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Relationships between exchangeable and water-soluble cations in the forest soil

Związki między wymienną i rozpuszczalną w wodzie formą kationów w glebach leśnych

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Abstract

The aim of this research was to assess the relationships between exchangeable and water-soluble cations in forest soil types. Three dominant soil types were distinguished on studied plots: Haplic Podzol, Dystric Arenosol and Dystric Cambisol. Ca, Mg, K, Na and Al in soil sorption complex and soil water extracts were determined. The differentiation of the ionic composition of soil sorption complex and soil water extracts within a soil type and amongst soil types was presented. The sum of cations in the soil and water extracts was the highest in Dystric Cambisol and the lowest in Haplic Podzol. Ca is a dominant cation in soil and soil water extracts in organic horizon, whilst Al is dominant in mineral soil horizons. The Ca/Al and the base cations to Al (BC/Al) molar ratios increased in the sequence of soils: Haplic Podzol < Dystric Arenosol < Dystric Cambisol. The parent material, soil-forming processes and vegetation cover affected the Ca/Al and BC/Al ratios.

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1. INTRODUCTION

Interactions between the soil and the plant can be described as a feedback. Soil properties affect the quantity and the quality of the vegetation cover, which in turn significantly affects the soil properties, including the development of the soil profile, although the weathering of minerals has a major influence on the development of genetic soil horizons. Lindroos et al. [2003] reported that the weathering of minerals is the main factor shaping the soil profile. The intensity of these processes is determined by the quality of soil organic matter (SOM), the rate of SOM mineralisation and leaching of dissolved organic matter with soil depth.

In acidic soils, the exchange reactions between the soil solution and the exchange site are mainly dominated by element concentration in solution, inputs of acidity, speciation of Al and ionic strength of the soil solution [Matschonat and Vogt 1998; Ross et al. 2008]. Because Al charge is larger than that of base cations, base cations are removed from the soil sorption complex to almost its trace quantities. In consequence, soil solutions are dominated by Al, thus causing a relative and even a real shortage of nutrients and an excessive Al uptake [Ostrowska and Porębska

Streszczenie

Celem pracy było ustalenie związków między kompleksem sorpcyjnym i roztworem glebowym w wybranych typach gleb leśnych. Do analizy wybrano trzy typy gleb: Haplic Podzol, Dystric Arenosol i Dystric Cambisol. Oznaczono Ca, Mg, K, Na i Al w kompleksie sorpcyjnym i w roztworach wodnych gleb. Przedstawiono zróżnicowanie składu jonowego kompleksu sorpcyjnego i roztworów wodnych w poszczególnych poziomach genetycznych danego typu gleby i między analizowanymi typami gleb. Sumaryczna zawartość badanych składników, zarówno w kompleksie sorpcyjnym, jak i roztworach wodnych gleb była największa w glebach Dystric Cambisol, a najmniejsza w Haplic Podzol. Stosunki molowe Ca/Al i BC/Al zwiększają się w szeregu gleb: Haplic Podzol < Haplic Arenosol < Dystric Cambisol. Zależność wskaźników Ca/Al i BC/Al od jakości materiału budującego gleby uwidacznia się przede wszystkim w poziomach C, a wpływ procesów glebotwórczych i jakości pokrywy roślinnej w poziomach głównego korzenia drzew.

2002]. In the case of an excessive Al uptake by plants, although it mainly accumulates in roots, it also moves to aboveground parts and thus enters the trophic chain and may potentially have an adverse effect in the next levels of the chain [Ostrowska et al. 2008].

Many authors deal with the acidification of forest soils and the indicators for assessing this process [Reuss 1983; Cronan and Grigal 1995; Schoenholtz et al. 2000; Blaser et al. 2008; Farr et al. 2009; Mellert and Ewald 2014]. The authors mostly used the indicators based on the basic-to-acidic cations ratio in the soil solution and in the cation-exchange capacity (CEC). A common indicator of soil acidification is the molar Ca/Al ratio, whose values in the soil solution and the plant roots were validated by Cronan and Grigal [1995] in the scale of Al toxicity to plants.

This study focused on the assessment of the impact of soil types on the distribution of exchangeable and water-soluble cations in soil profile and on the determination of the relationships between the soil sorption complex and the soil water extracts. The objectives of the study were to determine

- the differentiation within a soil type in terms of the ionic composition of soil sorption complex and soil water extracts in the individual soil horizons;
- the differentiation amongst the soils in terms of the contents of the cations in the soil and the soil water extract, as well as the relationships between them;
- the differentiation of the Ca/Al and base cations to Al (BC/Al) indicators amongst forest soil types.

2. MATERIAL AND METHODS

The study was conducted on the three research plots: Goleniowska Forest (the PG plot, 53°65'N, 14°76'E), Rajgrodzkie Forest (the LR plot, 53°68'N, 22°67'E) and Borecka Forest (the PB plot, 54°12'N, 22°06'E). All the plots comprised forest complexes with a surface area of about 400–600 ha and they composed a part of much larger forest complexes. On the PG plot, there were a coniferous forest, with Scots pine as a dominant species, and a coniferous-deciduous forest, with Scots pine, Norway spruce and oak. On the LR and the PB plots, there was mainly deciduous-coniferous forest, with oak, beech, hornbeam and Scots pine as a dominant species. On the PB plot, there was also a deciduous forest with hornbeam, oak and Norway spruce.

According to the World Reference Base for Soil Resources [WRB 2006], the following soil types were distinguished: Haplic Podzol on the PG plot, Dystric Arenosol on the LR and PB plots, Dystric Cambisol on the PG and PB plots. The soils in the coniferous and the coniferous-deciduous forest were developed from fluvioglacial or eolian sands, whereas the soils in the deciduous site were

emerged from glacial boulder clays. All soils were moderately to strongly acidic. The selected soil properties are presented in Table 1.

On each plot, 10–12 soils profiles were investigated. Soil samples were taken from the individual horizons down to the depth of the parent rock. All samples had been air-dried and sieved through a 2-mm mesh. Exchangeable base cations (Ca, Mg, K, Na) in 1 M NH₄OAc extracts was determined using the inductively coupled plasma atomic emission spectroscopy (ICP-AES; Varian, VISTA-PRO, Australia). Exchangeable acidity was determined by the titration of 1 M KCl extracts, and exchangeable Al in 1 M KCl extracts by the flame atomic absorption spectroscopy (FAAS) method (AA/AE AAS-30, C.ZEISS JENOPTIC, Germany).

The soil water extracts were prepared by adding Mili-Q water (at the 1:3 or 1:10 mass-to-volume ratio, respectively, for mineral and organic horizons) to soil samples that has been air dried and sieved and then incubating the solutions for 10 days at 25°C. In this way, the so-called simulated soil solutions, that is, soil water extracts, achieved the stability with respect to ion concentration [Ostrowska 1985]. After centrifuging (6,000 rpm.) the water extracts, the contents of Ca, Mg, K, Na and Al were determined by the FAAS method.

The results were presented as the mean values, for the individual horizons of the soils of a given type. Statistical analysis was performed using Statistica 10 [StatSoft 2010]. Mean values and standard deviations (SD), as well as Pearson's correlation coefficients, of the basic parameters were calculated. Level of significance for all analyses was set at $p < 0.05$. Analysis of variance (ANOVA) was used to assess the significant differences between soil types. Number of soil samples (n) for individual soil horizons

Table 1. Base characteristics of studied soils.

Soil type	Horizon	Thickness (cm)	Clay (%)	Silt (%)	pH (H ₂ O)	BS (%)	S-ex	S-ss
		min–max	min–max	min–max	min–max	mean ± SD	mmol _x /kg	mmol _x /kg
Haplic Podzol	O	5–10	-	-	3.6–4.3	39.9 ± 12.8 a	108.7 a	5.01 a
	AE	7–11	2–4	3–5	4.1–4.4	19.9 ± 19.5 a	19.8 a	0.98 a
	E	11–15	1–2	2–3	4.4–4.7	16.9 ± 5.4	11.8	0.69
	Bhs	16–28	0–2	2–7	4.5–5.0	15.8 ± 7.5 a	18.9 b	1.07 b
	BC	16–45	0–1	0–6	4.8–6.0	28.7 ± 6.5 a	6.7 a	0.55 a
	C	< 60–90*	0–1	1–8	5.1–5.5	36.3 ± 4.4 a	5.0 a	0.34 a
Dystric Arenosol	O	3–5	-	-	4.0–4.8	66.1 ± 5.9 b	137.4 b	13.13 b
	A	4–14	3–9	2–15	4.1–4.7	9.6 ± 3.3 a	48.3 b	0.81 a
	Bv	16–35	2–12	3–14	4.7–5.4	24.9 ± 8.3 a	11.7 a	0.45 a
	BvC	20–48	0–12	2–10	5.0–6.0	36.1 ± 15.9 a	12.5 a	0.42 a
	C	< 60–90*	0–9	2–27	5.3–6.5	65.7 ± 24.5 b	11.3 a	0.41 a
Dystric Cambisol	O	1–5	-	-	4.6–5.0	80.0 ± 9.4 b	269.0 c	24.81 c
	A	7–16	4–27	6–39	4.0–5.4	25.3 ± 23.5 a	46.4 b	1.86 b
	Bw	14–38	2–47	8–30	4.6–5.6	32.9 ± 18.6 a	47.7 c	1.06 b
	BwC	22–50	0–61	6–20	5.2–5.8	51.9 ± 17.8 a	58.2 b	2.14 b
	C	< 60–95*	0–53	0–18	5.1–6.0	58.0 ± 24.2 ab	54.8 b	1.21 a

BS, base saturation $(Ca + Mg + K + Na)/(Ca + Mg + K + Na + Al + H)$; S-ex, sum of exchangeable Ca, Mg, K, Na and Al; S-ss, sum of Ca, Mg, K, Na and Al in soil solution; SD, standard deviation; *, soil depth.

Differences in letters indicate differences within soil horizons at the 0.05 probability level.

in studied types of soil (n was from 2 to 9) was small, which could be the reason that, in many cases, despite the large differences between the mean values, there was no statistical significance.

3. RESULTS AND DISCUSSION

The summary content of Ca + Mg + K + Na + Al in the soil (S-ex) and the soil water extract (S-ss) was the largest in the organic horizon and decreased with the soil depth. In the O horizon, the values of these sums increased in the sequence: Haplic Podzol < Dystric Arenosol < Dystric Cambisol (Table 1). In the same sequence, the values of both sums grew in the parent rock.

The ionic composition of soil sorption complex and soil water extract in the individual horizons of the soil types considered is presented in Figure 1. In Haplic Podzol, Ca dominated in the soil sorption complex in the organic horizon (54%) and so did K and Na (28–30% each) in the water extract. In the mineral horizons, Al was the dominant in S-ex and S-ss, with its percentage share falling, respectively, within the ranges 50–80% and 51–72%, depending on the soil horizon (Fig. 1).

Organic horizons of Dystric Arenosol and Dystric Cambisol were saturated by Ca (approximately 70%), while the water extracts were dominated by Ca (36–43%) and K (34–36%). Mineral horizons in these soil types were dominated by Al. The shares of Al in S-ex decreased with the soil depth, whereby in the C horizons, they were less than those of Ca (Fig. 1). The soil water extracts from the mineral horizons of Dystric Arenosol and Dystric Cambisol were characterised by a smaller Al share and a larger Ca share in S-ss than that of Haplic Podzol.

In Haplic Podzol, the Ca-ex and Al-ex contents decreased from the O horizon to the C horizon, except for the Bhs horizon, where the

Al-ex content was greater than that in the adjacent horizons (Table 2), what is a natural result of the podzolisation. Thus, the Ca/Al-ex ratio was the lowest in the Bhs horizon, which subsequently increases to 0.8 in the C horizon (Table 3). In the soil water extracts, the Ca/Al-ss ratio was the lowest in the E horizon.

In Dystric Arenosol, changes in the contents of Ca and Al led to the highest Ca/Al-ex ratio in the O horizon and the lowest in the A horizon, with the values rising with soil depth. In the soil water extracts, the lowest Ca/Al-ss ratio was also noted in the A horizon, as in the deeper lying horizons, the Ca/Al-ss ratios were greater than 1. In general, the Ca/Al-ss values in Dystric Arenosol were higher than those in Haplic Podzol (Table 3). In Dystric Cambisol, the Ca/Al-ex values were higher than those in the other soil types. In the soil water extracts, the Ca/Al-ss value was the highest in the O horizon and the lowest in the Bw horizon (Table 3).

Changes in the Ca/Al-ss and BC/Al-ss values were related to the solubility of ions, measured by the ratio of their content in the soil water extract to their exchangeable content in the soil. In all the horizons of Haplic Podzol, the greatest solubility was demonstrated by Na and K. In Dystric Arenosol, the greatest solubility of K and Na was observed only in the O and A horizons. A greater Al solubility was observed in the O and C horizons of Dystric Arenosol than in the other soil types. In the parent rock of Haplic Podzol, greater Ca and Mg solubility was found than that in the other soil types (Fig. 2), possibly suggesting that these soil was the most impoverished because of the leaching of base cations as a result of soil acidification.

The contents of base cations in the soil water extract were strictly related to their contents in the soil exchange sites, with correlation coefficients within the range 0.83–0.94, except Al, for which $r = 0.20$ (Table 4).

Table 2. Ca and Al concentrations (mean and standard deviation) in the soil (ex) and soil solution (ss) in three soil types.

Soil type	Horizon	n	Ca-ex	Al-ex	Ca-ss	Al-ss
			mmol _e /kg	mmol _e /kg	mmol _e /kg	mmol _e /kg
Haplic Podzol	O	9	61.0 ± 28.1 a	22.4 ± 9.7 a	1.15 ± 0.70 a	0.63 ± 0.31 a
	AE	7	2.1 ± 0.4 a	15.9 ± 6.1 a	0.11 ± 0.09 a	0.61 ± 0.13 a
	E	4	1.8 ± 0.3	8.8 ± 7.3	0.03 ± 0.04	0.51 ± 0.21
	Bhs	9	1.5 ± 0.3 a	16.1 ± 11.5 a	0.13 ± 0.07 a	0.74 ± 0.31 b
	BC	9	1.4 ± 0.4 a	4.3 ± 3.1 a	0.09 ± 0.07 a	0.34 ± 0.30 a
Dystric Arenosol	C	9	1.4 ± 0.3 a	2.6 ± 0.9 a	0.07 ± 0.06 a	0.17 ± 0.11 a
	O	7	95.4 ± 12.6 b	9.4 ± 6.8 a	4.87 ± 1.84 b	1.61 ± 1.09 a
	A	3	3.4 ± 1.3 a	42.6 ± 15.6 b	0.13 ± 0.06 a	0.32 ± 0.26 a
	Bv	7	2.0 ± 0.6 a	7.8 ± 3.1 a	0.14 ± 0.07 a	0.14 ± 0.10 a
	BvC	7	2.5 ± 0.9 a	7.8 ± 9.2 a	0.11 ± 0.05 a	0.15 ± 0.16 a
Dystric Cambisol	C	6	5.7 ± 5.2 a	2.5 ± 2.6 a	0.11 ± 0.05 a	0.13 ± 0.09 a
	O	2	192.3 ± 12.6 c	8.9 ± 1.0 a	10.57 ± 0.30 c	0.82 ± 0.23 a
	A	4	10.9 ± 9.5 a	30.1 ± 19.3 ab	0.57 ± 0.62 a	0.51 ± 0.58 a
	Bw	5	14.0 ± 19.1 a	28.2 ± 19.7 a	0.21 ± 0.23 a	0.38 ± 0.29 ab
	BwC	5	28.7 ± 31.4 a	18.7 ± 19.8 a	0.48 ± 0.53 a	0.60 ± 0.32 a
	C	5	32.5 ± 35.0 a	11.1 ± 14.8 a	0.31 ± 0.36 a	0.25 ± 0.14 a

Differences in letters indicate differences within soil horizons: O, A/AE, Bhs/Bv/Bw, BC/BvC/BwC, C at the 0.05 probability level.

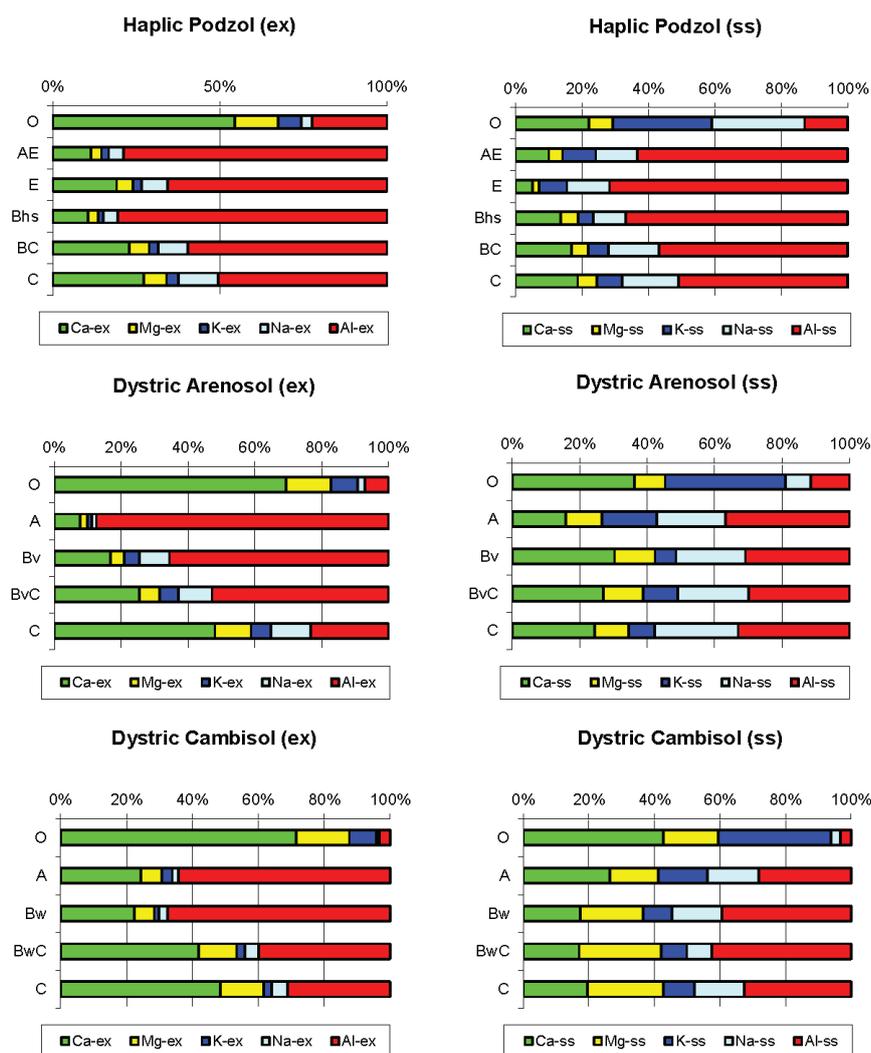


Figure 1. Ionic composition of the soil sorption complex (ex) and soil water extract (ss) for Haplic Podzol, Dystric Arenosol and Dystric Cambisol

Table 3. Molar ratios of Ca/Al, Ca+Mg/Al and base cations (Ca+Mg+K+Na)/Al in soil (ex) and soil solution (ss) for three soil types.

Soil type	Horizon	Ca/Al-ex	Ca/Al-ss	Ca+Mg/Al-ex	Ca+Mg/Al-ss	BC/Al-ex	BC/Al-ss
Haplic Podzol	O	4.1	2.7	5.1	3.6	6.5	17.2
	AE	0.2	0.3	0.3	0.4	0.5	1.5
	E	0.3	0.1	0.4	0.1	0.7	1.0
	Bhs	0.1	0.3	0.2	0.4	0.3	1.0
	BC	0.5	0.4	0.6	0.5	1.1	1.3
	C	0.8	0.6	1.0	0.8	1.9	2.2
Dystric Arenosol	O	15.3	4.5	18.2	5.6	22.8	15.8
	A	0.1	0.6	0.2	1.0	0.2	3.7
	Bv	0.4	1.5	0.5	2.0	1.0	4.4
	BvC	0.5	1.0	0.6	1.5	1.2	3.9
	C	3.4	1.2	4.2	1.7	6.1	4.8
Dystric Cambisol	O	32.4	19.3	39.8	26.9	47.9	60.7
	A	0.5	1.7	0.7	2.5	0.9	5.5
	Bw	0.7	0.8	0.9	1.8	1.1	3.6
	BwC	2.3	1.2	3.0	3.1	3.3	4.6
	C	4.4	1.9	5.6	4.4	6.2	7.3

Table 4. Correlation coefficients between the content of cations in soil (ex) and in soil solution (ss), share of cations in S-ex and S-ss and base saturation (BS) and Ca/Al ratios in soil and soil solution (n = 155).

Cation contents	r	Cation shares	r	Indicators	r
Ca-ex – Ca-ss	0.83	%Ca-ex – %Ca-ss	0.32	BS – Ca/Alex	0.69
Mg-ex – Mg-ss	0.85	%Mg-ex – %Mg-ss	0.36	BS – BC/Alex	0.69
K-ex – K-ss	0.94	%K-ex – %K-ss	0.56	BS – Ca/Alss	0.33
Na-ex – Na-ss	0.93	%Na-ex – %Na-ss	0.25	BS – BC/Alss	0.32
Al-ex – Al-ss	0.20	%Al-ex – %Al-ss	0.47		
S-ex – S-ss	0.87				

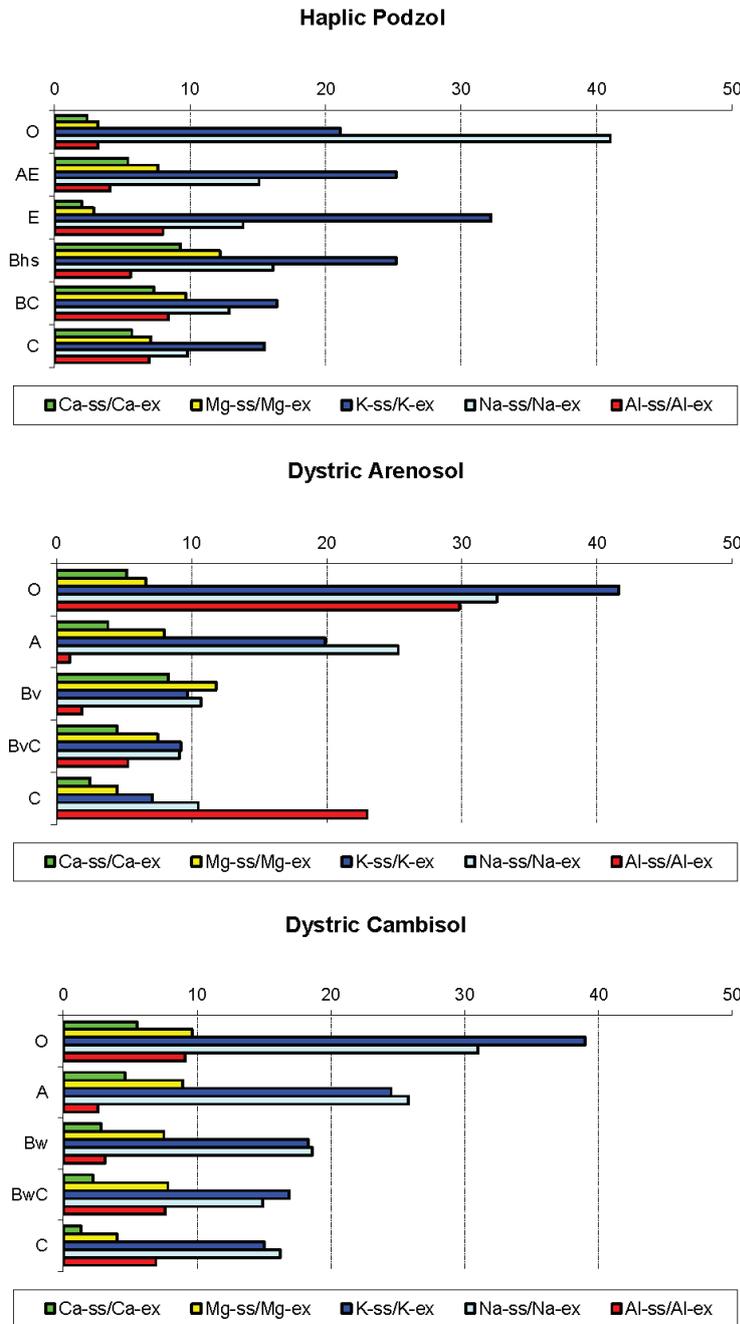


Figure 2. Solubility of Ca, Mg, K, Na and Al expressed as the ratio between their content in the soil water extract (-ss) and their content in the soil (-ex) for Haplic Podzol, Dystric Arenosol and Dystric Cambisol (in %)

The relationships between the contents of the different forms of elements in soil (total content and soluble forms) depend on their native contents and the factors determining the activity of their flows between these forms [Reuss 1983; Matschonat and Vogt 1998; Ostrowska et al. 2006]. The investigated soil types were differentiated by the parent rock. The ionic composition of the soil sorption complex of the soils types indicated that Haplic Podzol was the most acidified soil in the entire profile, with the largest Al share and the smallest Ca share in S-ex in the C horizon. The Al saturation in the soil water extracts of Haplic Podzol was found to be greater than in those of the other soil types. In Dystric Arenosol, the A horizon was the poorest in Ca and Mg content and the richest in Al content. In Dystric Cambisol, the poorest in Ca and the most enriched in Al was the Bw horizon.

The results indicated the soil impoverishment in Ca and Mg and the replacement of these cations by Al ions, particularly in the tree rooting layer. Changes in the soil were the result of cations uptake by plants and soil-forming processes. For example, leaching of base cations from the eluvial horizon and accumulation of Al compounds in the Bhs is characteristic for the podzolisation. The differentiation of the Ca/Al and BC/Al indicators in the soil and the soil water extract within a given soil type and amongst soil types confirmed the soil impoverishment in base cations and a higher Al content in both media. The values of these indicators increased in the sequence: Haplic Podzol < Dystric Arenosol < Dystric Cambisol.

In acidic soils, the exchange reactions between the soil solution and the soil sorption complex are mainly dominated by cation concentration in solution, inputs of acidity, speciation of Al and ionic strength of the soil solution [Ross et al. 2008]. Although the chemistry of soil solution reacts with the seasonal changes, Collignon et al. [2011] assumed that the quantity of exchangeable cations is relatively stable. Grand and Lavkulich [2013] found that the organic, eluvial and illuvial horizons had contrasting distributions of exchangeable cations and showed different relationships between variables, indicating that the main controls on soil chemistry were distinct in each soil horizon. Our results showed explicit differences in the ionic composition of the soil sorption complex between horizons in the soil profile, as well as differentiation between soil types, which is a result of soil processes.

Our results also indicated that the contents of base cations in the soil water extract were closely related to their contents in the soil exchange sites. These relationships were linked to the solubility of elements, that is, the fluxes of the individual elements between

the soil and the soil water, as well as their outflow (uptake, leaching). In turn, the relationships between the ionic composition of the soil sorption complex and the soil water extract, that is, the shares of the particular ions in their sum, were less strict. These relationships were linked not only to the solubility of the particular element but also to the solubility of other elements including in the sum. The intensity of cation leaching depends, among others, on the soil type and vegetation cover. Our earlier study showed that over the past 27 years, the composition of CEC, expressed as series of decreasing shares of cations, showed replacement of Ca with H ions in the Dystric Arenosol; a shift of Ca and Mg towards lower percentages and an increase in the share of H in the Dystric Cambisol and a drastic decrease in the Mg contribution in the Haplic Podzol [Porębska et al. 2008]. This suggests that the ion composition of soil sorption complex may be used as an efficient index for evaluating the acidification process.

According to Graf Pannatier et al. [2004], the soil base saturation (BS) and the BC/Al ratio in soil were related to BC/Al in soil solution. Our research found that the BS was not strongly related to the Ca/Al-ss and BC/Al-ss (Table 4). In turn, the BS showed a relationship with Ca/Al-ex and BC/Al-ex (correlation coefficients 0.69). The values of the Ca/Al varied both in the profile of a given soil type and amongst soil types. Their application can be useful for a quality assessment of soils, among others, the abundance of the pool of base cations available to plants, the degree of acidification and the advancement of the podzolisation process.

4. CONCLUSIONS

Our research indicated

- The differentiation of the ionic composition of soil sorption complex and soil water extracts within a soil type and amongst soil types; in the organic horizon as well as in the parent rock, the sum of Ca + Mg + K + Na + Al in the soil and soil water extract increased in a sequence: Haplic Podzol < Dystric Arenosol < Dystric Cambisol;
- Strong relationships between the soil sorption complex and the soil water extract, expressed by the correlation coefficients (>0.8) between the contents of base cations in both media;
- In both, the soil sorption complex and the soil water extracts of soil horizons, the values of the Ca/Al and BC/Al ratios increased in the sequence: Haplic Podzol < Dystric Arenosol < Dystric Cambisol.

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