Surface charge characteristics of coastal plain soils in Cross River State, Nigeria.

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Abstract

Physico-chemical and Point of Zero Charge (PZC) of coastal plain soils of Cross River State, Nigeria were studied. Four profiles representing coastal plain soils were studied in Calabar South and Akpabuyo Local Government Areas. The soils were coarse-textured with high sand content exceeding 70 % in the surface, giving surface textural classes of loamy sand or sandy loam overlying sandy clay and sandy clay loam subsurface. **.** *The soils were characterized as follows: soil reaction, very strongly acid (pH 4.0 - 4.5), mean organic carbon contents of 1.98 % for surface soils, available P (29.31mgkg^{-1}), effective cation exchange capacity (ECEC) was low (2.36-6.26 cmolkg^{-1}); base saturation (65 - 74 %) The ΔpH values (pH in KCl – pH in H_2O) were negative with mean values of – 0.63 and – 1.01 for surface and subsurface of coastal plain soils. PZC values were 3 and 3.9 for Calabar and Akpabuyo soils, indicating that the PZC values were typical of natural soils. These findings revealed that surface charge depends on the activities of potential determining ions (H^+ and OH^-) and electrolyte concentration (ionic strength), in the soil. With the negative delta pH (ΔpH) values in all the horizons, the coastal plain soils are negatively charged.*

Keywords: Surface charge, coastal plain soil, point of zero charge, ionic strength, Cross River State,

Introduction

Surface charge characteristics are based on the charge properties of soil constituents such as kaolinite, sesquioxides and organic matter. Kaolinite and organic matter can generate negative charges, while the sesquioxides (gibbsite, goethite and hematite) can bear positive charges (Shamshuddinn and Anda, 2008). Based on differences in surface characteristics, soils can be categorized as permanent charge soils and variable-charge soils. The permanent charge soils (constant surface charge type) are soils of the temperate region, where the charges arise from isomorphous substitution in the 2:1 clays, whereas, the variable-charge soils (constant potential type) where the charges arise from ionisation of hydroxyls of the 1:1 clays and hydrous oxides (Loganathan and

Fernando, 1977; Moghimi *et al.*, 2013) in tropical soils. Depending on soil pH, the variable charge surfaces can generate net negative, or positive or no charge. The pH at which the net electric charge is zero is called the point of zero charge (PZC), which is one of the most important parameters used to describe variable-charge surface (Appel *et al.*, 2003).

Surface charge of soil colloids is responsible for various important physicochemical properties such as ion exchange, ion mobility aggregate stability, erosivity among others (Loganathan and Fernando, 1977). Surface charge characteristics for colloids can predict the mechanisms of reactions with xenobiotic compounds and pathways of weathering reactions in soils (Schroth and Sposito, 1997; Shamshuddin and Anda, 2008).Surface charge characteristics for colloids with amphoteric surfaces influence soil management in agriculture and retention of ionic soil contaminants (Appel *et al.*, 2003). Surface charge characteristics control migration of ions in soils, the formation of organo-mineral complexes, soil structure, plant nutrition and the dispersion, flocculation, swelling and shrinkage of the soil fractions (Moghimi *et al.*, 2013).

Soils of Calabar and Akpabuyo (Coastal Plain Soils) are highly weathered and classified as *ultisols*. Being in humid tropical environment, the soils may be characterized as constant surface potential materials whose potential-determining ions (H^+ and OH^-) control the surface charge characteristics of the soils. This study was conducted to determine the physicochemical properties of the soils and the point of zero charge (PZC) of the soils using potentiometric titration and pH method.

Materials and methods

Description of the study area

The coastal plain soils of Calabar (04^0 57’ 04’’ N 008^0 21’ 28’’ E) and Akpabuyo (04 52’ 41’’ N , 008^0 25’ 08’’E) are located in Cross River State (Figure 1). Four profile pits were dug in the two locations namely; Calabar South and Akpabuyo Local Government Areas. The coordinates of the four profile sites were obtained using Garmin etrex (2000) GPS meter. Soil samples were collected from the bottom layer of the profile up to the surface soils so as to avoid contamination. Sixteen (16) soil samples were collected from the four profiles for study.

The climate of the coastal plain area is a typical of tropical humid region with a mean annual rainfall of 3500 – 4000 mm, a mean annual temperature of 26 – 27 ^{0}C and a mean relative humidity of 80 – 90 % (Akpan-idiok, 2012).

Figure 1. Map of Cross River showing the study areas and sampling points

Physico-chemical analysis

The particle size distributions of the soil were carried out using Bouyocous hydrometer method. The pH was determined with a pH meter in a 1:2.5 soil: water suspension using a glass-electrode. Total N was determined by micro-Kjeldahl method (Black, 1965) as modified by Jackson (1989).Available phosphorus was extracted with acidic fluoride using the Bray P 1method (Bray and Kurtz, 1945); phosphorus in the extract was determined calorimetrically by the molybdenum blue color method of Murphy and Riley (1962). Exchangeable bases (K, Ca, Mg and Na) were extracted with IN NH_4OAC using 1:10 soil solution ratio. Potassium and sodium in the filtrate were determined by flame photometer, while calcium and magnesium were determined with an atomic absorption spectrophotometer (Model 6405 UV/visible spectrophotometer, Jenway, U K).

The cation exchange capacity was determined by summation of exchangeable bases and exchangeable acidity (Juo, 1981). Exchangeable acidity was determined by successive leaching of the soil with neutral un-buffered IN KClusing a 1:10 soil liquid ratio. The amount of acidity (H and Al) in the leachate was estimated by titration with 0.05 NaOH to a permanent pink end point using phenolpthalein indicator (Maclean, 1982). The sum of the exchangeable bases and exchangeable acidity was taken as the effective cation exchange capacity (ECEC).Organic carbon was determined by the dichromate wet oxidation method of Walkley and Black (1934). The result was multiplied by Broadbent’s factor of 1.724

(Page *et al.,* 1982) to estimate the soil organic matter content.

Base saturation:

Percentage base saturation was calculated using the formula below:

$$\% \text{ B.S} = \frac{\text{Total Exchangeable Bases}}{\text{ECEC}} \times 100$$

Determination of point of zero charge:

This was carried out using the analytical method described by Longanathan and Fernando (1978).

Results and discussion

Physical properties: Particle size distribution.

The mean value of the sand fraction was 82 % in the surface soil (Table 1.) The mean value of silt fraction was 16.5 % whileclay fraction was 6.5 % in the surface soils. The coastal plain soils are coarse-textured with a high content of sand exceeding 70 % in the surface, giving surface textural classes of loamy sand overlying sandy clay loam subsurface soil respectively (Table 1). With clay content of 20 % in the subsurface the coastal plain soils can retain considerable amount of water for crop production. Similar results were obtained for coastal plain soils of Cross River State, Nigeria. *(*Akpan-Idiok, 2012*).*

Chemical Properties

The chemical characteristics of soil properties data are shown in Table 2. The pH values classify the coastal plain soils as very strongly acidic with mean values of 4.1 and 4.5 for surface and subsurface soils, respectively. The acidic conditions of the soils might be due to the high rainfall (2500-3500 mm) of the ecological zone which could leach out basic cations from the soil solum. The findings are consistent with the results of the earlier workers on coastal plain soils (Akpan-Idiok, 2012*).*

Mean value of organic carbon contents was 1.98 % in surface and 0.96% in subsurface soils, this level of organic carbon is rated medium as most values are lower than 1.5 % (Enwezor *et al.,* 1989). Such level of organic carbon cannot sustain the intensive and continous cropping system in the area. Total nitrogen contents were low 0.17 % as most values were below 0.2 % established for productive soils. This low content of total nitrogen could be ascribed to rapid microbial activities, leaching of nitrates and crop removal in the soil environment. Similar ranges of value (0.08-0.10 %) were reported for coastal plain soils in Cross River State of Nigeria (Akpan-Idiok and Ukwang, 2012*)*. Available P surface mean value was 29.31 $mgkg^{-1}$. The coastal plain soils are rated high in available phosphorus as the average value of available P exceeds 15 $mgkg^{-1}$ regarded for productive soils in the ecological zone (FPDD, 1990; Akpan-Idiok, 2012*)*

The mean values for exchangeable bases were as follows: Ca (2.75-3.40 $cmolkg^{-1}$) Mg (0.6-0.8 $cmolkg^{-1}$) K (0.07-0.08 $cmolkg^{-1}$) and Na(0.05-0.06 $cmolkg^{-1}$). These values are low when compared with the medium range critical values of individual basic cations; Ca, Mg, K, and Na: 5-10, 1-3, 0.3-0.6 and 0.3-0.7 $cmolkg^{-1}$, respectively (Holland *et al*., 1989) for crop production in the ecological zone.

Exchangeable acidity values were low with mean value of 1.30 – 1.41 for coastal plain soils (when compared with a medium range of 2.1-4.0 $cmolkg^{-1}$ (Holland *et al*, 1989) but impact of Al^{3+} in the soil solution could be significant in terms of influencing the biochemical behaviour in the soils (Akpan-Idiok, 2012). Effective cation exchange capacity (ECEC) value ranged from 2.36-6.26 $cmolkg^{-1}$ were rated low when compared with the threshold value of 10 $cmolkg^{-1}$ (FPDD, 1990) established for productive soils. The high rainfall (mean annual, 3500-4000 mm) for coastal plain soils might have enhanced the leaching of basic cations from the soil solum (Akpan-Idiok, 2012*)*. With mean percentage base saturation of 65-74 for both soil surface and subsurface, basic nutrients occurred in available forms in soil solution despite the low cation reserves in the soils (Akpan-Idiok, 2012*)*.

Surface charge characteristics

Delta pH values:

The difference between values of soil pH determined in IN KCl solution and in distilled water.

$$pH_{(KCl)} - pH_{(H_2O)} = \Delta pH$$

This is referred to as delta pH (ΔpH) and it illustrates that all the horizons of the soils posses net negative surface negative charge. The pH in water was higher that pH in I NKCl solution (Table 3). The ΔpH values (pH in KCl – pH in H_2O) are negative with mean values of – 0.63 and – 1.01 for surface and subsurface of coastal plain soils respectively. The soils with net negative charge can retain basic cations and heavy metal pollutants. The drop in pH in the KCl solution arises from the hydrolysis of Al^{3+}

displaced by potassium and being strongly acidic soils, the dominant cation on the exchange complex might be exchangeable Al^{3+} (Esu *et al*, 2008; Aki *et al*. 2014).

Potentiometric titrations:

The potentiometric titration curves at different ionic strength (0.001 M, 0.01 M, 0.1 M and 1.M) for surface of coastal plain soils are shown in Figures 1 & 2. The titration curves at varying ionic strength (I) tend to intersect one another at single point when pH is plotted against surface charge or amounts of acid or base added. The point of intersection is referred to as the point of zero charge (PZC) where the net total particle charge is zero. It is the pH where the net adsorption of potential-determining ions, H^+ and OH^- on variable charge surfaces is independent of electrolyte concentration. In this study, the points of zero charge values of 3.0 and 3.9 were recorded for coastal plain surface. The range of values is typical of natural surface soils with organic matter or iron/aluminum in the soils (Shamshuddin and Anda, 2008). Studies have shown that organic matter in the surface soils tends to lower the PZC when compared with the subsoil horizons within a given profile. quartz and kaolinite have PZC values below pH 3.0 whereas pure Fe and Al oxides and hydrous oxides such as hematite, goethite and gibbsite have PZC around pH 7 and 8.

Point of zero charge of the soils:

The point of zero charge (PZC) refers to the pH at which the net charge is zero and is expressed as pH_o. The PZC value is useful to predict the nature of the surface charge or the extent of a given soil to adsorb anions (NO_3^-, Cl^-) and cations (Ca, Mg, K) for coastal plain soils. The pH_o values are 3.0 for Calabar and 3.9 for Akpabuyo while the field condition pH stands at 4.1 and 4.5. With the field soil pH higher than pH_o (3.0 and 3.9) the coastal plain soils possess negative charges as confirmed by negative delta pH (ΔpH) values in all the horizons. With pH_O values of 3.0 and 3.9 for coastal plain soils, it can be inferred that the soils under study have achieved a more advanced chemical stage of weathering (Shamshuddin & Anda, 2008).

Conclusion

The soils are highly weathered with surface textural classes of loamy sand overlying sandy clay loam subsurface. Soil reaction varies from strongly to very strongly acid in coastal plain soils. The values of organic carbon and ECEC qualify coastal plain soils as moderate and low in fertility status, respectively. Generally, the coastal plain soils possess considerable negative charges, an indication that the soils have little or no capacity to adsorb anions but have capacity to retain cations.

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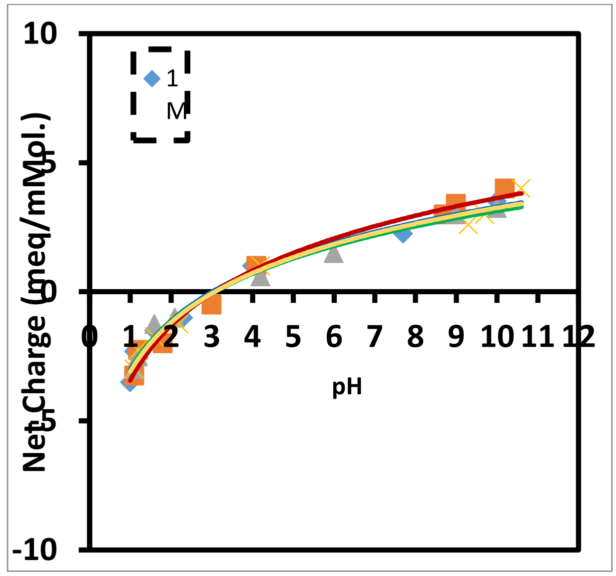

Figure 2. Point of zero charge for soils in Calabar South.

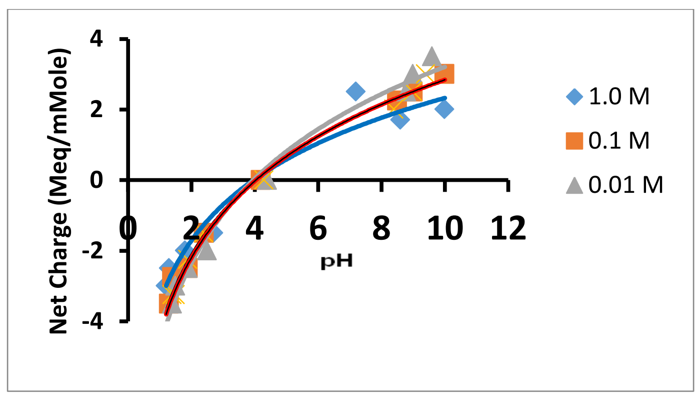

Figure 3. Point of zero charge for soils in Akpabuyo.

Table 1. Range, mean and standard error for some physical properties of the soil.

	Surface		Subsurface	
Parameters	**Range**	**Mean**	**Range**	**Mean**
Sand (%)	77-84	82±1.69	57-79	70.8±1.89
Silt (%)	10-13	11.5±0.65	3-17	8.4±1.13
Clay (%)	3-11	6.5±1.66	12-27	20.8±0.37
Texture	-	Loamy sand	-	Sandy clay loam

Table 2. Range, Mean and Standard error for some chemical properties of the soil

	Surface		Subsurface	
Parameters	**Range**	**Mean**	**Range**	**Mean**
Mg^{2+}(cmol/kg)	0.6-1.0	0.8±0.08	0.4-1.2	0.6±0.008
K^{+}(cmol/kg)	0.07-0.09	0.08±5x10^{-3}	0.06-0.09	0.07±2.89x10^{-3}
Na^{2+}(cmol/kg)	0.05-0.07	0.06±4.75x10^{-3}	0.04-0.7	0.05±2.79x10^{-3}
EA (cmol/kg)	0.96-1.60	1.30±0.14	0.72-1.26	1.00±0.06
ECEC (cmol/kg)	4.24-6.12	5.0±0.40	2.36-6.26	4.4±0.32
B.S (%)	73-75	74±0.41	54-81	65±2.74
pH	4.0-4.5	4.13±0.13	4.0-5.0	4.51±0.10
ΔpH	-0.4-(-1.0)	-0.63	-0.6-(-2.1)	-1.01
Organic Carbon (%)	1.49-2.69	1.98±0.28	0.26-1.34	0.56±0.09
T.N (%)	0.13-0.23	0.17±0.02	0.01-0.9	0.04±0.01
Avail. P (mg/kg)	16.75-37.50	29.31±5.08	7.87-40.0	20.16±3.34
Calcium (cmol/kg)	2.0-3.8	2.75±0.38	0.8-4.2	3.40±1.18