

Humic Substances and Mineral-Associated Soil Organic Carbon As Influenced By Land Use in Southeastern Adamawa State, Nigeria

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Abstract: Land use management has been observed to affect labile, stable and humified soil organic matter fractions, but the magnitude of these changes has not been established in the Southern Guinea savanna of Adamawa State, northeastern Nigeria. The study investigated effects of five land use management systems (undisturbed natural forest, crop land, grazing reserve, forest plantation and fallow land) on the status of humic substances and mineral-associated soil organic carbon. Three transects that are 100 m apart were cut in each of the study site and four sampling plots of 20 m × 20 m in dimension were laid in alternate positions along each transect at 50 m interval. Soil core samples were collected diagonally at a depth of 0-15, 15-30, 30-45 and 45-60 cm and at three points in each plot using a 3cm diameter soil auger. These results showed that both mineral-associated and humified organic matter are better protected under natural forest, plantation and grazing reserve and consequently less vulnerable to mineralization. The study revealed that seven years fallow contribution to soil organic carbon was minimal. This might be attributed to several factors such as livestock grazing, incidence of annual bush burning and cutting of vegetation for fuel wood. The relationship between stable soil organic carbon and various soil nutrients indicates that positive correlation exists. This shows that availability of humic, fulvic acid, exchangeable magnesium, exchangeable calcium, total phosphorus, cation exchange capacity and total nitrogen depend to some extent on the status of mineral-associated soil organic carbon. The content of humic was significantly influenced by land use and soil depth. Highest humic acid content (17.42 g/kg) was recorded under plantation in the soil surface layer (0-15 cm), followed by natural forest (15.16 g/kg), grazing reserve (14.16 g/kg), and fallow land (12.31 g/kg). The fulvic acid content also followed the same pattern as obtained for humic acid. The highest %mineral associated soil organic carbon was recorded for plantation and natural forest at the surface layer (0-15 cm) (1.19 and 1.15 respectively), followed by the grazing reserve (1.12). The crop land and the fallow land recorded 0.95 and 0.87 respectively. There exist differences across land use types in their potentials of storing total, particulate, mineral-associated organic carbon and humic substances in the Southern Guinea Savanna soils of Adamawa State, Nigeria. From the results it was noted that, natural forest, plantation and grazing reserve had potentials for storing organic carbon of appreciable concentration. This result provides valuable information for implementing tillage practices (such as zero tillage) that can favour carbon sequestration and improve soil quality.

Key words: Land Use, Humic substances, Mineral-associated soil organic carbon, Influence

I. Introduction

World soils are important reservoirs of active carbon and play a major role in the global carbon cycle. As such, soil can be either a source or sink for atmospheric CO₂ depending on land use and the management of soil and vegetation (Lal, 2005). Soil organic carbon (SOC) represents the largest terrestrial organic C pool and globally contains over 1550 Pg Carbon (A Pg is equal to 1000 million metric tons) (Lal, 2008), and this pool attracts considerable attention because of its potential to sequester Carbon (Baker *et al.*, 2007). The conversion of native forests for cultivation is usually accompanied by a decline in organic matter and soil structure deterioration (Resck *et al.*, 2008). Other authors also maintained that conversion of natural ecosystems to agriculture is known to cause large losses of SOC, but the SOC losses also depends on land use (Ogle *et al.*, 2005; Bayer *et al.*, 2006; Dolan *et al.*, 2006). In addition to changes in structure, organic matter reduction is associated with negative effects on nutrient concentrations (Ashagrie *et al.*, 2007), water storage (Resck *et al.*, 2008) and the emission of greenhouse gases (Lal, 2006).

In a previous study conducted by Alexandra and Jose (2005) they stated that, converting grassland and forest plantations to arable cropping results in the loss of 30 % of the soil organic carbon (SOC) originally present in the soil profile. This is an indication that continuous cultivation of these soils can accelerate depletion of the soil organic carbon content. It is obvious that, under natural conditions organic matter (OM) is returned to soil through leaf droppings particularly in the deciduous plants. Before the forest is cleared, a closed nutrient cycle exists in the soil-forest system. Within this system, most nutrients are stored in the biomass and topsoil,

and a constant cycle of nutrient transfer from one compartment of the system to another operates through the physical and biological processes of rain-wash (i.e. foliage leaching), litterfall; root decomposition, and plant uptake (Nair, 1993)

Most studies use the content of total organic carbon (TOC) to quantify the stocks and changes in organic matter. In many cases, the changes resulting from land use are not duly reflected in TOC values (Roscoe and Burman, 2003),

The soil organic matter (SOM) is located in different compartments that have different recycling times and forms of protection (Duxbury *et al.*, 1989). Soil organic matter can be analyzed on the basis of the different fractions. Changes in the levels of organic matter, caused by land use, can be better understood by alterations in the different compartments (Figueiredo *et al.*, 2010).

In recent decades, several techniques have been refined to separate the different fractions, trying to identify labile and stable fractions, and their location in the soil structure (Roscoe and Machado, 2002). One such technique, the physical fractionation allows the separation of particulate organic matter (labile) composed of readily available material for decomposition by microbial attack, e.g., leaves, roots, animal remains and mineral-associated organic matter soil (stable) (Cambardella and Elliott, 1992).

These fractions have been used in studies involving the storage of SOM under different management systems (Bayer *et al.*, 2004; Costa *et al.*, 2004; Conceição *et al.*, 2005; Vieira *et al.*, 2007; Sá and Lal, 2009), specifically on water-stable aggregates (Ashagrie *et al.*, 2007). It has been emphasized that these fractions can be used as an attribute of soil quality (Conceição *et al.*, 2005) and sensitivity and as an indicator of changes caused by farming (Ashagrie, *et al.*, 2007). Vieira *et al.*, (2007) showed that particulate organic matter (> 53 μm) can be used to determine the index that measures the lability of organic matter. The influence of SOM on aggregate formation and stability is proven, although the existing fractions act differently in these processes (Baldock, 2002). The particulate fraction acts as a cementing agent, to stabilize macroaggregates and as intra-aggregate protection of the proper organic matter (Six *et al.*, 2002). Adejuyigbe *et al.*, (2000) pointed out that particulate organic carbon is a more labile fraction of the soil organic carbon which is the most readily formed and when it decomposes, it serves as an important substrate for mineralization process in the soil. The level of this fraction therefore, could be an essential determinant of the fertility status of savanna soils.

Costa *et al.*, (2004) found differential contributions of total organic and particulate organic carbon (more labile) in the formation of soil aggregates. In a study of Bayer *et al.*, (2004), organic carbon in the particulate organic matter (POC) (> 53 μm) indicated management changes with greater sensitivity than TOC. Mineral-associated soil organic carbon is the soil separates that passed through the 53 μm sieve during separation of particulate organic carbon. Bayer *et al.*, (2001) found that, the C and N pools in mineral-associated soil organic carbon increased several times more than the particulate organic carbon fraction caused by greater physical recalcitrance of mineral-associated soil organic carbon to biological decomposition. The mineral-associated soil organic carbon is an excellent atmospheric carbon reservoir which is less affected by conventional tillage practices, and has smaller transference of soil C to the atmosphere.

Bayer *et al.*, (2006) further maintained that, the non significant effect of tillage on carbon stocks in mineral-associated soil organic matter is probably related to the high stability of this fraction to biological decomposition due to interaction with various charge minerals.

Management decisions that reduce tillage intensity, maximize residue return, eliminate bare fallow, and reduce water stress with irrigation (Follet, 2001; Hermle *et al.*, 2008) have all been suggested to increase SOC stocks and mitigate greenhouse gas (GHG) emissions, with soils serving as a Carbon sink for atmospheric CO₂ (West and Marland, 2002; Ogle *et al.*, 2005; Zinn *et al.*, 2005).

Savannas are a major component of the Earth's vegetation and occupy large areas in Sub-Saharan Africa. The savanna biome is characterized by the co-dominance of trees and grasses, but ranges from grasslands where trees are virtually absent to more forest-like ecosystems where trees are dominant. Most of the savanna areas are natural ecosystems; however, they can also be formed by the degradation of tropical forests by burning, grazing and deforestation.

Humic substances (HS) make up a large portion of the dark matter in humus and are complex colloidal supramolecular mixtures (Piccolo, 1996, 2001; MacCarthy, 2001). These substances arise by the microbial degradation of biomolecules (lipids, proteins, carbohydrates, lignin) dispersed in the environment after the death of living cells. Humic substances may chelate multivalent cations such as Magnesium²⁺, Calcium²⁺, and Iron²⁺. By chelating the ions, they increase the availability of these cations to organisms, including plants.

Humic substances play an important role from the agronomy point of view. They influence significantly the quality and productivity of the soil. In addition to the improvement of the soil's physical properties and moisture conditions, HS also show a high Base Exchange capacity, which is important for soil fertility (Lotosh, 1991, Zhang and He, 2004).

Currently, humic materials are used as additives in fertilizers (García *et al.*, 1994, Madejon *et al.*, 2001, Albiach *et al.*, 2001, Arancon *et al.*, 2004). Different salts of humic substances, such as calcium humate, were used to

increase soil fertility (Buckau *et al.*, 2000). Another role of humic substances lies in the enhancement of the quality of soils when they are very poor in organic matter. Previous research shows that humic acid can be used as farm animal feed (Kocabagli *et al.*, 2002).

Soil organic matter is composed of different compartments which differ from each other in biochemical composition, biological stability and carbon turnover rates (Paustian *et al.*, 1992). The humified SOM (Humic, Fulvic and Humin) represents the most microbially recalcitrant and thus stable reservoir of organic carbon (OC) in soil and an important component that controls nutrient absorption and release, and for the control of soil erosion by water and wind (Piccolo *et al.*, 1999).

Most studies on SOM dynamics in the tropics have focused on its absolute amount without recourse to their chemical fractions (Scholes *et al.*, 1997). However, not much information is available on chemical characteristics of humic substances and mineral-associated organic carbon and their modifications when forested sites are cleared for intensive cultivation, especially in the savannas and also when marginal land is afforested. Yet SOM and HAs, in particular, play important roles in these soils where 1:1, low activity clays, and low cation exchange capacity (CEC) are common. In these conditions, more than 70% of the CEC of such soils and, hence, of their chemical fertility is attributed to SOM (Asadu *et al.*, 1997). Soil monitoring is needed in order to assess the effects of land use change, as well as changes at the level of management types. Therefore, this study was carried out to characterize the humified OM fractions and mineral-associated soil organic carbon from natural forest, fallow land, grazing reserve, plantation and crop land soils of the southern guinea savanna of Adamawa State, Nigeria

II. Materials And Methods

The Study Area

The study was carried out in and around Gumti sector, the northern half of Gashaka-Gumti National Park, covering Toungo local government and Jada local government areas of Adamawa State. Toungo local government lies between latitude 8° 7' and longitude 12° 3' East. It is bounded by Ganye to the north, Taraba state to the west and south and to the east the Republic of Cameroon. It has a land mass of 5479.5km² and a population of 52,040 (Adebayo, 1999; NPC, 2007). Jada local government lies between latitude 8° 46' N and longitude 12° 9' East. It is bounded by Ganye to the east, Mayo-belwa and Taraba state to the west, Toungo to the south and to the east Republic of Cameroon (Adebayo, 1999). It has a population of 171, 672 (National Population Commission, 2007).

Climate

The area received an annual rainfall of 1000–1200 mm. Rainfall distribution is unimodal, with much of the rain falling between April and November. Day time temperatures may drop below 18°C at higher altitudes and gradually rise to 40°C. The rainy season is followed by a dry season. During this period, the area comes under the strong influence of the hammattan (November and March) a dry dusty wind blows from Sahara Desert and temperatures may be significantly cooler (Gashaka Gumti National Park, 2010).

Site Selection and Sampling procedure

The study area consists of five (5) selected sites; these include undisturbed natural forest, fallow land, grazing reserve, afforested land and a crop land. The undisturbed natural forest is strictly restricted as a National Park and hence no crop cultivation. The crop land is extensively cultivated with crops such as Maize, Sorghum, Cowpea, *Arachis hypogea*, Yam and livestock grazing is usually carried out on the site. In the grazing reserve no crop cultivation, the site is exclusively reserve for livestock grazing. The plantation was established with *Gmelina arborea* in 1993 and strictly protected against wildfire. Fallow land was left under natural fallow for seven years, livestock grazing and fetching of fuel wood also takes place. This site was under cultivation with crops such as *Arachis hypogea*, Yam, Maize, Sorghum and Cowpea. Prior to soil sampling, soil profile studies was carried out and the profile morphological characteristics of the dominant soil types in the study areas described based on (World Reference Base, 2006).

Systematic strip sampling was employed in laying out the plots. Three transects that are 100m apart were cut in each of the study site and four sampling plots of 20m × 20m in dimension were laid in alternate positions along each transect at 50m interval. Soil core samples were collected diagonally at the depths of 0-15, 15-30, 30-45 and 45-60cm and at three points in each plot using a 3cm diameter soil auger. Samples from each plot at each depth were bulked and the composite soil samples taken and analyzed in the laboratory for humic, fulvic acids, particulate soil organic carbon, mineral associated soil organic carbon and other physico-chemical soil properties. A total of forty eight (48) composite samples from each site were properly labeled for ease of identification.

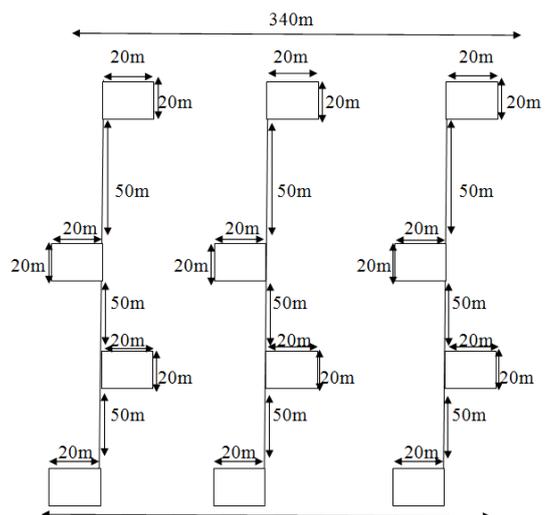


Fig. 1: Systematic Strip Transect Sampling Technique and Plot Layout

Design of the Study

The experiment was laid out in Randomized Complete Block Design (RCBD). The land use types constituted the treatments while soil depths constituted the blocks.

Physical and chemical soil analyses

Fractionation of soils for separation into particulate and mineral size fractions

The process of soil physical fractionation was based on the methodology proposed by Cambardella and Elliott (1992). 50g of $\geq 2\text{mm}$ soil sample was transferred into a 250 ml sample bottle and 105ml distilled water added. Soil suspension was then washed through a $>53\mu\text{m}$ sieve and the coarse fraction was separated. The soil samples above the $53\mu\text{m}$ sieve were considered particulate soil organic matter (SOM) while, those that pass through the sieve mineralized SOM. The particulate ($\geq 53\mu\text{m}$) and mineral ($<53\mu\text{m}$) soil fractions were dried in an oven at 100°C , and analyzed for organic carbon using the wet oxidation method.

Organic carbon determination in the various fractions

Organic carbon was determined in the bulk soil, $\geq 53\mu\text{m}$ and $<53\mu\text{m}$ soil fractions as total organic carbon (TOC), particulate organic carbon (POC) and mineral organic carbon (MOC) respectively, using the wet oxidation method of Walkley and Black (1934). One gram of soil sample was weighed into a 250mls conical flask, 10mls of 1N potassium dichromate added with the aid of a pipette, thereafter, 20mls of conc. Sulphuric acid added and allowed to cool to room temperature. 100mls of distilled water followed by 10mls of orthophosphoric acid was also added, after which 0.2g of Sodium fluoride and 5drops of diphenylamine indicator were added. The sample was titrated against 0.5N ferrous sulphate.

The colour change (end point) to bottle-green and the organic carbon calculated using the following formula:

$$\text{OC} = \frac{B - T \times F \times 0.39}{W}$$

Where:

B = Blank titre value

T = Sample titre value

F= Strength of Ferrous sulphate

W = Weight of sample.

0.39 = Constant

Routine Soil Analysis

The samples were also analyzed for pH (1:2.5soil to water ratio) using glass electrode pH meter as described by Bates (1954), particle size was determined using hydrometer method as described by (Bouyoucos 1951). Available Phosphorus was extracted with 1N NH_4F and 0.5N HCl (Bray and Kurtz, 1945) and measured at the wavelength of 660 nm. The titrimetric method was used for the determination of Calcium and Magnesium in the soil as described by Black, (1965) while the regular Macro-Kjeldahl Method as described by Black (1965) was used for the determination of soil total Nitrogen. Potassium and Sodium were determined in 1N neutral NH_4OAc soil extract using Flame Photometry and Exchangeable acidity was determined using the titration

method as described by Mclean (1965). The effective cation exchange capacity and cation exchange capacity (CEC) was determined by summation method.

Method of Extraction of Humic Substances

The simple and rapid method of isolating humic substances as described by Shamsuddin *et al.*, (2009). 5 grams of soil samples was transfer into a polyethylene centrifuge bottles (250 ml) and 50 ml 0.1M NaOH solution added and bottle stopped tightly with a rubber stoppers. The samples were equilibrated at room temperature (25⁰C) on a reciprocal mechanical shaker. The extraction period ranges from 4, 8, 12, 16, 20 and 24hours. At the end of each extraction period, the samples were centrifuged at 16, 211 G for 15 minutes. The dark-coloured supernatant liquors decanted, the pH of the solutions adjusted to 1.0 with 6M HCL and the humic acid (HA) allowed to stand at room temperature. At the end of each fractionation period, the excess supernatant liquors (Fulvic acid) were siphoned off from the acidified extracts. The remainder of the suspensions containing the HA was transfer to polyethylene bottles and centrifuge at 16,211 G for 10 minutes. The HA samples were purified by washing them in 50ml of distilled water through centrifugation at 16,211 G for 10 minutes to reduce mineral matter (e.g., Na⁺) and HCl (used during acidification). This procedure was repeated 5 times after which the washed HA samples were oven dried at 40⁰C to a constant weight, weighed and yields expressed as g/kg HA and FA (fulvic acid) in the soil samples.

Statistical Analyses

Data collected were subjected to analysis of variance (ANOVA) to determine statistical differences of selected soil properties. Correlation analysis was also employed to relate humic substances and mineral associated soil organic carbon to various soil nutrient elements. The Statistical analysis was performed with SPSS (V. 18), Mean separation was performed with Duncan's Multiple Range Test (DMRT) at p<0.05.

III. Results

Influence of land use on the status of humic substances and carbon fractions

The results of the influence of land use management on the status of humic substances and carbon fractions are shown in Table 1. The results of the analysis of variance (ANOVA) show that there was significant difference (P<0.05) in the status of humic acid, fulvic acid, %total organic carbon, % particulate organic carbon and % mineral associated organic carbon with respect to land use management. The highest humic acid and fulvic acid content was recorded for plantation (8.75 and 52.50g/kg soil), followed by the natural forest (6.38 and 40.97g/kg soil), grazing reserve (5.64 and 33.83g/kg soil), fallow land (5.30 and 31.80g/kg soil) and crop land (3.36 and 20.13g/kg soil) respectively. The result follows a decreasing order with land use management. Thus, Plantation>Natural forest>Grazing reserve>Fallow land>Crop land. For percentage particulate organic carbon (labile fraction), the highest (0.55) was obtained in the natural forest, followed by the grazing reserve, plantation and crop land (0.43, 0.42 and 0.39) and fallow land (0.32) respectively. Thus, Natural forest>Grazing reserve=Plantation=Crop land>Fallow land in a decreasing pattern. The highest %mineral associated (stable fraction) organic carbon (0.70) was recorded for plantation, followed by the natural forest (0.62), grazing reserve (0.54 and crop land (0.52), followed by fallow land (0.32) in a decreasing order respectively. Thus, Plantation≥Natural forest>Grazing reserve=Crop land≥Fallow land.

Correlation of percent mineral associated organic carbon with humic acid, fulvic acid and other soil nutrients

The relationship between percent mineral associated organic carbon with phosphorus, total exchangeable soil acidity, exchangeable Calcium, Humic and fulvic acids are presented in Table 2. Phosphorus was positively correlated with %mineral associated carbon (r=0.86). Total exchangeable acidity, exchangeable Calcium, Humic acid, fulvic acid, %total Nitrogen, exchangeable Magnesium and cation exchange capacity were also positively correlated with %mineral associated carbon (r=0.21, r=0.24, r=0.94, r=0.94, r=0.14, r-0.40 and r-0.40) respectively.

Effects of soil depth and land use on humic substances and organic carbon fractions

The effects of soil depth and land use management on humic substances and organic fractions are shown in Table 3. The results of the analysis of variance show that there was significant difference (P<0.05) in the contents of humic acid, fulvic acid, %particulate soil organic carbon and %mineral associated soil organic carbon with respect to soil depth and land use management. The content of humic acid was significantly influenced by land use and soil depth. Highest humic acid content (17.41 g/kg) was recorded under plantation in the soil surface layer (0-15 cm), followed by natural forest (15.16 g/kg), grazing reserve (14.16 g/kg), fallow land (12.31 g/kg) respectively. The subsurface layer of the plantation recorded the second highest content of humic acid (13.33 g/kg), followed by the natural forest (8.13 g/kg). Subsurface layers of the grazing reserve and

fallow land 15-30, 30-45 cm had the same content of humic acid (3.42, 3.46 g/kg) respectively. The last subsurface layer of the plantation and the natural forest 30-45 and 45-60 cm recorded the same and lowest content of humic acid (2.13 and 2.01 g/kg) followed by the fallow land (1.97 g/kg), crop land and grazing reserve (1.33 and 1.11g/kg respectively). The fulvic acid content also followed the same pattern as obtained for humic acid. The surface layer of the plantation (0-15cm) depth has the highest content (104.46 g/kg) of fulvic acid, followed by the natural forest (90.96 g/kg).

The results of analysis of variance revealed that there was significant difference ($P < 0.05$) in the contents of %particulate organic carbon and %mineral associated soil organic carbon with soil depth and land use type (Table 3). The highest (1.19 and 1.15) %mineral associated soil organic carbon was recorded for plantation and natural forest respectively at the surface layer (0-15 cm), followed by the grazing reserve (1.12). The crop land and the fallow land recorded 0.95% and 0.87% respectively. The subsurface layer (15-30 cm) of the plantation recorded the highest 0.84 % mineral associated soil organic carbon followed by the crop land and the natural forest (0.75 and 0.70 respectively). The grazing reserve and the fallow land subsurface layer (15-30cm and 30-45cm) had the same contents of %mineral associated soil organic carbon in a decreasing pattern (0.32 and 0.29 respectively). Also, the subsurface layers of the plantation and the natural forest 45-60 and 30-45cm) had the same contents of %mineral associated soil organic carbon (0.38 and 0.31) respectively.

IV. Discussion

Humic substances consist of the humic acid, fulvic acid and humin. These make up a large portion of the dark matter in humus and are complex colloidal supramolecular mixtures (Piccolo, 1996; 2001; MacCarthy, 2001). These organic substances play an important role from the agronomy point of view. They influence significantly the quality and productivity of the soil. In addition to the improvement of the soil's physical properties and moisture conditions, humic substances also show a high Base Exchange capacity, which is important for soil fertility (Lotosh 1991, Zhang and He, 2004).

The results of the analysis of variance show that there was significant difference ($P < 0.05$) in the contents of humic acid, fulvic acid (passive fraction soil organic carbon), %total soil organic carbon, %particulate (labile fraction) and %mineral associated (stable fraction) soil organic carbon. The result of the status of humic and fulvic acids follows a decreasing pattern with land use type. Thus, Plantation > Natural forest > Grazing reserve > Fallow land > Crop land. This result indicates that land use is an important factor that controls the content and availability of humic substances in the soil. High content of humic and fulvic acids that was recorded in the plantation can be attributed to the organic matter returned to the soil through the leaf litter of Gmelina and most important as a deciduous plant which sheds leaf during the dry season. In a previous study conducted by Oluwatosin *et al.*, (1999) they reported that, vegetation influences the quality of soils under it, which also in turn influence the growth and performance of crops. According to Juma, (1999) organic matter content, particularly the more stable (humic substances) increases the capacity of the soil to store water and sequester carbon from the atmosphere. Post and Kwon (2000) maintained that land use and soil management practices significantly influence soil organic carbon dynamics and carbon flux from the soil.

There was a marked decrease in the contents of humic acid and fulvic acid as a result of change in land use; Crop land recorded the lowest value of humic substances. This agrees with the findings of Alexandra and Jose (2005), who reported that conversion of grassland and forest plantations to arable cropping results in the loss of 30 % of the soil organic carbon originally present in the soil. This shows that continuous cultivation of these soils can accelerate depletion of the soil organic carbon content.

Fallow remains one of the traditional methods of land use management system that is used for soil fertility restoration through the buildup of soil organic matter. In this study it was noted that the contribution of seven years fallow to the status of humic, fulvic acids and soil organic carbon was minimal. This might be attributed to several factors such as livestock grazing, incidence of annual bush burning and cutting of vegetation for fuel wood which is more frequent in the study area. The natural forest and the grazing reserve recorded a relatively high content of humic and fulvic acids due to accumulation and humification of organic matter under these land use types.

The results of correlation between percent mineral associated (stable fraction) soil organic carbon with phosphorus, total exchangeable soil acidity, exchangeable Calcium, Humic acid, fulvic acid, %total Nitrogen, exchangeable Magnesium and cation exchange capacity showed positive relationship. This indicates that mineral associated organic carbon is both a carbon sink and also a source of soil nutrients. A high positive correlation exists between mineral associated organic carbon with humic acid, fulvic acid and phosphorus ($r^2=0.89$, $r^2=0.89$ and $r^2=0.74$)

The relationship between mineral-associated (stable fraction) soil organic carbon with various soil nutrients is a good indicator of soil fertility. Total organic carbon has been used as an indicator of soil fertility and productivity. The relationship between stable soil organic carbon and various soil nutrients in this study indicates that positive correlation exists. Some authors pointed out that this is attributed to the physical stability

of aggregates in variable charge soils (Janzen *et al.*, 1998; Bayer *et al.*, 2001). The mineral-associated soil organic carbon has been reported to be very important in increasing and/or maintaining soil quality and determining the soil's potential to act as an atmospheric CO₂ sink. Bayer *et al.*, (2006) pointed out that this is probably related to high stability of this fraction to biological decomposition due to interaction with various charge minerals.

In a study conducted by Tipping (1994), he found out that humic acids have the ability to form complexes with ions such as Mg²⁺, Ca²⁺, Fe²⁺ and Fe³⁺. Ghabbour and Davies (2001) confirmed that the formation of (chelate) complexes is an important aspect of the biological role of humic acids in regulating bioavailability of metal ions. Yang *et al.*, (2007) also found that soil organic matter plays an important role in nutrient availability and soil aggregate formation. The formation of stable macro aggregates is strongly linked to soil organic matter dynamics as well as nutrient supply. This shows that availability of humic, fulvic acids, exchangeable magnesium, exchangeable calcium, total phosphorus; cation exchange capacity and total nitrogen depend, to some extent, on the status of mineral-associated soil organic carbon. At the same time when the content of mineral-associated soil organic carbon is high this may also lead to a decrease in the availability of some soil nutrients. A negative relationship was observed between mineral-associated organic carbon and exchangeable soil potassium and sodium ($r=-0.20^{**}$ and $=-0.28^{**}$) respectively.

The content of humic was significantly influenced by land use and soil depth. Highest humic acid content (17.42 g/kg) was recorded under plantation in the soil surface layer (0-15 cm), followed by natural forest (15.16 g/kg), grazing reserve (14.16 g/kg), fallow land (12.31 g/kg) respectively. The fulvic acid content also followed the same pattern as obtained for humic acid. The highest %mineral associated soil organic carbon was recorded for plantation and natural forest at the surface layer (0-15 cm) (1.19 and 1.15 respectively), followed by the grazing reserve (1.12). The crop land and the fallow land recorded 0.95 and 0.87 respectively.

All the different land use types showed highest accumulation of the various carbon fractions in the surface layer (0-15cm). Burle *et al.*, (1997) also reported that highest soil organic matter increase on surface layers but soil organic matter storage in total soil profile was also positively affected. This high level of organic carbon stock in the surface layer could be due to the slow mixing of the soil and, the litter layer formed as a result of leaf-fall from the trees. In a 12-year experiment, Bayer *et al.*, (2000) found that by the third year, the increase in carbon and nitrogen stocks were minimal and occurred only in the 2.5cm top layer, however, by the 5th year, this effect had spread to the 7.5cm depth. In the 9th and 11th year, carbon and nitrogen stocks increased through to 12.5cm and 17.5cm depths respectively. In addition, soil organic carbon storage in deeper soil layer has been related to the development of roots systems (Pillon, 2000) and to the amount of above ground biomass addition on the soil surface (Burle *et al.*, 1997) implying that the trees will normally improve in their respective organic carbon addition potentials, depending on the length of time and fallow period since the biomass increase with age. The organic carbon fractions were observed to decrease with depth. The top layer recorded the highest concentration of these fractions.

V. Conclusion

There exist differences across land use types in their potentials of storing total, particulate, mineral-associated organic carbon and humic substances in the Southern Guinea Savanna soils of Adamawa State, Nigeria. From the results it could be observed that, natural forest, plantation and grazing reserve had potentials for storing organic carbon of appreciable concentration.

The organic carbon fractions were observed to decrease with depth. The top layer recorded the highest concentration of these fractions. All the different land use types showed highest accumulation of the various carbon fractions in the surface layer (0-15cm). This result provides valuable information for implementing tillage practices (such as zero tillage) that can favour carbon sequestration and improve soil quality

Recommendations

One strategy of increasing the humified and mineral-associated soil carbon in tropical soils is the use of management systems that provide large amounts of biomass, especially with deep root systems. Based on the results presented, pasture is an appropriate option, similar to natural forest in the amount of biomass it provides the soil with. However, the *Gmelina arborea* supported the highest accumulation of mineral-associated carbon making it a good candidate for trees which have carbon sequestration potentials in the savanna.

Table 1: Influence of land use management on the status of humic substances and carbon fractions

Land use	%TO/C	%P.OC	%M.OC	HA(g/kg)	FA(g/kg)
Natural forest	1.17a	0.55a	0.62ab	6.83ab	40.97ab
Plantation	1.12ab	0.42b	0.70a	8.75a	52.50a
Grazing reserve	0.98ab	0.43b	0.54bc	5.64b	33.84b
Crop land	0.92bc	0.39b	0.52bc	3.36c	20.13c
Fallow land	0.73c	0.32c	0.42c	5.30bc	31.80bc

Means with the same letter along the columns are not significantly different (Duncan's Multiple Range Test P< 0.05)

- %TOC =% Total organic carbon
- %P.OC =% Particulate organic carbon
- %M.OC =% Mineral associated organic carbon
- HA (g/kg) =Humic acid gram per kilogram soil
- FA (g/kg) =Fulvic acid gram per kilogram soil

Table 2: Correlation Coefficients between total, particulate, mineral associated organic carbon, humic acid, fulvic acid, total available phosphorus, %total Nitrogen and exchangeable cations

	%TOC	%P.OC	%M.OC	%TN	TEA	T-P	EK	ECa	EMg	ENa	ECE	HA	FA
%TOC	1.00												
%P.OC	0.96**	1.00											
%M.OC	0.99**	0.91**	1.00										
%TN	0.15*	0.15*	0.14*	1.00									
TEA	0.25**	0.30**	0.21**	0.26*	1.00								
T-P	0.85**	0.77**	0.86**	0.10	0.10	1.00							
EK	-0.20**	-0.24**	-0.17**	-0.09	-0.19**	-0.03	1.00						
ECa	0.29**	0.37**	0.24**	-0.02	0.03	0.33**	0.06**	1.00					
EMg	0.42**	0.44**	0.40**	-0.35**	-0.07	0.18**	-0.08	0.27**	1.00				
ENa	-0.28**	-0.21**	-0.31**	0.18**	0.22**	-0.45**	-0.70**	-0.43**	-0.18**	1.00			
ECE	0.45**	0.51**	0.40**	-0.26**	-0.03	0.29**	-0.01	0.73**	0.86**	-0.36**	1.00		
HA	0.93**	0.86**	0.94**	0.17*	0.26**	0.93**	0.28	0.39**	0.30**	-0.50**	0.42**	1.00	
FA	0.93**	0.86**	0.94**	0.17**	0.28**	0.93**	0.28	0.39**	0.30**	-0.50**	0.42**	0.97**	1.00

**Correlation if significant at 0.01 level, *Correlation is significant at 0.05 level

- %TOC =% Total organic carbon
- %P.OC =% Particulate organic carbon
- %M.OC =% Mineral associated organic carbon
- TEA =Total exchangeable acidity
- T-P = Total Phosphorus
- %TN = % Total Nitrogen
- EK = Exchangeable Potassium
- ECa = Exchangeable Calcium
- EMg = Exchangeable Magnesium
- ENa = Exchangeable Sodium
- ECE =Cation exchange capacity
- HA =Humic acid
- FA =Fulvic acid

Table 3: Effect of land use management and Soil Depth on Humic Substances and Mineral Associated Soil Organic Carbon

Soil depth (cm)	Natural forest	Plantation	Grazing reserve	Crop land	Fallow land
% Total soil organic carbon					
0-15	1.94a	1.91a	1.87a	1.46a	1.55a
15-30	1.33b	1.26b	0.80b	1.12b	0.54b
45-60	0.70c	0.65c	0.80b	0.55c	0.54b
30-45	0.70c	0.65c	0.38c	0.54c	0.34c
% Particulate soil organic carbon					
0-15	0.77a	0.73a	0.76a	0.50a	0.68a
15-30	0.62b	0.42b	0.39b	0.44b	0.24b
45-60	0.39c	0.27c	0.39b	0.31c	0.24c
30-45	0.39c	0.27c	0.185c	0.31c	0.11c
% Mineral-associated soil organic carbon					
0-15	1.15a	1.19a	1.12a	0.95a	0.87a
15-30	0.70b	0.84b	0.42b	0.75b	0.29b
45-60	0.31c	0.38c	0.20c	0.23c	0.23c
30-45	0.31c	0.38c	0.42b	0.23c	0.29b
Humic acid (g/kg)					
0-15	15.16a	17.41a	14.16a	7.58a	12.31a
15-30	8.13b	13.33b	3.42b	3.21b	3.46b
30-45	2.01c	2.13c	3.42b	1.32c	3.46b
45-60	2.01c	2.13c	1.11c	1.32c	1.97c
Fulvic acid (g/kg)					
0-15	90.96a	104.46a	87.66a	45.48a	73.86a
15-30	48.78b	79.98a	20.52b	19.26b	20.76b
30-45	12.06c	12.78c	20.52b	7.92c	20.76b
45-60	12.06c	12.78c	6.66c	7.92c	11.82c

Means with the same letter along the columns are not significantly different (Duncan's Multiple Range Test $P < 0.05$)

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