

# THE EXCHANGEABLE CATIONS IN ALLUVIAL SOILS FORMED FROM CALCAREOUS SINTER IN THE UNISŁAWSKI BASIN

**Agata Bartkowiak, Jacek Długosz**

**Department of Soil Science and Soil Protection  
University of Technology and Life Sciences Bydgoszcz**

## Abstract

The samples were taken from 7 profiles of alluvial soils formed from varied gytias on calcareous sinter. The research concerned determination of composition of exchangeable cations and basic saturation. In the analysed soils, lithologic discontinuities in the profile structure were observed. The calcareous sinter located in the lower part of the profile caused characteristic water properties and occurrence of gleyic process. The investigated soil profiles were varied in their morphological structure and physicochemical properties. Fluctuations in the content of carbonates, organic matter and non-carbonate mineral substance confirmed the existence of several cycles in the formation of these soils. The basic saturation (S) of the analysed soils ranged between 287.4 and 2238.7 mmol(+) kg<sup>-1</sup>. The highest values were detected in gytia horizons (gyd), and the lowest ones - in gleyic horizons (G). The dominant cation in sorption complex of all horizons was calcium, and its highly differentiated content ranged from 245.3 to 2089.6 mmol(+) kg<sup>-1</sup>. Magnesium was the second most abundant cation in sorption complex. The content of Mg<sup>2+</sup> ranged from 19.4 mmol(+) kg<sup>-1</sup> in clay-lime gytia horizons to 143.5 mmol(+) kg<sup>-1</sup> in lime gytia horizons. The lowest in the content among exchangeable cations in the analysed samples was potassium (0.6-12.9 mmol(+) kg<sup>-1</sup>). Our comparison of the divalent cation content (Ca<sup>2+</sup>, Mg<sup>2+</sup>) and monovalent cation content (Na<sup>+</sup>, K<sup>+</sup>) showed significant instability of the balance between these groups of cations, which was confirmed by a very wide range of the ratio (21.3-333.1) calculated between these two groups of cations. The amount of alkaline cations in the analysed soils followed this order: Ca<sup>2+</sup> > Mg<sup>2+</sup> > Na<sup>+</sup> > K<sup>+</sup>.

Key words: soil, cation capacity, exchangeable cations.

## KATIONY WYMIENNE W GLEBACH ALUWIALNYCH WYTWORZONYCH NA MARTWICY WAPIENNEJ W BASENIE UNISŁAWSKIM

### Abstrakt

W próbkach z 7 profili glebowych gleb aluwialnych, wytworzonych ze zróżnicowanych utworów gytiovych podścielonych martwicą wapienną, badano skład zasadowych kationów wymiennych oraz ich sumy. Analizowane gleby wykazały nieciągłość litologiczną w budowie profilowej i wyraźną trójczłonowość. Leżąca w spągu profilu glebowego martwica wapienna wpłynęła na gospodarkę wodną, powodując występowanie procesu glejowego. Profile glebo- we wykazały duże zróżnicowanie nie tylko w budowie morfologicznej, ale także we właści- wościach fizykochemicznych. Stwierdzone wahania zawartości węglanów, substancji orga- nicznej i niewęglanowej substancji mineralnej, wskazują na występowanie wielu cykli w kształtowaniu badanych gleb. Suma zasadowych kationów wymiennych (S) kształtowała się od 287,4 do 2238,7 mmol(+) kg<sup>-1</sup>. Najwyższą wartość stwierdzono w poziomach gytii detrytusowej (gyd), a najniższą w poziomach glejowych (G). Dominującym kationem wysy- cającym kompleks sorpcyjny był wapń, a jego ilości były zróżnicowane – od 245,3 do 2089,6 mmol(+) kg<sup>-1</sup>. Drugim kationem pod względem ilości występowania w kompleksie sorpcyj- nym był magnez. Zawartość magnezu w badanych glebach wynosiła od 19,4 mmol(+) kg<sup>-1</sup> w poziomach gytii ilasto-wapiennej do 143,5 mmol(+) kg<sup>-1</sup> w poziomach gytii wapiennej. W badanych profilach odnotowano najmniej potasu wymiennego (0,6-12,9 mmol(+) kg<sup>-1</sup>). Analiza zawartości kationów dwuwartościowych (Ca<sup>2+</sup>, Mg<sup>2+</sup>) oraz jednowartościowych (Na<sup>+</sup>, K<sup>+</sup>) wykazała, że w badanych glebach występuje wyraźne zachwianie równowagi między analizowanymi kationami. Oznaką zaburzenia równowagi był szeroki zakres omawianego ilorazu – od 21,3 do 333,1. Szereg ilościowy kationów o charakterze zasadowym w analizo- wanych glebach układał się następująco: Ca<sup>2+</sup> > Mg<sup>2+</sup> > Na<sup>+</sup> > K<sup>+</sup>.

Słowa kluczowe: gleby napływowe, pojemność sorpcyjna, kationy wymienne.

## INTRODUCTION

In Poland, soils formed from alluvial deposits account for a significant part of arable lands under intensive agricultural cultivation. The soils situated in river valleys, mainly those of the Odra and the Vistula, create highly varied soil cover. Although soils of Poland have been largely studied and classified, the above areas still need far more detailed research. One such location is the Unislaw Basin, where soils of a complex structure related to some sediment accumulation cycles occur. They are: calcareous sinter in the floor, covered with a gytia layer and surface alluvial formations with flood history. The flat situation, advantageous water conditions and high nutrient abundance result in high soil fertility and encourage intensive agricultural use. However, there are no detailed and exhaustive data concerning their chemical and mineralogical composition or physicochemical properties.

Sorption properties and the exchangeable cation content play an impor- tant role in the process of leaching nutrient components from soil, thus shaping the effectiveness of fertilization, which is of importance in plant nutrition processes, especially in soils used agriculturally (HARTMAN et al. 1998, SKŁODOWSKI and ZARZYCKA 1995). The aim of the study was to evaluate the composition of cations in sorption complex of some alluvial soils.

## MATERIAL AND METHODS

The research material consisted of 7 soil profiles localized in the Unislaw Basin area, which is an enlargement of the Vistula Valley, 8-9 km wide, situated north of the Fordon Brakeage (Figure 1). The dominant type of landscape, covering half the basin, is floodplain. The research showed lithologic discontinuities in the profile structures and clear trimembrality. The topmost layer consisted of alluvial material, which built the surface and

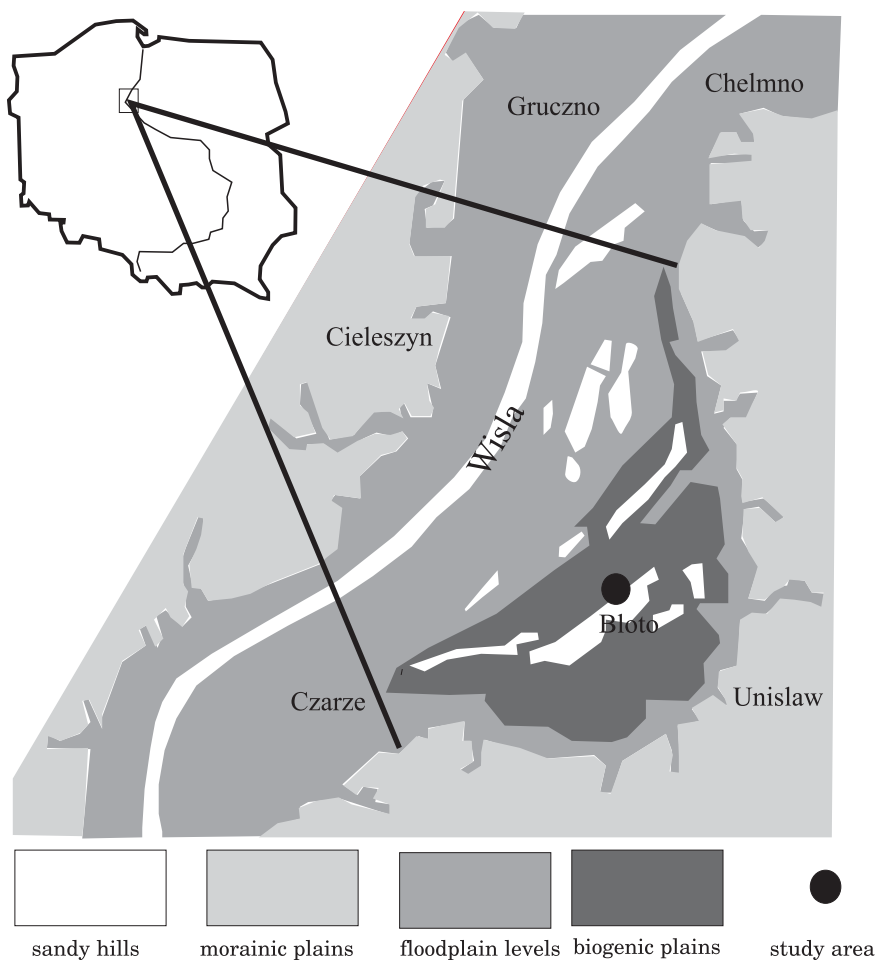


Fig. 1. Map of the analysed area (KORDOWSKI 2003)

subsurface horizons of the soil and showed high homogeneity in the granulometric and mineralogical composition. The alluvial layer was spread on gyttias, differentiated in mineral and organic fractions, which in turn were deposited on the calcareous sinter lying at the depth of 100-110 cm. The calcareous sinter in the investigated area originated from the shore and is the result of the  $\text{CaCO}_3$  sedimentations from the defluent waters from upland around the basin (SKOMPSKI 1961). It is most likely that the sediment of calc-sinter type characterised by very low porosity and very high hardness (SZULC 1983) consisted mainly of calcite and a small addition of quartz (Figure 2). Due to the very low porosity, the sediment is a barrier to water penetration, which becomes stagnant and therefore changes the oxy-reductive conditions. The sedimentation of gyttias on the calcareous sinter occurred in standing water bodies found in this lake-rich region. Both the water level and organic matter content played an important role in this process. Different kinds of the analysed gyttias were ruled out on the basis of MARKOWSKI's triangle (1980), where the principle for the division was the carbonate content and loss during calcination as a measure of the organic matter content.

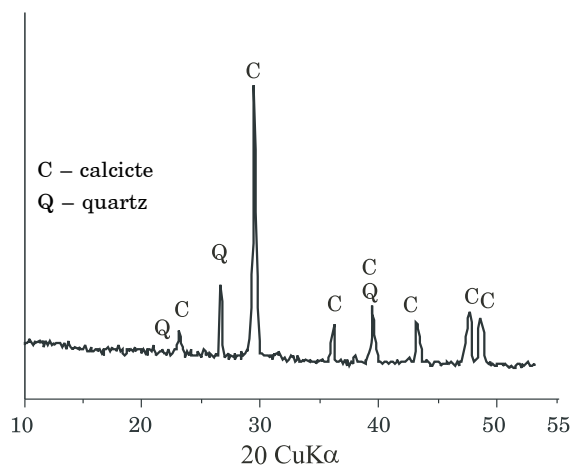


Fig. 2. Diffractogram of calcareous sinter

A great variety of factors affecting the processes of sedimentation and sedimentation led to the differentiation of morphology and physicochemical properties of the formed sediments and soils lying on these sediments. Some basic physicochemical properties are given in Table 1.

Exchangeable cations ( $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{K}^+$ ,  $\text{Na}^+$ ) in the soil samples were assayed in 0.5 M  $\text{NH}_4\text{Cl}$  (pH 8.2). Cation concentrations were determined in a filtrate by atomic absorptive spectroscopy and emissive spectroscopy using a Philips PU 9100x spectrometer (KOCIAŁKOWSKI et al. 1984). Saturation (S) with bases was also calculated.

Table 1

Selected physical and chemical properties of the analysed soils

Horizons	Content						pH 1MKCl	
	Corg (g kg <sup>-1</sup> )		CaCO <sub>3</sub> (%)		fraction < 0002 mm (%)			
	min	max	min	max	min	max	min	max
Surface horizons (Ap)	50.2	80.3	15.9	26.5	35.6	66.5	7.03	7.41
Subsurface horizons (Aa)	5.1	78.0	5.3	69.3	11.3	60.3	7.15	7.30
Gleyic horizons (G)	4.9	6.5	0.6	4.5	6.7	32.9	7.09	7.26
Detritus gytia (gyd)	46.5	342.8	21.0	48.7	n.o	n.o	7.09	7.40
Detritus-calcaric gytia (gydca)	112.9	195.2	36.7	56.5	44.1	71.3	6.88	7.16
Clay gytia (gyi)	1.4	7.9	8.5	12.1	35.0	42.0	7.14	7.41
Clay-calcaric gytia (gyica)	2.2	90.6	20.5	46.8	16.6	81.5	7.12	7.35
Calcaric gytia (gyca)	9.5	59.8	51.6	76.1	12.2	78.4	7.20	7.48

n.o.– not detected

## RESULTS AND DISCUSSION

Large amounts of CaCO<sub>3</sub> found in the analysed soil were determined as being either neutral or slightly alkaline in reaction. It was confirmed pH in 1M KCl ranged from 6.88 to 7.41 (Table 1). This parameter is extremely important as it influences the surface charge of soil colloids, which is reflected in the cation exchangeable capacity (JÓZEFACIUK 1998). Then, some balance between the content of exchangeable cations and the amount of soil mineral weathering products in soil solution is established in the soil (CRABTREE 1986).

Because of the high calcium carbonate content and a small share of absorbed acid cations (H<sup>+</sup> and Al<sup>3+</sup>), the basic saturation of the analysed soils was similar to the total cations exchangeable capacity. The highest basic saturation (S) values (2238.7 mmol (+) kg<sup>-1</sup>) were found in the detritus gytia horizons (gyd) enriched with calcium carbonate, while the smallest ones (287.4 mmol (+) kg<sup>-1</sup>) were assayed in the gleyic horizons (G) (Table 2). The research showed significant differentiation of the bases saturation (S) within the alluvial formation consisting of the surface (Ap) and subsurface (Aa) horizons, where S values ranged from 401.1 to 1175.4 mmol (+) kg<sup>-1</sup>, whereas in the Ap horizons the S variability was lower (Table 2). The high-

Table 2

Exchangeable cation content, basic saturation and ratios between cations in the analysed soils

Horizons	Exchangeable cation content mmol(+) kg <sup>-1</sup>												BS*		Ca		Na		Ca+Mg			
	Ca			Mg			K			Na			mmol(+) kg <sup>-1</sup>		Mg		K+Na					
	min	max		min	max		min	max		min	max		min	max	min	max	min	max				
Surface horizons (Ap)	640.9	1029.9		52.0	118.2		2.1	7.6		3.5	19.7		698.5	1175.4		12.3	8.7		1.7	2.6	123.7	145.5
Subsurface horizons (Aa)	362.7	912.7		34.2	117.9		1.0	4.6		3.2	12.5		401.1	1047.7		10.6	7.7		3.2	2.7	94.5	60.3
Gleyic horizons (G)	245.3	439.3		29.2	63.3		3.3	5.6		9.6	11.8		287.4	520.0		8.4	6.9		2.9	2.1	21.3	28.9
Detritus gytia (gyd)	640.6	2089.6		42.3	142.4		0.6	2.0		4.3	4.7		687.8	2238.7		15.1	14.7		7.2	2.4	139.4	333.1
Detritus-calcaric gytia (gydea)	862.8	982.4		83.7	88.1		3.0	4.0		12.0	12.2		961.5	1086.7		10.3	11.2		4.0	3.1	63.1	66.1
Clay gytia (gyi)	450.6	498.6		42.2	45.5		3.6	5.6		8.4	10.2		504.8	550.3		10.6	11.0		2.3	1.8	41.1	34.4
Clay-calcaric gytia (gyica)	362.7	1151.4		19.4	94.3		0.8	12.9		3.8	21.5		386.7	1280.1		18.7	12.2		4.8	1.7	83.1	36.2
Calcaric gytia (gyca)	474.3	685.7		31.5	143.5		1.2	10.5		6.7	12.4		513.7	852.1		15.1	4.8		5.6	1.2	64.0	36.2

\*BS – basic saturation

est S value was determined in the detritus gytia ( $2238.7 \text{ mmol (+) kg}^{-1}$ ), while in clay-lime and detritus-lime the S values were lower ( $1280.1 \text{ mmol (+) kg}^{-1}$  and  $1086.7 \text{ mmol (+) kg}^{-1}$ , respectively). The lowest saturation with bases (S) was found in the gytia-clay horizons (Table 2). The investigation showed that the lower the organic matter content, the lower the bases saturation (S) values. Similar regularity for many post-bog soils was also reported by PIAŚCIK et al. (1997) and ŁACHACZ (2001).

Calcium was the dominant cation in the sorption complex of all the horizons, which is characteristic for soils of alkaline reaction. The soil content of Ca ranged within  $245.3\text{-}2089.6 \text{ mmol (+) kg}^{-1}$ . The surface horizons were characterised by the Ca content fluctuating between  $640.9$  and  $1029.9 \text{ mmol (+) kg}^{-1}$ , while in the subsurface ones the range was  $362.7\text{-}912.7 \text{ mmol (+) kg}^{-1}$ . When comparing specific kinds of gytia, no significant differences in Ca saturation of the sorption complex were found, except the detritus gytia in profile 5, where  $\text{Ca}^{2+}$  ion content reached the value of  $2089.6 \text{ mmol (+) kg}^{-1}$ . The lowest amounts of calcium ions were determined in the gleyic horizons, where likewise the smallest amounts of the ions ( $245.3 \text{ mmol (+) kg}^{-1}$ ) were assayed. Despite such considerable  $\text{Ca}^{2+}$  differentiation, its contribution in the sorption complex was found to be in a narrow range of  $79.7\text{-}94.1\%$  (Figure 3). The  $\text{Ca}^{2+}$  ion concentrations were lower than the content found by ORZECZOWSKI et al. (2005) in their studies of sorption characteristics of alluvial soil in Żuławy Wiślane.

Magnesium was the second in the sequence of the abundance of cations in the sorption complex. The content of  $\text{Mg}^{2+}$  ranged from  $19.4$  in the clay-lime gytia horizons to  $143.5$  in the lime gytia horizons. The contribution

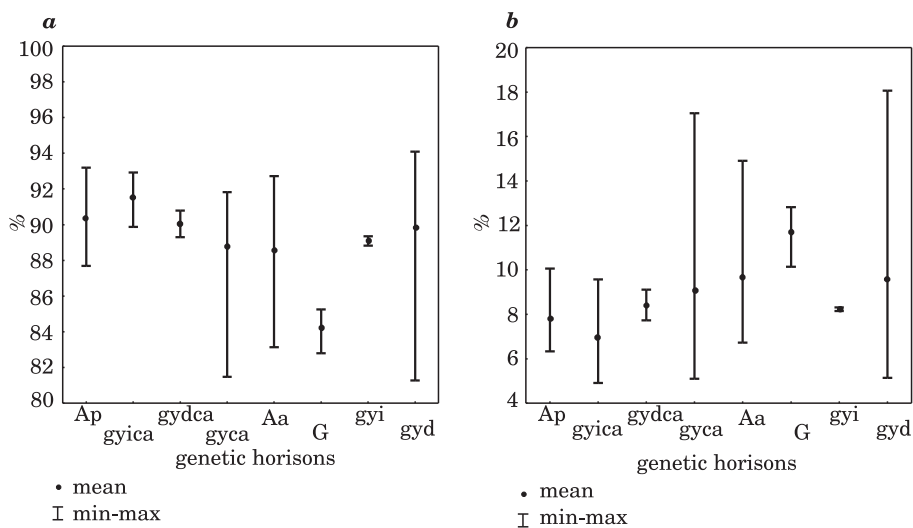


Fig. 3. Content of  $\text{Ca}^{2+}$  (a) and  $\text{Mg}^{2+}$  (b) in basic saturation (BS) in the analysed soils

of  $Mg^{2+}$  to the base saturation (S) values ranged from 4.9 to 19.4%. The base saturation analysis of the surface horizons showed that the  $Mg^{2+}$  ion content fluctuated between 52.0 mmol (+)  $kg^{-1}$  and 118.2 mmol (+)  $kg^{-1}$ , and their participation in the base saturation reached 6.3% and 10.1 %, respectively. According to the literature (NEMETH et al. 1970, LIPIŃSKI, BEDNAREK 1998, RUTKOWSKA et al. 2006), the concentration of calcium and magnesium in soil solution was observed along with an increase of particles  $<0.02$  content, which was attributed to a higher amount of clay minerals which contain these elements.

Exchangeable potassium occurred in the examined profiles in small amounts (from 0.6 mmol (+)  $kg^{-1}$  to 12.9 mmol (+)  $kg^{-1}$ ). The most rich in potassium were the levels of clay-lime and lime gytia, where the  $K^+$  content was 1.9 mmol (+)  $kg^{-1}$  and 10.5 mmol (+)  $kg^{-1}$ , respectively. In the Ap horizons the  $K^+$  affluence formed at the level of 2.1 to 7.6 mmol (+)  $kg^{-1}$ , what accounted for 0.2-0.7% of the base saturation. One should stated that most of all potassium ions were noted in the horizons which were enriched with organic matter, what may be the effect of biological accumulation of the component (ZASOŃSKI, SKIBA 1988). Similarly, a low potassium content was found by LASKOWSKI and SZOZDA (1985) in the alluvial soils along Odra.

The  $Na^+$  ion content was lower than that of  $K^+$  and reached 3.5 mmol (+)  $kg^{-1}$  in the Ap horizons and 21.5 mmol (+)  $kg^{-1}$  in the clay-lime gytia horizons. Our analyses of the arable horizons showed that the  $Na^+$  ion concentrations ranged between 3.5 mmol (+)  $kg^{-1}$  and 19.7 mmol (+)  $kg^{-1}$ , which corresponded to 0.2% and 4.5 % of the total content of these ions. Similarly, SAPEK (1979) found that calcium is the basic ion saturating the exchangeable complex of organic soils. It may account for 65-100% of the total calcium content, while the respective values are lower for magnesium (23-100%), potassium (16-66%) and sodium (52-84%).

The calcium to magnesium ion concentration ratio calculated for the analysed soils was rather narrow and varied from 8.4 to 18.7. A somewhat different picture appeared in the case of the quotient of monovalent ions ( $Na^+/K^+$ ), which was lower and ranged 1.2-7.2 (Table 2).

Our analysis of divalent and monovalent cation content showed that the balance between these groups of cations in the investigated soils was significantly unstable, which is bad for plant nutrition. The indication of some disturbance in the balance of cations is a very wide range of the ratio (333.1). A wide range of the analysed quotient (from 21.3 to 333.1) should be emphasized. The lowest value of the quotient was calculated for the gleyic horizons, while the highest one – for the detritus gytia horizons.



## CONCLUSIONS

1. The composition of cations saturating the exchangeable complex was mostly influenced by calcareous sinter, consisted mainly of calcite. Calcium was the dominating cation, while the potassium content was relatively low.

2. High differentiation of the absorbed exchangeable cations was probably due to a diverse exchangeable complex capacity resulting from the organic fraction content.

3. A very wide range of the divalent to monovalent cation ratio might lead to deficiency of plant-available potassium and sodium.

4. As regards the specific saturation of exchangeable complex with alkaline cations, the analysed soil requires application of physiologically acidic fertilizers.

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