

Soil Surface Charge is an Inherent Property of Soil Chemical Character

Sourav Kumar Khan and Sanjib Kar

Department of Agricultural Chemistry & Soil Science, Institute of Agricultural Science,
University of Calcutta, 35, B.C. Road, Kolkata-700019
E-mail: souravkhan.90@gmail.com, sanjib_cu@yahoo.co.in

Abstract—To investigate the distribution of the electric charges on some tropical soil of India was made by direct measurement of adsorption of ions in the presence of varying concentration of electrolyte. The results show that surface charge varies with soil according to the variation of organic matter and sesquioxide content. Surface charge also varies with organic carbon, composition of clay and chemical components of soil. Variability in the magnitude of this charge was attributed to the effect of contribution from various organic functional groups or Al / Fe blocked exchange sites of clay. Organic carbon and sesquioxide/allophone is responsible for charge variation. Composition of clay is an important factor for soil surface charge.

Keywords: Soil surface charge, clay composition, iron and aluminium oxide.

1. INTRODUCTION

One of the possible alternative approaches to the study of amorphous coatings on soil particles is to study the exchange reactions which take place at the interface between the soil particles and soil solution. This can be done using the potentiometric titration technique, which utilizes the adsorption and desorption of H^+ and OH^- ions to measure the surface charge characteristics. Specifically the titration curves at different ionic strengths cross at a common point, thus determining the zero point of charge, and providing a measure of the permanent or pH-dependent exchange capacity.

This technique has been applied to soils of tropical regions (Gallez et al., 1976), and to areas of soils developed on volcanic ash (Epinosa et al., 1975), to soils of temperate regions (Laverdiere et al., 1977).

The natural charge of soil particles is divided into permanent charge and variable charge components (Uehara and Gillman, 1981). A given soil may be dominated by either permanent charge or variable charge or their mixture, depending on the degree of its weathering and type on mineral constituents (Sparks, 2002; Chorover et al., 2004; Sposito, 2008). The objectives of this research, therefore, were to determine the charge characteristics of some tropical soils of India.

2. MATERIALS AND METHOD

Sampling sites

Three soil samples were collected from Nandigram, Patharpratima of South 24 parganas and Bethuadahari of Nadia district of West Bengal, India. The soils are mostly tropical climate with an annual rainfall of approximately 1250mm and mean temperature of approximately 24.8°C (Metrological department, 2017).

The sampling sites and classification of the soils in this study are given in Table 1. The soil samples are air dried, crushed, and then passed through 2mm sieve for laboratory analysis.

Physico-chemical Analysis

Soil pH as measured in a 1:1 soil : solution in H_2O and 1M KCl (National Soil Survey Centre, 1996), Organic Carbon (OC) was measured by the Walkley-Black method (Nelson and Sommers, 1996) and used to calculate the amount on Organic matter (OM) ($OM = OC \times 1.742$). Cation exchange capacity was determined by NH_4OAC at pH 7.0 and is defined by the some of the exchangeable cations that a soil can absorb (Chapman., 1965). Anion exchange capacity is determined by colorimetric methods (Frank E. Clarke, 1949). Particle size distribution was analysed by the pipette method (Gee and Bauder., 1986). The ΔpH index was calculated from the difference between pH_{KCl} and pH_{water} (Mekaru and Uehar, 1972). Calcium and Magnesium by Sparks (1996). Exchangeable Al (Bertsch and Bloom, 1996) and exchangeable Fe Sparks (1996). The Fe and Al contents associated with secondary minerals were determined in extracts obtained after boiling both 1g of soil for 30minutes in 20ml 9(M) H_2SO_4 . The acid extract were analysed for Al and Fe. Soil fused with alkali and total Fe and Al estimated by atomic absorption spectrometry (AAS) (Sparks, 1996).

3. SURFACE CHARGE ANALYSIS

Ion adsorption method

An estimate of the CEC and AEC as a function of pH was determined by measuring the amount of K^+ and Cl^- retained by the soils at different pH using a modification of Schofield's method (Schofield, 1949). Based upon the unknown mineralogy of these soils, it was assumed that the clays contained essentially no sites capable of specifically absorbing K^+ ; and therefore that KCl could be treated as an indifferent electrolyte. Triplicate 2g samples of soil were weighed in centrifuge tubes and washed with 0.1 (M) KCl to minimize soluble Al; after discarding the supernatants, 20ml of the same solution were added and the pH adjusted with KOH or HCl to give a pH range between 2 and 8. The samples were equilibrated at room temperature ($24 \pm 2^\circ C$) by shaking intermittently on a reciprocal shaker for 12 hr. Then the samples were centrifuged, the supernatants discarded, and 20ml 0.01 (M) KCl added; this (0.01)M KCl wash was repeated two more times. After the final washing, the supernatant pH was measured as well as the Cl^- , K^+ and Al concentrations. Next, the adsorbed K^+ and Cl^- ions were displaced by washing the soil with 0.5 (M) NH_4NO_3 . The amounts of K^+ and Cl^- displaced, after correction for the entrained KCl with in the soil volume, were used as estimates of the negative and positive charges, respectively. Chloride was measured using a specific ion electrode with a double junction reference electrode filled with $100gK_2SO_4$ solution in the outer chamber, and K^+ by flame photometer.

Statistical analysis

Each experiment was treated as a completely randomized design. Because the experiments were performed individually on each soil, comparisons of surface charge of the soils as a function of pH were accomplished by the use of correlation coefficient, were used to determine statistical significance of any differences in the surface charge measurements.

4. RESULT AND DISCUSSION

Important soil chemical and physical properties of the soil used in this study are given in Table 2. Clay content in the Bethuadahari soil was higher than Nandigram and Patharpratima, and this is reflected in the corresponding cation exchange capacity values of these soils with relatively higher cation exchange capacity of Bethuadahari soil than Nandigram and Patharpratima, indicated the dominance of Kaolinite mineral in the clay fraction of these soils.

Where it can be seen that Bethuadahari soils are more acidic (5.2) compare to Nandigram (7.8) and Patharpratima soil (7.1). All these experimental soils had ΔpH less than zero, which indicate they present net negative surface charge (Meakru and Uehara, 1972). Cation exchange capacity of Bethuadahari soil is higher than the Nandigram and

Patharpratima soil probably an effect of organic matter content (Morais et al., 1976).

Organic matter is an important source of cation exchange capacity in these soils (Carvalho et al., 2009). With increasing percent of organic matter, surface charge increases that increment is very high even in small increment of organic matter. In this study it appears that organic matter has an increasing effect on surface charge. The evidence presented is based on comparison of the surface charge characteristics of samples which contain different amounts of organic matter, but which are almost similar in other respects.

Surface charge of the soil is estimated by subtracting the cation exchange capacity value at a give pH from the corresponding anion exchange capacity value; these values are shown in Table 2 with the calculated surface charge values. Bethuadahari soil possesses higher surface charge than Nandigram and Patharpratima soil. This has been attributed to the negative charge arising from the greater organic matter content. Presence of dissociated organic functional groups and unblocked exchange sites and amount of iron and aluminium oxide are responsible for surface charge. Amount of clay and their composition is an important factor for surface charge formation (Table 2).

Total Fe and Al as well as Al and Fe oxide also contribute surface charge characters that are reflected in Table 2 with simultaneous contribution of soil organic matter. In all this samples pH in water was greater than the measured in KCl indicating that pristine point of zero charge of the untreated soil located below the zero point titration.

Variability in the magnitude of this charge was attributed to the effect of contribution from various organic functional groups or Al / Fe blocked exchange sites of clay. Organic carbon and sesquioxide/allophone is responsible for charge variation.

5. ACKNOWLEDGEMENTS

The authors are grateful to the University of Calcutta for Research Fund as a financial support for this investigation. The authors also thank the staff in the department of Agricultural chemistry and Soil Science, University of Calcutta, for their kind assistance

REFERENCES

- [1] Bertsch, P.M., Bloom, P.R., 1996. Aluminum. In sparks, D.L.(ed.) Methods of Soil Analysis. Part.3. Chemical Methods. American society of Agronomy and Soil Science Society of America, Madison. 3: 517-550.
- [2] Carvalho, J.L.N., Cerri, C.E.P., Feigl, B.J., Piccolo, M.C., Godinho, V.P., Cerri, C.C. 2009. Carbon sequestration in agricultural soils in the cerrado region of the Brazilian Amazon. Soil Tillage Research. Amsterdam. 103: 342-349.
- [3] Chapman, H. D., 1965. Cation exchange capacity. In Methods of Soil Analysis (Edited by Black, C. A.). Number 9 in the series

Agronomy: Am. Inst. Agronomy, Madison, Wisconsin. 2:891-901.

- [4] Chorover, J., Amistadi, M., Chadwick, O.A., 2004. Surface charge evolution of mineral-organic complexes during pedogenesis in Hawaiian basalt Geochim. Cosmochim. Acta, 68:4859-4876.
- [5] Espinoza, W., Gast, R.G., Adams, R.S., Jr 1975. Charge characteristics and nitrate retention by two Andepts from southern Chile. Soil Science Society of America Proceeding. 39: 842-846.
- [6] Frank, E. Clarke. 1949. Improved Colorimetric and Titrimetric Methods; Chemical Engineering Laboratory, U.S. Naval Engineering Experiment Station, Annapolis, Md.
- [7] Gallez, A., Juo, A.S.R., Herbillon, A.J., 1976. Surface and charge characteristics of selected soils in the tropics. Soil Science Society of America Proceeding. 40:601-608.
- [8] Gee, G.W., Bauder, J.W., 1986. Particle Size Analysis. In: Methods of Analysis; Part 1, Physical and Mineralogical methods, 2nd edn. (ed. A. Klute), American Society of Agronomy, Madison, WI. 2:383-411.
- [9] Laverdiere, M.R., Weaver, R.M 1977. Charge characteristics of spodic horizon. Soil Sci. Soc. Am. J. 41: 505-510.
- [10] Meraku, T., Uehara, G., 1972. Anion adsorption in Ferruginous tropical soils. Soil Science Society of America Proceeding. 36: 296-300.
- [11] Metrological department. Government of India, Regional Metrological Centre, Kolkata
- [12] Morais, F.I., Page, A.L., Lund, L.J., 1976. The effect of pH, salt concentration, and nature of electrolytes on the charge characteristics of Brazilian tropical soils. Soil Science Society of America Journal. 40:521-527.
- [13] National Soil Survey Center. 1996. Soil Survey Laboratory Methods Manual. U.S. Department of Agriculture, National Soil Survey Center., Soil Survey Laboratory., Soil Survey Investigation No. 42. Version J.
- [14] Nelson, D.W., Sommers, L.E., 1996. Total carbon and soil organic matter. In Methods of Soil Analysis. Part III. Chemical Methods. D.L. Sparks, A.L. Page, P.A. Helmke, and R.H. Loeppert (eds.) American Society of Agronomy, Inc, Madison, WI, 3:961-1010.
- [15] Schofield, R.K., 1949. Effect of pH on electric charges carried by clay particles. Journal of Soil Science. 1: 1-8.
- [16] Sparks, D.L. 1996 (Ed.) Method of Soil Analysis. Part 3. Chemical Methods. American Society of Agronomy and Soil Science Society of America, Madison, WI.
- [17] Sparks, D.L., 2002. Environmental Soil Chemistry, 2nd ed. Academic Press, San Diego. CA.
- [18] Sposito, G., 2008. The Chemistry of Soils. Oxford University Press, New York. 2:330.
- [19] Uehara, G., Gillman, G.P. 1981. The Mineralogy, Chemistry and Physics of Tropical Soils with Variable Charge Clays. West View Press, Boulder, 145.

Table 1: Sampling site, Soil order, Vegetation Type and texture

Sl. No.	Location	Soil order	Vegetation type
1.	Nandigram soil, West Bengal, India, 21.99°N, 87.88°E	Fluvaquent	Rice-rice-rice
2.	Patharpratima soil, West Bengal, India 21.63°N, 73.29°E	Endoaquepts	Rice-rice-rice
3.	Bethuadahari West Bengal, India 23.59°N, 88.39°E	Haplustepts	Tropical forest

Table 2: Chemical and Physical characteristics of soils

Soil Sample	pH _{water}	pH _{in 1(N) KCl}	*ΔpH	% O _C	% O _M	Fe ₂ O ₃ (g/Kg)	Al ₂ O ₃ (g/Kg)	Ex. Ca (g/Kg)	Ca _o (g/Kg)	Ex. Mg (g/Kg)	Mg _O (g/Kg)	% sand, silt, clay
Nandigram	7.8	6.5	-0.13	1.45	2.51	97.9	33.0	2.8	3.92	0.6	0.99	32, 33, 35
Patharpratima	7.1	6.4	-0.7	1.52	2.63	101.7	37.9	3.0	4.20	0.6	0.99	29, 32, 39
Bethuadahari	5.2	4.3	-0.9	1.98	3.42	265.2	86.5	5.2	7.27	1.8	2.98	30, 26, 44

*ΔpH = pH_{KCl} - pH_{water}, EC = electrical conductivity, OC = organic carbon, OM = organic matter, Ex = Exchangeable

Table 3: CEC, AEC, Surface charge and their relation with various chemical characters.

Soil Sample	AEC (Cmol _c Kg ⁻¹)	CEC (Cmol _c Kg ⁻¹)	Surface Charge (Cmol _c Kg ⁻¹)	Correlation between Surface charge & OC	Regression value (clay & OC) (r* < 0.05)
Nandigram	18.2	22.1	3.9	0.99842	0.94352
Patharpratima	19.7	24.2	4.5		
Bethuadahari	30.4	42.5	12.1		

AEC = Anion Exchange Capacity, CEC = Cation Exchange Capacity.