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Original Research Article

Chemistry and Mineralogy of soils derived from different Parent Materials in Southeastern Nigeria.

Abstract

Knowledge of the soil minerals is an important index in understanding the soil fertility properties since mineral surfaces serve as both source and sink of plant nutrients. Soils developed from contrasting parent materials viz: Coastal Plain Sand, Sandstone, Basalt and Shale at different soil horizons (0-20cm, 20-40cm and 40-60cm) in South Eastern Nigeria were studied for mineralogical properties. Soil samples were collected from the different parent material in three replicates and a total of thirty six composite samples were collected. These samples were subjected to X-ray diffraction analysis with Siemens D5000 diffractometer using Cuką radiation with Iron(fe) filter (λ = 1.5409A) at 40kv and 30mA, at a scan rate of 2^0 per minute The experimental design was a 4 x 3 factorial in Randomized Complete Block Design (RCBD). Statistical analysis revealed significant ($P<0.05$) variation in soil physical and chemical properties with parent material and soil depth except OM, TN, Mg^{+2} TEA and BS where variations were not significant. However, interaction between parent material and soil depth was only significant in influencing the pH. Top soil layers had significant greater amount of OM, TN, AP, cations, Sand and Silt. Generally, soil of shale formation was superior, followed by basaltic soil in these soil fertility indicators, while soil of Coastal Plain Sand formation had the least amounts. Parent material and depth played dominant roles in the type and distribution of clay minerals in the study area. The concentration of these minerals varied with parent material and soil depth. Significant variations with parent material were observed in the minerals identified except in Halloysite and Chlorite where non-significant variations were observed. While variations with depth were statistically significant ($P<0.05$) in Chlorite, Geothite, Hermatite, Montmorillonite and Quartz, the influence of the interaction between parent material and soil depth were only significant in Gibbsite, Kaolinite and Montmorillonite. Soil derived from Coastal Plain Sand had, Kaolinite (9.94 to 28.83%) and Quartz (56.4 to 87.3%) as the dominant clay minerals and these decreased with depth. Soil formed in shale had mixed clay mineralogy of montmorillonite (14.37 to 21.88%), goethite (23.58 to 25.09%) , hermatite (20.39 to 24.19%), gibbsite (8.48 to 12.10%), kaolinite (6.89 to 3.56%) and others with depth.Soil formed in sandstone has Kaolinite accounted for 26.42 to 31.26%, goethite, 7.77 to14.87%,, and quartz accounted for 35.4 to 51.8%. Other minerals identified were: hermatite (4.58 to 14.62%), gibbsite (1.70 to 5.23%), while soils derived from basalt had kaolinite (14.64 to 27.44%), quartz (23.7 to 42.5%), hematite (11.0 to 23.14%), goethite (13.94 to 26.48%) as the dominant crystalline minerals present in the soil. The study concludes that the mineralogy of Southeastern Nigeria consists of quartz, kaolinite, hermatite, goethite and gibbsite with traces of smectite in soil derived from shale as the dominant minerals and their percent mass occurrences varied with soil parent material and depth.

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Key words: soil chemistry, Clay mineral, parent material and soil depth.

Introduction

The challenge for agriculture over the coming decades will be to meet world increasing demand for food in a sustainable way (Idris and Ahmed, 2012). Declining soil fertility and management of plant nutrients have made this task more difficult (Gruhn *et al.,* 2000).With increasing demand of agricultural production due to the drastic increase in global population, there is urgent need to outline strategies that will ensure sustainable production of food through a holistic approach to soil nutrient management (Jones *et al.*,2013). A decisive and holistic approach to soil fertility study will in addition to investigating the nutrient content in a soil include a study of the mineralogical properties.

Soil minerals serve as both sources and sinks of essential plant nutrients. As primary minerals that originally formed at high temperatures and pressures in igneous and metamorphic rocks are weathered in soils, they release plant nutrients into the soil solution. New minerals form in the aqueous phase of soil environments.

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These secondary minerals which dominate the clay fraction of the soil (Clay minerals) serve as sources of nutrients themselves, or they precipitate or adsorb essential elements, keeping them from being taken up readily by plants. In many cases, secondary minerals serve as important reservoirs where nutrients are held strongly enough to prevent leaching, yet weakly enough to allow plants to draw on them to meet their nutritional needs. The availability of different nutrient elements such as P, Ca, K, $NH_{4,}$ Mg, etc is largely influenced by the clay minerals present in such soils.

Soils show tremendous variability with regard to their mineralogical properties (Nsalambi and Christopher, 2010). The types and amount of minerals present in soils from different regions vary greatly, hence the mineralogical constitution of soil is rather complex.

The mineralogical composition of the clay fraction of a soil is one of the critical factors in determining soil chemical and physical properties. In natural soils, (Borggaard and Elberling, 2004) concluded that mineralogy can be decisive for soil sensitivity and resilience, including the capacity of the soils to resist stress and recover after exploitation. Mineral types and amounts are influenced by several factors such as climate, topography, vegetation and bedrock type (Libo *et al*., 2015). Clay minerals are excellent tracers of weathering processes of bedrocks, especially some typical clay minerals such as kaolinite, montmorillonite and illite (Tang, *et al*., 2002). Quantitative analysis of clay minerals and their alteration provides invaluable information on the pedogenic history of soils (Wilson, 1999). Clay mineralogy in soils helps in better understanding soil genesis and development (Moore and Reynolds 1997). Moreover, the types and amount of clay minerals are considered as important constraints on the physical and chemical properties of soil.

Kaolinite, Quartz and different forms of iron (Fe) and aluminum (Al) oxides have been reported as the dominant minerals in the clay fraction of the highly weathered soils of most tropical and subtropical regions (Nitzsche *et al*., 2008; Schaefer *et al*., 2008). The concentration of these minerals in the soil and their characteristics such as crystalline and specific surface area vary with the parent materials, intensity of weathering, composition of soil solution and drainage conditions (Schaefer *et al.,* 2008) and may also be affected by soil management system (Silvaneto *et al.,* 2008).

The mineralogy and geochemistry of different geological formations such as shale, sandstone, coastal plain sand etc, influence to a large extent the nature of the overlying soils (Szilas *et al*., 2005). Norra *et al. (*2006) observed that the mineralogical and geochemical components of surface soils reflect the soil parent material and pedogenic minerals. Parent material has been recognized as an important factor in soil formation since the earliest scientific consideration of soils (Jenny, 1980). According to Joffe (1949) the formation of soil in a region can occur within a certain period of time depending on the parent material, climate, topography and vegetation of the region (Buol *et al*., 1980; Dinc *et al*., 1987). Different parent materials affect the morphology and chemistry of soils under the same conditions, such as topography and vegetation (Irmak et al.,2007). Differences in physical, chemical and mineralogical properties of soils are related primarily to parent material (Washer and Collins, 1988).

The clay mineral characteristics of a given soil type influence largely the capacity of the soil to supply nutrient to plants and the kinetics of its ability to replenish the soil solution after the depletion of the rhizosphere

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(Hinsinger *et al.,* 2009). Different types of clay mineral hold and retain different kind and amount of nutrients. Therefore characterizing the clay minerals present in a particular soil can be an important index in understanding and possibly predicting the degree to which the soil can retain and supply nutrients to plants. Also the soil clay mineralogy is closely related to soil fertility and the differences in soil clay mineralogy cause great differences in soil fertility. Thus, characterization of soils especially as it relates to mineralogical distribution provides useful information on their behaviour, fertility status and their agricultural productivity potentials since mineral surfaces serve as potential sites for nutrient retention and subsequent release to plants (Hinsinger *et al.,* 2009). Much work on the fertility status of the highly weathered soils of Southeastern Nigeria has been done, but little or none of these works provided information on the mineralogy. The unavailability of detailed information on the mineralogical properties of soils of Southeastern informed the choice of this study.

MATERIALS AND METHOD

Location

The study area, southeastern Nigeria lies between latitudes 4°20' and 7°25'N and longitudes 5°25' and 9°51'E (Nwagbara, 1997).It is made up of Abia, Akwa Ibom, Anambra, Cross River, Ebonyi, Enugu, Imo, and River States and occupies a land mass of about 12% of the total land area of Nigeria (Odurukwe *et al.,* 1995). It covers an area of about 37,845km^{2}land mass with 60 percent of this area covered by the tropical rainforest (Njoku *et al.,* 2006). It is bounded on the east by the Republic of Cameroon, on the North by Benue State and on the south by the Bight of Benin (Odurukwe *et al.,* 1995).

The climate is essentially humid Tropical with annual rainfall total not exceeding 3500mm (Njoku, *et al.,* 2006). There are two marked seasons in the study area: the wet and the dry seasons. The wet season begins in late April and last, till October with heavy rainfalls recorded in the months of June, July and September. There is usually a decline of rainfall in August. This is usually referred to as "August break" (Obasi *et al.,* 2015). Current mean maximum temperature of the area is 32°C while the mean minimum is 21°C, and a relatively high mean annual relative humidity, exceeding 75% (Njoku *et al.,* 2006).

Vegetation stretches from mangrove swamp in the coast through rainforest to derived savanna in the interior. According to Okorie and Okpala, (2000), the vegetation is essentially secondary forests tending towards derived savannah because of population pressure and repeated annual bush burning.

Geology

The extensive soil systems and landscape of South-eastern Nigeria are underlain by sedimentary materials of different ages and different formations (Igwe *et al*., 2015).The geological formations were described by Ofoegbu (1985) as materials within the "Benue trough". They are mainly weathered sandstones of Palaeocene/Pleistocene age and shales of the basement complex of Precambrian age (Oriajiaka, 1975). The underlying geology consist of heterogeneous materials, namely Basement Complex, Beach Sands, Coastal Plain Sand, Mangrove Swamp Deposits, Sandstones, Somberirio Warri Deltaic Deposits, Recent and Sub-recent Alluvium (FDALR, 1985). Crystalline rocks mainly gneisses and related rocks (metamorphic) are found around Oban hills and Obudu highlands, while basalt (igneous rock) is present around Ikom in Cross River State

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(Jungarius and Lavett 1964). Most of the reference are however under lain by sedimentary rocks from the earlier ones of the lower cretaceous era, through those of tertiary period (e.g. Imo shale group, the coastal plain sands, the Bende-Amaeke formation etc) to those of the quarternary period (alluvium) Oriajiaka (1975).

Soil of the Area

Most soils of this area belong to the order “Ultisol” and are classified as typic Hapludult (Federal Department of Agriculture and Land Resources, 1985; Nwaogu and Ebeniro, 2009). Soils formed on coastal plain sand and sandstone occupy most of Imo, Abia and Akwa Ibom States, a reasonable part of Rivers, Bayelsa States and a little of Cross River State. These soils are usually acidic, have low CEC, low base saturation and low fertility status (Okunami, 1981). Soils formed on shale are reddish-brown and gravely. They have high clay content, poorly drained, acidic with high exchangeable cations but are generally fertile. Soils formed from basalt are highly weathered, strongly acidic and a good number of them are low in available P, having high fixation capacity for P (Osodeke and Uba, 2005).

Soil Sampling

Thirty six soil samples representative of twelve (12) locations of contrasting parent materials comprising of Abakiliki (Shale), Afikpo (shale), Ikom (Basalt), Bende (Shale) Umudike (Coastal plain sand), Nssuka (Basalt), Etung (Basalt), Ikot-Ekpene (Coastal plain sand), Aba (Coastal plain sand), Amaeke (Sandstone), Ohafia (Sandstone), and Okigwe (Sandstone), at three depths (0-20cm, 20-40cm and 40-60cm) were collected using soil auger (Table 3.1 and Figure 3.1).

Table 3.1 Soil Parent Materials and Sample Locations.

Parent Material	Sample Location (Town and Cities)
Coastal plain sand	Umudike, Ikot-Ekpene, Aba
Shale	Afikpo, Abakiliki, Bende
Sandstone	Amaeke, Ohafia, Okigwe
Basalt	Ikom, Nsukka, Etung

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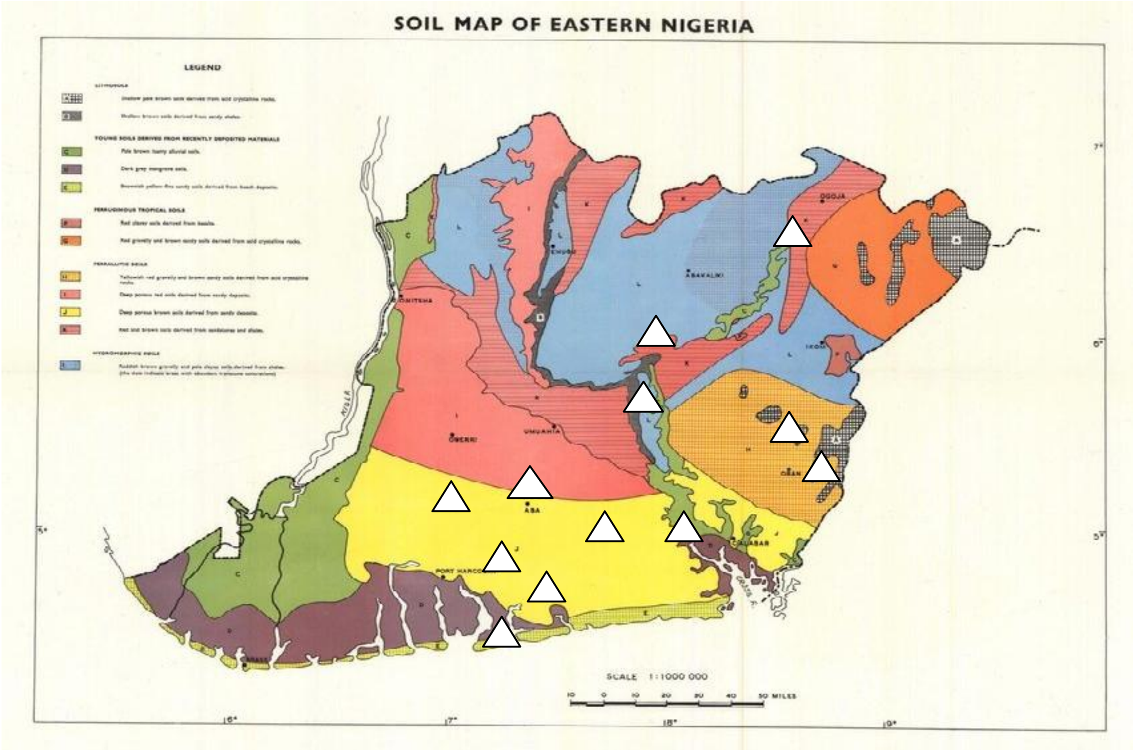

Fig. 3.1. Map of Southeastern Nigeria showing sample locations.

SAMPLE PREPARATION

The soil samples were air-dried, crushed and sieved through a 2mm sieve (Pansu and Gautheyrous, 2006). They were bagged and labeled accordingly for laboratory analyses. The samples chemical and mineralogical content were analyzed according to standard Laboratory procedures.

LABORATORY ANALYSES

Particles size distribution: This was determined using the Bouyocous hydrometer method as described by Benton (2001). Soil pH was determined in soil to water and soil to $CaCl_2$ at the ratio of 1:2.5, using glass electrode pH meter (Udo *et al*., 2009). Organic carbon was determined by the wet oxidation method of Walkey and Black as described by Pansu and Gautheyrous (2006).Total nitrogen determination was done by the macro Kjeidahl digestion method (Simmone *et al.,* 1994). Exchangeable acidity was determined by the 1M KCl extraction procedure as described by Udo *et al*., (2009).Exchangeable basic cations (K^+, Ca^{2+}, Mg^{2+}, Na^+) were determined by the ammonium acetate method (Carter and Gregoich, 2008). Ca and Mg in the extract were determined using the atomic absorption spectrophotometer, while K and Na were read using the flame photometer. Effective Cation Exchange Capacity (ECEC) was obtained by summation of all the exchangeable cations and exchangeable acidity as described by Udo, *et al*., (2009). Base Saturation was obtained mathematically with: BS (%) = $\frac{TEB}{ECEC}$ X $\frac{100}{1}$

BS = Base saturation, TEB =Total Exchandeable Bases, ECEC = Effective Cation Exchange Capcity

MINERALOGICAL ANALYSIS

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The qualitative determination of the mineralogical properties of the soil samples using X-ray diffraction were carried out at Sci-Ba Laboratory and Scientific Consultant, Cape Town South Africa. About 2g of each soil sample was dried, pulverized and milled using McCrone Mill with agate grinding element in a Jar. The unique grinding action of the mill rapidly reduces the soil particles to sub-micrometer sizes and mixes the sample for homogenization required for qualitative analytical methods (Approximately 10 µm). Pre-analysis sample preparation procedures included the removal of soluble salts and gypsum by washing out according to the method of Konse and Rich, (1959). Carbonates were removed by neutralization with sodium acetate (pH =5), according to Grossman and Millet, (1961), while organic matter was removed by oxidation with H_2O_2 (Konse And Rich, 1959). These samples were saturated with Magnesium (Mg^{2+}) and Potassium (K^+) using magnesium chloride ($MgCl_2$) and potassium chloride (KCl) solutions. About 0.5g of dried and prepared soil sample each was used for the X-ray analysis. The X-ray studies were performed with Siemens D5000 diffractometer using Cuką radiation with Iron (fe) filter ($\lambda = 1.5409A$) at 40kv and 30mA, at a scan rate of 2^0 per minute (Osabor *et al*., 2009). The diffraction patterns were obtained with the aid of computer, while the 2Θ, d-values and peak intensities yielded by the powder patterns were used to identify the minerals (Akhirevbulu *et al*., 2010). The interpretation of the diffractograms obtained for each sample was done by comparing the peaks obtained with those of standard minerals established by Brown (2008) and Joint Committee of Powder Diffractogram Standards (1980).

Statistical Analysis

This study was considered a 4 x 3 factorial in Randomized Complete Block Design (RCBD) in which the parent material and soil sampling depths were the two factors under consideration.

The data obtained were subjected to simple descriptive statistics and analysis of variance (ANOVA) as outlined by Steel and Torrie (1980) to test the differences between means. Least Significant Difference ($FLSD_{0.05}$) was used to separate the means that were significantly difference.

RESULTS AND DISCUSSION

4.1. Physical and Chemical Characteristics of the Soils used for the Study.

The physical and chemical characteristic of the soils used in the study are presented in Table 4.1. The results of the soil analysis showed that there were significant variability in both the physical and chemical properties among parent materials and sampling depth. Particle size analysis showed that the soils varied from sandy-loam, sandy-clay-loam to clay-loam. Soils of shale and basalt formations were generally clayey-loam irrespective of depth, while soils of coastal plain sand formation were more of sandy-clay-loam especially at the surface horizon. The variability observed in the textural properties of the soils studied could be a reflection of the differences in the parent materials (Enwezor *et al*., 1990). Parent material and soil depth significantly ($P<0.05$) influenced the textural properties of the soils studied. The sand component ranged from 77.1% in soil of coastal plain sand formation to 23.8% in soil formed form shale. The results showed that sand is the predominant particle size in soils formed on coastal plain sand. The sand component decreased with soil depth which is in accord with the findings of Aki and Antigha, (2015). Generally, it was observed that soils formed from shale

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and basalt had the least amount of sand, which is in line with the reports of Oti, (2015) and Osodeke and Ubah, (2005) for soils of southeastern Nigeria.

Silt fraction ranged from 26.53% in soils of basalt formation to 10.07% in soil of shale formation and this did not show a consistent distribution trend down the soil profile. Similarly, soils formed from Shale and Basalt had the highest percentage of silt, while soils formed from Coastal Plain Sand had the least proportion of silt. It was also observed that only the effect of parent material was significant ($P<0.05$) in influencing the silt distribution in these soils.

Percentage clay fraction distribution among the soils ranged from 62.2% to 12.6%. The clay content generally increased with soil depth and the highest clay contents were recorded in soils formed from Shale and Basalt. Other researchers such as Osodeke and Ubah, (2005), Wissen *et al*., (2015) have also reported similar trend in clay distribution of tropical soils. The relative low clay content at the surface horizon (0 -20cm), may be due to the sorting of soil materials by biological and agricultural activities, clay migration or combination of these activities as earlier reported by Malgwi *et al.,* (2000) and Adegbenro *et al.*, (2011).

Soil pH varied widely with soil depth and parent material. Apart from soils formed from coastal plain sand which exhibited slightly reverse trend, soil reaction in all soil types was slightly acidic at the surface horizon, grading towards strongly acidic down the soil profile. This observation can be due to high leaching potentials that characterized the acid sands of southeastern Nigeria as conditioned by the heavy tropical rainfall leading to loss of basic cations from the surface horizons as noted by Osodeke (1999) and Udo *et al.,* (2009). Upper horizons receive maximum leaching by rainfall, and by dissolved carbonic acids and organic acids which remove metal cations (e.g. Ca^{++}, K^{+}) and replace them with H^{+} ions, but the lower horizons are not so strongly leached, in fact, the dryer areas may accumulate calcium and other materials removed from the upper soil. The strongly acidic conditions observed at the lower depths in soils formed from shale and basalt could be attributed to the increasing clay content with its associated high Fe and Al concentrations and 1:1 clay minerals as observed in this study. The highest pH (H_20) of 5.83 was observed in soil of shale formation at 0 -20cm depth while the least (3.10) was noted in basaltic soils (Table 4.1). Other researchers (Onwuka *et al.,* 2007; Eneje and Azu 2009) have reported acidity in most soils of Southeastern Nigeria. Low pH is basically an indication of the presence of H^{+} or acidic cations which displaces the basic cations and result to low nutrient and low crop yield (Brady and Weil, 2008). The parent material, soil depth and their interaction generally showed significant influence on soil pH.

The organic carbon and organic matter content of the soils varied from 2.50% in soil of shale formation to 0.90% in basaltic soil and 4.33% in soil formed from shale to1.53% in soil of basalt formation respectively. Variability on both organic carbon and organic matter were observed, but at 5% probability level, only the soil depth showed significant difference. Organic carbon and organic matter content of these soils, irrespective of parent material declined exponentially with depths, probably due to a decrease in rooting density, litter fall, agricultural activities and soil management practices, which agrees with the report of Bowman and Savory (1992).

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Result of soil organic carbon and organic matter exhibited typical surface build-up from litter and root activities. There was no consistent variability in soil organic carbon and organic matter as related to the parent materials, which may probably due to the fact that organic carbon is build up from plant activities and human manipulations on natural soils. Osodeke, (1992) and Orhue and John (2015), have reported a decreasing trend in organic carbon content down the soil profile in most tropical regions of Nigeria. The present values fall within the low and very low category in broad rating of organic carbon (Udo *et al.,* 2009) and since organic matter content is related to soil fertility status (Enwezor *et al.,* 1990), the present values are indications that these soils are low in plant nutrients.

The total nitrogen ranged from 0.27% in soil of Shale formation to 0.08 % in soil of Sanstone and the nitrogen content followed similar trend of decreasing in quantity with soil depth as organic carbon with the exception of some soils formed on coastal plain sand where direct relationship between total nitrogen and soil depth were observed. This observation could be attributed to the large pore spaces and thus, high porosity that is associated with sand which encourages the eluviation from upper horizons and illuviation of nitrogen at higher depths especially in high rainfall zones (Brady and Weil, 2008). Similarly, this observation could be viewed from the angle of leaching away of nitrates from soil surface horizons due to the relatively high mobility of nitrate in soils, especially in highly porous soils. Most of the soils were low in total nitrogen content except the soil formed from shale which had moderate levels of nitrogen in relation to other soil types and these values were within the critical level set by Adeoye and Agboola (1984) for soils of the humid tropics. The order of abundance of exchangeable bases in the soils is Ca > Mg > K > Na. The exchangeable Ca^{2+} ranged from 4.37 Cmol/kg in soil of Shale formation to 1.72 Cmol/kg in soil Coastal Plain Sand formation. Generally, Ca^{2+} content decreased with soil depth and soils formed on shale had greater Ca^{2+} content relative to other soil types. With the exception of soil of Coastal Plain Sand formed soil at sub-soil levels, all the soils had Ca^{2+} level above the critical level of 2.0 cmol/kg reported by Agboola and Corey, (1982). It was also noted that soils from Coastal Plain Sand had the least values of Ca^{2+} and these values increased with increased soil depth, indicating evidence of high leaching.

The exchangeable potassium (K^{+}) varied from 0.37 Cmol/kg in soil of Shale formation to 0.14 Cmol/kg in soils formed from Coastal Plain Sand. Magnesium (Mg^{2+}) and Sodium (Na^{+}) varied from 1.24cmol/kg in Basaltic soil to 1.33cmol/kg in soil of Sandstone formation. The total exchangeable bases were low in line with the reports of other researchers (Adeoye and Agboola 1984; Enwezor et al., 1989; Osodeke and Ubah 2005). In relation to parent materials, it was observed that the exchangeable bases varied and the order of abundance is shale > basalt> sandstone> coastal plain sand. Sodium content did not show a uniform variation among the soils of contrasting parent material. The trend in the distribution of Na^{+} among different soil types was contrary to that of other basic cations.

Table 4.1. Some physical and chemical properties of the soils used for the study

Parent Material	Depth (cm)	Particle size distrib. (%) Sand	Silt	Clay	Texture	pH $CaCl_2$	H_20	Org.C (%)	OM (%)	TN (%)	Na	K Cmol/kg	Ca	Mg	TEB	TEA	ECEC	BS (%)	
Basalt	0-20	40.7	26.5	32.8	CL	4.03	5.03	1.90	3.27	0.22	0.09	0.28	3.22	1.24	4.70	2.72	7.42	63	
	20-40	26.3	20.3	53.4	CL	3.43	4.33	1.27	2.13	0.16	0.06	0.22	2.76	1.12	4.18	3.32	7.50	55	
	40-60	24.6	16.3	59.3	CL	3.10	4.07	0.90	1.53	0.10	0.05	0.21	1.82	0.34	2.41	3.47	5.88	41	
CPS	0-20	77.1	10.3	12.6	SCL	3.93	4.90	1.83	3.30	0.13	0.15	0.17	1.91	0.72	3.55	2.45	5.67	59	20-
40	72.7	10.1	17.4	SCL	4.20	5.13	1.40	2.30	0.18	0.10	0.20	2.13	1.69	4.41	2.42	7.00	64	40-60	
	69.6	11.1	19.3	SCL	4.00	5.00	1.10	1.43	0.16	0.10	0.14	1.72	0.57	3.19	3.11	6.29	51		
Shale	0-20	44.4	19.4	36.2	CL	4.67	5.83	2.50	4.33	0.27	0.07	0.37	4.37	2.43	6.83	2.81	9.64	68	20-
40	30.1	16.6	53.3	CL	4.40	5.30	1.53	2.73	0.23	0.02	0.32	3.89	1.68	5.30	3.43	8.73	59	40-60	
	23.8	14.6	62.2	CL	3.43	4.90	1.13	2.00	0.12	0.04	0.22	2.93	1.23	3.74	3.95	8.03	48		
SST	0-20	56.9	19.2	23.9	SCL	4.10	5.03	1.97	3.40	0.18	0.11	0.26	3.01	1.70	5.08	3.03	8.44	60	20-
40	51.0	16.6	32.7	CL	3.63	4.70	1.70	2.97	0.14	0.09	0.24	2.97	1.62	4.92	3.31	8.56	57	40-60	
	45.4	12.4	42.2	CL	3.50	4.57	1.13	1.97	0.08	0.06	0.17	2.65	1.33	4.20	3.43	7.63	54		
Mean		**46.9**	**16.1**	**37.1**		**3.87**	**4.90**	**1.53**	**2.61**	**0.17**	**0.08**	**0.23**	**2.78**	**1.31**	**4.38**	**3.12**	**7.57**	**56**	
LSD (0.05) PM		8.410	4.670	6.560		0.257	0.203	NS	NS	0.040	0.027	0.040	0.599	NS	NS	NS	1.413	NS	
LSD (0.05) DE		7.280	NS	5.680		0.222	0.176	0.339	0.583	0.034	0.024	0.035	NS	NS	NS	NS	NS	6.1	
LSD (0.05) PM X DE		NS	NS	NS		0.445	0.351	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	

SL =Sandy loam, SLC =Sandy clay loam, CL =Clay loam, CPS= Coastal plain sand, TEB=Total exchangeable bases, TEA=Total exchangeable acidity, ECEC= Effective cation exchange capacity, BS=Base saturation, PM=Parent material, DE=Depth.

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The highest amounts of Na^+ were found in soil formed from Coastal Plain Sand while soil formed from Shale had the least values and the order of the relative abundance of Na^+ is coastal plain sand > sandstone > basalt > shale. Sodium is a dispersing agent and its high proportion in sands may be responsible for their coarse nature and the strong aggregation and plasticity in clay soils may be an indication of low Na^+ content (Brady and Weil 2008).

While the total exchangeable bases decreased with soil depth for most soil types, the total exchangeable acidity generally increased with soil depth irrespective of parent material. A similar observation was made by Oti, (2015) for some soils of southern Nigeria. Both ECEC and base saturation were low which is an indication of low soil fertility as reported by Udo and Ogunwale (1977).

MINERALOGICAL COMPOSITION OF THE SOILS OF STUDIED AREA

The XRD results of the mineralogical analysis showed the mineralogical assemblages of the different soil samples. The relative abundance of clay minerals distinguished in the selected soil samples is presented in Table 2. The results indicated the predominating presence of kaolinite quartz, hermatite, goethite and gibbsite within the soils irrespective of the parent material. Identification of other secondary minerals was difficult, because their peaks were obscured by the greater peaks of the major minerals, kaolinite and quartz. All formations contained small amount of hollysite, but only shale contained measurable amount of this mineral. Other researchers Odoma *et al.,* (2013), Onyeogu *et al.,* (2016), Akhirevbulu *et al.,* (2010) Osabor *et al.,*(2009) and Nweke *et al.,* (2015) made similar observations for soils of southeastern Nigeria. However, montmorillonite, vermiculite, illite were present in trace amount in some of the soils, especially soils formed on shale at lower soils horizons.

Parent material and depth played dominant roles in the type and distribution of clay minerals in the study area. The concentration of these minerals varied with parent material and soil depth. Significant variations with parent material were observed in the minerals identified except in Halloysite and Chlorite where non-significant variations were observed. While variations with depth were statistically significant ($P<0.05$) in Chlorite, Geothite, Hermatite, Montmorillonite and Quartz, the influence of the interaction between parent material and soil depth were only significant in Gibbsite, Kaolinite and Montmorillonite. The vertical distribution pattern of goethite and hermatite, in profile varied with parent material, but contrary to the report of Mehmood *et al*. (2015), the interactive effect of depth and parent material was not significant. This result emphasis the influence of parent material and soil depth on clay mineral formation and distribution as reported by other Researchers ((Szilas *et al*., 2005; Norra *et al.,*2006).

Mineralogical composition of soils derived from Coastal Plain Sand at different soil depths.

Soils formed on Coastal Plain Sands showed that the dominant minerals present were kaolinite and quartz and this is similar in all the pedogenic horizons and this agreed with the report of Chikezie *et al.,* (2010) for soils derived from coastal plain sands of Southeastern Nigeria. Kaolinite accounted to 9.94 to 28.83%, while Quartz accounted to 56.4 to 87.3% and these decreased with depth. Other minerals which were present in trace amounts included Geothite (1.41 to 8.81%), Haematite (0.75 to 3.46%), Gibbsite (0.36 to 1.33%) and Mica (0.103%).The high dominance of quartz in the clay fraction of these soils clearly explains their grittiness and also suggests

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clay to be of residual origin (Akhirevbulu *et al.,* 2010). The presence of high amount of quartz, which acts as abrasive according to Apuo-Nwosu *et al.,* (2011), could lead to poor physico-chemical performance of the soil. Also, the presence of high amount of kaolinite in soil of Coastal Plain Sand formation indicates that they must have been subjected to strong chemical weathering with very good leaching, favoured by tropical and subtropical humid climates (Onyeogu *et al.,* 2016).

Similarly, Chikezie *et al.,* (2010) noted that the dominance of kaolinite suggests that the soils are at an advanced stage of weathering. High leaching, together with low pH and removal of basic cations have been reported as the ideal conditions for Kaolinite formation in soils (Branhisel and Bertesch 1992). Warm and humid climate with good drainage have been reported for kaolinite formation (Nadimi and Farpoor 2011; Khormali and Abtahi 2003). Since such an environment is found in the study area at present, kaolinite formatiom is highly favoured.

Kaolinite is a low activity clay and the effective surface of kaolinite (10-20m^2) is restricted to its outer faces, thus, kaolinite has low cation exchange capacity (CEC) with values ranging from 3-15 Cmol/kg (Brady and Weil, (2008). Kaolinite containing soils however, make good bases for road beds and building foundations because of the absence of interlayer spacing between them, but usually poor for agricultural production due to the low CEC except with good fertilizer management policies and practices. When related to the soil nutrient properties, it can be observed that soils formed on coastal plain sands were generally low in fertility status, which can be attributed to the high dominance of kaolinite and quartz in the clay fraction of the soils.

Mineralogical composition of soils derived from Shale at different soil depths.

Their mineralogical compositions of soil of shale formation differed significantly from those derived from other parent materials Table 2. X-Ray Diffraction analysis data showed that soil derived from shale had mixed clay mineralogy of montmorillonite, goethite, hermatite, gibbsite, kaolinite and others with depth and smectite was the dominant clay mineral in this soil especially at lower depth.. The presence of smectite was in agreement with the CEC and swelling properties of the soils. The level to very gently undulating landscape, high pH and saturation of the soils with water for a period of time in the study area may have ensured the accumulation of bases and therefore the formation of smectite and other 2:1 clay mineral (Buol *et al*., 1980; Dinc *et al*., 1987; Yesilsoy, 1994).

The mineralogy is kaolinitic in the upper 0-20cm (6.89 to 3.56%) of the profile and mixed mineralogy at the lower depths. At lower depths, the dominant minerals were montmorillonite (14.37 to 21.88%), goethite (23.58 to 25.09%), hermatite (20.39 to 24.19%), gibbite (8.48 to 12.10%) and Illite (0.68 to 1.26%). Chlorite and vermiculite were also present in small amounts (0.05 to 0.483% and 0.523 to 1.283% respectively) at lower depths. The mineralogy of soil of shale formation was much more complex than mineralogy of other soil formations studied. Apart of quartz and kaolinite which decreased in occurrence with depth, other minerals generally increased in proportion with depth. Nweke *et al.,* (2015) reported that illite and montmorillonite are the predominant clay minerals in soil of Abakaliki which is formed from shale. Other researchers have shown that montmorillonite is a significant component of several soils derived from shale in Southeastern Nigeria (Jungerius and Levelt, 1964; Chikezie *et al.,* 2010).

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The maximum amount of montmorillonite noticed at lower horizons of soil derived from shale could be as a result of the highly base accumulating environment, such as poor drainage, high water table and deep horizons which encourages montmorillonite formation. Barshad, (2006) stated that conditions that impose on the soil a base accumulating environment induces montmorillonite formation. Some researchers have claimed that excess Ca^{++} content in the soil would increase the formation of montmorillonite but decrease the formation of kaolinite (Yesilsoy, 1994). Many researchers have also reported that montmorillonite was the most abundant clay mineral in most of the soils formed on shale parent material (Singer, 1989; Yılmaz, 1990). Most soils of shale formation under the study areas have hydromorphic properties, poor internal drainage conditions which retard the alteration of these minerals and may account for the dominance of montmorillonite on these soils (Chikezie *et al.,* 2010). Similarly simple transformation of illite to montmorillonite may play a role in increasing the montmorillonite concentration, thereby decreasing the illite concentration on the surface soils, since illite is the main precursor mineral for the formation of smectite in soil, particularly at the surface horizon. Climatic condition of the study area provides a leaching environment that promotes detachment and release of K^+ from illite. Moreover, the high amount of Mg^{2+} notice in soil of shale formation, probably created the favourable condition for montmorillonite through transformations at the soil surface (Owliaie *et al.,* 2006).

Trace to very low amount of vermiculite was observed mostly at the middle horizon (20-40cm) of the soil. Even though, the alteration of mica is the main pathway for the formation of pedogenic vermiculite in soils (Churchman and Lowe 2012), but Barshad (2006) noted that conditions that impose on the soil an intermediate to moderate environment between highly base accumulating and highly base depleting, favour vermiculite formation.

The soils also contain, in low amounts, kaolinite and illite minerals. For kaolinite formation, the ratio of Si/Al must be under 2.0, the basic cation content must be less, pH<7.0 (Buol *et al*., 1980; Dinc *et al*., 1987; Dixon and Weed, 1989; Sumner, 2000). According to this theorem, the rainfall must be in a sufficient amount to translocate silicon and basic cations to a certain limit in the profile. Furthermore, a low amount of kaolinite mineral might have formed gradually over a very long period of time, due to high weathering and leaching of basic cations as conditioned by heavy tropical rainfall. Also, simple transformation of illite to montmorillonite may play a role in decreasing the illite concentration on the surface soils.

Soil derived from shale had significant higher concentration of Hermatite and Goethite followed by the groups of soils derived from basalt, sandstone and coastal plain sand in that order. Mehmood *et al*.,(2015) also reported similar observations in soils studied. The higher geothite and hermite content in shale derived soil may be due to higher clay content and lothogenic hermatite (Memo *et al.,* 2011; Mehmood *et al.,* 2015) The high hermatite and goethite content at the 40-60cm horizon may be due to weathering at surface and the resultant release of these minerals that are subsequently leached down and accumulate in the 40-60cm horizon of soil, relative at higher stage of soil development as reported by Memoon (2008).

The high CEC and relatively higher fertility status observed in soils form from shale could be a reflection of the high content of high activity clays such as montmorillonite in these soils. The large CEC which is consequent of the large surface area of these minerals increase their capacity to retain and supply large quantities of nutrients

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such as Ca, Mg, K and NH_4, thus, these soils tend to be of high fertile, especially when proper irrigation management is practiced (Brady and Weil, 2008).

Mineralogical composition of soils derived from Sandstone at different soil depths.

Soil formed in sandstone has a dominant clay mineralogy that consists of kaolinite, goethite and quartz. Okusami *et al*., (1985) had also reported the dominance of these minerals in soils of sandstone formation. Kaolinite accounted for 26.42 to 31.26%, goethite, 7.77 to14.87%,, and quartz accounted for 35.4 to 51.8%. Other minerals identified were: hermatite (4.58 to 14.62%), gibbsite (1.70 to 5.23%), chlorite (0.307 to 0.867%), illite (0.13 to 0.31%), mica (0.557 to 0.683%) and vermiculite (0.60 to 1.79%).

Mineralogical composition of soils derived from Basalt at different soil depths.

X-rays diffraction analysis of soils formed from basalt reveled that kaolinite (14.64 to 27.44%), quartz (23.7 to 42.5%), hematite (11.0 to 23.14%), goethite (13.94 to 26.48%) were the dominant crystalline minerals present in the soil. While the quartz and kaolonite content decreased with depth, geothite and hematite increased down the profile, but gibbsite was fairly constant. Esu *et al.,* (2015) have also reported the dominance of kaolinite, quartz and iron oxides in a basaltic soil of Ikom. They stated that basaltic soils are highly weathered to the extent that they no longer possess any further weathering potential. They have indeed reached the oxic state of weathering.

Table 2. Mineralogical properties of the soils used for the study

Parent Material	Depth (cm)	Mineralogical Distribution (% by mass)											
		Halloysite	Chlorite	Geothite	Gibbsite	Herm	Illite	Kaolinite	Mica	Mot	others	Quartz	Verm
Basalt	0-20	0.263	0.000	13.94	7.57	11.00	0.00	27.44	0.00	0.00	0.827	42.50	0.513
	20-40	0.000	0.000	24.54	3.82	14.88	0.00	28.08	0.00	0.00	0.290	32.80	0.560
	40-60	0.000	0.383	26.48	10.31	23.14	0.08	14.64	0.00	0.67	0.620	23.70	0.000
CPS	0-20	0.103	0.000	1.41	0.36	0.75	0.00	9.94	0.02	0.00	0.220	87.30	0.000
	20-40	0.000	0.000	2.84	1.33	2.56	0.00	19.83	O.00	0.00	0.513	72.60	0.000
	40-60	0.000	0.000	8.81	1.23	3.46	0.00	28.83	0.400	0.00	0.907	56.40	0.000
Shale	0-20	0.017	0.050	23.58	9.62	20.39	0.68	6.89	0.377	14.37	1.137	22.50	0.523
	20-40	0.027	0.047	24.43	12.10	21.65	0.92	5.09	0.290	20.09	0.537	13.40	1.283
	40-60	0.337	0.483	25.09	8.48	24.19	1.26	3.56	0.000	21.88	0.053	8.20	0.627
SST	0-20	0.210	0.000	7.77	1.70	4.58	0.31	31.26	0.557	0.00	1.267	51.80	0.600
	20-40	0.000	0.307	12.12	3.66	10.57	0.16	30.63	0.683	0.00	0.357	38.70	1.793
	40-60	0.000	0.867	14.87	5.23	14.62	0.13	26.42	0.643	0.16	0.227	35.40	1.017
GRAND MEAN		0.071	0.178	15.49	5.42	12.65	0.29	18.97	0.248	4.76	0.579	40.50	0.576
LSD (0.05) DE		NS	0.328	3.129	NS	2.592	NS	NS	NS	1.537	NS	5.20	NS
LSD (0.05) PM		NS	NS	3.614	2.303	2.993	0.734	3.828	0.431	1.775	NS	6.00	0.529
LSD (0.05) PM X DE		NS	NS	NS	3.900	NS	NS	6.630	NS	3.074	NS	NS	NS

CPS= Coastal plain sand, Sandstone, Herm = hermatite, Mot = Montmorillonite, Verm = Vermiculite, PM=Parent material, DE=Depth.

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Correlation between the major soil minerals and some soil properties.

Correlation analysis between the major soil minerals identified and some soil properties is presented in Table 3. Sand showed negative correlation with most of the major minerals identified except quartz and mica where the correlation was positive. The highly significant negative correlation ($P<0.01$) between sand and goethite, gibbsite and hermatite is an indication that soils with sand as dominant texture have low or insignificant amount of these iron oxides. Similarly, the highly positive correlation between sand and quartz shows that the higher the sand contents of a soil, the more the occurrence of quartz. The reverse trend was observed when sand was correlated with goethite, gibbsite, hermatite and quartz. Therefore, soils rich in clay, have more goethite, gibbsite, montmorillonite, illite and chlorite content, but less in quartz and clay. P^H correlated negatively with goethite, hermatite and kaolinite, but positively with montmorillonite, illite, and quartz.

Table 3. Correlation between the major minerals and some soil properties

	Sand	silt	clay	pH	Org.C	TEB	TEA	ECEC	BS
	(%)	(%)	(%)		(%)		(Cmol/kg)		(%)
Chlorite	-0.354	-0.24	0.468	-0.429	-0.479	-0.253	0.617*	0.26	-0.508
Geothite	-0.944**	0.429	0.937**	-0.155	-0.199	0.088	0.715**	0.371	-0.376
Gibbsite	-0.809**	0.427	0.785**	0.097	-0.20	0.210	0.507	0.394	-0.178
Hermatite	-0.914**	0.330	0.933**	-0.092	-0.182	0.109	0.724**	0.402	-0.364
Illite	-0.497	0.059	0.545	0.422	0.100	0.346	0.556	0.595*	-0.037
Kaolinite	0.327	0.171	-0.414	-0.313	-0.064	-0.097	-0.165	-0.113	0.039
Mica	0.197	-0.075	-0.201	0.168	0.216	0.391	0.166	0.483	0.149
Mont	-0.494	0.051	0.543	0.482	0.107	0.358	0.467	0.544	0.020
Quartz	0.910**	-0.424	-0.901**	0.300	0.154	-0.211	-0.805**	-0.560	0.316
Verm	-0.339	0.266	0.305	0.048	0.160	0.474	0.445	0.683*	0.136

Mont = Montmorillinite, Verm = Vermiculite.

*Correlation is significant at the 0.05 level (2-tailed). **Correlation is significant at the 0.01 level (2-tailed)

Significant negative correlation was observed between total exchangeable acidy and quartz, the correlation between total exchangeable acidy and goethite, hermatite , illite were positively significant. Base saturation showed negative correlation with chlorite, goethite, gibbsite, and hermatite, but positively with montmorillonite, mica, vermiculite and illite.

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CONCLUSION

The result of the present investigation on the chemistry and mineralogy of soils of contrasting parent materials at different depth suggests that the soils were generally poor in terms of fertility except the soil of shale formation where fertility indicators was relatively higher than in other soil types. Parent material and depth played dominant roles in the type and distribution of clay minerals in the study area. Mineralogy revealed the dominance of quartz, kaolinite in most of the soil studied. However a mixed mineralogy of quartz, kaolinite, goethite, hermatite and smectite was observed in soil derived from shale. Knowledge of different types of clay minerals in soil together with their distribution has greater relevance in assessing the long term nutrient supplying power of soil to crop. Also, such study will provide an important index in formulating a sound fertilizer programme for a given set of soil and crop. If suitable and efficient drainage programmes are employed, it is certain that soil of shale formation will be a potential source for plant cultivation in Southeastern Nigeria. However, for optimum and sustainable crop production in other soil types, external fertilizer imput and other fertility enhancement strategies must be adopted. A more detailed study of soil minerals as they relate with the chemical, physical and biological attributes of the soils of Southeastern Nigeria will not only provide a broad knowledge of the fertility status of these highly weathered soils, but will help farmers to formulate an effective nutrient management programmes in general for a soil and particularly for a soil type for sustainable food production.

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