

Cation exchange capacity and mineralogy of loess soils with different amounts of volcanic ashes



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ABSTRACT

The cation exchange capacity of soils (CEC) is largely affected by the mineralogy of their parent material. Soils of the Argentinean Pampas develop on illitic loess, mixed, in variable proportions, with volcanic ashes. It is whether a question of how pedogenesis can modify this mineralogy, affecting CEC differentially. In order to answer this question, we analyzed four soils, two of them placed in semiarid conditions and developing on parent materials with high volcanic ash contents, and two placed in the humid Pampas, developing on ash-free parent materials. Results indicated that pedogenesis transformed coarse lithogenic illites into smaller illites in ash free soils, accumulating them not only in clays but also in silts. In ash enriched soils, illites were not altered by pedogenesis but they were the volcanic glasses, which were transformed into less crystallized smectites. These smectites accumulated mainly not only in clays but also in fine silts. The mineral fraction of ash free soils had higher CEC ($15.07 \text{ cmol}_c \text{ kg}^{-1}$) than ash enriched soils ($9.50 \text{ cmol}_c \text{ kg}^{-1}$), being the contribution of the $<50 \mu\text{m}$ sized fractions to the total CEC similar in all the studied soils (on average, 54%). As a consequence of this, clays and silts of ash free soils made a relatively low contribution to the total CEC, while poorly crystallized smectites of ash enriched soils made a relatively high contribution. This was explained on the basis of the kind of minerals present (smectitic minerals with high CEC) rather than on the proportion of the mineral fraction itself in ash enriched soils, and on the relatively high content of the mineral fractions rather than on their mineralogy (illites with low CEC) in ash free soils. The contribution of silts to CEC was similar and relatively high in all the studied soils: 17.5% of the total CEC and 32% of the mineral fraction CEC. These results confirm that the electrochemical properties of the studied soils are defined not only by clays but also by silts, mainly those with sizes between 2 and $20 \mu\text{m}$.

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1. Introduction

The cation exchange capacity of soils (CEC) is one of the most important parameters defining soil fertility (Martel et al., 1978; Thompson et al., 1989). Besides organic matter- and clay contents, the clay mineralogy defines CEC. For example, it is largely known that 1:1 minerals have lower CEC than 2:1 minerals and that, within 2:1 minerals, illites contribute less to CEC than smectites (Martín-García et al., 1999; Peinemann et al., 2000).

Less attention has been paid to the contribution of fractions coarser than clays to CEC. This is a sound question for soils of the Argentinean Pampas, as their silt fractions show some cation sorption capacity. As a matter of fact, Morrás (1995) found that silts of soils of the Chaco region of Argentina have CEC varying from 8 to $23 \text{ cmol}_c \text{ kg}^{-1}$, while Peinemann et al. (2000), for Entic Haplustolls and Typic Hapludolls of

the semiarid Pampas, found that silts have CEC varying from 6.5 to $7.1 \text{ cmol}_c \text{ kg}^{-1}$. Thompson et al. (1989) found similar results for Mollisols and Alfisols of the USA, in which silt fractions had CEC between 2 and $29 \text{ cmol}_c \text{ kg}^{-1}$.

The origin of the electrostatic properties of silts of the Pampas soils seems to be related to their mineralogy. Though the pleistocenic and holocenic loess sediments on which the soils develop are mineralogically homogeneous, illites being the predominant minerals (Buschiazco, 1988; Zárate, 2003), the variable amounts of volcanic ashes, mixed with the loess, can modify this homogeneity.

The volcanic ashes were accumulated by frequent eruptions of Andes volcanoes during the Pleistocene and Holocene (Teruggi, 1957). One of the most recent events occurred in 1932, when the Quizapu volcano sedimented a 10 cm thick, 1000 km long and 30 to 50 km broad W–E oriented ash layer in the semiarid Pampas (Larsson, 1936). The highest amounts of volcanic glasses are currently found in soils of the dryer Pampas (Hepper et al., 2006).

The presence or absence of volcanic ashes seems to define the mineralogy of the clay fraction of Pampas soils: ash free soils contain illites

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with traces of kaolinite, while ash enriched soils contain poorly crystallized smectites with traces of kaolinite (González Bonorino, 1965, 1966; Nabel et al., 1999). Zárate and Blasi (1991) and Camilión (1993) told about a possible transformation of these volcanic ashes in new mineral species without defining which one.

The different behavior of ash enriched- and ash free soils of the Pampas was detected by Buschiazzo et al. (1998) and Urioste et al. (2006) through their different P-sorption capacities: ash enriched soils showed much higher P-sorption than ash free soils. Authors attributed these differences to the presence of minerals with high P sorption capacity in the ash enriched soils of the semiarid Pampas produced, apparently, by the transformation of volcanic ashes.

It is whether a question of how far lithogenic illites or volcanic glasses, originally accumulated in size fractions coarser than silts, transformed into new mineralogical species and how these transformations affected CEC of clays and silts in each soil group. It is known that under moist conditions illites can decrease their size, accumulating in the finer fractions changing little their crystallographic structure. In dry environments, on the other hand, illites mostly remain unaltered (Dahlgren et al., 2004; Hepper et al., 2006).

Volcanic glasses are known to transform rapidly in new clay species like amorphous oxides, allophane or even smectites, depending on the environmental conditions (Dubroeuq et al., 1998; Georgoulas and Moustakas, 2010; Shoji et al., 1993).

If the transformation of illites and volcanic glasses mentioned above occurred in the Pampas soils, the relative contribution of silts to CEC should be higher in ash free- than in ash enriched soils, due to the large presence of illites in silts. The opposite is expected in ash enriched soils, in which the newly formed minerals should be mostly accumulated in the clay fraction.

In view of the former queries, the aims of this study were to determine the mineralogy of different size fractions of soils containing different amounts of volcanic ashes, and to assess how this mineralogical composition affects CEC of different size fractions.

2. Materials & methods

2.1. Studied area and soils

Soil samples from the topsoil (0–20 cm) were randomly taken by triplicate from a 10 m² surface in four sites of the Pampean region of Argentina (Fig. 1). All the studied soils develop on the same parent material, the so-called Pampas loess (Buschiazzo, 1988; Teruggi, 1957; Zárate, 2003). The mineralogy of the loess is qualitatively- but not quantitatively homogeneous. This is because the sedimentation of the aeolian materials by winds of different speeds, and therefore different transport energies, sedimented variable amounts of minerals with different densities at different depths (Buschiazzo and Taylor, 1993). This makes the mineralogy of C-horizons of current soils to be not strictly related with the mineralogy of A horizons (Buschiazzo, 1988). Because of that, only the A- and not the C-horizon was analyzed in this study.

The studied soils were two ash enriched soils: an Entic Haplustoll (EH) and a Typic Hapludoll (TH-I), and two volcanic ash free soils: a Typic Hapludoll (TH-II) and a Typic Argiudoll (TA) (Table 1). Management conditions were similar in all the studied soils and representative of management systems of the whole Pampean region: a wheat (*Triticum aestivum*)–soybean (*Glycine max*) crop sequence, carried out under no-till conditions since more than 20 years.

2.2. Laboratory procedures

Soil samples were air dried and sieved through 2 mm. The pH was determined potentiometrically using a combined glass-calomel electrode, in both water (pH_{H2O}) and KCl 1 mol dm⁻³ (pH_{KCl}) (1:2.5 soil:liquid); the equation $\text{pH} = \text{pH}_{\text{KCl}} - \text{pH}_{\text{H}_2\text{O}}$ was used to determine charge characterization (Mekaru and Uehara, 1972). The organic

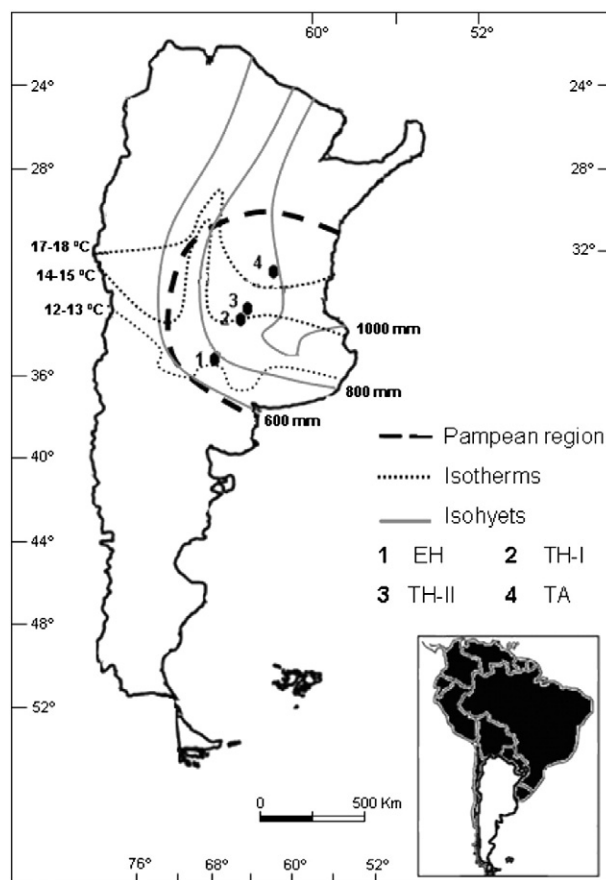


Fig. 1. Location of the studied soils. EH = Entic Haplustoll; TH-I = Typic Hapludoll I; TH-II = Typic Hapludoll II; TA = Typic Argiudoll.

matter content (OM) was determined by wet digestion (Walkley and Black, 1934) and the CEC by saturation with an ammonia acetate dissolution 1 mol dm⁻³ at pH 7 (Rhoades, 1982). Amorphous Al- and Fe oxides were extracted in the darkness with oxalic acid, and crystalline Al- and Fe oxides (Alos and Feos, respectively) with boiled oxalic acid (Schlichting et al., 1995). All procedures mentioned above were performed on triplicate samples.

Over a composed soil sample of each soil, the grain size distribution was determined by the combined pipette and sieving method (Gee and Bauder, 1986). Clays (C, soil particles with a diameter (ϕ) < 2 μm), fine silt (FSi, 2 μm < ϕ < 10 μm) and medium silt (MSi, 10 μm < ϕ < 20 μm) fractions, were separated and concentrated by centrifugation and siphoning, on organic matter-free and dispersed soil samples. The settling times were selected with the centrifugation methodology provided by Tanner and Jackson (1947). After this procedure, the sand fraction (S) was separated by wet sieving. Coarse silt (CSi, 20 < ϕ < 50 μm) was obtained as a remnant of the sand separation procedure and its content was calculated with Eq. (1):

$$\text{CSi} = \text{Soil} - (\text{C} + \text{FSi} + \text{MSi} + \text{S}) \quad (1)$$

where CSi, MSi, FSi, C and S are, respectively, the masses of coarse, medium and fine silts, clay and sand, and Soil is the mass of the soil sample. All the parameters of the equation are expressed in grams (g). In addition, on other < 2 mm fraction of a composed soil sample of each soil, fine clay fraction (FC; ϕ < 0.2 μm) was separated following the same procedure described for C, FSi and MSi.

Mineralogical analysis of the FC, C, FSi, MSi and CSi fractions was determined by X-ray diffraction on MgCl₂ saturated samples. For this determination a diffractometer with a Cu anticatode ($\lambda = 1.54 \text{ \AA}$), operating at 45 kV and 40 mA was used. The angular interval was

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