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Cations of Soil Minerals and Carbon Stabilization of Three Land Use Types in Gambari Forest Reserve, Nigeria

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Abstract

Predicting carbon distribution of soil aggregates is difficult due to complexity in organo-mineral formation. This limits global warming mitigation through soil carbon sequestration. Therefore, knowledge of land use effect on carbon stabilization requires quantification of soil mineral cations. The study was conducted to quantify carbon and base cations on soil mineral fractions in Natural Forest, Plantation Forest and Farm Land. Five 0.09 ha were demarcated alternately along 500 m long transect with an interval of 50 m in Natural Forest (NF), Plantation Forest (PF) and Farm Land (FL). Soil samples were collected with soil cores at 0-15, 15-30 and 30-45 cm depths in each plot. Soil core samples were oven-dried at 105°C and soil bulk densities were computed. Sample (100 g) of each soil core was separated into >2.0, 2.0-1.0, 1.0-0.5, 0.5-0.05 and <0.05 mm aggregates using dry sieve procedure and proportion determined. Carbon concentration of soil aggregates was determined using Loss-on-ignition method. Mineral fractions of soil depths were obtained using dispersion, sequential extraction and sedimentation methods of composite soil samples and sieved into <0.05 and >0.05 mm fractions. Cation exchange capacity of two mineral fractions was measured using spectrophotometry method. Data collected were analysed using descriptive and ANOVA at $\alpha_{0.05}$. Silt and sand particle size decreased while clay increased with increase in soil depth in NF and PF. Subsoil depth contained highest carbon stock in the PF. Carbon concentration increased with decrease in aggregate size in soil depths of NF and FL. Micro- (1-0.5, 0.5-0.05 and <0.05 mm) and macro-aggregates (>2.0 and 2-1.0 mm) were saturated with soil carbon in NF and FL, respectively. Cation exchange capacity of <0.05 mm was higher than >0.05 mm in soil depths of PF and FL. Fine silt (<0.05 mm) determine the cation exchange capacity in soil depths. Land use and mineral size influence the carbon and cation exchange capacity of Gambari Forest Reserve.

Key Words: soil carbon, soil mineral fractions, cation exchange capacity, soil aggregates, soil carbon sequestration

Introduction

The present extreme weather conditions in most part of the world is attributed to high concentration of greenhouse gases in the atmosphere and it is threatening human existence. Carbon dioxide is a major greenhouse gas with high latent heat and residence time and its concentration in the atmosphere is expected to double by in the next year 2100 (IPCC 2000). There are adaptive and mitigation options for the amelioration of climate change. However, soil carbon sequestration is inexpensive and cost effective than the other mitigation and adaptive strategies. Therefore, car-

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bon sequestration is viable option in the use of tropical soils.

Oades (1988) found that soils with 2:1 clay type show increase in organic carbon content with decreasing aggregate sizes pattern while most soils of the tropics with 1:1 clay type do not exhibit this pattern. Conversely, magnitude and distribution of carbon associated with soil aggregates is highly variable from site to site. Therefore, Kaiser et al. (2012) and Ramussen et al. (2018) opined that mechanism for carbon stabilization is site specific which is dependent on the type of interaction between organic compounds and cations of clay mineral. However, the understanding of interactions of organic matter with mineral surfaces in different land use types is limited.

The interactions include ligand exchange, polyvalent cation bridge, weak interactions and interaction with metal ions (Lützow et al. 2006). The adsorption of organic compounds on soil mineral leads to formation of organo-mineral complexes (Tan 2005; Sposito 2008; Chacón et al. 2015) which involves the substitution of inorganic cations in the interlayer position of clay minerals through organic cations ligard-exchange complexation (Sposito 2008). The exchangeable cations form cation bridges between the negatively charged clay surface and polar organic groups such as carboxylate, amines, carbonyl and hydroxyl alcoholic. This makes layer lattice structure and specific surface area of soil mineral important in the organo-mineral complex formation. Adsorption of carbon onto mineral surface is recognised as a dominant carbon stabilization mechanism in many soils (Sanderman et al. 2014). Variable and permanent charge clay minerals dominate tropical and temperate soils, respectively. However, variable charge properties are acquired not only by climate but also ambient PH condition of soil solution (Sposito 2008). Furthermore, most of the tropical soils compose mixture of different clay minerals because soils with specific and homogenous clay mineral are not common (Righi and Elsass 1996). This is attributed to frequent soil disturbances. However, there are few studies on the basic processes that cause adsorption of carbon on soil mineral. Most times, prediction of carbon distribution on soil aggregate sizes is not realistic. Therefore, knowledge of organic carbon stabilization on variable charge soil mineral will help to evaluate changes in mineral properties caused by soil disturbance in tropics. Consequently, detail understanding of the mechanisms that promote soil carbon adsorption is required to manage soil for carbon sequestration. The organic matter sorption is dependent on mineral surface characteristics (Kaiser and Guggenberger 2003) and clay surface property (de Oliveira Ferreira et al. (2018) but not organic matter inputs. Conversely, Rasmussen et al. 2018 reported that the formation of organo-mineral complexes is dependent on physico-chemical properties of soil mineral but less on clay surface properties. Sausen et al. (2014) reported that the strength of the organo-mineral complex is dependent on the surface properties of soil mineral but less on surface area. There is controversy on mineral property that influence carbon stabilization of tropical soils. Therefore, accurate prediction of carbon distribution on aggregate fractions requires identification and quantification of base cations on mineral fractions in tropical soils. Tan (2005) stated that clay size of silicate minerals has different layer lattice structures and specific surface areas. Therefore, clay minerals with different layer lattice structures do not have the same organo-mineral structural formation and consequently, cause them to have different reactivity, solubility and sorption capacity (Mitchell and Soga 2005; Sposito 2008). Previous studies have shown that organic matter retention and stabilization is primarily promoted by sorption of organic matter to soil minerals through cations ionization (Sposito 2008; Ramussen et al. 2018) and there are several cations responsible for the formation of organo-mineral (Lützow et al. 2006). Clay minerals have high specific surface area and exhibit permanent structural charge and variable pH-dependent surface charge. These allow clay size particles to exhibit mineral-mineral, mineral-organic, mineral-metal and mineral-water interaction in soil (Oades 1988; Sposito et al. 1999). Thus, some authors suggested the involvement of polyvalent cations (Jiang et al. 2011; Kaiser et al. 2012; O'Brien et al. 2015) and others indicated monovalent cations (Morris et al. 2007; Kaiser et al. 2012) as most important factors enhancing the formation of organo-mineral complexes and carbon stabilization. These uncertainties are limiting prediction of global warming mitigation through soil carbon sequestration. Therefore, detail knowledge of soil carbon stabilization mechanism requires identification and quantification of basic cations facilitating sorption of soil organic matter on clay mineral especially in different land use types. However, depletion of soil carbon through

inappropriate land use practices could increase greenhouse gases in the atmosphere. Improved knowledge of the distribution of carbon and cations among different land use types will provide information on land use practice that enhances optimum carbon storage. Also, cation distribution and pattern could be effectively compared in selected land use types since they are located on the same soil type and series with the same isothye. Therefore, the study was conducted to quantify carbon and base cations on soil mineral fractions in Natural Forest, Plantation Forest and Farm Land.

Materials and Methods

The study area

The soil samples for the study were collected at Gambari Forest Reserve which is first forest reserve to be established in Nigeria and gazzeted in 1887. It is located between Latitude 7° 25' and 7° 55' N and Longitude 3° 53' and 3° 9' E within the low land semi-deciduous rainforest vegetation of Nigeria and covers a total land area of 17,984 ha. Gambari Forest Reserve is situated at the southern part of Ibadan and bounded on the west by River Ona and east by of Ibadan-Ijebu-Ode road (Akinyemi 1998). Dry and rainy seasons are experienced in the Reserve. Dry season lasts for 3 months (December-February). The average annual rainfall is about 1,140 mm and average annual temperature is about 26.4°C (Akinyemi 1998). The Reserve was delineated into fragments include natural and plantation forests and agroforestry plots.

Its monthly temperature ranged from 31°C (January) to 20°C (June) and relative humidity ranged from 83% (June to September) to 75% (December to January). The soil is Alfisol (Egbeda series) and derived from complex basement rock overlain by crystalline rock of in-differentiates of gneiss, quartz and schist. The topsoil is free drainage with good base accumulation (Fig. 1).

Sampling procedures

Natural Forest (NF), Plantation Forest (PF) and Farm Land (FL) were selected for this study in Gambari Forest Reserve in March 2018. Sample plot demarcation and collection of soil samples were conducted in April, 2019. Five (30 m×30 m) plots were alternately established along a 500 m long transect with 50 m distance between each plot in each of the selected land uses. Soil core samples were collected from 8 m×8 m subplots demarcated at the four corners and centre of each plot using stainless steel soil cores with (diameter=7.5 cm and height=15 cm). Soil cores were taken at 0-15 (Surface soil), 15-30 (subsoil) and 30-45 cm (deep soil) depths. The soil core samples were labelled and transported to the laboratory in rigid and sealed plastic containers so as to preserve their structures.

Carbon stock estimation

Soil core samples were oven dried at 105°C to a constant weight and bulk densities of the samples were computed with the final weight of the soil. Subsample of oven dried soil (100 g) from each core sample was separated into aggregate size fractions using dry sieving method as described by Yang et al. (2016). Briefly, a fragment (100 g) of oven dried core soil sample was placed on the top of a stack of four sieves (2.0, 1.0, 0.5, 0.05 mm) and agitated for one minute with sieve shaker. The aggregate fractions remained on each sieve was collected and weighed. Subsequently, five aggregate sizes (>2.0, 2.0-1.0, 1.0-0.5, 0.5-0.05 and <0.05 mm) were obtained and carbon content of soil aggregates was estimated using Loss-on-ignition method at 500°C for 4 hours (Soil and Plant Analysis Council 1999; Schumacher 2002). Organic carbon content of the bulk soil was also determined for surface soil (0-15 cm), subsurface soil (15-30 cm) and deep soil (30-45 cm) and carbon concentrations of each soil depth were converted to carbon stock (Mg/ha). The carbon stock of soil depths was ob-

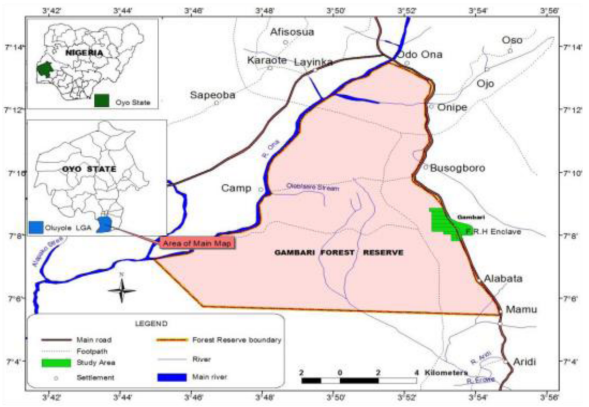

Fig. 1. Map of the study area.

tained by multiply carbon concentration by soil bulk density and thickness of each soil layer (equation 1) and conversion factor.

The soil carbon stock for each layer within the upper 45 cm depth of soil was estimated using the following equation:

SCS (Mg/ha)=SOC×BD×Depth×α×
(100 − Aggregate size ≥2.0 mm (g/100g)) ····· 1

Where,

SCS=soil carbon stock

SOC=concentration of soil carbon (%),

Depth=thickness of soil layer (cm),

BD=bulk density of the soil (g/cm^3),

α=constant for conversion of 1 cm^2 to hectare (1 ha= 1.0×10^{10} cm^2) and

Aggregate size ≥2.0 mm=proportion of gravel in the soil (%)

To obtain the soil carbon stock for 0-45 cm depth, the carbon stock of 0-15, 15-30 and 30-45 cm horizons were summed.

Soil mineral cation analysis

Five hundred grammes (500 g) of air dried soil samples (<2.0 mm) from topsoil (0-15 cm depth), subsoil (15-30 cm depth) and deep soil (35-40 cm depth) for each land use type were dispersed with $Na_4P_2O_7$ and oxidized with 20ml of 30% of H_2O_2 to remove organic matter. Four replicates of soil samples were taken from each soil depth. The mixture was shaken for 16 to 24 hours. The dispersed soil minerals were removed and oxidation process was repeated many times as required until reddish and brown colouration of the soil samples disappeared and the distilled water used for rinsing was clear (Lopez-Sangil and Rovira 2013). Furthermore, the samples were treated by adding a few drops of 0.5 M HCl and then heated to 80°C on water bath to eliminate the carbonates (Whitton and Churchman 1987; Eusterhues et al. 2005). The samples were washed several times with deionized water over a sieve of 0.02 mm mesh size. The dispersed soil minerals obtained were sieved with 0.05 mm mesh size sieve into two soil mineral sizes Coarse silt >0.05 and fine silt <0.05 mm) and thereafter were air-dried. Cation exchange capacity of two fractions (>0.05 and <0.05 mm) were measured by the ammonium acetate method (1 M, pH 7.0) by following the procedure described by Soil and Plant Analysis Council, 1999 and analysed by Buck Scientific Atomic Absorption Spectrophotometer model 210/211 VGP. Soil texture was determined by using hydrometer method after removal of organic matter with 20 ml of 20% of H_2O_2 and 6% $Na_4P_2O_7$.

Data analysis

The cation exchangeable capacity (CEC) of >0.05 and <0.05 mm fractions was computed as sum of exchangeable basic and acidic cations (Bruun et al. 2010) and its coefficient of variation in the three depths was computed in order to establish the variation of exchangeable capacity between soil mineral sizes. The significant difference in carbon concentration associated with aggregate sizes among three soil depths in each land use and among land use types were tested using two-way analysis of variance (ANOVA). Furthermore, significant difference in cation concentration of two particle sizes among three soil depths and three land use types were tested using three-way analysis of variance (ANOVA). The mean separation was done using Duncan Multiple Range Test (DMRT). All statistical analyses were computed using the univariate of General Linear Model of SPSS.

Results

The proportion (%) of clay fraction increased with increase in soil depth while silt and sand decreased with increase in soil depth of Natural Forest, Plantation Forest and Farm Land. Therefore, the three land use types had similar soil texture at the topsoil, subsoil and deep soil (Table 1).

Soil carbon concentration decreased with increase in soil depths in Farm Land and Natural Forest (Table 2). The soil carbon concentration was more variable along the three soil depths in Farm Land (Coefficient of Variation= 47.61%) followed by soil depths of Plantation Forest (Coefficient of Variation=28.46%). Therefore, there was significant difference in soil carbon concentration among three soil depths of Natural Forest (Sum of square=57.03, df=2, p=0.001) and Farm Land (Sum of square=116.34, df=2, p=0.001). The subsoil of Farm Land and the topsoil of Natural Forest had the highest Coefficient of Variation (27.80%) and highest soil carbon concentration among the soil depths of the three land use types,

Table 1. Particle size of soil depths in Natural Forest, Plantation Forest and Farm Land in Gambari Forest Reserve

Sampling depth (cm)	Particle size (g)								
	Natural Forest			Plantation Forest			Farm Land		
	Clay	Silt	Sand	Clay	Silt	Sand	Clay	Silt	Sand
0-15	6.36±1.80	10.85±2.84	82.78±3.30	6.74±2.83	9.49±2.31	83.76±2.46	5.85±2.46	9.16±1.60	84.98±2.60
15-30	9.12±2.63	9.60±2.36	81.19±3.42	9.96±3.21	8.03±2.04	82.01±3.46	6.98±0.88	7.58±1.41	85.44±1.55
30-45	11.69±2.78	8.18±2.84	80.13±3.76	10.57±3.62	6.96±2.13	82.46±3.89	7.07±1.51	7.08±2.04	85.84±1.89

Mean±standard deviation.

Table 2. Soil carbon concentration of Natural Forest, Plantation Forest and Farm Land of Gambari Forest Reserve

Sampling depth (cm)	Soil carbon concentration (gC/100 g)		
	Natural Forest	Plantation Forest	Farm Land
0-15	9.70±2.48aA	7.81±2.30aA	9.31±3.39aA
15-30	6.55±1.58aA	6.85±1.40aA	5.73±2.50aB
30-45	7.07±0.86aB	7.89±2.02aA	4.72±0.89bB

Means with different lowercase letters along a role are significantly different at $p < 0.05$ (DMRT).
Means with different uppercase letters along a column are significantly different at $p < 0.05$ (DMRT).

Table 3. Soil carbon stock of Natural Forest, Plantation Forest and Farm Land in Gambari Forest Reserve

Sampling depth (cm)	Soil carbon stock (Mg/ha)		
	Natural Forest	Plantation Forest	Farm Land
0-15	2.63±0.95aA	1.32±0.32bA	1.49±0.52bA
15-30	2.00±0.93aA	3.45±3.29aB	1.81±1.09aB
30-45	1.68±0.41aA	4.15±0.87bB	2.54±1.03cB

Means with different lowercase letters along a role are significantly different at $p < 0.05$ (DMRT).
Means with different uppercase letters along a column are significantly different at $p < 0.05$ (DMRT).

respectively. The values of soil carbon concentration was significantly different among the three land use types ($p \leq 0.05$) at deep soil (30-45 cm depth). Therefore, mean separation test showed that carbon concentration of Farm Land (2.54 g/100 g) was significantly different from carbon concentration of Natural Forest (7.07 g/cm^3) and Plantation Forest (7.89 g/100 g) at deep soil (30-45 cm depth). Conversely, the value of soil carbon concentration was not significantly different among the three land use types at topsoil (Sum of square=19.91, df=2, p=0.290) and subsoil (Sum of square=6.80, df=2, p=0.405).

The soil carbon stock decreased with increase in soil depth of Natural Forest. Conversely, soil carbon stock increased with increase in soil depth of Plantation Forest and Farm Land Therefore, surface soil of Natural Forest contributed the highest carbon concentration and stock to soil. The carbon stock of Natural Forest was 6.31 Mg/ha at the top 45 cm soil depth and ranged from 1.68 (30-45 cm) to 2.63 Mg/ha (0-15 cm). Soil carbon stock of Plantation Forest was 8.92 Mg/ha at the top 45 cm depth and ranged from 1.32 (0-15 cm) to 4.15 Mg/ha (30-45 cm) (Table 3). Therefore, deep soil depth contributed highest carbon concentration and stock to soil of Plantation Forest. The value of soil carbon stock was significantly different among the three land use types ($p \leq 0.05$) at topsoil (0-15 cm) and deep soil (30-45 cm) depths. Therefore, mean separation

test showed that carbon stock of Natural Forest (2.63 Mg/ha) was significantly different from carbon stock of Plantation Forest (1.32 Mg/ha) and Farm Land (1.49 Mg/ha) at topsoil (0-15 cm depth). Also, carbon stock of Natural Forest (1.68 Mg/ha) and Farm Land (2.54 Mg/ha) and Plantation Forest (4.15 Mg/ha) were significantly different from each other at deep soil (Table 3). The value of soil carbon stock was significantly different among the three soil depths of Plantation Forest (Sum of square=43.33, df=2, $p \leq 0.05$) and Farm land (Sum of square=5.82, df=2, $p \leq 0.05$). The mean separation test showed that carbon stock of topsoil was significantly different from carbon stock of subsoil and deep soil in Plantation Forest and Farm land.

The carbon concentration of aggregate size increased with decrease in aggregate size in soil depths of Natural Forest and Farm land (Fig. 2A, C). Carbon concentration associated with individual aggregate sizes decreased with increase in soil depth of Natural Forest, Plantation Forest and Farm land (Fig. 2A-C). There was significant difference in carbon concentration associated with aggregate sizes among soil depths of Natural Forest ($F_{142.01}=57.03$ df=2 p=0.001) and Farm Land ($F_{285.21}=116.34$, df=2, p=0.001). The mean separation test showed that carbon concentration of aggregates at topsoil (9.70 gC/100 g) was significant different from subsoil (6.55 gC/100 g) and deep soil (7.07 gC/100 g) in Natural Forest (Fig. 2A). Also, the mean separation test showed that carbon concentration of aggregates at topsoil (9.31 gC/100 g) was significantly different from carbon concentration of aggregate sizes of subsoil (5.73 gC/100 g) and deep soil (4.72 gC/100 g) depths of Farm Land (Fig. 2C). Conversely, there was no significant difference in soil carbon concentration associated with aggregate sizes of subsoil (15-30 cm) and deep soil (30-45 cm) except for aggregate size >2.0 mm in Natural Forest (Fig. 2A). The mean separation test showed no significant difference between carbon concentration of aggregates in subsoil (15-30 cm) and deep soil (30-45 cm) depths of Natural Forest. Although, soil carbon associated with aggregate size >2.0 mm of subsoil depth was higher than aggregate >2.0 mm of deep soil depth in the Natural Forest (Fig. 2A). However, there was no significant difference in the carbon concentration associated with five aggregate sizes in each soil depth of Natural Forest (F=70.19, df=4; p=0.473).

Aggregate size < 0.05 mm contained highest proportion of soil carbon concentration at subsoil and deep soil of Plantation Forest. Therefore, carbon concentration associated with aggregate sizes of topsoil (7.53 gC/100 g) were not significantly different from those of subsoil (6.22

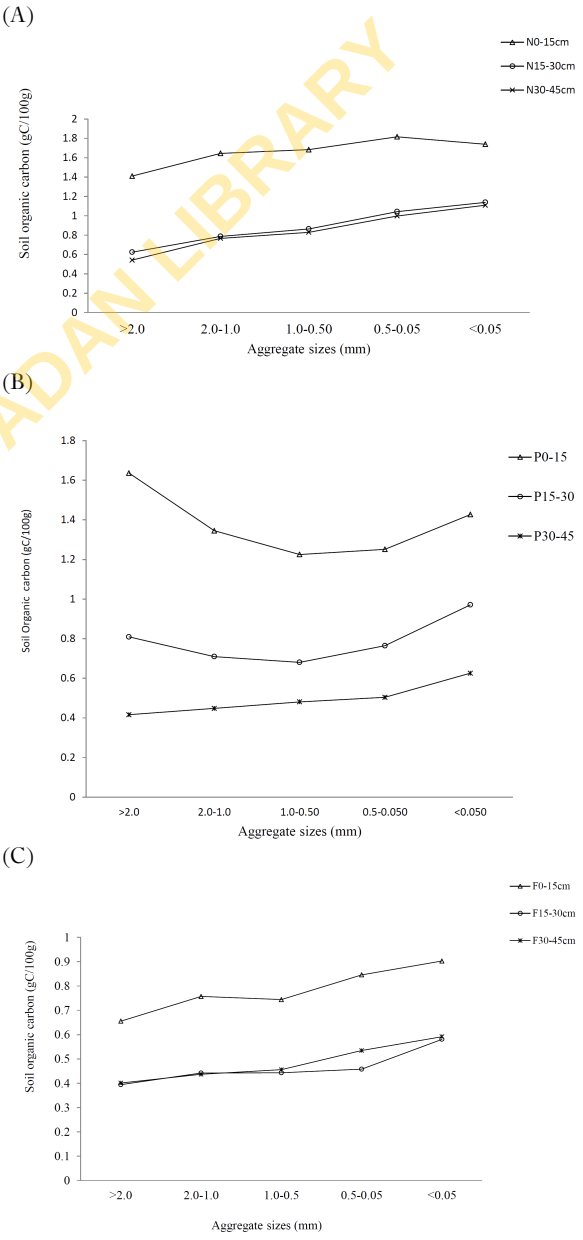

Fig. 2. (A) Organic carbon of aggregate sizes in the soil depths of Natural Forest, (B) organic carbon of aggregate sizes in soil depths of Plantation Forest, (C) organic carbon of aggregate sizes in the soil depths of Farm Land.

gC/100 g) and deep soil (6.71 gC/100 g) depths in Plantation Forest ($F_{109.38}$=6.57, df=2, p=0.433). Aggregate size >2.0 mm contained the highest carbon concentration in the topsoil depth, followed by <0.050 mm (Fig. 2B). However, there was significant difference in the carbon concentration associated with five aggregate sizes in each soil depth of Plantation Forest (F=50.87, df=4; p=0.000). Therefore, mean separation test showed carbon associated with aggregate >2.0 mm (8.32 gC/100 g) was significantly higher than aggregate size 0.5-0.05 mm (5.48 gC/100 g) and 0.5 mm (6.44 gC/100 g).

There was significant difference in carbon concentration associated with the five aggregate sizes at topsoil (8.54 gC/100 g), subsoil (5.16 gC/100 g) and deep soil (4.44 gC/100 g) of Farm Land (F=192.46, df=2, p=0.000), except for aggregates 0.5-0.05 and <0.05 mm. Also, there was significant difference in the carbon concentration associated with five aggregate sizes in each depth of Farm Land (F=11.65, df=4, p=0.025). Therefore, mean separation test showed that carbon associated with aggregate size >2.00 mm was significantly higher other aggregates in Farm Land. Conversely, soil carbon concentration associated with the two aggregates 0.5-0.05 and <0.05 mm of deep soil was higher than subsoil depths (Fig. 2C). There was no significant difference in the carbon concentration associated with aggregate sizes among the three soil depths of Farm Land (F_{285}=11.38, df=8, p=0.171).

The concentration of Ca^{2+} of two soil mineral fractions (>0.05 mm and <0.05 mm) was significantly higher than other basic cations (Mg^{2+}, K^{+} and Na^{+}) in the soil depths of Natural Forest, Plantation Forest and Farm Land (Tables 4-6). Therefore, there was significant different in the concentration of basic cations (F=537.48, df=3, p=0.000) in Natural Forest, in Plantation Forest (F=695.23, df=3, p=0.000). The mean separation test showed that Ca^{2+} was significantly higher than other basic cations in three land use types. The coarse silt (>0.05 mm) contained higher concentration of basic cations ($Ca^{2+}$and Mg^{2+}) than fine silt (<0.05 mm) in the soil depths of Natural Forest, except for K^{+} at subsoil (15-30 cm depth) (Table 4). Therefore, fine silt (<0.05 mm) contained higher concentration of K^{+} and Na^{+} in the subsoil (0-15 cm depth). Conversely, fine silt (<0.05 mm) contained higher concentration of basic cations (Ca^{2+}, $Mg^{2+}$and K^{+}) than coarse silt (>0.05 mm), except for Na^{+} at subsoil (15-30 cm depth) depth of Farm Land (Table 6). The exchange capacity of coarse silt (>0.05 mm) was higher than fine silt (<0.05 mm) in the soil depths of Natural Forest while exchange capacity of fine silt (<0.05 mm) was higher than coarse silt (>0.05 mm) in the soil depths of Plantation Forest and Farm Land. Furthermore, exchange capacity of two soil mineral fractions (>0.05 mm and <0.05 mm) in-

Table 4. Cation exchange capacity of two soil mineral fractions in three depths of Natural Forest

Soil particle	Cation	n=4	cmolc/100 g				CV
			0-15 cm depth	15-30 cm depth	30-45 cm depth	Mean	
<0.05 mm	Ca^{2+}	4.0	6.42±4.93	3.66±0.62	0.23±5.81	5.44	0.77
>0.05 mm	Ca^{2+}	4.0	9.86±11.18	6.73±5.92	3.10±0.70	6.56	0.97
<0.05 mm	Mg^{2+}	4.0	0.73±0.61	0.21±0.07	0.34±0.33	0.43	0.99
>0.05 mm	Mg^{2+}	4.0	0.90±0.76	0.42±0.37	0.37±0.35	0.57	0.95
<0.05 mm	K^{+}	4.0	0.06±0.00	0.05±0.06	0.06±0.07	0.06	0.24
>0.05 mm	K^{+}	4.0	0.09±0.01	0.01±0.01	0.02±0.01	0.07	0.22
<0.05 mm	Na^{+}	4.0	1.36±0.23	1.24±1.50	1.31±1.10	1.31	0.12
>0.05 mm	Na^{+}	4.0	1.51±0.30	0.15±0.19	1.34±0.24	1.45	0.16
<0.05 mm	Acidity	4.0	0.65±1.30	1.07±0.95	0.52±0.33	0.75	0.79
>0.05 mm	Acidity	4.0	0.23±0.90	0.50±0.14	1.07±0.35	0.95	0.64
<0.05 mm	CEC		9.24	6.25	8.48		
>0.05 mm	CEC		13.67	9.24	5.97		

Mean±standard deviation.
Coefficient of variation, CV; Replicate, n.

Table 5. Cation exchangeable capacity of soil mineral particles at three depths of Plantation Forest

Soil particle	Cation	n=4	cmolc/100 g				CV
			0-15 cm depth	15-30 cm depth	30-45 cm depth	Mean	
<0.05 mm	Ca^{2+}	4.0	8.25±5.35	8.65±5.87	5.49±0.52	7.46	0.59
>0.05 mm	Ca^{2+}	4.0	7.85±4.28	4.95±0.98	5.35±0.65	6.04	0.44
<0.05 mm	Mg^{2+}	4.0	0.58±0.32	0.39±0.20	0.32±0.05	0.43	0.53
>0.05 mm	Mg^{2+}	4.0	0.67±0.65	0.29±0.11	0.32±0.03	0.43	0.89
<0.05 mm	K^{+}	4.0	0.05±0.11	0.04±0.00	0.04±0.00	0.05	0.19
>0.05 mm	K^{+}	4.0	0.06±0.01	0.05±0.00	0.05±0.00	0.05	0.17
<0.05 mm	Na^{+}	4.0	1.43±0.41	1.44±0.05	1.53±0.20	1.47	0.16
>0.05 mm	Na^{+}	4.0	1.59±0.35	1.42±0.18	1.67±0.16	1.56	0.16
<0.05 mm	Acidity	4.0	0.62±0.22	0.47±0.28	0.47±0.17	0.52	0.42
>0.05 mm	Acidity	4.0	0.60±0.46	0.57±0.23	0.47±0.15	0.55	0.52
<0.05 mm	CEC		10.96	11.01	7.86		
>0.05 mm	CEC		10.78	7.30	7.88		

Mean±standard deviation.
Coefficient of variation, CV; Replicate, n.

Table 6. Cation exchangeable capacity of soil mineral particles at three depths of Farm Land

Soil particle	Cation	n=4	cmolc/100 g				CV
			0-15 cm depth	15-30 cm depth	30-45 cm depth	Mean	
<0.05 mm	Ca^{2+}	4.0	6.46±4.87	8.63±3.49	9.05±3.57	8.05	0.47
>0.05 mm	Ca^{2+}	4.0	7.68±2.73	7.89±2.96	7.94±2.97	7.83	0.33
<0.05 mm	Mg^{2+}	4.0	0.46±2.73	0.39±0.13	0.38±0.25	0.41	0.45
>0.05 mm	Mg^{2+}	4.0	0.42±0.11	0.32±0.05	0.29±0.07	0.34	0.26
<0.05 mm	K^{+}	4.0	0.08±0.26	0.06±0.01	0.06±0.02	0.07	0.31
>0.05 mm	K^{+}	4.0	0.07±0.01	0.06±0.00	0.05±0.01	0.06	0.16
<0.05 mm	Na^{+}	4.0	1.55±0.06	1.56±0.06	1.54±0.35	1.55	0.12
>0.05 mm	Na^{+}	4.0	1.72±0.18	1.56±0.11	1.64±0.05	1.64	0.08
<0.05 mm	Acidity	4.0	0.45±0.37	0.35±0.12	0.52±0.40	0.44	0.69
>0.05 mm	Acidity	4.0	0.32±0.17	0.52±0.34	0.57±0.35	0.47	0.62
<0.05 mm	CEC		9.01	11.02	11.57		
>0.05 mm	CEC		10.23	10.36	10.51		

Mean±standard deviation.
Coefficient of Variation, CV; Replicate, n.

creased with increase in soil depths of Farm Land. The exchange capacity of the coarse silt (>0.05 mm) and fine silt (<0.05 mm) ranged from 5.97 to 13.67 cmolc/100 g and 6.25 to 9.24 cmolc/100 g in the soil depths of Natural Forest, respectively (Table 4). The two mineral fractions (>0.05 mm and <0.05 mm) had the highest exchange capacity in topsoil (0-15 cm depth) of Natural and Plantation Forests. The mean and coefficient of variation (CV) of the concentration of basic cations in coarse silt (>0.05 mm) were higher than fine silt <0.05 mm of Natural Forest. The coarse silt (>0.05 mm) showed wide variation (CV) of exchange capacity when compare with fine silt (<0.05 mm) in Natural Forest.

However, concentration of Mg^{2+} and Na^{+} of fine silt (<0.05 mm) decreased and increased with increase in soil depth of Plantation Forest, respectively. Fine silt fractions

contained higher concentration of Ca^{2+} than coarse silt fractions in the three soil depths of Plantation Forest. Concentration of Mg^{2+} and Na^{+} were higher in coarse silt fractions than fine silt fractions in 0-15 and 30-45 cm depth of Plantation Forest (Table 5).

Concentration of Na^{+} ion was higher in coarse silt fraction than fine silt fraction at three soil depths of Farm Land (Table 6). Fine silt fraction contained higher concentration of exchangeable cations than coarse silt fractions of subsoil (15-30 cm depth) and deep soil (30-45 cm depth). The concentration of basic cations at topsoil (0-15 cm depth) was higher than that of subsoil (15-30 cm depth) and deep soil (30-45 cm depth) of Farm Land, except Ca^{2+} and Na^{+}. High exchange capacities are characteristics of fine silt in Farm Land. Therefore, concentration of basic cations is dependent on the particle size.

Discussion

The proportion (%) of clay fraction increased with increase in soil depth while silt and sand decreased with increase in soil depth. Therefore, three land use types had similar soil texture at surface, subsoil and deep soil. This indicates that soil texture is a comparatively stable property which is not likely to undergo changes as a result of vegetation changes of the study area. Plantation Forest had the largest carbon stock at the top 45 cm of soil depth (894.00 Mg/ha), followed by Natural Forest (633.11 Mg/ha) and Farm Land (585.37 Mg/ha). The highest carbon stock occurred at deep soil of Plantation Forest. This may be attributed to the effect of dissolved organic carbon that moved from topsoil to deep soil depths and deep tree roots at the deep soil depths of Plantation Forest. Sá (2001) reported that increase in litter-fall from vegetation increase soil aggregation and organic carbon content but the increase is restricted to the surface soil. Therefore, the values of carbon stock increased with increase in soil depth of Plantation Forest. However, highest carbon stock was obtained at the deep soil and followed by subsoil of Plantation Forest. This indicated that large soil carbon could be sequestered at deep soil and subsoil of Plantation Forest. Hence, deep soil and subsoil layers of Plantation Forest may be good option for carbon sequestration in Gambari Forest Reserve. The amount of soil organic carbon stock of surface soil in the land use types may be due to effect of land uses (Forth 1990) while the amount in subsoil and deep soil may be due to vertical distribution of deep plant roots.

The aggregate <0.05 mm contributed large proportion of carbon to carbon stock in the soil depths of Natural Forest and Farm Land while fractions >2.0 and <0.05 mm contributed large proportion of carbon to carbon stock in soil depths of Plantation Forest. Therefore, the aggregate size <0.05 dominated the soil depths of the three land use types and hence, influence the soil carbon distribution of Gambari Forest Reserve.

This supported the studies of Yang et al. (2016) and Oades (1988) that organic carbon storage of most land use types is determined by mass proportion of its fine-size particle. There was no difference in the carbon concentration of aggregates of subsoil and deep soil of Natural Forest, except for aggregate >2.0 mm. This indicated that micro-aggregates (1-0.5, 0.5-0.05 and <0.05 mm) of subsoil and deep soil of Natural Forest had reached carbon saturation limit and therefore could not adsorbed more carbon.

Also, there was no difference in carbon concentration of aggregates at subsoil and deep soil of Farm Land, except for aggregate of 0.5-0.05 and <0.05 mm. This indicated that macro-aggregates (>2.0, 2-1.0 mm and 1-0.5 mm) had reached carbon saturation limit. This is contrary to the common assumption of Yang et al. 2016 that macro-aggregates start to accumulate carbon after the micro-aggregate are saturated. The two unsaturated aggregates (0.5-0.05 and <0.05 mm) in soil depths of Farm Land was probably caused by tillage which affected the distribution of organic carbon at subsoil depth and led to release of stored carbon to the atmosphere and consequently cause carbon saturation deficit in aggregates 0.5-0.05 and <0.05 mm at the subsoil. According to Khandakar et al. (2017) and Souza et al. (2017), individual soil aggregate has definite carbon saturation limit but aggregate stabilizes organic carbon if it is carbon saturation deficit. Khandakar et al. (2017) reiterated the fact that carbon saturation limit of soil is determined by the adsorptive capacity of individual aggregate fractions. The organic carbon concentration of aggregate size <0.05 mm was higher than other aggregates in soil depths of the three land use types and therefore, aggregate <0.05 mm has higher carbon adsorptive capacity than oth-

er aggregate sizes in the three depths. Although, the carbon concentration of individual aggregate decreased gradually down the soil depths of the three land use types. This indicated that carbon adsorptive capacity increased with decrease in soil aggregate size in the three land use types.

Coarse silt contributed large proportion of base cations to the exchange capacity in the soil depths of Natural Forest and highest proportion of base cations to the exchange capacity of subsoil. Conversely, fine silt contributed large proportion of base cations to the exchange capacity in the soil depths of Plantation Forest and Farm Land. High concentration of base cations and exchange capacity of coarse silt (>0.05 mm) at subsoil of Natural and Plantation Forests may be attributed to accumulation of base cations which leached from the surface soil depth. The amount of K^+ in the surface soil was lower than that in the subsoil due to the leaching process in both fractions. A high value of Na^+ accumulated on coarse and fine silt of subsoil could be due to high mobility of Na^+ from decomposed litter material with considerable leaching losses.

Fine silt minerals were responsible for high cation exchange capacity in the subsoil of Plantation Forest and Farm Land. Therefore, high cation exchange capacity of fine silt minerals could be attributed to high specific surface area when compare to coarse silt particles (Tan 2005). This shows that land use type can affect decomposition and leaching of soil mineral (Velde and Peck 2002) and consequently, it could affect the surface properties of clay mineral.

The cation exchange capacity of coarse and fine silt ranged from 5.23 to 13.40 cmolc/100 g. The extremely low values of cation exchange capacity of soil mineral fractions in three land use types may be due to the presence of kaolinite. Tan (2005) considered low cation exchange capacity and low adsorption capacity as attributes of kaolinite silicate clay minerals.

The exchange capacity of mineral size of >0.05 and <0.05 mm was highest at subsoil of Natural and Plantation Forests but increased with increase in depth in Farm Land. However, carbon concentration decreased with increase in soil depth in Farm Land. This implied absence of the influence of exchange capacity on carbon concentration in Farm Land. Decrease in exchange capacity with increase in soil depth may be due to leaching effect of soluble salts.

The exchange capacity of clay and coarse silt was low at the surface layer in the three land use types. The exchange capacity of fine silt fractions at subsoil and deep soil layer of Plantation Forest was higher than that of Natural Forest and Farm Land. This may be attributed to high carbon concentration at subsurface soil depth of Plantation Forest. Oades (1988) demonstrated positive relationship between soil organic carbon and high base status. The exchange capacity of coarse silt minerals at the subsoil of Natural Forest was higher than Plantation Forest and Farm Land. Also, exchange capacity of coarse silt at deep soil layer of Farm Land was higher than that of Natural Forest and Plantation Forest.

Calcium ion (Ca^{2+}) and sodium ion (Na^+) were the dominant cations in the soil depths of the three land use types. The significant difference in the quantity of cations on coarse and fine silt minerals in the soil depths of the three land use types despite the same soil type may be due to leaching and weathering of Ca^{2+} and Na^+ on silicate minerals that is probably caused by land use types. Ca^{2+} is the dominant cation in tropical soils and more strongly adsorbed by clay mineral than other ions because Ca^{2+} is divalent with smallest hydrated radius and strong energy of adsorption (Foth 1990). Also, as a result of the strong energy of adsorption, calcium ion is typically more abundant as an exchangeable cation than Mg^{2+}, K^+ and Na^+. The energy of adsorption of specific cation is related to valency and degree of hydration. Thus, the energy of adsorption of divalent cations is about twice that of mono-valence cations (Foth 1990; Tan 2005). Presence of Ca^{2+} protects organic carbon from mineralization in neutral and alkaline soils (Oades 1988) and Rowley et al. (2018) indicated positive relationship between Ca^{2+} and high soil organic carbon storage.

Conclusion

The aggregates of subsoil (15-30 cm depth) and deep-soil (30-45 cm depth) of Natural Forest and Farm Land seem to have reached carbon saturation limit. The carbon saturation limit among aggregates of subsoil and deep soil depths may be due to effect of high cation exchange capacity at subsoil and land use type. Coarse silt was

the dominant carrier of base cations in soil depths of Natural Forest while fine silt was the dominant carrier of base cations in soil depths of Plantation Forest and Farm land. Calcium ion dominated the exchangeable basic cations and may responsible for high sorption of carbon in soil depths of Gambari Forest Reserve. The fine silt (<0.05 mm) had high basic exchange capacity and total exchange bases than course silt in Plantation Forest and Farm Land. Apparently are responsible for most of the cation exchange capacity of the soil. Land use and mineral characteristics may responsible for carbon storage capacity of soil in Gambari Forest Reserve. Cation exchange capacity enhanced carbon storage at subsoil while organic matter inputs enhanced carbon storage at surface soil of Gambari Forest Reserve.

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