

## Nota

# QUANTIFICATION OF PERMANENT AND VARIABLE CHARGES IN REFERENCE SOILS OF THE STATE OF PERNAMBUCO, BRAZIL<sup>(1)</sup>

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### SUMMARY

The electrical charges in soil particles are divided into structural or permanent charges and variable charges. Permanent charges develop on the soil particle surface by isomorphic substitution. Variable charges arise from dissociation and association of protons ( $H^+$ ), protonation or deprotonation, and specific adsorption of cations and anions. The aim of this study was to quantify the permanent charges and variable charges of Reference Soils of the State of Pernambuco, Brazil. To do so, 24 subsurface profiles from different regions (nine in the Zona da Mata, eight in the Agreste, and seven in the Sertão) were sampled, representing approximately 80 % of the total area of the state. Measurements were performed using cesium chloride solution. Determination was made of the permanent charges and the charges in regard to the hydroxyl functional groups through selective ion exchange of  $Cs^+$  by  $Li^+$  and  $Cs^+$  by  $NH_4^+$ , respectively. All the soils analyzed exhibited variable cation exchange capacity, with proportions from 0.16 to 0.60 and an average of 0.40 when related to total cation exchange capacity.

**Index terms:** clays, cation exchange capacity, structural charges, pH dependent charges.

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<sup>(1)</sup> Part of the Master Dissertation in Soil Science and Plant Nutrition of the first author, University of Viçosa - UFV. Received for publication on September 13, 2013 and approved on May 16, 2014.

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**RESUMO: QUANTIFICAÇÃO DE CARGAS PERMANENTES E VARIÁVEIS EM SOLOS DE REFERÊNCIA DO ESTADO DE PERNAMBUCO, BRASIL**

*As cargas elétricas nas partículas dos solos são divididas em estruturais ou permanentes e variáveis. As primeiras desenvolvem-se na superfície da partícula do solo por substituição isomórfica; as segundas, no entanto, evidenciam-se por meio de dissociação e associação de prótons ( $H^+$ ), protonação ou desprotonação e adsorção específica de cátions e ânions. O objetivo deste trabalho foi quantificar as cargas permanentes e as variáveis, em solos de referência do Estado de Pernambuco. Para atingir os objetivos, foram retiradas amostras subsuperficiais de 24 perfis em diferentes regiões (nove da Zona da Mata, oito do Agreste e sete do Sertão), que representam aproximadamente 80 % da área total desse Estado. As determinações realizadas, utilizando solução de cloreto de cézio, permitiram quantificar as cargas permanentes e as referentes aos grupos funcionais hidroxila, por meio da troca iônica seletiva de  $Cs^+$  por  $Li^+$  e de  $Cs^+$  por  $NH_4^+$ , respectivamente. Todos os solos analisados apresentaram capacidade de troca catiônica variável, com proporções no intervalo de 0,16 a 0,60 e média de 0,40, quando relacionada com a capacidade de troca catiônica total.*

*Termos de indexação: argilas, capacidade de troca catiônica, cargas estruturais, cargas dependentes do pH.*

## INTRODUCTION

The study of electric charges in clays is important for an understanding of various physicochemical phenomena in the soil because most electrochemical reactions take place at the surface of these clay particles. This analysis is also important for interpreting the results of soil dispersion in response to the use of different sodic solutions in soil particle-size analysis.

Electric charges of soil mineral particles are divided into structural or permanent charges and variable charges. Permanent charges develop on the soil particle surface through isomorphic substitution. Variable charges, in contrast, result from proton ( $H^+$ ) dissociation and association, protonation or deprotonation, and specific adsorption of cations and anions.

Permanent charges originate from isomorphic ionic substitution in the mineral structure and are manifested at any soil pH (Sposito, 2008). This charge is inherent to the mineral and can also be called a structural charge. Isomorphic ionic substitutions, also referred to as isomorphic substitutions, occur in primary minerals, in their magmatic differentiation, and in secondary minerals in their formation in the soil or through inheritance from primary minerals.

Permanent charges can be either negative or positive. Nevertheless, due to the ionic dimensions, a lower valence cation usually substitutes a higher valence one ( $Al^{3+}$  replacing  $Si^{4+}$ ,  $Mg^{2+}$  replacing  $Al^{3+}$ , etc.), which causes a positive charge deficit in the crystalline structure and leads to the emergence of negative charges at the surface of soil mineral particles.

Data on permanent electric charges, which constitute the surface charge of soil particles, are

extremely important for an understanding and prediction of the fate of chemical elements in the soil. The 2:1-type clay minerals have predominantly permanent charges. The presence of structural electric charges in minerals is essential for maintaining nutrients in the soil since they appear at any pH value, unlike variable-charge minerals, which mostly have a high zero point charge (ZPC), thus originating a net positive charge at a pH considered optimal for most crops.

Variable charges are those originating from the adsorption of ions onto the surface of organic and mineral soil particles, with the net charge being determined by the ion adsorbed in excess. Ions capable of interfering with the charge when adsorbed are called potential-determining ions,  $H^+$  and  $OH^-$  being the main ones in the soil solution. Kaolinite, goethite, hematite, and gibbsite are the main soil minerals with this characteristic (Fontes et al., 2001).

The possibility of hydroxylation at the surface is essential to the formation and development of charges in the inorganic constituents with predominance of variable charges. In the presence of water, elements such as Si, Al, or Fe, for instance, located at the surface of minerals like kaolinite, goethite, hematite, and gibbsite, fill their coordination layer with hydroxyl ions, such that the surface becomes hydroxylated.

Some methods have been proposed to quantify the surface charges of soil particles, among which are ion retention, potentiometric titration, electrokinetic techniques, salt titration, and the mineral addition technique.

A method proposed in the 1990s allows measurement of the structural permanent charge ( $\sigma_o$ ) and, at the same time, measurement of the proton charge density ( $\sigma_H$ ), together with cation and ion adsorption (Anderson & Sposito, 1991). This method is based on the use of a cesium chloride solution and it allows quantification of the structural permanent

charge and the charges related to the hydroxyl functional groups through ionic exchange of  $\text{Cs}^+$  by  $\text{Li}^+$  and  $\text{Cs}^+$  by  $\text{NH}_4^+$ , respectively. The success of the method has been shown by Chorover & Sposito (1995), Fontes & Sposito (1995), Peixoto et al. (1995), and Weber et al. (2005).

The State of Pernambuco, Brazil, has a soil heterogeneity represented by a network of 35 profiles with distinct classifications, allowing thorough examination regarding the origin of the electric charges in the soil. Identification of the contribution of each component to the generation of electric charges in soil particles (permanent or variable electric charges) allows us to obtain important information to understand soil behavior in regard to genesis, chemistry, physics, and fertility, among other areas of soil science.

The aim of this study was to quantify the permanent and variable charges in Reference Soils of the state of Pernambuco, Brazil, according to the classification of a team of soil scientists from the Universidade Federal Rural de Pernambuco (Federal Rural University of Pernambuco) (Ribeiro et al., 1999; Biondi et al., 2011).

## MATERIALS AND METHODS

To achieve these objectives, subsurface samples were taken from 24 profiles (nine from the Zona da Mata, eight from the Agreste, and seven from the Sertão), which represent approximately 80 % of the total area of the state (Table 1). The Zona da Mata, Agreste, and Sertão are meso-regions of the state of Pernambuco arising from division of Brazil into geographic meso- and micro-regions (IBGE, 1990).

After collection, samples were air dried, soil clods were broken up, and the material was passed through a No. 10 sieve (2-mm grid). The pH in water and in 1 mol L<sup>-1</sup> KCl (1:2.5 ratio) (Embrapa, 1997) were determined to characterize the samples and to allow calculation of the pH. Organic carbon was measured through the wet oxidation method (Yeomans & Bremner, 1988) (Table 2). Clay proportion was also determined (Ruiz, 2005) (Table 3). In addition, mineralogical analysis was performed through X-ray diffraction of the clay fraction, which was separated from the samples after particle-size analyses and mounted on an oriented glass slide through the smear technique. A diffractometer X'Pert Pro (PANalytical) was used, with  $\text{CoK}\alpha$  radiation and irradiation from 4 to 45 °2 $\theta$ , with a 2 $\theta$  step size of 0.01 and a step time of 1 s<sup>-1</sup>, tension of 40 kV, and current of 30 mA.

In order to quantify the permanent and variable electric charges, the method proposed by Anderson & Sposito (1991) and modified by Weber et al. (2005) was adapted. The different steps are presented below:

- 24 g of a 0.5 mol kg<sup>-1</sup> solution of CsCl was added to 3.5 g samples of air-dried soil in 50 mL polycarbonate centrifuge tubes. The suspension was shaken for 25 min using a reciprocal shaker, removing the light organic fraction from the supernatant. It was then centrifuged for 35 min with a relative centrifugal force (RCF) of 1,710 g, discarding the supernatant solution. The ion Cs<sup>+</sup> present in the reagent is non-radioactive (Cs-133), of low risk, and when combined with Cl<sup>-</sup> it forms a compound similar to K compounds; therefore, no special caution is required regarding its disposal, but the basic recommendations of reagent use and disposal must be strictly followed;
- RCF was calculated as follows:  $\text{RCF} = 0.0001118 \times R \times N^2$ , where R is the centrifugation radius, in cm, and N is the centrifugation speed, in rotations per minute;
- The previous procedure of shaking and centrifugation was repeated with the remainder of the soil sample, adding 20 g of CsCl solution, but with the concentration reduced to 0.1 mol kg<sup>-1</sup>. The supernatant solution was then discarded and the procedure was performed two more times, one with a 0.1 mol kg<sup>-1</sup> solution and another with a 0.05 mol kg<sup>-1</sup> solution. The supernatant solutions were discarded;
- The remaining soil paste was homogenized with the aid of a glass stirring rod, and then put in porcelain evaporating dishes. Then, two 0.5 g subsamples were taken in order to determine moisture content and assist in calculations involving the mass of the dry soil paste ( $M_{\text{DSP}}$ );
- After drying (100 °C) for 48 h, quantities of 0.35 g of  $M_{\text{DSP}}$  from each previous subsample were transferred to 50 mL centrifuge tubes which received 3.5 g of a 0.05 mol kg<sup>-1</sup> solution of CsCl at pH 7.0. The suspensions were shaken for 60 min in a horizontal shaker and centrifuged at 1,710 g for 15 min, discarding the supernatant;
- After that, subsamples were washed in 30 g of an ethanol:water solution (95:5, volume:volume). In this procedure, the suspensions were shaken for 10 s in a Vortex mixer, immersed in an ultrasonic bath for 5 min, and once more shaken in a Vortex mixer for 10 s;
- The suspensions were once more centrifuged at 1,710 g for 30 min, discarding the supernatant solutions. Washing was repeated until no chloride was detected after a test with a 0.01 mol kg<sup>-1</sup> solution of AgNO<sub>3</sub>. The centrifuge tubes were placed in a laboratory oven and dried at 65 °C for 48 h;
- The purpose of washing with ethanol and drying the samples was to reduce the concentration of embedded Cs<sup>+</sup> and favor the formation of internal sphere complexes between Cs<sup>+</sup> and siloxane surfaces;
- The soil samples prepared as indicated received 30 g of a 0.01 mol kg<sup>-1</sup> solution of LiCl, at pH 7.0, and were shaken for 30 min in a horizontal shaker and centrifuged at 1,710 g for 40 min, thus extracting Cs<sup>+</sup> ions from the ionizable functional groups;

**Table 1. Classification lithology and sampled horizon (H) of the studied reference soils of the State of Pernambuco**

Profile <sup>(1)</sup>	SiBCS <sup>(2)</sup>	Soil Taxonomy <sup>(3)</sup>	Lithology	H
Zona da Mata <sup>(4)</sup>				
1	Argissolo Vermelho-Amarelo	Ultisols. Oxisols (Kandic)	Gneiss	Bt1
2	Argissolo Amarelo	Ultisols. Oxisols (Kandic)	Barreiras Group	Bt1
4	Argissolo Vermelho-Amarelo	Ultisols. Oxisols (Kandic)	Gneiss e migmatites	Bt1
5	Chernossolo Argilúvico	Molisols	Gneiss	Bt
6	Latossolo Amarelo	Oxisols	Similar material to Barreiras Group covering again crystalline basement	Bw1
7	Nitossolo Vermelho	Ultisols. Oxisols (Kandic). Alfisols	Basic volcanic rocks	Bt1
8	Argissolo Vermelho	Ultisols. Oxisols (Kandic)	Gneiss	Bt1
9	Plintossolo Argilúvico	Ultisols (Plintaquults)	Barreiras Group	2Bt
10	Argissolo Amarelo	Ultisols. Oxisols (Kandic)	Barreiras Group	Btx
Agreste				
14	Planossolo Háptico	Ultisols (Albaquults and Plintaquults). Alfisols (Albaquults and Plintaquults)	Medium equigranular leucocratic biotite-gneiss	2Bt
15	Planossolo Háptico	Ultisols (Albaquults and Plintaquults). Alfisols (Albaquults and Plintaquults)	Coarse equigranular diorite	2Bt
16	Argissolo Vermelho	Ultisols. Oxisols (Kandic)	Coarse equigranular leucocratic biotite-gneiss	Bt1
18	Argissolo Amarelo	Ultisols. Oxisols (Kandic)	Biotite-muscovite- quartzite of fine to medium-grained. with quartz veins	Bt
19	Planossolo Nátrico	Alfisols (Natrusalfs and Natrudalfs)	Banded biotite-gneiss of medium-grained with quartz veins	2Btn
20	Latossolo Vermelho-Amarelo	Oxisols	Coarse titanite-amphibole-biotite-granodiorite with plagioclase porphyry	Bw1
21	Argissolo Vermelho-Amarelo	Ultisols. Oxisols (Kandic)	Leucocratic sillimanite-biotite-muscovite-gneiss of medium grained	Bt
22	Argissolo Amarelo	Ultisols. Oxisols (Kandic)	Covering little thick on crystalline rocks	Btx
Sertão				
23	Argissolo Amarelo	Ultisols. Oxisols (Kandic)	Crystalline rocks (Mica Schist)	Bt1
24	Planossolo Nátrico	Alfisols (Natrusalfs and Natrudalfs)	Covering little thick of material reported to Tertiary/Quaternary about rocks from Precambrian	Btn2
29	Luvissolo Crômico	Adirisols (Argids)	Mica Schist and gneiss from Undivided Precambrian	2Bt
30	Latossolo Amarelo	Oxisols	Material from Undivided Precambrian with covering again de material reported to Tertiary/Quaternary	Bw1
31	Cambissolo Háptico	Inceptisols	Granites and syenites	Bi1
32	Vertissolo Crômico	Vertisols	Shale with intercalation of limestones. marls. siltstone and gibbsite	Biv
33	Argissolo Amarelo	Ultisols. Oxisols (Kandic)	Material from Precambrian with covering again of material reported to Tertiary/Quaternary	Bt

<sup>(1)</sup> Numbering attributed by the Federal Rural University of Pernambuco to the reference soils of the state. <sup>(2)</sup> Brazilian Soil Classification System. <sup>(3)</sup> Correspondence based on Embrapa (2013). <sup>(4)</sup> Location region of the profile in the State of Pernambuco.

**Table 2. pH (H<sub>2</sub>O and KCl), ΔpH, organic carbon (OC) and principal clay minerals of the sampled horizons (H) of reference soils of the State of Pernambuco**

Profile <sup>(1)</sup>	SiBCS	H	pH(H <sub>2</sub> O)	pH(KCl)	ΔpH	CO	Clay minerals
						g kg <sup>-1</sup>	
						Zona da Mata <sup>(2)</sup>	
1	Argissolo Vermelho-Amarelo	Bt1	4.34	3.80	-0.54	11.3	Kaolinite
2	Argissolo Amarelo	Bt1	4.67	3.97	-0.70	6.7	Kaolinite
4	Argissolo Vermelho-Amarelo	Bt1	4.36	3.87	-0.49	7.5	Kaolinite
5	Chernossolo Argilúvico	Bt	6.12	4.40	-1.72	7.4	Kaolinite, Illite
6	Latossolo Amarelo	Bw1	4.53	4.10	-0.43	6.7	Kaolinite, Goethite
7	Nitossolo Vermelho	Bt1	5.03	4.96	-0.07	11.9	Kaolinite, Goethite, Hematite
8	Argissolo Vermelho	Bt1	4.98	4.21	-0.77	4.5	Kaolinite
9	Plintossolo Argilúvico	2Bt	4.83	3.94	-0.89	5.9	Kaolinite, Illite
10	Argissolo Amarelo	Btx	4.75	4.26	-0.49	3.7	Kaolinite, Goethite
						Agreste	
14	Planossolo Háplico	2Bt	5.70	4.47	-1.23	2.2	Kaolinite, Illite
15	Planossolo Háplico	2Bt	7.30	5.48	-1.82	3.0	Kaolinite, Smectite
16	Argissolo Vermelho	Bt1	4.53	4.16	-0.37	3.7	Kaolinite, Quartz
18	Argissolo Amarelo	Bt	4.98	4.02	-0.96	5.2	Kaolinite, Goethite, Quartz
19	Planossolo Nátrico	2Bt <sub>n</sub>	6.57	4.64	-1.93	3.7	Kaolinite, Illite
20	Latossolo Vermelho-Amarelo	Bw1	4.27	4.06	-0.21	8.2	Kaolinite, Gibbsite
21	Argissolo Vermelho-Amarelo	Bt	4.75	3.86	-0.89	2.2	Kaolinite, Illite, Quartz
22	Argissolo Amarelo	Btx	4.69	4.24	-0.45	3.7	Kaolinite, Goethite
						Sertão	
23	Argissolo Amarelo	Bt1	5.12	4.01	-1.11	5.9	Kaolinite, Goethite, Illite
24	Planossolo Nátrico	Bt <sub>n</sub> 2	7.74	6.35	-1.39	1.5	Kaolinite, Smectite
29	Luvissolo Crômico	2Bt	6.49	4.42	-2.07	5.9	Kaolinite, Illite
30	Latossolo Amarelo	Bw1	4.34	3.87	-0.47	3.0	Kaolinite, Goethite, Illite
31	Cambissolo Háplico	Bi1	5.97	5.09	-0.88	7.4	Kaolinite, Illite
32	Vertissolo Crômico	Biv	5.54	3.79	-1.75	3.0	Kaolinite, Illite, Quartz
33	Argissolo Amarelo	Bt	5.40	4.72	-0.68	3.7	Kaolinite, Goethite, Illite
	Mean		5.29	4.36	-0.93	5.33	

<sup>(1)</sup> Numbering attributed by the Federal Rural University of Pernambuco to the reference soils of the state. <sup>(2)</sup> Location region of the profile in the State of Pernambuco.

• The supernatant solutions were transferred to plastic containers and weighed. The centrifuge tubes, with the remaining soil and the embedded solution, were also weighed [ $M_{(CTS+ES)}$ ], obtaining the mass of the embedded solution through this difference [ $M_{ES} = M_{(CTS+ES)} - M_{CTS}$ ];

• The Cs<sup>+</sup> was then extracted from the sites with structural charge by adding 30 g of 1.0 mol kg<sup>-1</sup> solution of ammonium acetate (NH<sub>4</sub>OAc). The suspension was shaken for 30 min in a horizontal shaker and centrifuged at 1,710 g for 10 min. This extraction was performed three times, gathering the supernatant in a plastic container;

• Cs<sup>+</sup> determinations in the extracts of LiCl and NH<sub>4</sub>OAc were performed through ICP-OES (Inductively Coupled Plasma - Optical Emission Spectrophotometry), belonging to the Federal University of Viçosa, at the wavelength of 455.5 nm;

• The variable charge, CECV (mol<sub>c</sub> kg<sup>-1</sup> of soil), was determined by quantifying the exchangeable Cs<sup>+</sup> released from the surface after equilibrium of the sample with LiCl:

$$CECV = k_{Cs(LiCl)} \left( \frac{M_{LiCl(added)}}{M_{CTS}} \right) \quad (1)$$

where  $k_{Cs(LiCl)}$  is the Cs<sup>+</sup> concentration in the LiCl supernatant, and  $M_{LiCl(added)}$  is the mass of the added LiCl solution (supernatant solution + embedded solution);

The permanent charge, CECP (mol<sub>c</sub> kg<sup>-1</sup> of soil), was calculated as the excess of retained Cs<sup>+</sup> after saturation of the exchange complex with NH<sub>4</sub><sup>+</sup> to substitute the Cs<sup>+</sup> present in the structure of the minerals (Anderson & Sposito, 1991):

$$CECP = k_{Cs(NH_4OAc)} \left( \frac{M_{NH_4OAc(added)}}{M_{CTS}} \right) - (k_{Cs(LiCl)} M_{LiCl(embedded)}) \quad (2)$$

**Table 3. Clay content, permanent cation exchange capacity (CECP), variable cation exchange capacity (CECV), total cation exchange capacity (CECT = CECP + CECV) and relation CECV/CECT (V/T) in the sampled horizons (H) of reference soils of the State of Pernambuco**

Profile <sup>(1)</sup>	SiBCS	H	Clay	CECP	CECV	CECT	V/T
			kg kg <sup>-1</sup>	cmol <sub>c</sub> kg <sup>-1</sup>			
				Zona da Mata <sup>(2)</sup>			
1	Argissolo Vermelho-Amarelo	Bt1	0.590	6.56	2.89	9.45	0.31
2	Argissolo Amarelo	Bt1	0.297	5.44	1.61	7.05	0.23
4	Argissolo Vermelho-Amarelo	Bt1	0.376	3.57	2.32	5.89	0.39
5	Chernossolo Argilúvico	Bt	0.377	9.76	5.62	15.38	0.37
6	Latossolo Amarelo	Bw1	0.570	2.48	2.52	5.00	0.50
7	Nitossolo Vermelho	Bt1	0.693	5.07	4.56	9.63	0.47
8	Argissolo Vermelho	Bt1	0.419	3.17	2.99	6.16	0.49
9	Plintossolo Argilúvico	2Bt	0.195	3.23	1.73	4.96	0.35
10	Argissolo Amarelo	Btx	0.589	2.98	2.00	4.98	0.40
				Agreste			
14	Planossolo Háplico	2Bt	0.146	2.89	1.01	3.90	0.26
15	Planossolo Háplico	2Bt	0.268	15.84	3.42	19.26	0.18
16	Argissolo Vermelho	Bt1	0.417	2.50	1.79	4.29	0.42
18	Argissolo Amarelo	Bt	0.419	2.79	2.11	4.90	0.43
19	Planossolo Nátrico	2Btn	0.221	5.46	3.80	9.26	0.41
20	Latossolo Vermelho-Amarelo	Bw1	0.516	2.75	2.34	5.09	0.46
21	Argissolo Vermelho-Amarelo	Bt	0.308	2.70	1.59	4.29	0.37
22	Argissolo Amarelo	Btx	0.627	2.54	1.85	4.39	0.42
				Sertão			
23	Argissolo Amarelo	Bt1	0.232	2.67	1.61	4.28	0.38
24	Planossolo Nátrico	Btn2	0.240	3.76	2.57	6.33	0.41
29	Luvissolo Crômico	2Bt	0.130	2.44	2.57	5.01	0.51
30	Latossolo Amarelo	Bw1	0.234	1.93	1.17	3.10	0.38
31	Cambissolo Háplico	Bi1	0.307	2.03	3.03	5.06	0.60
32	Vertissolo Crômico	Biv	0.311	3.88	5.36	9.24	0.58
33	Argissolo Amarelo	Bt	0.065	2.66	1.08	3.74	0.29
	Mean		0.356	4.13	2.56	6.69	0.40

<sup>(1)</sup> Numbering attributed by the Federal Rural University of Pernambuco to the reference soils of the state. <sup>(2)</sup> Location region of the profile in the State of Pernambuco.

where  $k_{Cs(NH_4OAc)}$  is the concentration of  $Cs^+$  in the supernatant solution of  $NH_4OAc$ ;  $M_{NH_4OAc(added)}$  is the mass of the  $NH_4OAc$  solution added, and  $M_{LiCl(embedded)}$  is the mass of  $LiCl$  embedded per mass unit of the dry adsorbent.

• The total surface charge, CECT (mol<sub>c</sub> kg<sup>-1</sup> of soil) was calculated by the sum of CECP and CECV:

$$CECT = CECP + CECV \quad (3)$$

## RESULTS AND DISCUSSION

In general, the sampled soils show low values of organic matter (OM), high amplitude in the clay content, and predominance of negative electric charge, indicated by the negative value of  $\Delta pH$  (Tables 2

and 3). Organic carbon (OC) contents ranged from 1.5 to 11.9 g kg<sup>-1</sup> (average of 5.33 g kg<sup>-1</sup>), clay contents from 0.065 to 0.693 kg kg<sup>-1</sup> (average of 0.356 kg kg<sup>-1</sup>), and  $\Delta pH$  from -0.07 to -2.07 (average of -0.93).

Values of the permanent cation exchange capacity (CECP), variable cation exchange capacity (CECV), total cation exchange capacity (CECT) [CECT = CECP + CECV], and the ratio CECV/CECT (V/T), an indication of the proportion of pH-dependent charges in the diagnostic horizon of the soils studied, are shown in table 3. In four soils, V/T was equal to or greater than 0.50, which corresponds to approximately 17 % of the diagnostic horizons studied. The lowest V/T value was 0.18, indicating that all the diagnostic horizons studied showed CEC derived from variable-charge material.

Considering all the profiles analyzed, the average V/T ratio was 0.40 (Table 3). It should be noted that

there was no removal of OM from soils in the CEC determination, thus not allowing differentiation between the amounts of OM and clay minerals contributing to the variable charges for the CECV. To reduce the possible contribution of the OM, determinations were purposely performed with samples from subsurface horizons. Some soils, such as profiles 26 and 33, have low contents of clay and OC, which makes it difficult to infer the amount of CECV originating predominantly from inorganic material. Thus, further research is needed to identify the separate contribution of each constituent present in the soils.

The predominance of CECV in the subsurface horizons of profiles 1, 2, and 4 (Table 3), despite the prevalence of kaolinite in their clay fractions (Table 2), can be explained by the possibility that the method of CEC determination through Cs<sup>+</sup> adsorption registers the charges available in the 2:1 clay minerals that may be present but not detected by X-ray diffraction applied to the natural clay fraction (with no treatment application).

The Cs<sup>+</sup> adsorption method, though little studied in Brazilian soils, proves to be an excellent line of research for soil science because despite detecting electric charges originating from 2:1 minerals not identified with X-ray diffractograms in the absence of treatments, such as clay saturation by cations (Mg<sup>2+</sup> and K<sup>+</sup>, for instance) to identify materials with uniform expansion of the expansible phyllosilicate (smectites and chlorites, for instance), it would be important in studies on soils with different mineralogies, as well as allowing the observation of the contribution of organic and inorganic constituents to net soil electric charge.

Specifically regarding the representative soils of the State of Pernambuco, the presence of variable charges in all soils of the region should be pointed out. It is sometimes suggested that these soils, especially those from the Sertão region, could have a high proportion of permanent charges in their exchange complexes due to the climatic conditions of the region. The marked presence of materials with variable charge is an indication of past climate conditions that led to the predominant formation of variable charge clay minerals, as well as the possible contribution of kaolinite, which, despite having a low CEC, in large amounts can provide variable electric charges of considerable proportion. The predominance of a more humid past climate in the Northeast region was indicated by De Oliveira et al. (1999) and Pessenda et al. (2010).

## CONCLUSIONS

1. The cesium adsorption method was efficient in the determination of electrical charges in Reference Soils of the state of Pernambuco, allowing to identify different amounts of variable and permanent cation exchange capacity in all analyzed soils.

2. All the soils analyzed exhibited variable cation exchange capacity, with proportions from 0.16 to 0.60 and an average of 0.40 when related to total cation exchange capacity.

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