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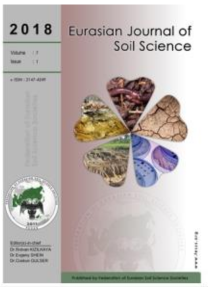

Surface charge is a function of organic carbon content and mineralogical compositions of soil

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Abstract

A study of the distribution of the electric charges in the surface horizons of two highly weathered soils Fluvaquent and Haplaquept of West Bengal, India was made by direct measurement of adsorption of ions in the presence of varying concentration of electrolyte. The objective of this study was to evaluate charge properties of two highly weathered soil of India. The results show that pH_0 varies with soil according to the variation in organic carbon and sesquioxide/allophone content. Organic carbon strongly affects the variation of negative charge with pH, but sesquioxide/allophone is responsible for positive charge variation. Results used the difference between the soil pH values measured in 1M KCl and in water for estimating the point zero charge of the soil and ΔpH values estimating the net surface charge character. Surface charges is a function of organic carbon, clay content, composition of clay and amount of Fe, Al and there oxides.

Keywords: Soil surface charge, organic matter, clay content, mineralogical composition.

Introduction

Solid particle surfaces in soils develop an electrical charge in two principal ways: either from isomorphic substitutions in soil minerals among ions of differing valence, or from the reactions of surface functional groups with ions in the soil solution. The electrical charge developed by these two mechanisms is expressed conventionally in moles of charge per kilogram ($mol_C\ kg^{-1}$). For different types of surface charge contribute to the net total particle charge in soils, denoted σ_p. Each of these components can be positive, zero, or negative, depending on soil chemical conditions.

Previous researchers (Espinosa et al., 1975; Gallez et al., 1976; Van Raij and Peech, 1972) have examined the surface charge characteristics of a number of soils of varying pedogenic age from different parts of the world.

In discussing surface charge characteristics it is important to classify the definitions of the terms used. The zero point charge is the pH at which the net total charge on the solid phase is zero, whether the charge arises from the pH-dependent charge associated with isomorphus substitution or from pH-dependent charge associated with hydroxylated oxide or organic matter surfaces. The isoelectric point is the pH at which the net charge on the hydroxylated surface is zero. The zero point of titration is the pH or range of pH values resulting from the reaction of the solid species with the indifferent electrolyte of varying concentrations in the absence of added acid or base (Parks, 1967). In a pure oxide system the ZPC, IEP and ZPT are coincident.

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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 of mineral constituents (Sparks, 2002; Chorover et al., 2004; Sposito, 2008). Soils in the humid tropics cover nearly 22% of the earth surface. These soils are dominated by mineral and amorphous colloids possessing amphoteric surfaces. Surface charge in this system depends on the activities of potential determining ions (H^+ and OH^-) and electrolyte concentration (Van Olphan, 1977).

This study aims to contribute towards an understanding of surface charge properties of two highly weathered soils of India by Ion adsorption methods.

Material and Methods

Sampling sites

Six soil samples were collected (0-15cm depth) from Sarisha and Lataguri of south 24 parganas and Jalpaiguri district of West Bengal, India for the study. The soils are mostly in tropical monsoonal climate with a mean annual rainfall of approximately 12000mm and approximate average temperature 27^{o}C. The classifications of the soils in this study are given in Table 1. The soil samples were air-dried, crushed and then passed through a 2mm sieve for laboratory analysis.

Table 1. Sampling site, Soil order, Vegetation Type

No.	Location	Soil order	Vegetation type	Texture	Textural class
1	Sarisha soil West Bengal, India 22^{0}35´N, 88 ^{0}44´E	Fluvaquent	Rice-rice-rice	34% silt 26% clay 40% sand	Silty clay loam
2	Lataguri soil West Bengal, India 26.32^{0}N,89.45^{0}E	Haplaquept	Tropical decudious forest	32% silt 38% clay 30% sand	Clay loamy

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= OCx1.724). 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 (Clarke, 1950). 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 Uehara, 1972). Exchangeable Al (Bertsch and Bloom, 1996) and exchangeable Fe Sparks et al. (1996). The Fe and Al contents associate d with secondary minerals were determined in extracts obtained after boiling both 1g of soil for 30minutes in 20ml 9M H_2SO_4. The acid extract were analysed for Al and Fe and soil fused with alkali and total Fe and Al estimated by Atomic Absorption Spectrometry (AAS) (Sparks et al., 1996).

Surface charge analysis

Ion adsorption method

An estimate of the CEC (Cation exchange capacity) and AEC (anion exchange capacity) 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 Schofields 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 minimise 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+/-2°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 0.01M 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 100gKg^{-1} KNO_3 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.

Results and Discussion

Important soil chemical and physical properties of the soils used in this study are given in Table 2, where it can be seen that Haplaquept are more acidic (4.65) than Fluvaquent (6.25). Fluvaquent are poor in organic carbon (1.25%) compare to Haplaquept (1.85%). Exchangble Fe, Al and total Fe, Al both are much higher in Haplaquept than Fluvaquent. Both soil had ΔpH less than zero, which indicates that they present negative net surface charge (Mekaru and Uehara, 1972). With increasing percent of organic matter and clay content point of zero charge reduces. In the present study a significant positive relationship observed between point zero charge and content of soil organic carbon and clay. The result can be ascribed to the positive correlation ($r= 0.2242$, $p<0.05$) between clay and soil organic carbon contents with surface charge. In both soil PZC value lower than pH water, so the net surface charge is negative.

Table 2. Chemical characteristics of soils

	Sarisha soil	Lataguri soil
pH $_{\text{water}}$	6.25	4.65
pH in 1N KCl	5.92	4.20
ΔpH *	-0.33	-0.45
Electrical Conductivity (EC), mSm^{-1}	0.08	0.23
Organic Carbon (OC), %	1.35	1.85
Organic Matter (OM), %	2.35	3.22
Exchangble Fe g kg^{-1}	0.26	0.58
Exchangble Al, g kg^{-1}	0.14	0.52
Total Fe, g kg^{-1}	28.6	52.80
Fe_2O_3, g kg^{-1}	40.85	75.42
Total Al, g kg^{-1}	21.90	58.60
Al_2O_3, g kg^{-1}	41.38	110.72

*$\Delta pH= pH_{KCl}-pH_{water}$

Clay content in the Haplaquept was significantly higher than the Fluvaquent, and this is reflected in the corresponding CEC values of these soils, with relatively higher CEC for Haplaquept than the Fluvaquent indicated the dominance of kaolinite mineral in the clay fraction of this soils.

The magnitudes of charges in the Haplaquept are higher than those of Fluvaquent because of dissociation of organic matter functional groups. Organic matter is an important source of CEC in these soils (Carvalho et al., 2009). Thus CEC and organic matter affected charges in these soils (Oorts et al., 2000).

Determination of surface charge by ion adsorption

The ion adsorption method allows the determination of positive and negative electric charge, as well as the net charge, as a function of pH. Figure 1-4 show the surface charge as a function of pH determined by the adsorption of K^+ and Cl^- at an ionic strength of 0.01M for the two soil samples.

Cation exchange capacity of Haplaquept is higher than Fluvaquent presumably an effect of organic matter content (Morais et al., 1976; Van Raij and Peech., 1972). This was observed that CEC of Haplaquept is higher in magnitude than Fluvaquent. Blocking of the exchange sites of organic matter by Al^{3+}/Fe^{3+} could explain this phenomenon. Iron and aluminium oxide are high in Haplaquept than Fluvaquent provide a positive surface charge in the soil.

As a certain pH CEC and AEC are same that is zero point net charge (ZPNC), that value is much higher in Haplaquept than Fluvaquent (Figure 1 and 2) due to the presence of higher organic carbon.

Haplaquept possess higher AEC than Fluvaquent. Organic matter and clay fraction play important role for AEC. These soils also differ in mineralogical composition. Organic groups displace water ligands at positive sites on the oxide surfaces (Mc Bride and Wesselink, 1988), reduce AEC in Fluvaquent.

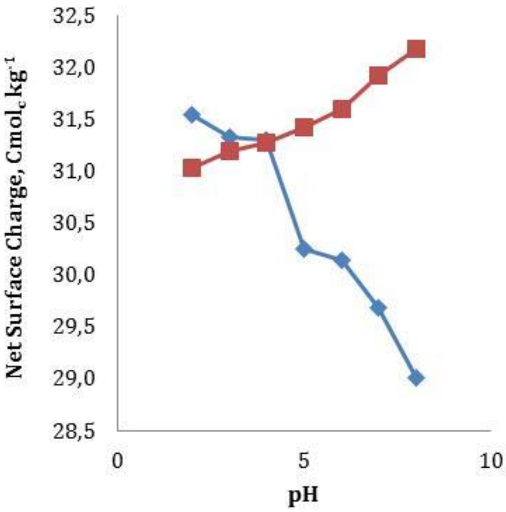

Figure 1. Estimation of net surface charge of Sarisha soil at different pH by ion adsorption Method

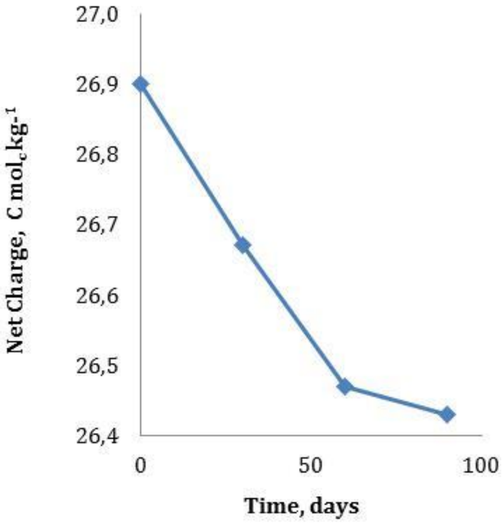

Figure 2. Net Charge vs Time curve in Sarisha soil

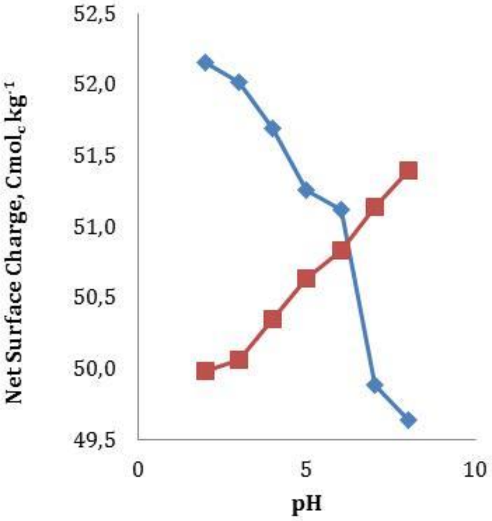

Figure 3. Estimation of net surface charge of Lataguri soil at different pH by ion adsorption method

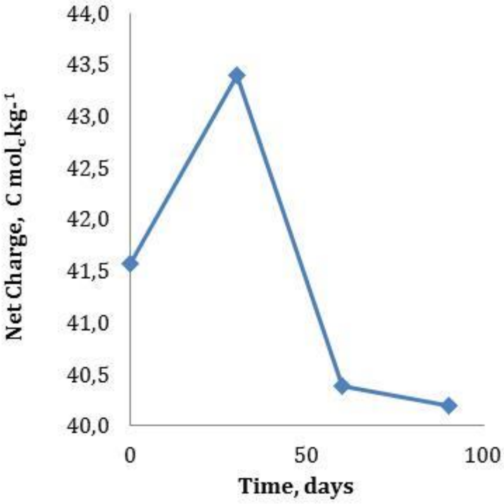

Figure 4. Net Charge vs Time curve in Lataguri soil

The net charge of the soil is estimated by subtracting the the CEC value at a given pH from the corresponding AEC value, these values are shown in Table 3 with calculated net charge values.

Table 3. PZC, CEC, AEC, Net charge and their relation with various chemical characters

	Sarisha soil	Lataguri soil
Point of Zero Charge (PZC) *	5.59	3.75
Anion Exchange Capacity (AEC), Cmol$_c$ kg^{-1}	26.14	41.12
Cation Exchange Capacity (CEC) Cmol$_c$ kg^{-1}	31.5	48.28
Net Charge (Cmol$_c$Kg^{-1})	5.36	7.16
Correlation between pH & Net Charge	-0.9672*	
Correlation between soil OC& PZC	-0.9997*	
Correlation between pH & PZC	0.9988^{nd}	
Regression value(Clay & OC) (r*<0.05)	0.2242*	

* (PZC= 2pH$_{KCl}$-pH$_{water}$)

Haplaquept possesses higher net charge value than Fluvaquent. This has been attributed to the negative charge arising from the greater organic matter content. These two soils are more different by net charge due to the presence of dissociated acidic organic functional group or greater unblocked exchange sites and amount of iron, aluminium oxide and content of clay.

Conclusion

The charge characteristics of the two highly weathered soils Haplaquept and Fluvaquent indicate that organic matter plays an important role on soil surface charge. Results clearly indicate that clay and organic matter fraction have important effects on the negative surface charge. Iron and aluminium oxide provide a positive surface charge in the soil. Point of zero charge varies with soil according to the variation of organic carbon and sesquioxide/allophone content. Charge characteristics of soil are a function of organic carbon content and mineralogical composition of soil.

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