al increases significantly with the increase of the content of individual less available Al forms – Al_{Cu} (high correlation), Al_{EDTA} and Al_{dit} (crystalline) (medium correlation), but the correlation with amorphous Al is low, for which the previous investigations (Juo and Kamprath 1979) considered that it is a more reactive Al reserve than Al crystalline. The explanation could be the fact that, as already noted, EDTA and $CuCl_2$ can extract the organic Al, Al in interlayers of three-layered minerals and other Al forms comprised in the amorphous Al. Moreover, exchangeable Al makes a significant part of Al reserves which are shown to be more reactive (especially in the deepest horizon): on average 12–22% Al_{dit}, about 22–59% Al_{Cu} and Al_{EDTA}. Furthermore, the question is how much the applied methods for the determination of less available forms of Al are selective (as also reported by Bertsch and Bloom 1996).

The results of our study point to the need of further research of the mobility of Al reserves in different types of acid soils.

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