Surface charge characteristics of selected Philippine soils

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ABSTRACT

Tulin .A.B. 2000. Surface charge characteristics of selected Philippine soils. *Ann. Trop. Res.* 22[1&2]:60-77.

The surface charge characteristics of selected Philippine soils, namely: Andisols, Alfisols, Ultisols and Vertisols were studied in relation to the nature of their colloidal components and other soil chemical and mineralogical properties. Sixteen soil samples representing the A and B horizons of 8 soil profiles sampled in different provinces were used in this study. Based on clay mineralogy, the Andisols and Ultisols were dominated by variable charge colloids while the Alfisols and the Vertisols consisted mainly of permanent charge colloids. The magnitudes of increase in negative charge and decrease in positive charge with an increase in pH were indicative of predominant variable charge behavior even for montmorillonitic and/or vermiculitic soils (Vertisols). The KCl adsorption method of determining negative and positive charges was inapplicable to illitic soils. Because of these observations, zero point of charge (ZPC) of tropical soils require careful interpretation. Generally, ZPC values varied among soil orders, with the Vertisols and the Alfisols exhibiting lower ZPC values (from < 2.0 to 5.3) as compared to the Ultisols and the Andisols (from 2.5 to 8.5). Variations in ZPC values among soil orders were attributed to differences in mineralogy, clay free oxides and organic matter contents.

Keywords: permanent charge colloids. Philippine soils. surface charge. variable charge colloids. zero point of charge.

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INTRODUCTION

Surfaces of soil particles develop electrical charge either from isomorphous substitutions among ions of differing valence in soil minerals, or from reactions of surface functional groups with ions in the soil solutions (Sposito, 1984). Based on the above, soil colloids may be grouped into two general types: constant surface charge colloids and constant surface potential colloids (Uehara and Gillman, 1981).

The constant surface charge colloids consist of 2:1 type clay minerals which possess permanent negative charges that originated from isomorphous substitution in their crystal structures. On the other hand, pH-dependent charge colloids (constant surface potential colloids) are made up of both organic and inorganic colloids consisting mainly of 1:1 type minerals, oxides and hydrous oxides of iron and aluminum in crystalline and amorphous forms, amorphous and poorly crystalline alumino-silicates such as allophane and imogolite as well as soil organic matter (Parfitt, 1980; McBride, 1989). Negative and positive charges on these materials arise from deprotonation and protonation of functional groups exposed on their surfaces, respectively, and ions with opposite charge which are adsorbed on charged sites (Sposito, 1984).

Since the surface charge of pH-dependent charge colloids vary with pH, salt concentration and other factors, these soil constituents are widely known as variable charge colloids. The parameters commonly used to characterize such soils include zero point of charge (ZPC), surface area, surface potential, and the magnitude and distribution of electric charges. Much emphasis though is given on ZPC as the most important criterion used in describing a variable charge system (Sakurai *et al.*, 1988 & 1989).

The chemical behavior of variable charge soils is not as intensively and extensively studied as the constant charge soils. In fact, in Asia, very limited studies have been reported until now. This situation is particularly true for soils in the Philippines such as Ultisols, Alfisols and Andisols which cover the most extensive agricultural lands (Briones, 1982).

The main objective of this study was to evaluate the surface charge characteristics (ZPC, and magnitude and distribution of electric charges) of some variable and constant charge soils in the Philippines and evaluate their relationships with the nature of their colloidal components and other soil chemical and mineralogical properties.

MATERIALS AND METHODS

Soil samples

Sixteen soil samples were collected from eight soil profiles in different provinces of Luzon, Philippines. The sampling sites and classification of the soils are presented in Table 1. It should be noted that the Andisols (Taal and Tagaytay) and the Ultisols (Luisiana and Antipolo) represented the variable charge soils while the Alfisols (Annam and Ibaan) and the Vertisols (Binangonan and Sibul) represented the permanent charge soils.

Table 1.   Some site characteristics of the eight soils studied

Profile No.	Soil Series	Horizon	Depth (cm)	Location	Soil Order
1	Taal	Ap	0 - 8	Kawit, Taal,	Andisol
		B	8 - 46	Batangas	
2	Tagaytay	Ap	0 - 40	Alfonso,	Andisol
		Bt	50 - 100	Cavite	
3	Annam	Ap	0 - 9.5	Pagbilao,	Alfisol
		B2	9.5 - 19	Quezon	
4	Ibaan	Ap	0 - 20	Pagbilao,	Alfisol
		B2	20 - 47	Quezon	
5	Luisiana	Ap	0 - 5	Caliraya,	Ultisol
		B21t	5 - 30	Laguna	
6	Antipolo	Ap	0 - 15	Siniloan,	Ultisol
		B21t	15 - 30	Laguna	
7	Binangonan	Ap	0 - 6	Teresa,	Vertisol
		B22	19 - 35	Rizal	
8	Sibul	Ap	0 - 27	Catalagan,	Vertisol
		B21t	27 - 41	Batangas	

Soil characterization

Soil samples were analyzed for physical, chemical and mineralogical properties. Particle size distribution was determined by the pipette method. Soil pH was determined potentiometrically both in water and 1 M KCl at

1:2.5 soil: water/KCl ratio; cation exchange capacity (CEC) and exchangeable bases using 1 M NH$_4$OAc buffered at pH 7 (Chapman, 1965); organic matter by wet oxidation (Walkley and Black, 1934); exchangeable Al by colorimetry (Yuan and Fiskell, 1959); and exchangeable Fe by atomic absorption spectrometry following 1 M NH$_4$OAc (pH 4.8) extraction (Olson, 1948). For mineralogical analyses, the clay fraction of each sample was pretreated with 6% H$_2$O$_2$ for the removal of organic matter and with dithionite-citrate bicarbonate for the removal of free oxides following the recommended method (Whittig, 1965) and the identification were carried out using the Rigaku Miniflex X-ray diffractometer using Ni-filtered CuKa radiation generated at 30 kV and 10 mA.

Distribution of electric charges

The magnitude and distribution of the positive and negative electric charges of the different soil samples were determined by measuring the adsorption of both positive and negative ions as a function of electrolyte concentration and pH. The method was the modified Schoefield method (1949) described by Gillman (1979) as follows:

A 2-g soil sample (oven dry basis) was placed in a preweighed 30 ml plastic centrifuge tube, and 10 ml of 2 M KCl was added. The pH was adjusted to the desired value (pH 3, 4, 6, and 8) by addition of 0.1 M HCl or 0.1 M KOH. Water was then added to make the final volume of 20 ml. On the next day, the pH was readjusted and the supernatant separated by centrifugation.

The soil sample was then washed 3 times with 25 ml of 0.2 M KCl and then 5 times with 0.01 M KCl as the saturating solution. Some readjustments of the pH was made with HCl or KOH before the last two washings. After the final centrifugation, the centrifuge tube containing the washed soil was drained and weighed immediately to determine the occluded solution volume. The pH of the final extract was determined and considered as the equilibrium pH. The sample was then washed five times with 20 ml of 0.5 M ammonium nitrate. The collected washings were analyzed for K and Cl and the amount of each ion adsorbed at each equilibrium pH was calculated after correcting for the entrained KCl solution. Potassium was determined using the EEL flame photometer while chlorine was analyzed by potentiometric titration using Beckman chloride electrode. The amounts of cation and anion extracted and corrected for the occluded salt solution were expressed as equivalent amounts of negative and positive charges, respectively.

Zero point of charge (ZPC)

The potentiometric titration curves were plotted to determine the ZPC at varying pH levels and electrolyte concentrations. In this study, the electrolyte used was $CaCl_2$ with concentrations of 2, 0.2, 0.02, and 0.004 *M*. Series of titrations were done on individual soil samples following the procedure outlined by Van Raij and Peech (1972) as follows:

Four grams of soil (oven dry basis) were placed into each of sixty 50 ml beakers arranged in 4 rows of 15 beakers each. Ten ml of electrolyte with concentrations of 2, 0.2, 0.02, and/or 0.004 *M* were added to each beaker in rows 1, 2, 3, and 4, respectively. After designating the middle beaker in each row as zero, increasing amounts (i.e. 0.5, 1.0, 1.5, 2.0, 3.0, and 3.5 ml) of 0.1 *M* HCl were added to the beakers at the left of zero, while increasing amounts (same volume as the acid used) of 0.1 *M* KOH were added to the beakers at the right of zero. Then distilled water was added to each beaker to make a total volume of 20 ml.

The solution was allowed to equilibrate for 4 days, with occasional stirring. Titration curves from the titration with acid and base of each of the 4 electrolyte solution were constructed to represent the blanks. After 4 days, the pH of the solution was recorded and the H or OH adsorbed was plotted against pH for each electrolyte concentration on one graph. The ZPC was then determined as the common intersection point of the titration curves.

RESULTS AND DISCUSSION

Soil physical and chemical characteristics

The distribution of sand, silt and clay fractions and textural classes of the soil samples are presented in Table 2. The data showed that with the exception of Taal, Tagaytay and Ibaan series which were moderately-textured, the soils were generally clayey.

Table 3 shows the soil chemical properties of the soils studied. The pH values in KCl were lower than the pH values in water except for the second layer of Taal soil (8-46 cm depth). This means that the delta (Δ) pH values of the samples were negative except for Taal soil. A negative Δ pH indicates that the soil is dominated by variable charge minerals, as shown by Luisiana and Antipolo series.

Table 2. Particle size distribution and textural classes of the eight soils

Profile No.	Order/Soil Series Name	Horizon	Sand	Silt	Clay	Textural Class*
			(-------------%-------------)			
	Andisols					
1	Taal	Ap	4.3	58.8	39.9	SiC
		B	80.4	3.2	16.4	SL
2	Tagaytay	Ap	63.4	14.1	22.9	SCL
		Bt	55.1	15.9	29.1	L
	Alfisols					
3	Annam	Ap	30.3	27.5	42.2	C
		B2	25.9	14.4	59.7	C
4	Ibaan	Ap	27.5	40.1	32.6	SiCL
		B2	56.7	2.0	41.3	SC
	Ultisols					
5	Luisiana	Ap	48.1	7.0	44.9	C
		B21t	25.5	21.3	53.2	C
6	Antipolo	Ap	14.0	17.4	68.6	C
		B21t	18.3	21.0	60.7	C
	Vertisols					
7	Binangonan	Ap	13.8	10.0	76.2	C
		B22	17.4	19.2	63.4	C
8	Sibul	Ap	25.6	13.8	60.6	C
		B21t	22.2	17.0	60.8	C

* C - clay; Cl - clay loam; SiC - silty clay; SiCL - silty clay loam; SC - sandy clay; SL - sandy loam; SCL - sandy clay loam

The organic matter (OM) contents of the different soil samples varied among soil orders and also with soil depth. Higher amounts of OM were consistently obtained in the surface than in the subsurface layers for the rest of the samples.

The values for cation exchange capacity (CEC) among the four soil orders generally followed the trend: Vertisols > Alfisols > Andisols, Ultisols. This could be attributed to differences in their mineralogy, clay and OM contents.

The amounts of exchangeable Fe varied with soil series. The highest value was obtained in the surface layer of Ibaan soil followed by Annam Ap soil. These 2 soil series were classified as Alfisols. Exchangeable Al, on the

Table 3. Chemical properties of the eight Philippine soils studied.

Order/Soil Series Name	Horizon	pH H₂O	pH KCl	ΔpH	OM (%)	Free Oxides (%)	Ex.Fe (mg.kg⁻¹)	Exch. Al	Ca	Mg	K	Na	CEC	BS (%)
Andisols														
Tall	Ap	7.0	5.5	-1.5	0.8	3.3	6.8	0.8	10.8	4.4	0.6	1.2	24.7	68.8
	B	5.1	7.1	+2.0	0.3	4.4	3.0	0.8	2.2	0.6	0.2	1.6	7.2	63.9
Tagaytay	Ap	7.2	5.9	-1.3	3.8	3.8	12.0	0.8	6.8	4.0	0.2	1.4	21.5	57.7
	Bt	7.2	5.7	-1.5	2.5	2.6	20.3	0.9	7.7	3.4	0.2	2.0	31.6	42.7
Alfisols														
Annan	Ap	5.1	4.0	-1.1	3.0	1.6	30.1	11.6	9.8	5.4	0.4	0.1	44.6	35.2
	B2	5.2	3.8	-1.4	1.7	5.0	13.0	14.1	3.1	2.7	0.2	0.0	25.1	23.9
Ibaan	Ap	5.9	4.6	-1.3	3.5	1.9	47.1	0.4	13.0	3.8	0.3	0.3	42.2	44.3
	B2	6.5	4.5	-2.0	1.2	1.7	19.3	0.9	17.0	3.4	2.2	0.0	39.2	57.7
Ultisols														
Luisiana	Ap	5.9	5.0	-0.9	4.7	4.4	12.4	2.7	3.4	4.5	0.2	0.5	28.0	30.7
	B21t	5.3	4.1	-1.2	1.3	2.7	17.8	4.3	6.9	3.1	0.2	0.1	32.5	31.7
Antipolo	Ap	4.8	4.1	-0.7	2.1	1.9	1.7	5.8	2.1	0.2	0.1	0.2	10.3	25.2
	B21t	4.6	4.0	-0.6	1.1	2.2	2.2	7.3	1.6	0.2	0.1	0.1	12.1	16.5
Vertisols														
Binagonan	Ap	6.2	4.9	-1.3	1.7	1.4	25.7	1.2	16.0	4.4	0.6	0.1	39.5	53.4
	B22	6.5	5.2	-1.3	1.1	1.7	23.7	1.1	15.5	6.1	0.4	0.1	39.5	55.9
Sibul	Ap	6.8	5.7	-1.1	2.2	2.2	0.2	0.9	18.8	3.4	0.4	2.5	46.4	54.1
	B21t	6.7	5.5	-1.2	1.4	3.0	0.7	1.3	17.3	3.6	0.4	3.1	47.3	51.6

ΔpH = (KCl) - pH (H₂O)   CEC = cation exchange capacity
OM = organic matter   BS = base saturation

other hand, was generally high in the acidic soils (Luisiana, Antipolo and Annam) but low in the slightly acid to neutral soils. Higher values of free oxides were obtained in the Ultisols than in the vertisols.

Soil mineralogy

Table 4 shows the dominant clay minerals present in the clay fraction of the soils studied. The Andisols contained amorphous clay minerals such as allophane and imogolite. The Alfisols (Annam and Ibaan) consisted of a mixture of kaolinite, illite, and vermiculite as the dominant clay minerals while the Ultisols (Luisiana and Antipolo series) consisted mainly of kaolinite and goethite. The Vertisols (Binangonan and Sibul series) were dominated by montmorillonite followed by vermiculite, illite and kaolinite in variable compositions. These clay minerals are responsible for the constant charge behavior of vertic soils (Ahmad, 1983).

Table 4.   Mineralogical compositions of the clay fraction of the A horizons of selected Philippine soils

Order/Soil Series Name	Dominant minerals in the exchange complex
Andisols	
Taal	allophane, imogolite, allophane like minerals
Tagaytay	allophane, imogolite
Alfisols	
Annam	illite, vermiculite > kaolinite
Ibaan	vermiculite, illite >> kaolinite > montmorillonite
Ultisols	
Luisiana	kaolinite >> goethite > vermiculite
Antipolo	kaolinite >> goethite
Vertisols	
Binangonan	montmorillonite >> illite > kaolinite
Sibul	montmorillonite >> vermiculite > kaolinite

Surface charge characteristics

Electric charge distribution

The magnitude of negative and positive charges of the soil samples at different pH levels as determined by the adsorption of K and Cl ions are

shown in Figure 1. The data showed that the amounts of negative charge or adsorbed K ions consistently increased with an increase in pH, while positive charge or adsorbed Cl ions decreased. Results showed a certain degree of variations in the A and B horizons among soil orders. The above results conform to the data of Van Raij and Peech (1972), and Gallez et al. (1976). The results clearly showed the coexistence of both positive and negative charges on soils which are responsible for their amphoteric properties.

At the same pH levels, the magnitude of negative charge of the Alfisols was higher than that of the Ultisols. The highest magnitude of negative charge was obtained in the surface layer of Annam soil. High magnitude was also obtained from the subsurface layer of Ibaan. Both soils are classified as Alfisols (Figure 1).

The predominance of illitic clay in the Alfisols could have caused the adsorption of K ions in excess of the negative charges that should characteristically be counterbalanced at the specified electrolyte concentration. High affinity of K ions to illites has long been widely recognized. The mineral properties that influence K affinity are charge density and origin of layer charge (Rich and Black, 1964). Total charge density and the distribution of the charge between the tetrahedral and octahedral sheets are also important characteristics that influence the extent of K fixation by 2:1 phyllosilicates (Inoue, 1983). The higher the charge density, the stronger the K affinity, and the tetrahedral charge favors a strong affinity (Fanning et al., 1989).

Selectivity is of particular interest with mica-expansible 2:1 minerals (edge-weathered mica) because these materials have high affinity (thus selectivity) for large monovalent cations such as K^+, NH^{4+}, Rb^+ and Cs^+ (Sawhney, 1972) with ionic radii of 0.133, 0.143, 0.148 and 0.169 nm, respectively. In addition, once the wedge zones become saturated with K ions, the selectivity is then determined by the planar surface sites, which have relatively lower affinity for K. Thus, the K selectivity coefficient of mica-expansible 2:1 minerals decreases as K saturation is increased (Singh et al., 1981), implying higher K activities in the equilibrium solution as the degree of K saturation increased. This situation was observed in the study as indicated by the magnitude of negative charges in the illitic soils which showed an increased K saturation of the equilibrium solution. Our results also implied that the amount of adsorbed K ions have been effectively replaced by NH^4 ions; otherwise, the adsorbed K ions could have been very low. The latter case could have resulted in low magnitudes of negative charge.
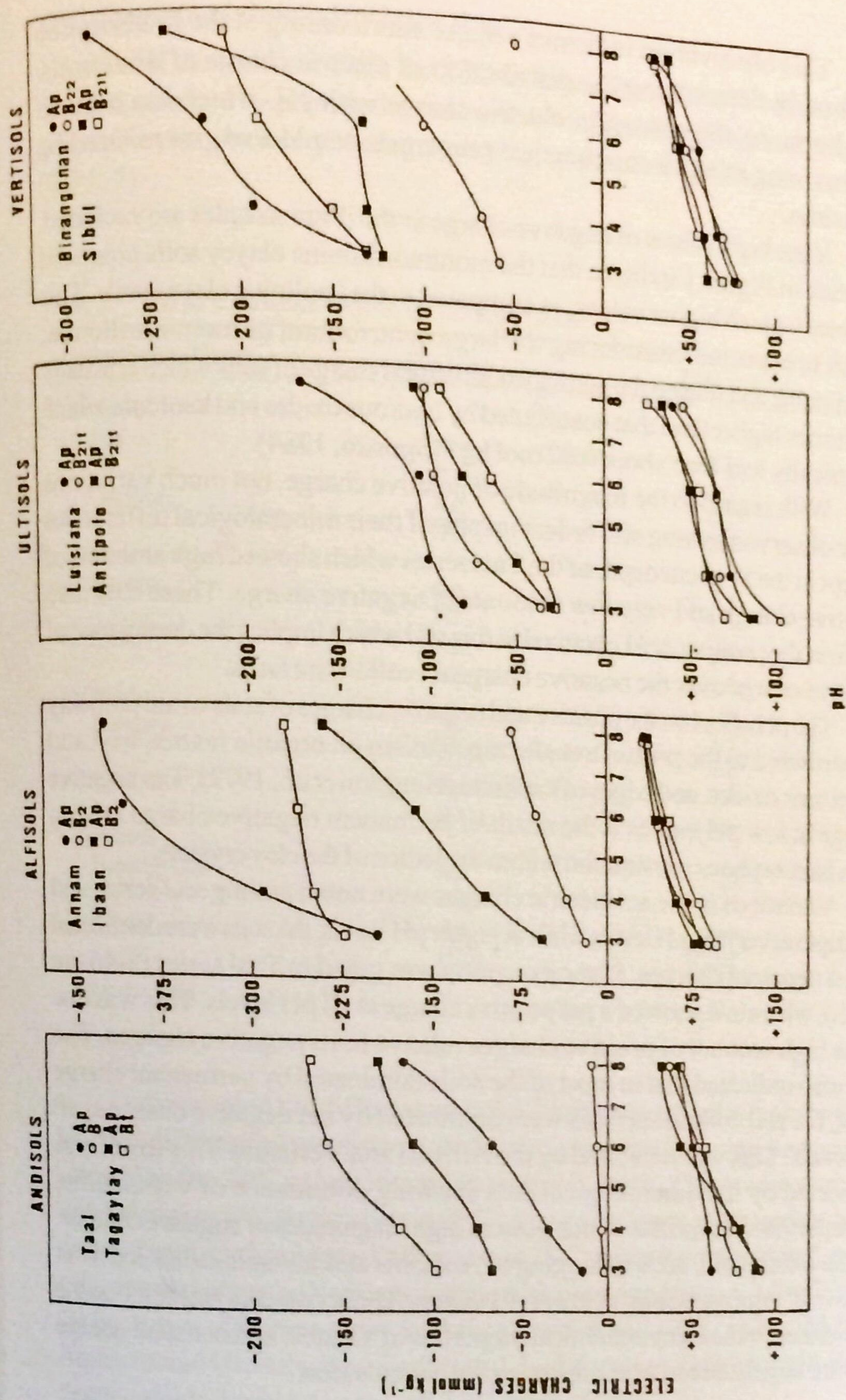
Figure 1.   Variations in the negative and positive charges of the surface and subsurface horizons of Andisols, Alfisols, Ultisols and Vertisols as determined at four pH levels.

This observation indicates a major shortcoming of the K adsorption method in determining the distribution of electric charge of illitic soils. Furthermore, the change in electric charge with pH, which is a basis of determining other electrochemical properties, would also give misleading quantities.

If the high values of negative charge in the illitic samples are excluded, the data in Figure 1 indicate that the montmorillonitic clayey soils produced distinctly much higher values, as compared to the kaolinitic clayey soils. This result is expected considering the large contribution of montmorillonite, vermiculite and illite to the permanent structural charge of soils which is usually 100 times higher than that contributed by hydrous oxides and kaolinite which is typically less than about 0.02 mol kg⁻¹ (Sposito, 1984).

With regard to the magnitude of positive charge, not much variations were observed among soil orders inspite of their mineralogical differences except in the 8-46 cm depth of the Taal series which showed high amounts of positive charge and very low amounts of negative charge. These data also confirm the positive ΔpH obtained in this soil which implies the dominance of positive charge over the negative charge on colloid surfaces.

The pH effect on the positive and negative charges of soils could probably be attributed to the proton transfer mechanism on organic matter, iron and aluminum oxides, and edges of kaolinite (Hingston *et al.*, 1972). The negative charge at low pH values is the result of permanent negative charge arising from isomorphous substitution within the lattice of the clay crystals.

Variations in the net electric charges were noted among soil series and soil depth at varying pH levels while at higher pH levels, the soils were dominated by net negative charges. Some exception was noted in Taal series (8-46 cm depth), wherein it showed a net positive charge at all pH levels. This was due to the high amount of positive charges relative to its negative charges. The data also indicated that in most of the soils dominated by permanent charge clays, the soil colloid surfaces were dominated by net negative charge at all pH levels. This was exhibited by the Alfisols and Vertisols. This result was supported by the mineralogical data showing dominance of vermiculite, montmorillonite and illite which possess high magnitudes of negative charges. On the other hand, soils belonging to Andisols and Ultisols exhibited a net positive charge especially at lower pH values. The above data suggest that the differences in the electrochemical properties of variable and constant charge soils are largely due to their mineralogical composition.

ZPC determined from adsorption data

For all the soils sampled, the ZPC as determined from ion adsorption data was obtained by piloting the values of net surface charge against pH, and when necessary by interpolating the curves to pass through the zero charge (Table 5).

Table 5. The ZPC values of selected Philippine soils

Order/Series Name	Horizon	ZPC values
Andisols		
Taal	Ap	5.2
	B	> 8.5
Tagaytay	Ap	4.1
	Bt	2.5
Alfisols		
Annam	Ap	< 2.5
	B2	5.3
Ibaan	Ap	3.3
	B2	< 2.0
Ultisols		
Luisiana	Ap	3.1
	B21t	3.8
Antipolo	Ap	4.4
	B21t	5.6
Vertisols		
Binangonan	Ap	< 2.5
	B22	3.7
Sibul	Ap	nd
	B21t	< 2.0

nd = no data

Data revealed the differences in ZPC values among the eight pedons. Marked differences were also noted among layers of a given soil profile. Generally, the ZPC values increased with soil depth. This was apparent in soils belonging to Ultisols wherein ZPC values were lower in the surface layers than in the subsurface layers. Differences in ZPC values were also noted among soil orders wherein the Vertisols and the Alfisols ranged from < 2.0 to 3.7 with the exception of Annam series for Alfisols, which had a ZPC value of 5.3. For Andisols and Ultisols, it ranged from 2.5 - 5.6 except Taal series (8-46 cm depth) which showed a very high ZPC value of >8.5.

Soils classified as Ultisols like the Luisiana series exhibited a lower ZPC value in the surface horizons as compared to the underlying horizon. Since the mineralogy and clay content in these layers are comparable, the variation in ZPC values could be attributed to the organic matter content which decreased with soil depth. This implies that the addition of OM in soils is an important strategy in managing variable charge soils since it would lower the ZPC values thereby increasing net negative charges which are important in the retention of cations.

Results also revealed the effects of mineralogy on the variation of ZPC values among soil orders. The Vertisols and the Alfisols had very low ZPC values compared to the Ultisols and Andisols. This suggests that the dominance of permanent charge minerals impart lower ZPC values to the soil as compared to variable charge minerals (Sposito, 1984).

The amount of free oxides also affect ZPC values. Soils with high free oxides had high ZPC values. This was exhibited by the Andisols and the Ultisols which possessed higher free oxides (having an average value of 3.2% free oxides) than the Vertisols and Alfisols (having an average value of 2.3% free oxides).

From the above results, it can be deduced that ZPC reflects the overall clay mineralogy and organic matter content of the soil. This is supported by the results obtained for the Luisiana and Antipolo series whose ZPC values were within the limit expected on these soils based on their mineralogical composition. The ZPC of kaolinite lies between 3.3 and 5.0, those for crystalline iron oxides between 6.6 and 8.7, and crystalline aluminum oxides generally above 7.7 (Breeuwsma, 1973). Soils dominated by amorphous silicates (as in allophane and imogolite) have ZPC values greater than 5.5 (Sakurai *et al.*, 1989). For a Hydrandept, El-Swaify and Sayegh (1975) reported ZPC values which ranged from 4.4 to 6.3.

ZPC determined by potentiometric titration

As a basis for comparison, the ZPC values of six soil samples were determined by potentiometric titration following the procedure of Van Raij and Peech (1972) and the values were compared with those obtained from ion adsorption data. In general, the ZPC values obtained by potentiometric titration were higher than those obtained by measurement of ion adsorption (Table 6). This may be attributed to the fact that the permanent negative charge was now balanced by K^+ instead of the strongly adsorbed trivalent Al^{3+} which

Table 6.   The position of the ZPC in relation to the zero point of titration (ZPT) and the ZPC as determined by potentiometric titration of some Philippine soils.

Soil Series	Horizon	Position of ZPC with respect to ZPT (mmol kg^{-1})	ZPC from titration curves using CaCl$_2$ solution
Luisiana	Ap	10, acid side	4.6
	B21t	2.5, acid side	6.1
Antipolo	Ap	22, acid side	3.8
	B21t	5, acid side	4.0
Taal	Ap	10, acid side	6.1
	B	1, alkaline side	6.5

would tend to increase the values for the ZPC obtained by potentiometric titration. A further complication in the different values obtained is the strong adsorption of cations and anions such as phosphate which decrease the ZPC and of chemisorbed cations which increase the ZPC . As a result, the crossover of titration in electrolytes other than those considered indifferent (i.e. salts of cations and anions that are not specifically adsorbed) does not produce ZPC values in agreement with those obtained in ionic media that interact only electrostatically with the surface. Since Ca^{2+} has a higher affinity for the oxide surface than Na$^+$ (an indifferent ion), the relative tendency for proton release as shown by the reaction

$$xFeOH + Mx \; r \; (Fe\text{-}O)xM + xH^+$$
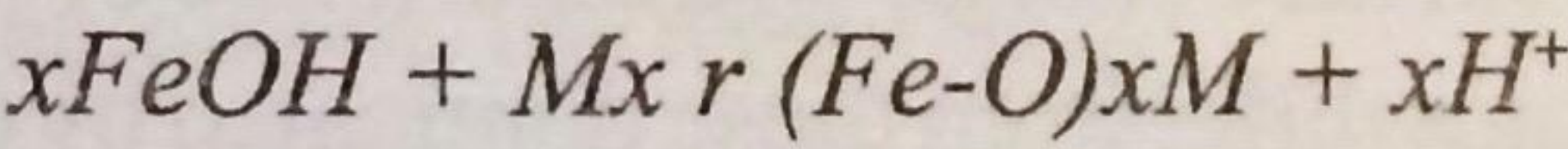
is increased in the presence of Ca^{2+} (McBridge, 1989). The ZPC estimated from titration curves or ion adsorption data is thereby shifted to lower pH (Breeuwsma, 1973).

In ascertaining the position of ZPC with regard to the zero point of titration (ZPT), results indicated that ZPT (the pH of the soil in 0.02 M CaCl$_2$ solution before any addition of acid or base) did not coincide with ZPC, it is displaced several units away either from the acid or the alkaline side of ZPC. In general, results from potentiometric titration indicated that the ZPC was displaced from 1 to 22 mole/kg on the acid side from the ZPT. This amount of H$^+$ adsorbed by the soil before reaching the ZPC, with consequent development of equivalent amount of positive charge, represents the permanent negative charge present in these soils (Van Raij and Peech, 1972; Espinosa et al., 1975). Furthermore,

results indicated that the magnitude of the distribution of the net electric charge was influenced by pH as well as by $CaCl_2$ concentration. The use of $CaCl_2$ as an indifferent electrolyte in this determination was based on the suggestion of Uehara and Gillman (1981), considering the dominance of cations in most tropical soils. Another striking observation made from potentiometric titration data was the difference in the net electric charges as measured by the amount of H^+ or OH^- adsorbed at different electrolyte concentration, wherein higher values were produced at 2 M $CaCl_2$ as compared to 0.004 M $CaCl_2$. This finding is again in accordance with the observations of Van Raij and Peech (1972) and Espinosa et al., (1975), for some tropical soils of Brazil and Santa Barbara, California, respectively.

Comparing the two methods of ZPC determination, the ZPC from the adsorption data is recommended over potentiometric titration. In the ion adsorption data, aside from the ZPC values, the magnitude of positive, negative and net electric charges are also determined. Moreover, the ZPC by potentiometric titration is not ideal for routine analysis since determination for one sample alone needs 60 beakers in order to establish the different pH levels at four electrolyte concentration. Aside from this, the equilibration period for potentiometric titration takes four days compared to the ion adsorption which needs only an overnight euqilibration for each pH level and analysis on a greater number of samples could be done simultaneously.

Implications for CEC measurements and soil management

This study showed that the surface charge characteristics of the soils dominated by variable charge colloids differ from those dominated by constant charge colloids. This difference in electrochemical behavior has important implications on the way these soils are managed for crop production. One important soil property that will be greatly affected is the CEC of the soil. On the basis of the influence of pH, electrolyte concentration, and the valence of counter-ions on the electric charge of the soils, most conventional methods (such as the use of buffered 0.25 M $BaCl_2$ at pH 8 or buffered 1 M NH_4OAc at pH 7) for the determination of exchange capacity appear to be inappropriate for tropical soils.

In an evaluation study of CEC measurements of some Philippine soils, Bautista and Briones (1988) found that the magnitude of CEC values followed the order: Method 2 (unbuffered M NH_4OAc - extractable bases + $BaCl_2$ - TEA extractable acidity at pH 8) > Method 3 (unbuffered M NH_4OAc -

extractable bases + exchangeable Al) $\geq$ Method 4 (unbuffered $M\,NH_4OAc$ - extractable bases + exchange acidity) > Method 5 (0.01 M KCl adsorption) > Method 6 (0.002 M $CaCl_2$ adsorption) > Method 7 ($BaCl_2$ compulsive exchange). They recommended either Method 3 or 4 as appropriate for CEC determination of tropical soils on the premise that these two methods eliminate the effects of high pH in the buffered salt solution which create additional negative charges on the soil as shown by the inflated CEC values obtained in Methods 1 and 2. A similar finding was observed by Gallez et al. (1976) for Nigerian soils.

Finally, the study of electric charges on soil colloids/aqueous solution interphase is relevant to soil fertility management. The role of OM in determining the sign of the net charge of soils emphasizes the need for management systems designed to maintain high levels of OM in tropical soils. Thus, proper management strategies should be evolved for tropical soils dominated by variable charge colloids to make them more productive for crop production.

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