

Point of Zero Salt Effect: Relationships with Clay Mineralogy of Representative Soils of the São Paulo State, Brazil*¹

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ABSTRACT

The point of zero salt effect (PZSE) is the soil pH value at which the magnitude of the variable surface charges is not changed due to variations in the ionic concentration of the soil solution. This property influences not only electrochemical phenomena occurring at the solid-solution interface but also the flocculation degree of the soil particles. In this study we investigated the relationships between the clay mineralogy and the PZSE values of representative soils of the São Paulo State, Brazil. The results confirmed the usefulness of the difference between the soil pH values measured in 1 mol L⁻¹ KCl (pH_{KCl}) and in water (pH_{H₂O}) ($2 \text{ pH}_{\text{KCl}} - \text{pH}_{\text{H}_2\text{O}}$) for estimating the PZSE of tropical soils, except for the ones rich in exchangeable Al; furthermore, the ΔpH index ($\text{pH}_{\text{KCl}} - \text{pH}_{\text{H}_2\text{O}}$) was highly correlated with the difference between the PZSE and pH_{H₂O} values, reiterating the ΔpH utility for estimating both the signal and the magnitude of the net surface charge of tropical soils. Finally, correlation and multiple regression analyses showed that the PZSE value of weathered non-allophanic tropical soils tends to increase and to equal the soil pH due to the weathering-induced kaolinite destabilization and concomitant Fe- and Al-oxide accumulation.

Key Words: electrochemical properties, iron oxides, kaolinite, tropical soils, weathered soils

INTRODUCTION

The point of zero salt effect (PZSE) is the designation proposed by Parker *et al.* (1979) for the soil pH value at which the ionic concentration of the soil solution does not influence the magnitude of the variable surface charges. The study of this property is of great interest for the chemistry of variable charge soils because the electrochemical phenomena occurring at the soil-solution interface have their magnitudes influenced by the balance between negative and positive variable surface charges, whose proportions, for weathered soils, depend practically on the difference between the PZSE and soil pH values (Van Raij and Peech, 1972). Furthermore, the difference PZSE – pH is inextricably related to the flocculation degree of soil particles and, consequently, to water dynamics, gas transfer and susceptibility to erosional losses. Finally, the PZSE determination can be useful for the elucidation of the mechanisms associated with the specific adsorption of cations (*e.g.*, Cd²⁺, Cu²⁺, Pb²⁺ and Zn²⁺) and the adsorption of some anions (*e.g.*, F⁻, PO₄³⁻ and SO₄²⁻), which can modify the proportion between the negative and positive surface charges of the soils (Yu *et al.*, 1997; Zhang, 1997).

São Paulo State is covered by weathered soils whose clay mineralogies are comprised mainly of kaolinite, gibbsite, hematite and goethite (Schwertmann and Herbillon, 1992). Other minerals such as vermiculite, illite, anatase and rutile as well as amorphous phases are also found in these soils, however at minor levels. Contrary to other regions of the South America, allophane and other similar tephra-derived materials are not constituents of the soils of São Paulo State (de Oliveira, 1999). It is probable, as verified by Varajão *et al.* (2002), that the small amounts of noncrystalline aluminosilicates present in the São Paulo State soils are derived from kaolinite and/or gibbsite weathering-induced destabilization.

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Although the crystallochemical properties that define the point of zero charge (PZC) values of oxides and phyllosilicates, including those of pedological interest, were well described by Parks (1965, 1967), since the seminal work of Van Raij and Peech (1972), there has been a lack of quantitative studies dealing on the direct influence of clay mineralogy on the PZSE values of tropical non-allophanic soils. Thus, the present research aims to evaluate the clay mineralogy effects on the PZSE values of representative soils of São Paulo State, Brazil.

MATERIALS AND METHODS

Air-dried samples (< 2 mm) of the B horizon of 7 Ferralsols, 4 Acrisols and 1 Nitisol (FAO *et al.*, 2002), soil units that comprise about 74 % of the mapping units of the soil map of São Paulo State (de Oliveira, 1999), were used in the present research. General information on these samples including classification, parent materials, localization, and depth of sampling is presented in Table I. The soil samples were characterized for contents of clay (Gee and Bauder, 1986), organic carbon (Nelson and Sommers, 1982) and exchangeable Al (Bertsch and Bloom, 1996). Soil pH values were measured in water ($\text{pH}_{\text{H}_2\text{O}}$), 0.01 mol L⁻¹ CaCl₂ ($\text{pH}_{\text{CaCl}_2}$) and 1 mol L⁻¹ KCl (pH_{KCl}) at 1:2.5 soil (g)/solution (mL) ratio (EMBRAPA, 1997). The ΔpH index was calculated from the difference between pH_{KCl} and $\text{pH}_{\text{H}_2\text{O}}$ values (Mekaru and Uehara, 1972).

TABLE I

Classification, parent materials, localization in the São Paulo State and sampling depths of the soils

Soil	Classification	Parent material	Localization	Depth
				cm
1	Acric Ferralsol	Basalt	Ribeirão Preto	100–140
2	Rhodic Ferralsol	Basalt	Itacemópolis	100–110
3	Rhodic Ferralsol	Basalt	Luís Antonio	80–100
4	Acric Ferralsol	Basalt	Luís Antonio	150–170
5	Orthic Ferralsol	Schist	Piracicaba	100–110
6	Orthic Ferralsol	Sandstone	Piracicaba	100–110
7	Orthic Ferralsol	Sandstone	São Carlos	80–100
8	Eutric Nitisol	Diabase	Piracicaba	30–40
9	Orthic Acrisol	Sandstone	Pindorama	100–120
10	Orthic Acrisol	Sandstone	Vera Cruz	100–120
11	Orthic Acrisol	Schist	Rio Claro	70–80
12	Orthic Acrisol	Basalt	Piracicaba	100–110

The Si, Fe and Al contents associated with secondary minerals were determined in extracts obtained after boiling both 1 g of soil for 30 min in 20 mL of 9 mol L⁻¹ H₂SO₄ (Fe and Al) and the remaining solid for 1 min in 150 mL of 0.2 mol L⁻¹ NaOH (Si). The acid extracts were analyzed for Al and Fe by atomic absorption spectrometry (AAS) whereas Si was quantified in the alkaline extracts by colorimetry (EMBRAPA, 1997). With these data the weathering indices K_i ($\text{SiO}_2/\text{Al}_2\text{O}_3$, mol mol⁻¹) and K_r ($\text{SiO}_2/(\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3)$, mol mol⁻¹) were calculated (EMBRAPA, 1999). Dithionite- and ammonium-oxalate-extractable Fe and ammonium-oxalate-extractable Al were determined by AAS after extractions carried out directly in the clay fraction (< 2 μm), previously separated by gravity settling (Jackson, 1969), following the procedures outlined by Buurman *et al.* (1996) (Fe_d) and by Mckeague and Day (1966) (Fe_o and Al_o).

X-ray diffraction analyses were performed on non-oriented powder samples of the clay fractions after their treatments with boiling 5 mol L⁻¹ NaOH for concentration of iron oxides (Kämpf and Schwertmann, 1982). The patterns were recorded with a Siemens D5000 computer-oriented diffractometer using monochromated CoK α radiation at 25 mA and 35 kV. The scans were obtained from 20 to 45° 2θ at a speed of 0.6° 2θ min⁻¹, and both peak positions and raw areas were determined using the software EVA 3.09.

Kaolinite and gibbsite contents were semiquantified by differential thermal analysis (Tan *et al.*, 1986) carried out in the dithionite-treated clay previously mixed with anhydrous Al_2O_3 as inert material. The analyses were performed under N_2 atmosphere in a Shimadzu DSC-50 analyser operated at the heating rate of $10^\circ\text{C min}^{-1}$. The results were corrected to the total-clay fraction considering the weight difference of the clay fraction before and after iron oxides removal. Clay contents of hematite (Hm) and goethite (Gt) were semiquantified from the ratio $\text{Hm}/(\text{Hm}+\text{Gt})$ and the difference Fe_d-Fe_o . The ratio $\text{Hm}/(\text{Hm}+\text{Gt})$ was calculated using the following equation derived by Resende *et al.* (1987):

$$R = \frac{0.708A_{\text{Hm}104}}{A_{\text{Gt}110} + 0.708A_{\text{Hm}104}} \quad (1)$$

where $R = \text{Hm}/(\text{Hm} + \text{Gt})$; $A_{\text{Hm}104}$ and $A_{\text{Gt}110}$ = areas of the hematite (104) and goethite (110) diffraction peaks in the XRD patterns of the iron-oxide-concentrated clay. The factor 0.708 corresponds to the ratio $A_{\text{Gt}110}/A_{\text{Hm}104}$ found by Jones (1981) in a 1:1 hematite and goethite mixture.

For clays that had goethite and hematite, the following equations were used:

$$\text{Gt} = \frac{\text{Fe}_d - \text{Fe}_o}{\frac{160(1-x)}{160 - 58x} \frac{R}{(1-R)} + \frac{80(1-y)}{89 - 29y}} \quad (2)$$

where Gt = goethite clay content (g kg^{-1}); Fe_d = dithionite-extractable iron ($\text{g kg}^{-1} \text{Fe}_2\text{O}_3$); Fe_o = ammonium oxalate-extractable iron ($\text{g kg}^{-1} \text{Fe}_2\text{O}_3$); x and y = respective aluminium substitutions in hematite and in goethite (mol mol^{-1}).

$$\text{Hm} = \frac{R}{1-R} \text{Gt} \quad (3)$$

where Hm = hematite clay content (g kg^{-1}).

For clays that did not have hematite, the goethite clay content was determined with the following equation:

$$\text{Gt} = (\text{Fe}_d - \text{Fe}_o) \frac{(89 - 29y)}{80(1 - y)} \quad (4)$$

Equations 2, 3 and 4 were derived considering that the respective chemical formulas of Al-substituted hematite and goethite are given by $\text{Fe}_{(2-2x)}\text{Al}_{2x}\text{O}_3$ and $\text{Fe}_{(1-y)}\text{Al}_y\text{OOH}$ and that the iron content associated with hematite plus goethite corresponds to $\text{Fe}_d - \text{Fe}_o$. The aluminium substitutions were determined from iron-oxide-concentrated XRD data using the equations derived by Schwertmann *et al.* (1979) for hematite and by Schulze (1984) for goethite.

The soil PZSE values were determined through the potentiometric titration method (Van Raij and Peech, 1972) with a few modifications: 4 g soil samples and 20 mL of 0.1, 0.01 and 0.001 mol L^{-1} NaCl were separately added to 50-mL vessels, being prepared 6 soil-solution mixtures for each salt concentration. Afterwards, in each salt series, 3 vessels were treated with HCl (0.3, 0.2 and 0.1 mL of 0.4 mol L^{-1} HCl), 2 received NaOH (0.2 and 0.1 mL of 0.4 mol L^{-1} NaOH) and 1 received neither acid nor base. Neglecting the changes in the salt concentrations promoted by the addition of the small volumes of acid and base, all vessels were stirred during 5 min and left on the bench for 24 h. After this period, the pH values of the soil suspensions were measured. In order to avoid the errors associated to the manual drawing of the titration potentiometric curves, the experimental data (*i.e.* $\text{cmol kg}^{-1} \text{H}^+$ or OH^- added and pH values) were submitted to the software PZSE 1.0 for Windows (Alves *et al.*, 2002) which fits them to the 4th-degree polynomial model, calculates the pH values associated to the crossing points of each one of the 3 pairs of titration curves (0.1 and 0.01 mol L^{-1} , 0.1 and 0.001 mol L^{-1} , and 0.01 and 0.001 mol L^{-1}) and finally computes the mean of these 3 pH values, which consists of

the PZSE value of the soil. In addition to the PZSE, the point of zero charge (PZC) values of the soils were estimated using the following equation proposed by Keng and Uehara (1974): $PZC = 2 \text{pH}_{\text{KCl}} - \text{pH}_{\text{H}_2\text{O}}$.

All determinations were performed in triplicate and the experimental data were submitted to correlation and regression analyses. The influence of clay mineralogy on the PZSE was assessed through multiple regression analysis in which the PZSE figured as dependent variable of the clay contents of kaolinite, gibbsite, hematite, goethite, Fe_o and Al_o , all previously corrected to the whole soil using the soil clay content values. Both the incorporation and permanence of each predictor variable in the model were defined using the stepwise procedure (SAS, 1994). The presence of multicollinearity in the model was assessed through the calculations of the variation inflation factor associated to each predictor variable (Neter *et al.*, 1990).

RESULTS AND DISCUSSION

Soil and clay properties

The soil and clay properties are summarized in Table II, where it can be seen that most soils were acidic ($\text{pH}_{\text{CaCl}_2} \leq 5$), clayey (clay $> 350 \text{ g kg}^{-1}$) (EMBRAPA, 1999), poor in organic carbon ($1.5\text{--}7.8 \text{ g kg}^{-1}$) and had no exchangeable Al. All soils, except soils 1 and 4, had $\Delta\text{pH} < 0$, which indicates that they present negative net surface charge (Mekaru and Uehara, 1972).

TABLE II

Selected soil and clay properties

Soil	Al^{3+}	Clay	OC^{a}	pH^{b}	$\Delta\text{pH}^{\text{c}}$	PZSE ^d	PZC ^e	K_i^{f}	K_r^{f}	Ka^{g}	Gb^{g}	Hm^{g}	Gt^{g}	Fe_o^{g}	Al_o^{g}	Ka_d^{h}	Gb_d^{h}
	$\text{cmol}_c \text{ kg}^{-1}$	g kg^{-1}	g kg^{-1}							g kg^{-1}							
1	0	529	6.0	5.0	0.1	5.6	5.4	0.72	0.42	234	459	226	33	150	130	332	650
2	0	481	7.8	5.5	-0.8	5.8	5.0	1.14	0.71	405	245	205	37	120	110	557	337
3	0.7	543	4.5	4.3	-0.1	4.5	4.4	0.97	0.61	408	337	213	9	110	100	542	448
4	0	647	4.9	5.4	0.4	6.1	6.3	0.49	0.30	150	543	226	40	140	160	216	781
5	0.1	774	7.4	4.9	-0.8	4.1	3.9	1.44	1.18	522	119	23	110	50	80	616	141
6	0	244	2.1	4.8	-1.0	3.5	3.5	1.65	1.29	632	10	20	83	60	60	718	12
7	0	421	2.4	4.8	-0.4	4.5	4.5	0.69	0.56	256	553	2	160	30	110	313	675
8	0	597	1.8	5.0	-0.7	4.8	4.6	1.56	1.00	535	23	128	84	170	70	705	31
9	8.2	347	1.5	4.0	-1.2	2.9	2.6	1.75	1.48	601	2	3	83	50	70	671	3
10	6.6	205	2.1	3.7	-0.7	3.5	3.3	1.81	1.56	773	0	14	56	50	60	844	0
11	0	475	3.0	5.2	-0.8	4.0	4.3	1.63	1.12	530	0	23	124	140	90	645	0
12	25.4	632	2.4	3.8	-1.1	3.6	2.7	1.66	1.34	513	9	26	90	90	90	596	10

^a) Organic carbon; ^b) pH measured in $0.01 \text{ mol L}^{-1} \text{ CaCl}_2$; ^c) $\Delta\text{pH} = \text{pH}_{\text{KCl}} - \text{pH}_{\text{H}_2\text{O}}$; ^d) Point of zero salt effect; ^e) Point of zero charge ($\text{PZC} = 2 \text{pH}_{\text{KCl}} - \text{pH}_{\text{H}_2\text{O}}$); ^f) Weathering index [$K_i = 1.7 \text{ SiO}_2 / \text{Al}_2\text{O}_3$; $K_r = 1.7 \text{ SiO}_2 / (\text{Al}_2\text{O}_3 + 0.64 \text{ Fe}_2\text{O}_3)$] where SiO_2 , Al_2O_3 and Fe_2O_3 are the respective soil contents of Si, Al and Fe associated to secondary minerals; ^g) Clay contents of kaolinite (Ka), gibbsite (Gb), hematite (Hm), goethite (Gt) and ammonium-oxalate-extractable Fe (Fe_o) and aluminum (Al_o); ^h) Dithionite-treated clay contents of kaolinite (Ka_d) and gibbsite (Gb_d).

The K_i and K_r indexes are used in the Brazilian System of Soil Classification to characterize the soil weathering status. As weathering increases, there is a progressive silica loss from clay minerals and a concomitant accumulation of iron and aluminium oxides. Therefore, the lower K_i and K_r values are, the more weathered the soil is. The K_i range (0.49–1.81) shows the wide variation of the weathering status of the studied soils whereas the K_r values separate them into oxidic ($K_r < 0.75$) and kaolinitic ($K_r > 0.75$) (EMBRAPA, 1999), which agrees with the clay mineralogy data (Table II). The soil PZSE values, which consisted of the calculated crossing point of three potentiometric titration curves (Fig. 1), ranged from 2.9 to 6.1.

Although the lowering effect of the organic matter on the PZSE is well known (Hendershot and Lavkulich, 1979), in the present study a significant positive relationship was observed between PZSE

and organic carbon soil content (% OC): $PZSE = 3.3611 + 2.8206OC$; $P > F = 0.0279$; $R^2 = 0.38$.

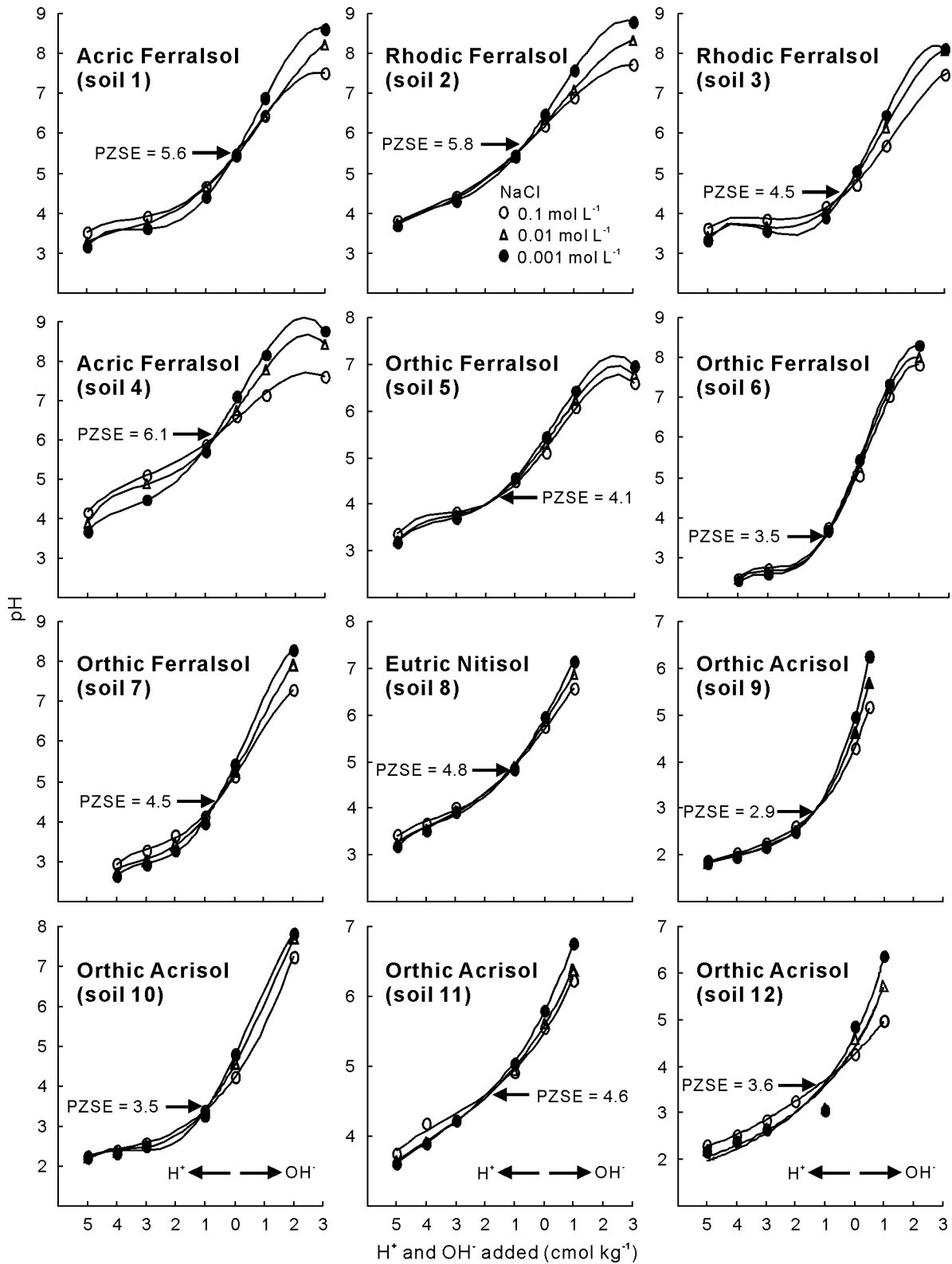


Fig. 1 Potentiometric titration curves of the studied soils.

Probably, this result can be ascribed to the positive correlation ($r = 0.58$, $P < 0.05$) between the soil contents of OC and ammonium-oxalate-extractable Al (Al_o), whose high positive correlation with the PZC of Thai and Japanese soils was verified by Sakurai *et al.* (1989).

The soil PZC, whose estimated values ranged from 2.7 to 6.2, is the soil pH value at which the total negative surface charge (*i.e.* variable + permanent negative charge) is equivalent to the total positive one. Considering that both negative and positive permanent charges are less expressive in weathered soils, their PZC values tend to the PZSE ones. This explains the high correlation observed between the PZC and the PZSE values ($r = 0.96$, $P < 0.01$).

The PZC and PZSE values show a major discrepancy associated with soil 12, which has the highest content of 1 mol L⁻¹ KCl-extractable Al. After the soil is in contact with 1 mol L⁻¹ KCl solution, the Al ions displaced by the K ones from the exchange sites promote hydrolysis giving rise to H₃O⁺ ions which lower the solution pH value. In fact, the soil PZC as estimated from pH_{KCl} and pH_{H₂O} was inversely correlated to the Al³⁺ soil content ($r = -0.65$, $P < 0.05$), whereas no correlation was observed between the soil PZSE and Al³⁺. Therefore, PZSE estimates using the approach of Keng and Uehara (1974) are valid only for soils having low levels of exchangeable Al.

Taking into consideration the Gouy-Chapman model for the electric double layer (Singh and Uehara, 1999), it can be observed that both the signal and magnitude of net surface charge are dependent on the difference $PZC - pH_{H_2O}$. Thus, when $PZC < pH_{H_2O}$ the net surface charge is negative, whereas PZC values higher than the pH_{H₂O} ones define positive net surface charge. The high similarity between PZC and PZSE observed here allows the same comparisons to be made between PZSE and pH_{H₂O} values. For the two samples presenting $\Delta pH > 0$ (soils 1 and 4), the differences between the PZSE and pH_{H₂O} were also positive whereas for all remaining soils both ΔpH and the difference ($PZSE - pH_{H_2O}$) were lower than zero. These observations and the high correlation between PZSE and pH_{KCl} ($r = 0.94$, $P < 0.01$) support the usefulness of the ΔpH index for estimating both the signal and magnitude of the net surface charge of non-allophanic tropical soils.

Relationships between soil weathering and PZSE

The inverse correlations between the soil PZSE values and the weathering indexes K_i ($r = -0.77$, $P < 0.01$) and K_r ($r = -0.87$, $P < 0.01$) show that the PZSE values tend to be higher in more weathered soils. As will be shown later, these relationships are explained by the enrichment in oxides and the concomitant destabilization of clay minerals, mainly kaolinite, which takes place in such soils as weathering advances. These weathering trends are in agreement with the direct correlations between dithionite-treated clay content of kaolinite and the K_i index ($r = 0.94$, $P < 0.01$) and the inverse correlation between the gibbsite dithionite-treated clay content and the above-mentioned weathering index ($r = -0.99$, $P < 0.01$).

The absolute difference between the soil PZSE and pH_{H₂O} correlated directly with the K_i ($r = 0.79$, $P < 0.01$) and K_r ($r = 0.83$, $P < 0.01$) indexes showing that the PZSE values tend toward the soil pH ones as weathering advances. These results are quite similar of those found by Hendershot *et al.* (1979) who suggested that the absolute difference between PZC and pH_{KCl} could be used as a measure of pedogenic development of Canadian soils. However, for our tropical soils, the absolute difference between PZSE and pH_{KCl} was less correlated to the weathering indexes K_i ($r = 0.59$, $P < 0.05$) and K_r ($r = 0.64$, $P < 0.05$) than the difference $|PZSE - pH_{H_2O}|$. These results can be attributed to both the high correlation between PZSE and pH_{KCl} and to the fact that the PZSE and pH_{H₂O} values of our soils were uncorrelated. Taking into consideration that the pH_{H₂O} values are closer to the soil solution pH values than the pH_{KCl} ones, the absolute difference $PZSE - pH_{H_2O}$ seems to be a better indicator of the pedogenic development of non-allophanic tropical soils than the absolute difference between soil PZSE and pH_{KCl} values.

As mentioned earlier, according to the Gouy-Chapman model for the electric double layer, the net electric surface charge is proportional to the difference $PZC - pH$. Therefore, considering the relation-

ships found here between the PZSE and the soil weathering degree, as the tropical soils become more weathered their net surface charges tend to zero. This favours the strong aggregation of the soil particles as normally verified for the highly weathered Brazilian Ferralsols (Fontes, 1992).

Clay mineralogy influence on PZSE

The results of multiple regression analysis carried out among PZSE and clay component contents (Table III) show that the soil contents of kaolinite, hematite and goethite were able to explain 81 % of the variation of the soil PZSE values.

TABLE III

Results of the multiple regression analysis relating the point of zero salt effect (PZSE) to the clay component contents (% whole soil) ($PZSE = a_0 + a_1 \text{ kaolinite} + a_2 \text{ hematite} + a_3 \text{ goethite}$)

Coefficient	Value	Standard error	<i>t</i>	<i>P</i> > <i>t</i>	VIF ^{a)}
<i>a</i> ₀	3.5465	0.4010	8.844	0.0001	0.0000
<i>a</i> ₁	-0.0382	0.0172	-2.216	0.0576	1.5413
<i>a</i> ₂	0.1796	0.0273	6.578	0.0002	1.2849
<i>a</i> ₃	0.2159	0.0706	3.056	0.0157	1.8401

^{a)} VIF means variance inflation factor. *F*-value = 16.2, *P* > *F* = 0.0009, *R*² = 0.81, *n* = 12.

According to Neter *et al.* (1990), when the predictor variables of a multiple regression model are correlated among themselves, multicollinearity among them is said to exist. In this case, the following problems can occur in the multiple regression analysis: i) parameter estimates may not be significant, even though a definite statistical relationship exists and ii) a parameter estimate may have a sign that is different from what is expected. One way of detecting multicollinearity consists of calculating the variance inflation factors (VIF), which measure the inflation of the variances for the regression coefficients above what would be expected if there was no correlation among the predictor variables. A VIF value greater than 10 indicates the presence of strong multicollinearity.

Preliminary regression analysis carried out with all clay components in the model showed VIF values greater than 10 for all of them. For this reason, not all clay components figured in the model when the stepwise procedure was applied. Despite this, the obtained equation was coherent with the expected effects of the clay mineralogy on the PZSE. The negative value found for the kaolinite coefficient demonstrates that this mineral lowers the soil PZSE value, which, in turn, is increased by the increments of both hematite and goethite soil contents.

The lowering effect of kaolinite on PZSE is probably due to its edge single OH groups coordinated with Si⁴⁺, the silanol (SiOH) groups. Being more easily ionizable than the single OH groups coordinated with the Al³⁺ (AlOH) and to Fe³⁺ (FeOH), the silanol groups tend to only dissociate protons (Sparks, 1995). For this reason, the protonation of silanol groups takes place only at higher H⁺ concentrations (low pH values), which contributes to the lowering of PZSE of the soils, mainly in non-allophanic kaolinitic ones. These trends are supported by the correlations between the PZSE and the relationships Al/(Al + Si) (*r* = 0.75, *P* < 0.01) and (Al + Fe)/(Al + Fe + Si) (*r* = 0.89, *P* < 0.01), similar to the findings of Zhang and Zhang (1992) for Chinese Ferralsols.

As these soils become more weathered, the kaolinite is destabilized and there is a progressive accumulation of gibbsite, hematite, goethite and amorphous phases. Thus, despite not considering all of the clay components, the multiple regression results are in agreement with the inverse correlation verified between the PZSE and the degree of soil weathering.

CONCLUSIONS

The PZSE of non-allophanic tropical soils having low levels of organic matter can be reasonably estimated from the soil pH values measured in both water and 1 mol L⁻¹ KCl, except for such soils rich

in exchangeable Al. In the same way, the difference $\text{pH}_{\text{KCl}} - \text{pH}_{\text{H}_2\text{O}}$ can provide a good estimation of the net surface charge of these soils.

As the above-mentioned soils become more weathered, their PZSE values increase due to kaolinite destabilization and tend toward the soil pH values, dropping the soil net surface charge to values near zero.

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