MONITORING OF ACTUAL STATUS AND DEVELOPMENT OF ACTIVE ALUMINIUM IN SOILS IN SLOVAKIA

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Active aluminium contents in agricultural soils of Slovakia were evaluated in the frame of partial-monitoring system – soil. The soil samples were taken in 5 years regular intervals from depths of 0–0.10 and 0.35–0.45 m. In the dry homogenised samples, soil reaction (pH in CaCl₂), exchangeable cation Ca²⁺ and active Al content by Sokolov (soil is extracted with 1 N KCl and Al is precipitated with NaF) in the samples with pH value lower than 6.0 were measured. Active Al content was in the range 0.10–684.0 mg/kg with the average value 59.28 mg/kg and median value 8.30 mg/kg in the depth 0–0.10 m. In the depth 0.35–0.45 m,

the average value was 59.30 mg/kg and the median value was 9.00 mg/kg. Significant differences in average and median values between the arable land and permanent grassland are determined as a consequence of the relationship between soil quality and its use. The increase in the active aluminium content (between first and last monitoring cycles) was determined in the group Podzols, Lithic Leptosols used as the permanent grassland as well as in the group Cambisols on the crystalline rocks and in the group Fluvisols used as arable land.

Key words: active aluminium content, acidification, soil degradation

Aluminium (Al) is the third most abundant element in the earth crust (Hiradate 2004) as well as a major element in soils. Al total content in soils is depended on the primary and secondary minerals content and it ranged in Slovakian soils from 0.76% to 14.48% in A-horizon and from 0.22% to 13.88% in C-horizon (Čurlík & Šefčík 1999). It is not an essential element, and its impacts on live organisms including man are highly toxic (Horák *et al.* 1995; Kozák & Borůvka 1998). Al toxicity to plants manifests in low acidic and acidic soils. High Al concentrations such as Al³⁺ represent an important growth and yield-limiting factor for crops in acidic soils (pH ≤ 5.5; Makovníková & Kanianska 1996a; Mačuha 1999; Kanianska 2000; Meriño-Gergichevich 2010). Al toxicity results in alterations of the physiological and biochemical processes of plants and consequently their productivity. The decrease in

root growth is one of the initial and most evident symptoms of Al toxicity at micromolar concentrations in plants (Rincón-Zachary 2010), inducing reduced capacity for water and nutrient uptake. It may possibly penetrate plant-root cells, and under certain conditions may be translocated within the plant body in at least four different forms (simple ions, more complex colloidal electrolytes, co-ordinated complex anions and organic compound). Phosphorus uptake is inhibited in plants, as well as growth and branching of root hairs; it negatively affects the ability of the plants for the uptake of Ca, Mg, Mn and Zn. Al is one of the major limiting factors for root growth in acidic subsoil. Al is present in soils in a variety of forms and bound to the soil constituents, particularly onto clay particles and organic matter independent from environmental conditions. Al phytotoxicity depends on its chemical forms. Many

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authors reported that only mobile and exchangeable forms of Al play a significant role in Al toxicity (Mačuha 1999; Hiradate 2004; Makovníková 2005; Meriño-Gergichevich 2010). The solubility of Al increases with the decrease in the soil reaction (Makovníková & Kanianska 1996b; Hiradate 2004; Mrvic *et al.* 2007; Meriño-Gergichevich 2010). Till the boundary pH in $\text{CaCl}_2 = 6$, the dominant Al forms in soil solution are aqua-hydroxo-Al complexes; these include monomeric Al ions forming complexes with OH and/or OH_2 groups, such as $\text{Al}(\text{H}_2\text{O})_6^{3+}$, $\text{Al}(\text{H}_2\text{O})_5(\text{OH})^{2+}$ and $\text{Al}(\text{H}_2\text{O})_4(\text{OH})^+$ (Hiradate 2004; Meriño-Gergichevich 2010). The Al monomeric ions are less phytotoxic than Al_{13} , but more phytotoxic than Al–organic acid complexes as published by Hiradate (2004). The toxic form is cation Al^{3+} ; phytotoxicity, however, also shows ions $\text{Al}(\text{OH})_2^+$, or $\text{Al}(\text{OH})_2^+$, with them Al^{3+} ions are equally present in soil solution (Hue 1986). Most of the Al in soil solution is in the form of compounds with organic substances, whereby the capability of organic ligands to decrease Al phytotoxicity depends on the stability of the complexes (Mládková *et al.* 2004; Makovníková 2005). With increasing pH value, Al ions are changed to insoluble aluminium hydroxide. Al substances are also dissolved in strong alkaline soil reaction and they form negatively loaded tetrahydroxy aluminium ions (Hue 1986).

The active Al content in context with soil reaction is monitored in partial monitoring system – soil – from 1993 year in 5-year cycles in basic monitoring network and yearly in key localities network. The aim of this work was to evaluate the distribution of active Al in the last sampling cycle as well as to compare the active aluminium content determined in all the sampling cycles.

MATERIAL AND METHODS

Status and development of active Al contents in agricultural soils of Slovakia was evaluated in the frame of partial monitoring system – soil (CMS-P), created by basic monitoring network and key monitoring sites (Kobza *et al.* 2009). Monitoring network of CMS-P is created on the basis of ecological principle (polluted as well as unpolluted regions) and represents all the most frequent soil types and sub-

types in Slovakia climate regions. Soil samples were collected from the depths of 0–0.10 and 0.35–0.45 m from agricultural soils (arable land and permanent grassland) in 5-year repetitions (in 1993, 1997, 2002 and 2007 years). Samples were air-dried and passed through 0.002 m sieves. In the samples, soil reaction (exchangeable pH in CaCl_2 potentiometrically (Kolektív 2011)), exchangeable cation Ca^{2+} and active Al content by Sokolov (soil is extracted with 1 N KCl and Al is precipitated with NaF) in the samples with pH value lower than 6.0 (Kolektív 2011)) were measured (115 samples, 62 samples from arable land and 53 samples from permanent grassland). All the methods (soil sampling, chemical and physical procedures) used are described in more detail in the publication unified working methods of soil analysis (Kolektív 2011).

Statistical analysis and evaluation of the results were carried out using the program Statgraphics XV Centurion.

RESULTS AND DISCUSSION

Active Al content was in the range 0.10–684.0 mg/kg with an average value of 59.28 mg/kg and median value of 8.30 mg/kg in the depth 0–0.10 m (Figure 1 – Al status in the year 2007).

Similar values of active Al content were measured in the depth 0.35–0.45 m, the average value was 59.30 mg/kg and the median value was 9.00 mg/kg. High differences between average and median values suggest an abnormal statistical distribution of this parameter. Table 1 shows the statistical distribution of active aluminium content in arable lands and permanent grasslands (actual status in the last sampling cycle – 2007 year).

Significant difference in average and median values between the arable lands and permanent grasslands is a consequence of the relationship between soil quality and its use. On the one hand, it is influenced by the parent substrate, its acidity or alkalinity; on the other hand, especially in the depth of 0–0.10 m the influence of anthropogenic factors such as tillage, fertiliser application, the impact of the emission components of the atmosphere and land utilities is also included. Attention must be given to

high maximum values of active aluminium on arable land, which can significantly inhibit the growth of cultivated crops and subsequently contaminate the nutrient chain.

Negative correlation between active Al content and soil reaction values and between active Al content and exchangeable Ca^{2+} cation content in soil (Table 2) is consistent with the work of various authors (Makovníková & Kanianska 1996b; Makovníková 2002; Hiradate 2004; Kobza *et al.* 2009; Meriño-Gergichevich 2010) and highlights the potential danger of acidification. Mrvic *et al.* (2007) reported similar coefficient of correlation between pH value and active Al content ($r = -0.65$) for Stagnosols in Serbia, whereas Mládková *et al.* (2004) determined a slightly lower coefficient for grassland in the Jizera Mountains region in the Czech Republic. Active Al content is maximally affected by the

parameters of soil acidity, and investigation of other parameters (humus content, fine sand and clay content) show only weak correlation (Mrvic *et al.* 2007).

Active Al content's statistical distribution within profiles of CMS-P according to soil representatives' groups [according to WRB (The World Reference Base for Soil Resources) 2006] in context with pH values and $\text{Al}^{3+}/\text{Ca}^{2+}$ ratio is presented in Table 3 (actual status in the last sampling cycle – 2007 year).

The measured average value of active Al content was from 3.43 mg/kg (Stagnosols used as arable land) to 455.57 mg/kg (group Podzols, Lithic Leptosols used as permanent grassland) in the depth 0–0.10 m. The higher total content of Al in soils developed on the crystalline rocks in comparison to the soil developed on the flysch as published by Čulík & Šefčík (1999) is not reflected in active Al content, which

T a b l e 1

Statistical distribution of active Al in arable lands and permanent grasslands

Depth [m]	Active Al [mg/kg]							
	Arable land				Permanent grassland			
	Average	Median	Min	Max	Average	Median	Min	Max
0–0.10	14.04	7.70	0.10	195.30	109.97	25.60	0.10	684.00
0.35–0.45	28.40	2.70	0.10	488.00	77.78	18.30	0.10	470.00

Figure 1. Active aluminium content (status in the last sampling cycle)

is conditioned not only by Al total content but also by soil reaction. The high differences between average and median values are caused by outlying high values in the evaluated soil groups. The higher content of active aluminium in the subsoil in the case of Cambisols on the acidic crystalline rocks and Stagnosols used as arable land (as indicated by the median) may result in depression root penetration depth as well as in reducing the depth of the root system and thereby increasing water deficit in subsequent crops. Exchangeable cation Ca^{2+} plays a fundamental role in the Al toxicity through Al–Ca interactions

improving physiological and biochemical processes in plants, and it is a useful amendment for correcting Al negative effects on crops growing in acidic soils. It has also been recognised that the ratio of equivalent amounts of cations $\text{Al}^{3+}/\text{Ca}^{2+}$ (Grishina & Baranova 1990; Meriño-Gergichevich 2010) is a good indicator of Al stress in nutrient solutions and may be used to predict acidity effect on plant growth and development. Grishina and Baranova (1990) reported that there is a 50% risk of negative effect on sensitive crops when the $\text{Al}^{3+}/\text{Ca}^{2+}$ ratio in soil is greater than 0.50 and greater than 1.00 for the less sensitive

T a b l e 2

Spearman correlation analysis

	Spearman correlation coefficient					
	Arable land			Permanent grassland		
	Active Al	pH	Ca^{2+}	Active Al	pH	Ca^{2+}
Active Al [mg/kg]	1	–0.77 ⁺⁺	–0.58 ⁺⁺	1	–0.66 ⁺⁺	–0.55 ⁺⁺
pH		1	0.57 ⁺⁺		1	0.52 ⁺⁺
Ca^{2+} [cmol/kg]			1			1

⁺⁺Statistically significant at the level $\alpha = 0.05$

Explanatory notes: 1 – Cambisols on the flysch, 2 – Cambisols on the crystalline rocks, 3 – Luvisols, 4 – Fluvisols, 5 – Mollic Fluvisols, 6 – Stagnosols

Figure 2. Active aluminium content in soil groups used as grassland (1993, 1997, 2002 and 2007 year) in the depth 0–0.10 m

crops (Grishina & Baranova 1990). The Al^{3+}/Ca^{2+} ratio greater than 1.00, which is the important growth and yield-limiting factor for crops, was determined in the groups of soils used as arable land (Cambisols on the crystalline rocks and Cambisols on the flysch and Fluvisols). The influence of exchangeable Ca on active Al content was also confirmed by Mládková *et.al* (2004).

The comparison of active Al content (average and median values) determined in the sampling cycles in arable land and permanent grassland groups is shown in Figures 2 and 3.

The apparent increase in the active aluminium content (between first and last monitoring cycles) was measured in the group Podzols, Lithic Leptosols used as permanent grassland as well as in the

group Cambisols on the crystalline rocks and Fluvisols used as arable land. These results are consistent with the pH value trends during the observed period (Makovníková & Dodok 2012). Comparison of the third and fourth cycle shows a decrease in the active aluminium content in the group Podzols, Lithic Leptosols used as permanent grassland as well as in the case of Fluvisols used as arable land. The average active Al content decreased in the group Podzols, Lithic Leptosols used as permanent grassland and in the groups Cambisols on the flysch and Fluvisols used as arable land. Negative trends, increase in median value, were observed in the case of Cambisols on the flysch, Luvisols and Fluvisols used as arable land.

T a b l e 3

Statistical distribution of active aluminium content in soil representative groups
(in the last sampling cycle)

Soil representative group	Active Al [mg/kg]						
	Depth [m]	Average	Median	Min	Max	pH in $CaCl_2$	Al^{3+}/Ca^{2+}
Podzols, Lithic Leptosols – PG	0–0.10	455.57	482.00	295.00	684.00	3.38	38.73
	0.35–0.45	159.00	138.00	120.00	259.00	4.20	–
Cambisols on the crystalline rocks – PG	0–0.10	38.46	19.40	2.70	182.00	4.68	12.31
	0.35–0.45	61.97	16.70	0.45	357.00	4.82	–
Cambisols on the crystalline rocks – AL	0–0.10	11.27	4.95	0.10	49.50	5.66	3.01
	0.35–0.45	24.90	13.50	0.10	72.90	5.55	–
Cambisols on the flysch – PG	0–0.10	87.28	30.95	0.45	308.00	4.91	25.99
	0.35–0.45	115.71	18.30	0.27	470.00	5.18	–
Cambisols on the flysch – AL	0–0.10	10.67	5.35	0.45	41.90	5.87	2.10
	0.35–0.45	4.10	2.47	0.45	9.49	6.05	–
Stagnosols – PG	0–0.10	12.52	13.00	3.60	30.60	5.41	0.92
	0.35–0.45	36.30	14.45	0.10	194.00	5.28	–
Stagnosols – AL	0–0.10	3.43	0.45	0.10	14.40	5.71	0.33
	0.35–0.45	38.71	0.67	0.10	418.00	5.66	–
Fluvisols – AL	0–0.10	54.34	14.40	4.77	195.00	5.64	5.13
	0.35–0.45	60.45	9.79	0.45	179.00	5.95	–
Luvisols – AL	0–0.10	11.67	11.10	0.10	28.40	6.20	0.63
	0.35–0.45	63.02	4.50	0.10	488.00	6.20	–
Mollic Fluvisols – AL	0–0.10	4.86	3.82	0.10	11.70	5.99	0.26
	0.35–0.45	22.38	4.50	0.10	66.60	6.08	–

AL – arable land; PG – permanent grassland

Explanatory notes: 1 – Podzols and Lithic Leptosols, 2 – Cambisols on the flysch, 3 – Cambisols on the crystalline rocks, 4 – Stagnosols

Figure 3. Active aluminium content in soil groups used as grassland (1993, 1997, 2002 and 2007 year) in the depth 0–0.10 m

CONCLUSIONS

The status of active aluminium content in the last monitoring cycle in agricultural soils of SR was significantly lower in the arable land compared with permanent grassland, which is a consequence of the relationship between soil quality and its use. Attention must be given to high maximum values of active aluminium on arable land, which can significantly inhibit the growth of the cultivated crops. In one of the four evaluated soil groups used as permanent grassland, the median value increased in the last sampling cycle compared with first sapling cycle. On the other hand, in the case of arable land, the median values of active Al content increased in all the evaluated soil groups. It is necessary in the future to pay attention to the arable land with the values of soil reaction in weak acid and the acidic range as well as with a lower quantity and quality of soil organic matter. To overcome the limitations of Al phytotoxicity, Ca amendments are an agronomic practice commonly used to reduce the acidic effect on plant growth and development.

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