

CATION EXCHANGE CAPACITY OF CLAY RICH SOILS IN RELATION  
TO MINERALOGICAL COMPOSITION AND ORGANIC MATTER  
CONTENT

*H. Dąbkowska-Naskręt, H. Jaworska, M. Kobierski*

Department of Soil Science, University of Technology and Agriculture  
Bernardyńska 6/8, 85-029 Bydgoszcz, Poland

**A b s t r a c t.** Contribution of clay mineral phase ( $<2 \mu\text{m}$ ) and organic matter to the cation exchange capacity (CEC) of two clayey soils (gleytic black earths from Gniew) was investigated. The XRD analysis showed dominance of illite and mixed layer illite/smectite as well as the presence of smectite, chlorite and trace of kaolinite in the clay fraction of studied soils. CEC of the soils ranged between 22.08-32.64  $\text{cmol}(+)/\text{kg}$ . After removal of organic matter with 30%  $\text{H}_2\text{O}_2$ , CEC the above values decreased significantly. However, the CEC of organic and inorganic components is not an additive. This may be explained by the formation of organo-mineral complexes, which might lower the CEC of the soil as a whole.

**K e y w o r d s:** cation exchange capacity, clay fraction, organic matter.

INTRODUCTION

Contribution of particulate soil components: organic matter, clay, free iron, manganese and aluminium oxides in the cation exchange capacity of the whole soil is difficult to evaluate. It is recognised that most of the capacity for cation exchange is related to clay minerals and soil organic matter [5,13]. However, in order to understand the phenomenon of cation exchange, it is necessary to learn quantitative data concerning the relative importance of inorganic and organic "active" (colloidal) phase in the cation retention by the soil.

The objective of the investigations reported here was to estimate contribution of mineral clay fraction and organic matter in the cation exchange capacity of two soils, rich in organic matter, formed from glacial clay material in relation to the mineralogical composition of the mineral phase.

## MATERIALS AND METHODS

Soils samples from two sites near Gniew were taken. Soils from each genetic horizon were sampled. After drying and sieving through 1 mm sieve, the following analyses were made using standard methods: particle size analysis according to Bouyoucos-Casagrande, organic C by wet oxidation with dichromate and back titration with 0.5 M  $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$ . Soil pH was measured in the supernatant of a 1:2.5 soil /deionized water suspension after a 1-h equilibration period.

Samples for mineralogical analysis were pre-treated with 30%  $\text{H}_2\text{O}_2$  adjusted to pH5 with 1 M NaOAc to remove organic matter and with sodium dithionite-citrate-bicarbonate to remove Fe-oxides. Oriented mounts for X-ray diffraction were prepared by depositing of clay ( $<2 \mu\text{m}$ ) suspension on glass slides.

Diffraction patterns were obtained from Mg-saturated, ethylene glycol solvated samples and from K-saturated samples with no heat treatment and after 4 hrs heating  $550^\circ\text{C}$ . Samples were scanned with  $\text{CuK}\alpha$  radiation using a HZG-4 X-ray instrument (step size  $2^\circ 2\theta$ , counting time 4 s).

Cation exchange capacity (CEC) was determined with  $\text{BaCl}_2$  according to Gillmann after Stuart and Viickers [9].

The CEC of the natural soils samples as well as CEC of the modified samples, after organic matter removal were determined. To remove organic matter soils were digested in the water bath with 30%  $\text{H}_2\text{O}_2$  according to Lavkulich and Wiens [6]. All the analyses were made in triplicate; only mean values are presented.

## RESULTS AND DISCUSSION

Soils taken for investigation are rich in clay fraction (30-71%) with the pH range 7.09-7.94 in water and between 6.59 and 7.40 in KCl. In each soil horizon, presence of  $\text{CaCO}_3$  (0.1-17.5%) was detected. The A horizon, (0-85 cm thick), rich in organic matter with the content of organic C in the range 1.90-3.11% is also very characteristic (Table 1).

Among exchangeable cations, Ca dominates (Table 2). The highest exchangeable Ca values were measured in the organic surface horizons.

Mg exceed K and Na in all the analysed horizons. A relatively high content of exchangeable Na in the studied black earths is very unusual.

Cation exchange capacity of the natural soil samples ranged between 22.08 and 32.64  $\text{cmol}(+)/\text{kg}$ , which is only slightly higher than cation exchange capacity of the

**Table 1.** Physical and chemical properties of analyzed soils

Pedon No.	Horizon	Depth (cm)	pH		CaCO <sub>3</sub>	C-org.	Content of fraction (%)			
			H <sub>2</sub> O	KCl			1.0-0.1	0.1-0.02	<0.02	<0.002
						(%)	(mm)			
Gniew I	Apg	0-30	7.31	6.93	0.9	2.96	19	21	60	40
	Aag	30-85	7.58	6.69	0.1	1.98	21	26	53	39
	C1cagg	85-115	7.90	7.11	15.1	-	7	11	82	60
	C2cagg	115-150	7.89	7.14	17.4	-	4	10	86	60
	Gca	150-170	7.94	7.14	14.2	-	2	3	95	61
Gniew II	Apg	0-30	7.09	6.59	1.9	3.11	23	20	47	30
	Aag	30-80	7.23	6.97	1.3	1.9	4	32	64	39
	C1cagg	80-104	7.74	7.40	16.8	-	3	19	78	38
	C2cagg	104-130	7.75	7.01	17.5	-	1	8	91	71
	Gca	130-150	7.64	7.06	16.2	-	0	2	98	66

**Table 2.** Exchangeable cations, total cation exchange capacity of natural soils and total cation exchange capacity of modified samples after removal of organic matter

Pe-don No.	Horizon	Depth (cm)	Ca <sup>++</sup>	Mg <sup>++</sup>	K <sup>+</sup>	Na <sup>+</sup>	H <sup>+</sup>	CEC	CEC <sub>t</sub> in modified samples
			(cmol(+)/kg)						
Gniew I	Apg	0-30	20.51	1.92	1.03	1.35	0.37	25.18	21.31
	Aag	30-85	15.06	4.31	0.92	1.36	0.45	21.10	14.64
	C1cagg	85-115	15.15	4.33	0.89	1.73	0.90	23.00	-
	C2cagg	115-150	15.47	4.74	1.11	1.07	0.37	22.76	-
	Gca	150-170	14.57	4.52	1.32	1.43	0.30	22.14	-
Gniew II	Apg	0-30	16.88	2.01	1.06	2.12	0.67	22.74	19.12
	Aag	30-80	22.43	3.09	0.95	1.47	0.82	28.76	17.26
	C1cagg	80-104	16.77	1.77	0.24	0.74	0.30	19.82	-
	C2cagg	104-130	23.62	3.37	1.02	1.46	0.60	30.07	-
	Gca	130-150	16.19	3.04	1.19	1.52	1.20	23.14	-

CEC - cation exchange capacity.

parent rock material (Table 2). Thus, the presence of organic matter does not influence cation sorption capacity of the soils rich in clay mineral fraction too much.

Such weak impact of organic matter on the soil properties may be caused by the high amounts of clay rich in illite, smectite and illite/smectites. In all other horizons the CEC values are usually a bit lower and ranged between 22.56 and 32.64 cmol(+)/kg.

Similarity in cation exchange capacity is caused by small variation in the mineralogical composition of soil clay fraction (Table 3). The dominant clay minerals are illite and mixed layer illite/smectite. In the gleyic horizon, small amounts

**Table 3.** The relative abundance of clay minerals in clay fraction of analyzed soils

Pedon No.	Horizon	I	I/S	I/Ch	Ch	Ch/S	S	K
Gniew I	Apg	+++	++	+	tr	++	tr	+
	Aag	+++	+	+	+	++	tr	+
	C1cagg	+++	+	+	+	++	+	+
	C2cagg	+++	++	+	tr	+	++	+
	G1ca	+++	++	+	tr	+	++	+
Gniew II	Apg	+++	++	+	tr	++	tr	+
	Aag	+++	++	+	tr	++	tr	+
	C1cagg	+++	++	+	tr	++	tr	+
	C2cagg	+++	++	+	tr	++	tr	+
	G1ca	+++	++	+	tr	++	+	+
	G2ca	+++	++	+	tr	+	++	+

Mineral contents: + small; ++medium; +++ high; tr - traces. Minerals: I-illite; S-smectite; Ch-chlorite; K-kaolinite; I/S-illite/smectite; I/Ch-illite/chlorite; Ch/S-chlorite/smectite.

of smectite and pedogenic chlorite were identified. Kaolinite occurred as accessory mineral in all the samples and its content does not exceed 5%. Predominance of illite minerals in the surface horizons is very characteristic. This part of the soil profile is “enriched” in this mineral when compared to the amounts of illite and smectite in the subsurface horizons. Such a distribution of minerals maybe caused by the aggravation process of smectite and the formation of illite minerals due to intensive, long-time K-fertilisation of these soils. The fixation of potassium by smectite layers in arable soils, described as an illitisation process, is proved by other authors [1,3].

Such a distribution of clay minerals within the soil profile with dominance of the illitic phase, with lower CEC in the surface horizon and relative high amounts of smectite in the parent material may also explain small differences between CEC of organogenic and mineral horizons in the studied soils. After removal of organic matter, CEC decreased and were in the range 14.64-21.31 cmol(+)/kg. Lower amount of CEC after treatment was attributed to destruction of organic matter. A decrease of the CEC values was relatively small and not related to the content of organic matter. Organic matter is usually considered to be a soil component with the highest contribution in the cation exchange capacity [4,8]. In the studied soils, the mineral phase is equally important. Several investigations indicate that the CEC of organic and inorganic components is not additive. Organic matter may coat inorganic surfaces making the CEC level lower than predicted [8,11].

Interaction between organic matter and clay in the studied soils yielded a synergistic effect on the surface charge. Such a situation may have even increased

CEC after organic matter removal due to unblocking of the active surface centre on colloidal particles [10]. Interaction between organic and inorganic components are controlled largely by the mineralogy of the soil [10].

It is also possible that destruction of organic matter with 30% H<sub>2</sub>O<sub>2</sub> is not complete. Organic matter forms complexes with clay. They are resistant to oxidation by peroxide [7]. In such a situation, modified samples still contain organic matter which influences CEC and makes its level high, even after H<sub>2</sub>O<sub>2</sub> destruction.

In the present study, calculation of CEC of organic matter was done according to the hypothesis of Turpalt *et al.* [12]. The calculated CEC of organic matter ranged between 26.0 and 35.0 cmol(+)/kg (Table 4). These values are rather low as compared to Turpalt *et. al* [12] report for a forest soils in France. However, the estimated CEC of organic matter in the studied black earths are difficult to compare with other reports in literature due to different methodology and composition of soil samples. The results suggest that the contribution of organic matter and mineral clay fraction are comparable in the studied black earths.

**Table 4.** Calculated CEC of organic matter according to Turpalt *et al.* [12]\*

Pedon No.	Horizon	CEC of organic matter (cmol(+)/kg)
Gniew I	Apg	29.0
	Aag	35.0
Gniew II	Apg	26.0
	Aag	28.0

\*calculation not shown.

## CONCLUSIONS

The present study showed that contribution of clay and organic matter in CEC is difficult to evaluate. It is assumed, however, that clay contribution is quite high, comparable to organic matter due to the mineralogical composition of colloidal mineral phase in the studied soils rich in clay. Although organic matter is usually considered a soil component which the highest contribution in the exchange capacity, it was not confirmed in this study.

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