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Charge sparsity: An index to quantify cation effects on clay dispersion in soils

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ABSTRACT: Few approaches have been developed to measure the isolated effect of exchangeable cations on clay dispersion in soils. In this study, the charge sparsity (CS) index was proposed using the ratio between the cations hydrated ionic radius and valence. The index capacity to measure cation effects on clay dispersion in soils was also evaluated. Three Ferralsols, sampled at different sites in Paraná State, Brazil, were homoionized with Ca^{2+}, Mg^{2+}, K^+, or Na^+ prior to evaluation of the clay dispersion degree. Published independent data for two soils and clays were also used. We tested the capacity of CS and II, the latter proposed by Marchuck and Rengasamy (2011), to predict clay dispersion in soils. The CS predicted the dispersion degree more accurately than the ionicity index did, in soils where Ca^{2+} and Mg^{2+} behaved similarly. The response of Paraná soils to CS varied with soil characteristics. Soils with a lower pH at the isoelectric point were more dispersible by cations with high CS (K^+ and Na^+). The CS was efficient to quantify the isolated effect of cations on the clay dispersion process in soils. Therefore, qualitative and quantitative studies can benefit from the CS as an index to understand the effect of cations on clay dispersion in soils.

Keywords: Colloids, Electrical double layer, aggregation, flocculation, zeta potential

Introduction

Soil structure is essential for ensuring its quality (Bronick and Lal, 2005) and results from aggregating primary particles and porous spaces between aggregates (Marshall et al., 1996). In Brazil, especially in the southern region, most soils are highly weathered. In these soils, distribution of surface charges on kaolinite minerals and coexistence with sesquioxides allow the formation of well-developed and stable microstructure (Trefalt et al., 2014). However, inadequate management of soils can affect the forces that hold particles together and degrade their structure.

Dispersion of the clay fraction from aggregates favors the formation of superficial crusts (Rosa et al., 2013), reduction of macroporosity (Spera et al., 2008), reduction of pore connectivity (Marchuk et al., 2012), and reduction of hydraulic conductivity (Arienzo et al., 2012). These characteristics affect vegetal production and favor the transport of particles, nutrients, and other contaminants to water bodies (Wang and Keller, 2009). Changing the nature of cations in the exchange complex regulates clay dispersion by affecting the repulsive forces between particles (Mahanta et al., 2012). Although cations are known to affect clay dispersion, few approaches quantify the isolated effect of cations on clay dispersion.

Marchuk and Rengasamy (2011) developed the ionicity index (II) for cations and predicted turbidity of suspensions of homoionic soils and clays, obtaining a linear model with $R^2 = 0.93$. Their study was based on Rengasamy and Sumner (1998), which concluded that clay dispersion is regulated by the ionicity/covalence of clay-cation bonds.

The effect of cations on dispersion is based on their ability to neutralize the electric field on clay surfaces; therefore, cations with higher valence and lower hydrated radius are more efficient in promoting flocculation. These two variables were combined in this study to generate an index based on charge sparsity (CS), corresponding to the ratio between the hydrated radius and the cations valence. A higher CS value indicates sparser cation charges, decreased electric field neutralization, and lower clay flocculation ability.

We hypothesize that CS expresses the isolated effect of cations on clay dispersion in soils. Here, we proposed and tested the CS index in soils.

Materials and Methods

Site description, soil characterization, and sampling

The study sites are located in the municipalities of São João do Oeste (S. J. do Oeste) (Latitude: -25°44′16″, Longitude: -52°53′54″, Altitude: 509 m), Santa Fé (Latitude: -23°0′22″, Longitude: -51°48′56″, Altitude: 538 m), and Londrina (Latitude: -23°20′28.9″, Longitude: -51°12′49.6″, Altitude: 577 m), in Paraná State, Brazil (Figure 1). The soils were classified as Ferralsols (FAO, 2015) and their characteristics are summarized in Table 1. Deformed samples were randomly collected from the superficial layer, air dried, and sieved (2 mm).

Particle size distribution, mineralogical analysis, and zeta potential analysis

To determine the soil particle size distribution, 20 g of sieved sample (2 mm) were mixed with 100 mL of NaOH solution (0.1 mol L⁻¹), shaken for 16 h at 200 rpm, and transferred to 1 L beakers. After adequate sedimentation time, according to the Stoke law, the silt and clay fraction were pipetted and gravimetrically
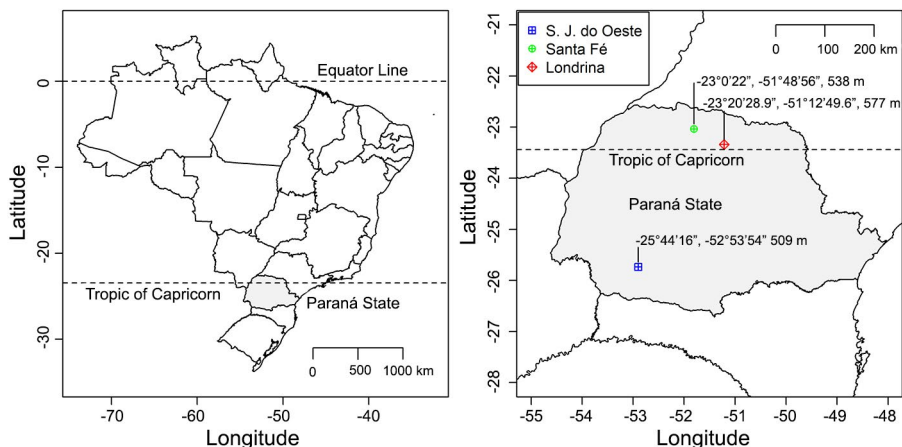
Figure 1 – Soil sampling locations.

Table 1 – Soil characteristics under field conditions.

Attribute	S. J. do Oeste	Santa Fé	Londrina
Parent material	Basalt	Sandstone	Basalt
Classification	Ferralsol	Ferralsol	Ferralsol
Altitude (m)	509	538	577
Use	Annual crops	Pasture	Annual crops
Samples (n)	5	5	10
Layer (cm)	0-10	0-20	0-10
Clay (g kg^{-1})[a]	535	216	616
Silt (g kg^{-1})[a]	278	25	180
Sand (g kg^{-1})[a]	187	759	204
Fe$_{ox}$ (g kg^{-1})[b]	6.00	1.87	7.38
C (g kg^{-1})[c]	21	9.1	16
H+Al^{3+} (cmol$_c$ kg^{-1})[d]	7.2	3.5	2.4
Al^{3+} (cmol$_c$ kg^{-1})[e]	0.4	0.0	0.0
Ca^{2+} (cmol$_c$ kg^{-1})[d]	7.4	1.6	9.4
Mg^{2+} (cmol$_c$ kg^{-1})[e]	1.5	0.6	2.3
K$^+$ (cmol$_c$ kg^{-1})[f]	0.4	0.1	0.2
Na$^+$ (cmol$_c$ kg^{-1})[f]	0.0	0.0	0.0
P (mg kg^{-1})[f]	4.1	10.1	7.2
pH$_{H2O}$[g]	5.1	5.7	6.3
ΔpH[h]	-0.90	-0.26	-0.64

[a]Quantified after shaking of 20 g of soil in 100 mL of a solution of NaOH (0.1 mol L^{-1}) during 16 h; [b]Oxalate extractable Fe, expressed on the clay basis; [c]Quantified by the oxidation of K$_2$Cr$_2$O$_7$ in sulfuric medium; [d]Estimated by the SMP method; [e]Extracted with KCl 1 mol L^{-1}; [f]Extracted with MEHLICH-1; [g]Measured in a 1:2.5 soil:water (*m:v*) ratio; [h]ΔpH = pH$_{KCl}$ − pH$_{H2O}$.

quantified. The suspension containing the clay fraction was used for the X-ray diffraction analysis and zeta potential analysis, measured by electroacoustic spectroscopy.

Homoionic saturation and desalinization of samples

Soil (5 g) was mixed with 50 mL of M^{x}Cl$_x$ solution (1 mol$_c$ L^{-1}), where M represents the evaluated cation (Ca^{2+}, Mg^{2+}, K$^+$, or Na$^+$) and "x" the corresponding valence. The suspension was shaken at 200 rpm in a horizontal orbital shaker for 15 min, allowed to rest for 1 h, and then the solution was separated from the soil by vacuum filtration. This procedure was repeated once using an M^{x}Cl$_x$ solution (0.5 mol$_c$ L^{-1}), allowing to rest for 16 h.

The homoionic soil was desalinated by successive washing with ethanol (50 mL, 70 % (v/v)) until the electrical conductivity was lower than 0.035 mS cm^{-1}. Desalination was performed to reduce the influence of concentration and reveal the effect of cation properties, such as valence and hydrated radius, on the clay fraction dispersion. The washing extract was translucent, indicating no significant loss of clay. After desalinization, the samples were dried at 50 °C in a forced-circulation stove for 1 h and sieved again (2 mm) before the evaluation of clay dispersion.

Clay dispersion evaluation

Exactly 0.500 g of dried, homoionic, desalinated, and sieved soil was shaken with 50 mL of distilled water for 1 h at 200 rpm in a Falcon tube on a horizontal orbital shaker. The time taken to pipette the clay fraction (< 2 × 10^{-6} m) was calculated according to the Stoke law and clay in the suspension was quantified in triplicate using a spectrophotometer at 420 nm. The dispersion degree was calculated in terms of the total clay obtained by the particle size distribution analysis.

Charge sparsity and ionicity index

The CS measures the cation capacity to neutralize the excess of charge on the surface of particles. To obtain the CS, the hydrated ionic radius (obtained from Volkov and Deamer, 1997) was divided by the valence, as shown in Eq. 1:

$$CS\ (10^{-10}\,m) = \frac{Hydrated\ ionic\ radius}{Valence} \tag{1}$$

The hydrated ionic radius, valence and CS of the cations evaluated in this study, as well as II, according to Marchuck and Rengasamu (2011), are shown in Table 2.

Statistical analysis

The significance of the exponential model parameters was determined according to the "t" distribution. The model was used to express the relationship between clay dispersion degree and CS or II. The Friedman test was used to compare the values of dispersion degree among treatments (cations) for each soil and the Kruskal-Wallis test was used to compare the values of dispersion degree among soils for each cation. All analyses were performed using R Software v. 3.4.0 (R Core Team, 2017).

Results and Discussion

Comparison of charge sparsity and ionicity index

Both CS and II-based models were able to predict the clay dispersion degree with high accuracy in the Ferralsols from Paraná State (Figures 2A and 2B). For the soil from S. J do Oeste, R^2 values (0.98) of the models generated were the same, whereas for soils from Santa Fé and Londrina, the CS-based models had better R^2 values (0.93 and 0.98, respectively) than the II-based models (0.90 and 0.91, respectively).

The advanced weathering stage of the Ferralsols under study, along with the organic matter content (Table 1), allows good stability of aggregates under field conditions, which is consistent with the high physical quality of these soils. Because the clay fraction tends remain aggregated, Ca^{2+} and Mg^{2+} behaved similarly, mainly in soils from Santa Fé and Londrina (Table 3 and Figures 2A and 2B). The CS-based models for these two soils were superior because the CS values for Ca^{2+} and Mg^{2+} are more similar than the corresponding II values. Thus, the CS values better represent the effect of these cations on clay dispersion in highly weathered soils (Table 2 and Figures 2A and 2B).

Kaolinite minerals contain positively and negatively charged sites over a wide pH range (Tombácz and Szekeres, 2006). Coexistence with metallic sesquioxides, which have isoelectric points at high pH values, makes these soils less responsive to variations in the electric potential (Trefalt et al., 2014). This possibly explains why Ca^{2+} and Mg^{2+} behaved similarly in the Ferralsols under study. These findings corroborate Ahmed et al. (1969), who also studied soils with a predominance of kaolinite and iron oxides and found that the stability of artificially prepared aggregates, saturated with different cations, followed the order: $Ca^{2+} = Mg^{2+} > K^+ \geq Na^+$.

Table 2 – Cation parameters.

Cation	HIR[1]	Valence	CS[2]	II[3]
	10^{-10} m		10^{-10} m	
Ca^{2+}	4.12	2	2.06	0.67
Mg^{2+}	4.28	2	2.14	0.73
K^+	3.31	1	3.31	0.86
Na^+	3.58	1	3.58	0.89

[1]Hydrated ionic radius (Volkov and Deamer, 1997); [2]Charge sparsity, CS = HIR/Valence. [3]Ionicity Index (Marchuk and Rengasamy, 2011).

Table 3 – Comparison of the dispersion degree values of different soils and cations.

Cation	S.J. do Oeste	Santa Fé	Londrina
		Dispersion degree	
		%	
Ca^{2+}	5.29 cA	2.16 cC	2.94 cB
Mg^{2+}	8.16 cA	2.55 cB	2.59 cB
K^+	30.87 bA	5.70 bC	12.09 bB
Na^+	57.28 aA	12.43 aC	22.63 aB

Lower case letters compare the cations within each soil by Friedman test. Upper case letters compare soils within each cation by the Kruskal-Wallis test, both at 5 % of probability.
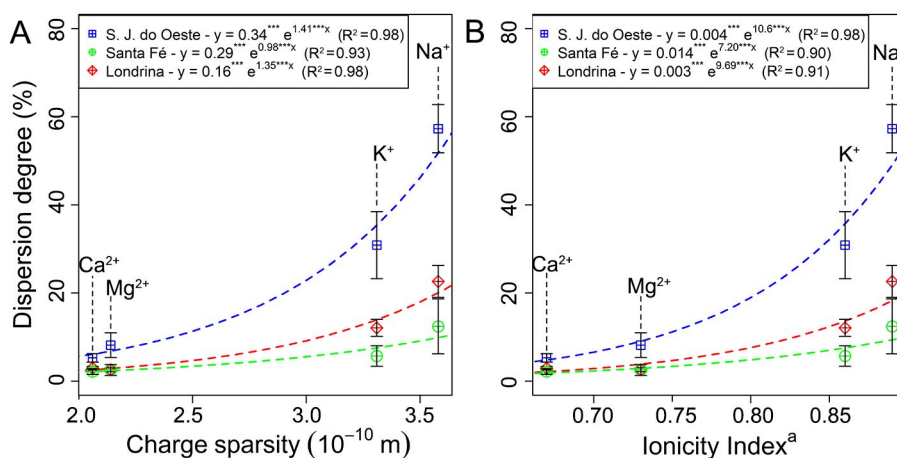

Figure 2 – Clay dispersion degree as a function of charge sparsity (A) and ionicity index (B) of cation in the exchange complex. Error bars represent the standard deviation. Model parameter ***significant at 0.1 %. [a]According to Marchuk and Rengasamy (2011).

We plotted the turbidity and zeta potential data published in Marchuk and Rengasamy (2011) as a function of CS and II (Figures 3A, 3B, 3C and 3D) to evaluate the CS behavior in independent samples. The increase in the R^2 value of the CS-based model compared with that of the II-based model for the Claremont sample was again associated with the similarity between Ca^{2+} and Mg^{2+}. The superiority of the II-based models for illite and bentonite clays was associated to the different effect of these cations. The difference between these samples is also evident in Figure 2 in Marchuk and Rengasamy (2011), where larger error bars are shown for Ca^{2+} and Mg^{2+} than for K^+ and Na^+.

The soils and clays studied by Marchuk and Rengasamy (2011) were predominantly composed of primary or moderately weathered minerals (Barzegar et al., 1995; Marchuk and Rengasamy, 2011). Thereby, the similarity between the effects of Ca^{2+} and Mg^{2+} on the Claremont sample is not associated to a high weathering stage, but with another factor that needs further investigation. However, slightly or moderately weathered soils usually seem to respond differently to Ca^{2+} and Mg^{2+}. Zhang and Norton (2002) studied soils with predominance of illite and smectite in the clay fraction and found higher clay dispersion and smaller hydraulic conductivity in soils saturated with Mg^{2+} than in soils saturated with Ca^{2+}. Smith et al. (2015) concluded that approximately 13 times more Mg^{2+} than Ca^{2+} is required to achieve the same beneficial effect on the hydraulic conductivity in a calcareous soil.

The goodness of fit of the CS-based models suggests that CS accurately measures the isolated effect of cations on clay dispersion. Smaller CS values indicate a greater capacity to neutralize the electric field created by the particle. This reduces the electric-double-layer thickness, as indicated by the capacity of cations to neutralize the zeta potential of electronegative clays and promote flocculation (Figures 2A, 3A and 3C). The II quantifies the degree of ionicity and covalency in clay-cation bonds and, consequently, indicates hydration reactions (Rengasamy et al., 2016). However, as these indices are highly correlated, this study does not reveal whether the importance of these phenomena vary in different soil types.

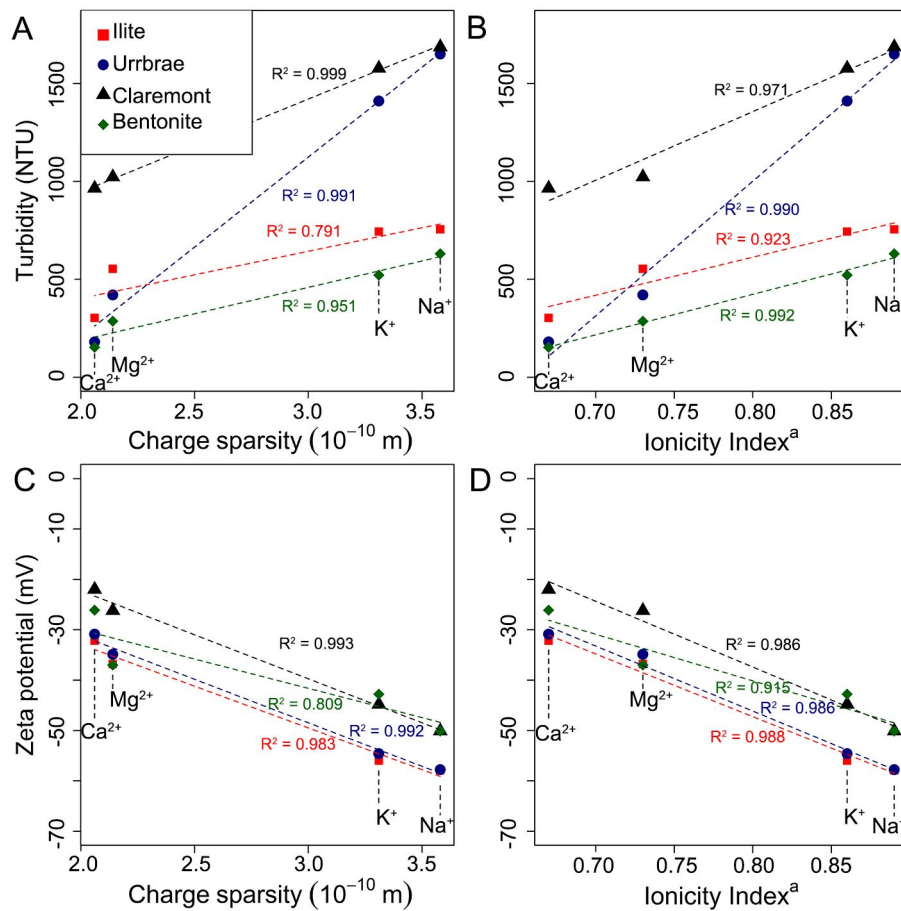Further, despite the similarity between CS and the ionic potential (both ratios use an ionic radius and

Figure 3 – Turbidity (A and B) and zeta potential (C and D) as a function of the charge sparsity and ionicity index of cation in the exchange complex. [a]According to Marchuk and Rengasamy (2011).
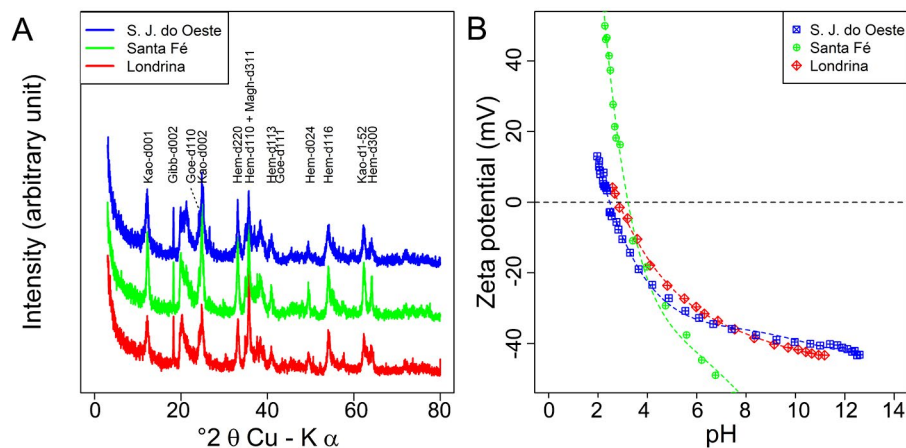
Figure 4 – X-ray diffractogram (A) and zeta potential (B) of the clay fraction of soils. Kao = kaolinite; Gibb = gibbsite; Goe = goethite; Hem = hematite; Magh = maghemite.

valence), CS considers the hydrated radius of the cations, whereas ionic potential considers the anhydrous radius. Thus, the ionic potential explains the tendency of cations to solvate, hydrolyze, or form oxyanions in the environment (Sposito, 2008), whereas the CS explains the capacity of cations to neutralize the electric field of particles.

Differences between the studied soils

The soils from S.J. do Oeste had the highest dispersion degrees for all the studied cations, followed by the soils from Londrina and Santa Fé. The soil from Londrina exhibited higher values than the soil from Santa Fé, except for Mg^{2+}, which had no statistical difference (Table 3). These differences were also reflected in the parameters of the CS-based models (Figure 2A), revealing that some soils respond more intensely to cations CS. This behavior seems to be associated with the charge balance of the particles (Figure 4B). The clay fraction of soils from S. J. do Oeste, Londrina, and Santa Fé reached electrostatic balance (zeta potential = 0 mV) at pH 2.47, 2.82, and 3.22, respectively (Figure 4B). Soils that reached charge equilibrium at lower pH values (S.J. do Oeste < Londrina < Santa Fé) (Figure 4A) exhibited higher dispersion when saturated with cations of high CS (K^+ and Na^+) (Figure 2A).

Adsorption of organic compounds and phosphate increases the negative electric potential on particle surfaces, favoring their dispersion after the mechanical breakdown of aggregates (Lee et al., 2012; Plaza et al., 2015; Ribeiro et al., 2012). Nguyen et al. (2013) studied the effect of different anions on dispersion of kaolinite minerals and observed that organic molecules intensify charge imbalance, favoring particle dispersion. Additionally, Ribeiro et al. (2012) tested the response of zeta potential of three Brazilian soils to vinasse and observed that adsorption of organic molecules reduces the pH of isoelectric point. Soils from S.J. do Oeste, Londrina, and

Santa Fé have very high, high, and moderate organic C levels, respectively (Pauletti and Motta, 2017). Thus, the organic matter content is the main factor that contribute to charge imbalance and responsiveness to high CS cations (Table 1 and Figure 2A).

The behavior of the soil from Londrina showed greater similarity with the soil from Santa Fé (Figures 2A and 2B), whereas soils from Londrina showed greater similarity to the soil from S.J. do Oeste (Table 1 and Figures 4A and 4B). This difference is associated to the nonlinear relationship between zeta potential and responsiveness of soils to high CS cations and to the higher microstructural stability of the soil from Londrina (Reichert et al., 2009) caused by a higher Fe_{ox} content (Table 1). Amorphous Fe forms play a crucial role in microstructure stabilization due to a higher specific superficial area (Camêlo et al., 2017). As we used the < 2 mm fraction, soil microaggregates were still stable after the methodological procedures, leading the soil from Londrina to have lower responsivity to CS than the soil from S.J. do Oeste.

The influence of several variables on clay dispersion limits the use of CS under field conditions, where there are variations in mineralogy, organic matter content and quality, pH, zeta potential, and cations in the exchange complex. However, in controlled conditions, CS represented effectively the isolated effect of cations in the clay dispersion process.

Conclusion

The CS of cations in the exchange complex explains their capacity to neutralize the repulsive forces between particles and, consequently, can predict the clay dispersion degree of homoionized samples from different soils. Therefore, qualitative and quantitative studies can benefit from CS as an index to understand the effect of cations on clay dispersion in soils.

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Authors' Contributions

Conceptualization: Melo, T.R. Data acquisition: Melo, T.R.; Machado, W. Data analysis: Melo, T.R. Design of Methodology: Melo, T.R. Writing and editing: Melo, T.R.; Tavares Filho, J.; Machado, W.

References

Ahmed, S.; Swindale, L.D.; El-Swaify, S.A. 1969. Effects of adsorbed cations on physical properties of tropical red earths and tropical black earths. I. Plastic limits, percentage of stable aggregates, and hydraulic conductivity. Journal of Soil Science 20: 255-268.

Arienzo, M.; Christen, E.W.; Jayawardane, N.S.; Quayle, W.C. 2012. The relative effects of sodium and potassium on soil hydraulic conductivity and implications for winery wastewater management. Geoderma 173-174: 303-310.

Barzegar, A.R.; Oades, J.M.; Rengasamy, P.; Murray, R.S. 1995. Tensile strength of dry, remoulded soils as affected by properties of the clay fraction. Geoderma 65: 93-108.

Bronick, C.J.; Lal, R. 2005. Soil structure and management: a review. Geoderma 124: 3-22.

Camêlo, D.L.; Ker, J.C.; Fontes, M.P.F.; Corrêa, M.M.; Costa, A.C.S.; Melo, V.F. 2017. Pedogenic iron oxides in iron-rich oxisols developed from mafic rocks. Revista Brasileira de Ciência do Solo 41: e0160379.

Food and Agriculture Organization [FAO]. 2015. International Soil Classification System for Naming Soils and Creating Legends for Soil Maps. FAO, Rome, Italy. (World Soil Resources Reports, 106).

Lee, B.J.; Schlautman, M.A.; Toorman, E.; Fettweis, M. 2012. Competition between kaolinite flocculation and stabilization in divalent cation solutions with anionic polyacrylamides. Water Research 46: 5696-5706.

Mahanta, K.K.; Mishra, G.C.; Kansal, M.L. 2012. Estimation of electric double layer thickness from linearized and nonlinear solutions of the Poisson-Boltzman equation for single type of ions. Applied Clay Science 59-60: 1-7.

Marchuk, A.; Rengasamy, P. 2011. Clay behavior in suspension is related to the ionicity of clay-cation bonds. Applied Clay Science 53: 754-759.

Marchuk, A.; Rengasamy, P.; McNeill, A.; Kumar, A. 2012. Nature of the clay-cation bond affects soil structure as verified by X-ray computed tomography. Soil Research 50: 638-644.

Marshall, T.J.; Holmes, J.W.; Rose, C.W. 1996. Soil Physics. 3ed. Cambridge University Press, Cambridge, UK.

Nguyen, M.N.; Dultz, S.; Tran, T.T.T.; Bui, A.T.K. 2013. Effect of anions on dispersion of a kaolinitic soil clay: a combined study of dynamic light scattering and test tube experiments. Geoderma 209-210: 209-213.

Pauletti, V.; Motta, A.C.V. 2017. Manual of Fertilizations and Liming for the State of Paraná = Manual de Adubação e Calagem para o Estado do Paraná. SBCS/NEPAR, Curitiba, PR, Brazil (in Portuguese).

Plaza, I.; Ontiveros-Ortega, A.; Calero, J.; Aranda, V. 2015. Implication of zeta potential and surface free energy in the description of agricultural soil quality: effect of different cations and humic acids on degraded soils. Soil & Tillage Research 146: 148-158.

Reichert, J.M.; Norton, L.D.; Favaretto, N.; Huang, C.; Blume, E. 2009. Settling velocity, aggregate stability, and interrill erodibility of soils varying in clay mineralogy. Soil Science Society of America Journal 73: 1369-1377.

Rengasamy, P.; Sumner, M.E. 1998. Processes involved in sodic behaviour. p. 35-50. In: Sumner, M.E.; Naidu, R., eds. Sodic soils: distribution, properties, management and environmental consequences. Oxford University Press, New York, NY, USA.

Rengasamy, P.; Tavakkoli, E.; McDonald, G.K. 2016. Exchangeable cations and clay dispersion: net dispersive charge, a new concept for dispersive soil. European Journal of Soil Science 67: 659-665.

Ribeiro, B.T.; Lima, J.M.; Curi, N.; Oliveira, G.C.; Lima, P.L.T. 2012. Surface charge of clay fraction as affected by vinasse and phosphorus. Química Nova 34: 5-10 (in Portuguese, with abstract in English).

Rosa, J.D.; Cooper, M.; Darboux, F.; Medeiros, J.C. 2013. Influence of tillage systems and simulated rainfall on the process of surface crust formation. Revista Brasileira de Ciência do Solo 37: 400-410 (in Portuguese, with abstract in English).

Smith, C.J.; Oster, J.D.; Sposito, G. 2015. Potassium and magnesium in irrigation water quality assessment. Agricultural Water Management 157: 59-64.

Spera, S.T.; Denardin, J.E.; Escosteguy, P.A.V.; Santos, H.P.; Figueroa, E.A. 2008. Clay dispersion in microaggregates of soil incubated with limestone. Revista Brasileira de Ciência do Solo 32: 2613-2620 (in Portuguese, with abstract in English).

Sposito, G. 2008. The Chemistry of Soils. Oxford University Press, New York, NY, USA.

Tombácz, E.; Szekeres, M. 2006. Surface charge heterogeneity of kaolinite in aqueous suspension in comparison with montmorillonite. Applied Clay Science 34: 105-124.

Trefalt, G.; Ruiz-Cabello, F.J.; Borkovec, M. 2014. Interaction forces, heteroaggregation, and deposition involving charged colloidal particles. The Journal of Physical Chemistry 118: 6346-6355.

Volkov, A.G.; Deamer, D.W. 1997. Two mechanisms of permeation of small neutral molecules and hydrated ions across phospholipid bilayers. Bioelectrochemistry 42: 153-160.

Wang, P.; Keller, A.A. 2009. Sorption and desorption of atrazine and diuron onto water dispersible soil primary size fractions. Water Research 43: 1448-1456.

Zhang, X.C.; Norton, L.D. 2002. Effect of exchangeable Mg on saturated hydraulic conductivity, disaggregation and clay dispersion of disturbed soils. Journal of Hydrology 260: 194-205.