

Effect of Topographic Position and Parent Material on the Abundance and Distributions of Oxides of Fe And Al In Selected Soils of Akwa Ibom State, Nigeria

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Abstract

The study was conducted to assess the effect of topographic position and parent material on the abundance and distributions of oxides of Fe and Al in selected soils of Akwa Ibom State. Four toposequences from coastal plain sands and shale parent materials were selected for the study. In each toposequence, soil profile pits were sunk at three topographic positions: summit, middle slope and footslope. A total of twelve (12) profile pits were sunk and described based on FAO 2013 guidelines for profile description. Soil samples were collected based on genetic horizons for laboratory analysis. The results revealed that the silt and clay fractions of shale soils were significantly higher ($p < 0.05$) than that of coastal plain sand soils, while sand fraction of coastal plain sand soils was significantly higher ($p < 0.05$) than that of shale soils. The study revealed that the silt and clay fractions of shale soils were significantly higher ($p < 0.05$) than that of coastal plain sand soils, while sand fraction of coastal plain sand soils was significantly higher ($p < 0.05$) than that of shale soils. Based on the abundance of amorphous and crystalline Fe, the footslope of coastal plain sand soils was more reactive, high surface charge and more ions adsorption capacity, followed by the summit and middle slope had the least while in shale soils, high reactivity, high surface charge and more

ions adsorption capacity was at the summit, followed by footslope and middle slope had the least. This was so because contents of amorphous Al and Fe were more abundant in the footslope than the summit and middle slope had the least in the study area. Coastal plain sand soils had more abundant of amorphous and crystalline Al than shale soils. Amorphous Fe was also more abundant in coastal plain sand soils than shale soil. Crystalline Fe was more abundant in shale soils than coastal plain sand soils due to relatively low Al content and the presence of dissolved organic matter, indicating that the two parent materials were not the same. At the summit and middle slope, profile distributions of oxides of Fe and Al indicated high contents of crystalline and amorphous Fe and Al in the B-horizon than other horizons (A and C) in the study area. But at footslope, the contents of crystalline and amorphous Fe and Al were more in the A-horizon than other horizons (A and C) in both coastal plain sand and shale soils, indicating little or no depletion of Al and Fe from the A-horizons. Thus, the two parent materials are not the same and should be managed differently.

Keywords: parent materials, topographic position, Fe and Al oxides

INTRODUCTION

Most oxides, hydroxides and oxyhydroxides of iron and aluminium occur in soils as precipitate of iron and aluminium released during the weathering of the Fe and Al bearing primary minerals (parent materials). Oxides, hydroxides and oxyhydroxides of Fe and Al are major components of the clay fraction of highly weathered soils such as Ultisols (some soils of Akwa Ibom State) (Pettersset al., 1989).

The bioavailability, potential toxicity and distribution of Al in soils and waters are highly dependent on chemical interactions with organic matter. Solution Al^{3+} is the most chemically and biologically available Al form, although this pool represents an extremely small fraction of total Al in the environment. (Sposito, 1996). Within the aqueous phase, Al may be associated with a variety of inorganic or organic ligands (oxygen-bearing ligands e.g water where water molecules act as ligands and coordinate to the Al ion via the oxygen donor atoms). The extent of complexation depends on the availability of soil Al, pH of the solution,

concentration of complexing ligands, ionic strength and temperature (Driscoll and Schecher, 1990). Aqueous Al may be redeposited to free soil, assimilated by living biomass or transported from the system (Driscoll and Schecher, 1990). Organic matter has been described to flocculate with Al salts. Maison *et al.* (2000) reported the existence of specific binding sites for Al for a given structures or ligands within the organic matter composition. This suggests that the organic ligands present in the organic matter are responsible for the distribution of Al. Solution properties of Al are complex in soil. At a pH of < 5, it is present as Al^{3+} , $Al(OH)^{2+}$, $Al(OH)_2^+$ but above pH 7.5, present as $Al(OH)_4^-$ (McBride, 1994). Al is a strong hydrolysing metal and relative insoluble in the neutral pH range (6.0-8.0). Under acidic (pH < 6.0) or alkaline (pH > 8.0) conditions, and /or in the presence of complexing ligands, the solubility of Al is enhanced, making it more available for biogeochemical transformation (May *et al.*, 1979).

Iron exists in soils either in divalent (Fe^{2+}) state (or ferrous state) or trivalent (Fe^{3+}) state (or ferric state). Iron occur predominantly as ferric (Fe^{3+}) oxides in soils. Ferrihydrite is the poorly crystalline (amorphous form) of Fe oxide and constitutes an initial product of weathering, which are converted to hematite and goethite with age. Ferrihydrite is unstable while hematite and goethite are stable in an oxidizing environment. Goethite (α - $FeOOH$) is the predominant mineral form which

Forms of iron and aluminium are important parameters for a proper understanding of soils. Their abundance and distribution in the soils are known to influence some soil properties such as anions adsorption, surface charges, specific surface area and aggregate formation, nutrient transformation and pollutant retention (Aghimienet *et al.*, 1988). The various forms have been extracted using different reagents (Mckeague and Day, 1966; Blume and Schwertmann, 1969). Dithionite extractable iron has been widely considered to give a reasonable estimate of pedogenic free iron in soils while Oxalate extractable represents amorphous forms of iron and aluminium and the differences between the two chemical forms give a measure of crystalline iron and aluminium oxides in soils. In the tropics, these amorphous (mobile) and crystalline (immobile) oxides occurring in soils could be used in the understanding of the genesis, properties and classification of the soils. The percentage of free Fe has been used as an aid in distinguishing soil types and differentiating soil horizons (Obi *et al.*, 2008). The percentage of free Fe has been used as an aid to determining relative soil age (Obi *et al.*, 2008). The reactivity of these sesquioxides is usually assessed by the value of the active ratios. Information obtained is extremely useful for planning, use and management of the soils. Therefore, the objectives of this study

imparts a brown to yellowish brown colour to soils (Kabata-Pendias and Pendias, 1984). Hematite (α - Fe_2O_3) imparts strong, almost blood red colouration to soil and lepidocrocite (γ - $FeOOH$) found mostly in concretion imparts orange colour to the soil. The ferrous iron (Fe^{2+}) is more soluble and bioavailable to plant than ferric iron. Ferrous iron can be oxidized to the ferric iron, where it may form oxide or hydroxide precipitates, and become unavailable to plant as a micronutrient. Iron oxides in soils are dependent on the moisture content, pH and oxygen content of the soil. The acidic and reducing conditions promote the solution of ferrous (Fe^{2+}) compound while oxidizing and alkaline conditions promote the precipitation of insoluble iron (Fe^{3+}) oxides. In some soils, oxides of Fe are present as coatings on mineral grains, where they influence aggregation by cementing primary particles into aggregate. Iron oxides have high surface area, a small amount can greatly enhance aggregation and effect soil colour. These amorphous coating transform to crystalline forms when aged (Dragun, 1988). Organic matter and some bacteria (Ferrobacillus, gallionella etc) affected the formation of iron oxides. Iron forms metal chelates with organic matter. Soil humic acid strongly adsorbs or complexes with iron at pH > 3 (Bodek *et al.*, 1988). Fe oxides have positively charged surface groups that can bind to negatively charged sites on clays and organic matter, and possess negatively charged sites that adsorb cations (Borgaard, 1983).

were to determine the abundance and profile distributions of Fe and Al Oxides in soils formed from coastal plain sand and shale parent materials in Akwa Ibom State, Nigeria for effective soil management.

MATERIALS AND METHODS

Description of the Study Area

The study area lies between latitudes $5^{\circ} 2''$ and $5^{\circ} 52''$ North and longitudes $7^{\circ} 60''$ and $8^{\circ} 20''$ East (Udoh *et al.*, 2007). The study area is underlain mainly by coastal plain sands, sandstone, shale and alluvial deposits (Petterset *et al.*, 1989). The area is under tropical humid climate. The annual rainfall varies from 3000 mm to 2250 mm at the extreme north. The annual temperature varied from 26- 28^o C while relative humidity varies between 75 – 80 %. The original natural vegetation which comprised lowland rainforest, mangrove forest and coastal vegetation, has given way to a mosaic farmland, riparian forest and oil palm forest (Petters *et al.*, 1989).

Field Sampling

Two parent materials, coastal plain sands and shale were selected. Three profile pits were sunk

– at the summit, middle slope and foot slope of each of the toposequences. Based on the topounits identified, twelve (12) standard profile pits were prepared, described and sampled according to the (FAO, 2006) guidelines. The soils were classified according to the USDA Soil Taxonomy (Soil Survey Staff, 2010) and correlated with FAO/UNESCO/World Reference Base (FAO, 2006).

Laboratory Analysis

The soil samples collected from genetic horizons were air-dried under laboratory conditions for three (3) days and passed through a 2 mm mesh-sieve and the following determinations were carried out using appropriate standard procedures. Particle size distribution was determined by the modified Bouyoucos hydrometer method as described by Gee and Or (2002). Soil pH was determined in 1: 2.5 soil: water ratio using a pH metre (Thomas, 1996). Organic carbon was determined as described by Nelson and Sommers (1996). Total Nitrogen was determined by the regular Macro-Kjeldahl digestion and distillation method as described by Bremner and Mulvaney (1996). Available Phosphorus was determined by the Bray-1 method as described by Udo *et al.* (2009). Exchangeable cations were extracted with 1 M NH_4OAc (pH 7.0) and the concentration of Ca and Mg in the extract was determined by EDTA titration method, K and Na by flame photometer (Udo *et al.*, 2009). Exchangeable acidity was extracted with 1 M KCl and titrated with 0.01 NaOH (Thomas, 1996). Effective cation exchange capacity (ECEC) was obtained by the summation of exchangeable bases ($\text{Ca}^{2+} + \text{Mg}^{2+} + \text{K}^+ + \text{Na}^+$) and exchangeable acidity ($\text{Al}^{3+} + \text{H}^+$). Base saturation was calculated as percentage of total ECEC occupied by Ca, Mg, K and Na. Crystalline forms of Fe and Al oxides were extracted from the soil samples using the Dithionite Citrate Bicarbonate procedure while the amorphous forms of Fe and Al were extracted using ammonium Oxalate acidified at pH 5.7. The content of Fe and Al in the extracts was determined by Atomic Absorption Spectrophotometer (Udo *et al.*, 2009).

RESULTS AND DISCUSSION

1. Physical properties of soils of the study area

Soil Texture

In soils developed from coastal plain sand parent material, the mean sand fraction was 90.26% at the summit, 90.54% at the middle slope and 92.22% at the footslope. The mean silt fraction was 0.80% at the summit, 1.99% at the middle slope and 2.74% at the footslope. The mean clay fraction was 6.58 % at the summit, 7.47% at the middle slope and 5.04% at the footslope. In soils developed from shale parent material, the mean sand fraction was 87.15 % at the summit, 88.24 % at the middle slope and 87.99 % at

the footslope. The mean silt fraction was 2.51% at the summit, 2.18 % at the middle slope and 4.93 % at the footslope. The mean clay fraction was 10.34 % at the summit, 10.49 % at the middle slope and 7.09 % at the footslope. The silt and clay fractions of shale soils were significantly higher ($p < 0.05$) than that of coastal plain sand soils. But sand fraction of coastal plain sand soils was significantly higher ($p < 0.05$) than that of shale soils. The high silt and clay fractions of shale soils could be due to the fact that shale is a fine grained sedimentary rock that forms from the compaction of silt and clay-size mineral particles such as quartz, chert, feldspar, iron oxides, sulphide mineral etc. (Donatus *et al.*, 2018).

Bulk density

The mean bulk density of coastal plain sand soils was 1.1 g/cm^3 at the summit, 1.4 g/cm^3 at the middle slope and 1.2 g/cm^3 at the footslope. In shale soils, the mean bulk density was 1.3 g/cm^3 at the summit, 1.4 g/cm^3 at the middle slope and 1.6 g/cm^3 at the footslope. The mean bulk density of coastal plain sand soils was not significant different ($p < 0.05$) from that of shale soils.

Total porosity

The mean total porosity of coastal plain sand soils was 58.6 % at the summit, 49.7% at the middle slope and 53.4 % at the footslope. In shale soils, the mean total porosity was 49.6 % at the summit, 46.1 % at the middle slope and 50.0 % at the footslope. The mean total porosity of coastal plain sand soils was not significant different ($p < 0.05$) from that of shale soils. The mean porosity of coastal plain sand soil at the summit was significantly higher than that of shale soils but not different at middle slope and footslope. The low porosity in shale soils could be due to tiny pore space due to silt and clay fractions that are major component of the soil.

Saturated hydraulic conductivity

The mean saturated hydraulic conductivity of coastal plain sand soils was 21.0 cm/hr at the summit, 5.2 cm/hr at the middle slope and 4.7 cm/hr at the footslope. In shale soils, the mean saturated hydraulic conductivity was 14.9 cm/hr at the summit, 7.8 cm/hr at the middle slope and 1.4 cm/hr at the footslope. The mean saturated hydraulic conductivity of coastal plain sand soils was not significant different ($p < 0.05$) from that of shale soils.

Moisture content

The mean moisture content of coastal plain sand soils was 13.12% at the summit, 10.17 % at the middle slope and 11.49 % at the footslope. In shale soils, the mean moisture content was 15.67% at the summit, 16.32 % at the middle slope and 21.41 % at the footslope. The mean moisture content of shale soils was significantly higher ($p < 0.05$) than that of coastal plain sand soils. The high moisture content in

shale soils could be due to tiny pore space due to silt and clay fractions that make up the texture of the soil.

2. Chemical properties of soils of the study area

Soil pH

The mean soil pH of coastal plain sand soils was 4.4 at the summit, 4.2 at the middle slope and 4.2 at the footslope. In shale soils, the mean soil pH was 4.7 at the summit, 4.5 at the middle slope and 4.9 at the footslope. The mean soil pH of shale soils was significantly higher ($p < 0.05$) than that of coastal plain sand soils. The high soil pH of shale soils could be due to the presence of smectite and other 2: 1 clay minerals with basic cations in their crystal lattice (Donatus *et al.*, 2018)

Electrical conductivity

The mean electrical conductivity of coastal plain sand soils was 0.033 dSm^{-1} at the summit, 0.031 dSm^{-1} at the middle slope and 0.033 dSm^{-1} at the

footslope. In shale soils, the mean electrical conductivity was 0.036 dSm^{-1} at the summit, 0.038 dSm^{-1} at the middle slope and 0.050 dSm^{-1} at the footslope. The mean electrical conductivity of shale soils was not significantly different ($p < 0.05$) than that of coastal plain sand soils

Organic matter

The mean organic matter content of coastal plain sand soils was 2.4 % at the summit, 2.1 % at the middle slope and 2.0 % at the footslope. In shale soils, the mean organic matter content was 2.0 % at the summit, 1.9 % at the middle slope and 2.3 % at the footslope. The mean organic matter content of coastal plain sand soils was significantly higher ($p < 0.05$) than that of shale soils only at the summit. There was no difference at the middle slope and footslope. The variation may be due to variation in land use types.

Table 1: Physical and chemical properties of soils of the study area

Parent materials	Topographic Positions			Parent materials	Topographic positions	LSD (0.05)	Interaction
	Summit	Middle slope	Footslope				
Physical properties							
Sand (%)							
CPS	90.26a	90.54a	92.22a	2.917	3.573	5.053	
Shale	87.15b	88.24a	87.99b				
Silt (%)							
CPS	0.80a	1.99a	2.74a	1.353	1.657	2.343	
Shale	2.51b	2.18a	4.93b				
Clay (%)							
CPS	6.58a	7.47a	5.04a	2.046	2.506	3.544	
Shale	10.34b	10.49b	7.09b				
Bulk Density (g/cm^3)							
CPS	1.1a	1.4a	1.2a	4.28	5.24	7.41	
Shale	1.3a	1.4a	1.6a				
Total Porosity (%)							
CPS	58.6a	49.7a	53.4a	5.09	6.23	8.81	
Shale	49.6b	46.1a	50.0a				
Saturated hydraulic conductivity (cm/hr)							
CPS	21.0a	5.2a	4.7a	8.07	9.89	13.99	
Shale	14.9a	7.8a	1.4a				
Moisture content (%)							
CPS	13.12a	10.71a	11.49a	1.735	2.125	3.005	
Shale	15.67b	16.32b	21.41b				
Chemical properties							
p^H							
CPS	4.4a	4.2a	4.2a	0.20	0.2420	0.3422	
Shale	4.7b	4.5b	4.9b				
Electrical Conductivity (dSm^{-1})							
CPS	0.033a	0.031a	0.033a	0.007	0.00816	0.01154	
Shale	0.036a	0.038a	0.050a				
Organic Matter (%)							
CPS	2.4a	2.1a	2.0a	0.3	0.4129	0.5839	
Shale	2.0b	1.9a	2.3a				
Total Nitrogen (%)							
CPS	0.061a	0.051a	0.051a	0.008	0.00980	0.01386	
Shale	0.050b	0.049a	0.056a				
Available Phosphorus (mg/kg)							
CPS	10.0a	6.6a	17.2a	4.54	5.56	7.87	
Shale	1.5b	0.7b	6.8b				
Exchangeable Ca (cmol/kg)							
CPS	9.9a	7.9a	8.1a	1.2	1.484	2.098	

Shale	6.5b	7.0a	7.0a			
			Exchangeable Mg (cmol/kg)			
CPS	3.3a	2.6a	2.7a	0.4	0.4613	0.6524
Shale	2.5b	2.3a	2.3a			
			Exchangeable K (cmol/kg)			
CPS	0.04a	0.04a	0.04a	0.05	0.0660	0.0934
Shale	0.06a	0.05a	0.19b			
			Exchangeable Na (cmol/kg)			
CPS	0.051a	0.039a	0.052a	0.013	0.01685	0.02382
Shale	0.053a	0.049a	0.053a			
			Exchangeable Acidity (cmol/kg)			
CPS	2.5a	1.3a	1.2a	1.1	1.371	1.939
Shale	1.0b	1.5a	2.6b			
			ECEC (cmol/kg)			
CPS	15.8a	11.8a	12.1a	2.3	2.778	3.928
Shale	11.1b	6.6b	12.1a			
			Base Saturation (%)			
CPS	84.6a	88.9a	90.0a	6.4	7.84	11.08
Shale	90.3a	86.9a	81.7b			

Total Nitrogen

The mean total N content of coastal plain sand soils was 0.061 % at the summit, 0.051 % at the middle slope and 0.051 % at the footslope. In shale soils, the mean total N content was 0.050 % at the summit, 0.049 % at the middle slope and 0.056 % at the footslope. The mean total N content of coastal plain sand soils was significantly higher ($p < 0.05$) than that of shale soils only at the summit. There was no different at the middle slope and footslope. The variation may be due to variation in land use types, like the organic matter.

Available P

The mean available P content of coastal plain sand soils was 10.0 mgkg⁻¹ at the summit, 6.6 mgkg⁻¹ at the middle slope and 17.2 mgkg⁻¹ at the footslope. In shale soils, the mean available P content was 1.5 mgkg⁻¹ at the summit, 0.7 mgkg⁻¹ at the middle slope and 6.8 mgkg⁻¹ at the footslope. The mean available P content of coastal plain sand soils was significantly higher ($p < 0.05$) than that of shale soils. The high content of available P in coastal plain sand soils could be attributed to high content of amorphous Fe and Al, which is more reactive, high surface charge and more ions adsorption capacity compared to shale soil (Schertmann, 1988).

Exchangeable Bases

In coastal plain sand soils, the mean content of exchangeable Ca was 9.9 cmol/kg at the summit, 7.9 cmol/kg at the middle slope and 8.1 cmol/kg at the footslope. The mean content of exchangeable Mg was 3.3 cmol/kg at the summit, 2.6 cmol/kg at the middle slope and 2.7 cmol/kg at the footslope. The mean exchangeable K was 0.043 cmol/kg at the summit, 0.039 cmol/kg at the middle slope and 0.043 cmol/kg at the footslope. The mean exchangeable Na was 0.051 cmol/kg at the summit, 0.039 cmol/kg at the middle slope and 0.052 cmol/kg at the footslope. In shale soils, the mean content of exchangeable Ca was 6.5 cmol/kg at the summit, 7.0 cmol/kg at the

middle slope and 7.0 cmol/kg at the footslope. The mean content of exchangeable Mg was 2.5 cmol/kg at the summit, 2.3 cmol/kg at the middle slope and 2.3 cmol/kg at the footslope. The mean exchangeable K was 0.064 cmol/kg at the summit, 0.051 cmol/kg at the middle slope and 0.190 cmol/kg at the footslope. The mean exchangeable Na was 0.053 cmol/kg at the summit, 0.049 cmol/kg at the middle slope and 0.053 cmol/kg at the footslope. The mean exchangeables Ca and Mg of coastal plain sand soils were significantly higher ($p < 0.05$) than that of shale soils only at the summit. There was no significant different at the middle slope and footslope, also no significant different in exchangeables K and Na in the study area. The variation in Ca and Mg at the summit may be due to variation in land use types.

Exchangeable Acidity

In coastal plain sand soils, the mean exchangeable acidity was 2.5 cmol/kg at the summit, 1.3 cmol/kg at the middle slope and 1.2 cmol/kg at the footslope. In shale soils, the mean exchangeable acidity was 1.0 cmol/kg at the summit, 1.5 cmol/kg at the middle slope and 2.6 cmol/kg at the footslope. Mean exchangeable acidity of coastal plain sand soils was significantly higher ($p < 0.05$) than that of shale soils at the summit, while that of the shale soils was significantly higher than that of coastal plain sand soils at the footslope. The variation at the summit and footslope may be due to variation in land use types.

Effective cation exchange capacity (ECEC)

In coastal plain sand soils, the mean ECEC was 15.8 cmol/kg (moderate) at the summit, 11.8 cmol/kg (low) at the middle slope and 12.1 cmol/kg (moderate) at the footslope. In shale soils, the mean ECEC was 11.1 cmol/kg (low) at the summit, 6.6 cmol/kg (low) at the middle slope and 12.1 cmol/kg (moderate) at the footslope. The mean ECEC of coastal plain sand soils was significantly higher ($p < 0.05$) than that of shale soils at the summit and middle slope but not different at the footslope. This

variation could be attributed to variation in landuse types and Al and Fe contents.

Base saturation

In coastal plain sand soils, the mean base saturation was 84.6% (high) at the summit, 88.9% (high) at the middle slope and 90.0% (high) at the footslope. In shale soils, the mean base saturation was 90.3% (high) at the summit, 86.9% (high) at the middle slope and 81.7% (high) at the footslope.

3. Effect of parent materials and topographic positions on the abundance of oxides of Fe and Al

Crystalline and amorphous Fe

The effect of parent material and topographic positions on the abundance of oxides of Fe and Al are shown in Table 2. In soils developed from coastal plain sand parent material, the mean content of crystalline Fe was 0.07 % at the summit, 0.06 % at the middle slope and 0.073% at the footslope. The mean content of amorphous Fe was 0.12 % at the summit, 0.10 % at the middle slope and 0.15% at the footslope. In soils developed from shale parent material, the mean content of crystalline Fe was 0.076 % at the summit, 0.084 % at the middle slope and 0.089% at the footslope. The mean content of amorphous Fe was 0.12 % at the summit, 0.09 % at the middle slope and 0.11 % at the footslope. Amorphous Fe was more in abundance than crystalline Fe in the study area. The mean content of crystalline Fe in the middle slope and footslope of soils developed from shale was significantly higher ($p < 0.05$) than that of coastal plain sand soils; while the mean content of amorphous Fe at the footslope of coastal plain sand soils was significantly higher ($p < 0.05$) than that of shale soils. There was no significant different in amorphous Fe content between summits and middle slope of coastal plain sand and shale soils. There was no significant different in content of crystalline Fe among topographic positions in both coastal plain sand and shale soils. But the content of amorphous Fe in coastal plain sand soils was significant higher ($p < 0.05$) at the footslope than summit and middle slope. The trend was footslope > summit > middle slope; whereas in shale soils, the content of amorphous Fe was significantly higher ($p < 0.05$) at the summit than footslope and middle slope. The trend was summit > footslope > middle slope. Middle slope had the least content of amorphous Fe in the study area. Based on

the abundance of amorphous and crystalline Fe, the footslope of coastal plain sand soils was more reactive, high surface charge and more ions adsorption capacity due to high content of amorphous Fe/Al. This was followed by the summit and middle slope had the least while in shale soils, high reactivity was at the summit, followed by footslope and middle slope had the least. Studies have shown that amorphous Fe/Al carried the majority of charge surfaces despite abundance of crystalline Fe/Al oxides (Arai and Livi, 2013; Arai *et al.*, 2005). The footslope of shale soils had more abundance of crystalline Fe when compared with coastal plain sand soils. The variation in the formation of crystalline Fe between soils of coastal plain sand and shale parent materials could be attributed to variation in the content of Al in the parent material and the presence of dissolved organic matter (organic acid) in the soil. For instance, dissolved organic matter impedes ferrihydrite growth, resulting in smaller crystal sizes and more crystallographic defects. Also, the stability of goethite and hematite depend on the degree of Al-substitution which depends on the stability of other Al –minerals which they are associated (Schertmann, 1988). This is an indication that the two soils developed from different parent material. In the study area, the colour of the subsoil developed from shale parent material varied from dark reddish brown (5YR 3/4), red (2.5YR 4/6) to light gray (7.5YR 7/1), indicating the presence of hematite (α -Fe₂O₃), while that coastal plain sand varied from brown (7.5YR 4/4), strong brown (7.5YR 5/6) to reddish yellow (7.5YR6/6), indicating the presence of goethite (α -FeOOH) (Kabata-Pendias and Pendias, 1984)

Ratio of amorphous Fe to crystalline Fe

In coastal plain sand soils, the mean ratio of amorphous Fe to crystalline Fe was 1.8 at the summit, 1.7 at the middle slope and 2.1 at the footslope. In soils developed from shale parent material, the mean ratio of amorphous Fe to crystalline Fe was 1.4 at the summit, 1.2 at the middle slope and 1.3 at the footslope. The ratio was significantly higher ($p < 0.05$) in coastal plain sand soils than shale soils at the summit, middle slope and footslope. This shows that the abundance of amorphous Fe was more than that of crystalline Fe in both coastal plain sand and shale soils. This low crystalline Fe could be due to inhibiting effect of organic matter on the process of crystallination and Al content of the soil (Schertmann, 1988).

Table 1: Effect of parent materials and topographic positions on the abundance of Al and Fe

Parent material	Topographic positions	LSD (0.05)
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	Summit	Middle slope	Footslope	Parent materials	Topographic positions	Interaction
Amorphous Al						
CPS	0.065a*	0.088a	0.11a*	0.014	0.017	0.024
Shale	0.065a	0.068a	0.069b			
Crystalline Al						
CPS	0.048a	0.045a	0.053a	0.007	0.008	0.011
Shale	0.041a	0.035b	0.041b			
Al₀/Al_d						
CPS	1.40a*	2.03a	2.29a*	0.40	0.49	0.69
Shale	1.61a	1.90a	1.77b			
Amorphous Fe						
CPS	0.120a*	0.104a*	0.154a*	0.024	0.029	0.041
Shale	0.118a*	0.085a*	0.106b			
Crystalline Fe						
CPS	0.070a	0.060a	0.073a	0.011	0.014	0.020
Shale	0.076a	0.084b	0.089b			
Fe₀/Fe_d						
CPS	1.80a	1.70a*	2.08a*	0.28	0.34	0.48
Shale	1.40b	1.15b	1.27b			

Note: CPS = coastal plain sand

Crystalline and amorphous Al

In soils developed from coastal plain sand parent material, the mean content of crystalline Al was 0.05 % at the summit, 0.05 % at the middle slope and 0.05% at the footslope. The mean content of amorphous Al was 0.07 % at the summit, 0.09 % at the middle slope and 0.11% at the footslope. In soils developed from shale parent material; the mean content of crystalline Al was 0.04 % at the summit, 0.04 % at the middle slope and 0.04% at the footslope. The mean content of amorphous Al was 0.07 % at the summit, 0.07 % at the middle slope and 0.07 % at the footslope. The mean content of amorphous and crystalline Al at the footslope of coastal plain sand soils was significantly higher ($p < 0.05$) than that of shale soils. The mean content of amorphous Al was significantly higher ($p > 0.05$) at the footslope than summit and middle slope in coastal plain sand soils and no different in shale soils. There was no significant different in crystalline Al content among topographic positions in both coastal plain sand and shale soils. The high content of crystalline and amorphous Al in coastal plain sand than shale soils could be attributed to variation in parent material. Coastal plain sand soils contain high content of quartz of 56.4 to 87.3% which may account for the high Al content of the soil (Donatus *et al.*, 2018).

Ratio of amorphous Al to crystalline Al

In coastal plain sand soils, the mean ratio of amorphous Al to crystalline Al was 1.4 at the summit, 2.0 at the middle slope and 2.3 at the footslope. In soils developed from shale parent material, the mean ratio of amorphous Al to crystalline Al was 1.6 at the summit, 1.9 at the middle slope and 1.8 at the footslope. At the footslope, the ratio of amorphous Al to crystalline Al was significantly higher ($p < 0.05$) in coastal plain

sand soils than shale soils. This shows that coastal plain sand soils had more abundance of amorphous Al than shale soils.

Profile distribution of oxides of Fe and Al

The profile distributions of crystalline and amorphous Fe and Al are shown in Figures 1,2 and 3. In soils developed from shale parent material, at the summit, the abundance of crystalline and amorphous Al was more in B-horizon than other horizons (A and C). The abundance of crystalline and amorphous Fe was more in the A- horizon than other horizons. In coastal plain sand soils, crystalline Al was more in the A and B-horizons than C-horizon while amorphous Al was more in the B and C-horizon than A-horizon. Crystalline and amorphous Fe was more in the B-horizon than other horizons, indicating illuviation. This shows that the two parent materials (shale and coastal plain sand) were not uniform in the profile distribution of Fe and Al. Soils developed from shale parent material showed evidence of depletion of crystalline and amorphous Al in A-horizon and accumulation in B-horizon (illuviation of Al oxides), but crystalline and amorphous Fe were not depleted. In soils developed from coastal plain sand, evidence of translocation and accumulation of amorphous Al, crystalline and amorphous Fe in the B-horizon was observed. Crystalline Al was not depleted from the A-horizon. The depletion of crystalline and amorphous Al in shale soils and depletion of crystalline and amorphous Fe in coastal plain sand soils could be attributed to the association of these oxides with simple organic acid (organic matter form). This is because simple organic acids are generally soluble and mobile themselves. When growing older, the conditions for a rapid decomposition of organic matter deteriorate and more condensed and polymerized organic substances are formed, becoming insoluble and immobile (Bodek *et al.*, 1988).

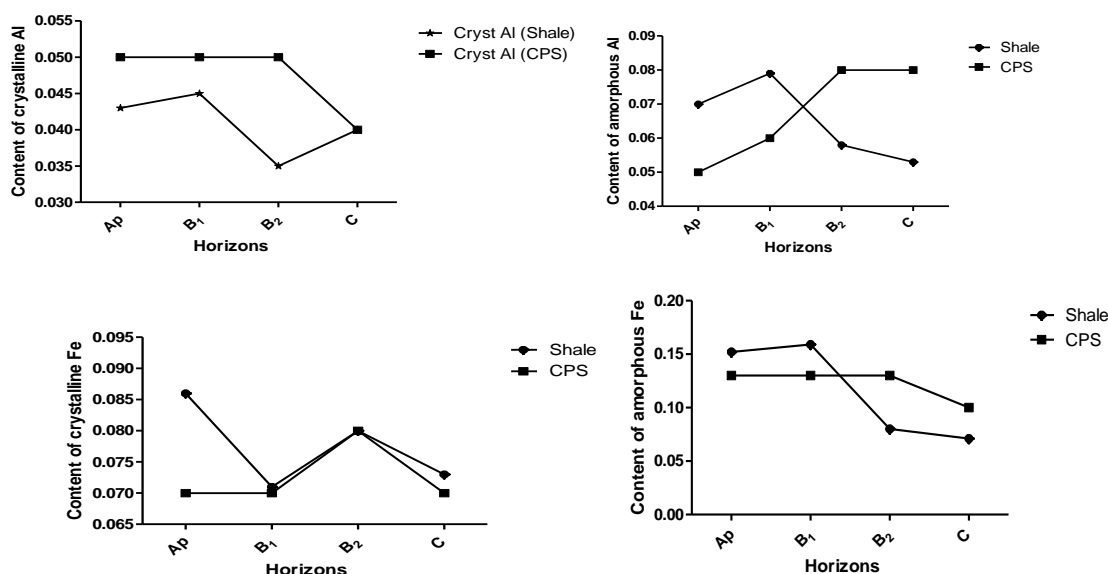


Fig. 1: Profile distribution of crystalline and amorphous Fe and Al at the Summit of the study area

At the middle slope, the contents of crystalline and amorphous Al in soils developed from shale parent material showed slight evidence of translocation and accumulation in the B-horizon. The contents of crystalline and amorphous Fe were more in the B-horizon. In coastal plain sand soils, evidence of translocation and accumulation of crystalline and amorphous Al in the B-horizon was observed. The content of crystalline Fe was not different between the A, B and C-horizons, but amorphous Fe was more

in the lower B and C-horizons. The non-variation of crystalline Fe between the A, B and C-horizons in coastal plain sand soils could be due to low concentration of this form of Fe in the soil. The extent of complexation of Fe with organic acid depends on the availability of soil Fe (metal), pH of the solution, concentration of complexing ligands (organic acid), ionic strength and temperature (Driscoll and Schecher, 1990).

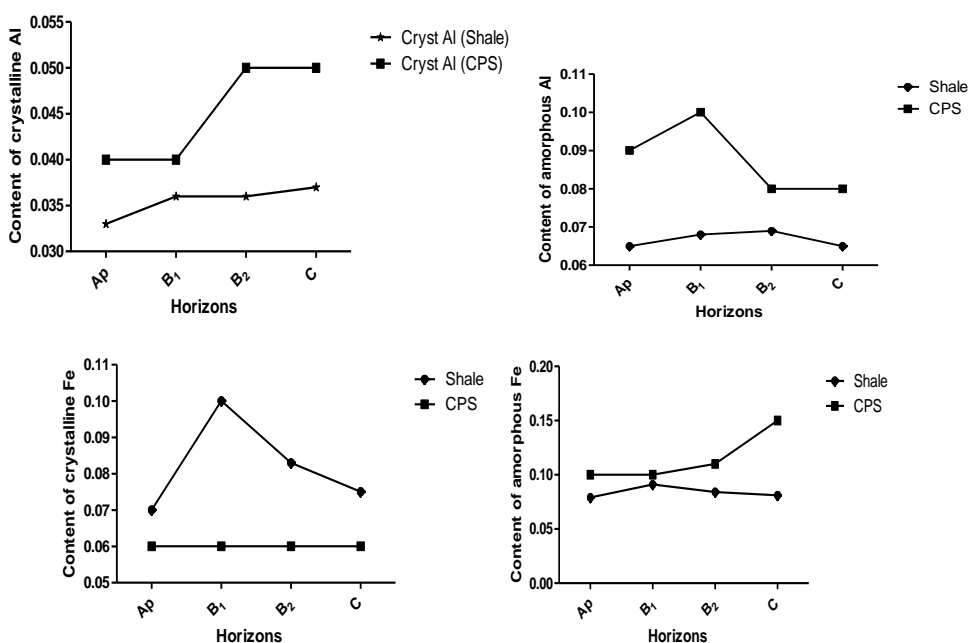


Fig. 2: Profile distribution of crystalline and amorphous Fe and Al at the middle slope of the study area

At the footslope, there was no evident of depletion of crystalline Fe and Al from A-horizon to B-horizon whereas amorphous Fe and Al showed evidence of translocation from A-horizon to B-horizon in soils developed from shale parent material. In coastal plain

sand soils, crystalline Al was not depleted from the A-horizons while amorphous Al, crystalline and amorphous Fe showed evident of translocation from the A-horizon to the B-horizon. The low translocation of crystalline Fe and Al from the A-horizon to B-

horizon in shale soils and crystalline Al in coastal plain sand soils could be due to low concentration of this form of Fe and Al in the soil, which makes

complexation with organic acid difficult thereby affecting their translocations (Driscoll and Schecher, 1990).

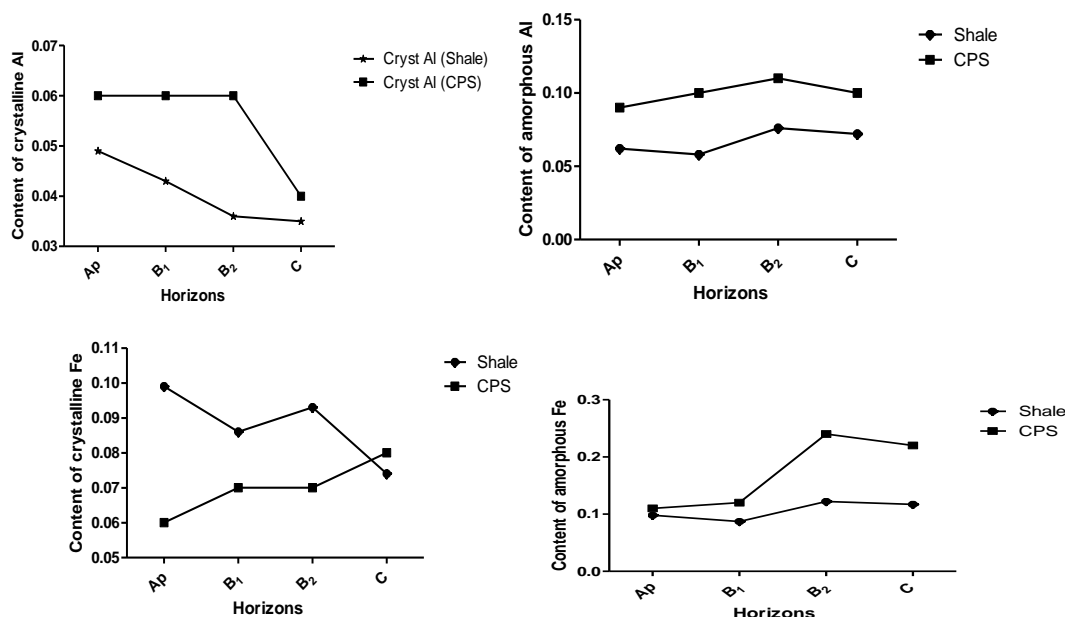


Fig. 3: Profile distribution of crystalline and amorphous Fe and Al at the footslope of the study area

Conclusion

The study revealed that the silt and clay fractions of shale soils were significantly higher ($p < 0.05$) than that of coastal plain sand soils, while sand fraction of coastal plain sand soils was significantly higher ($p < 0.05$) than that of shale soils. Based on the abundance of amorphous and crystalline Fe, the footslope of coastal plain sand soils was more reactive, high surface charge and more ions adsorption capacity, followed by the summit and middle slope had the least while in shale soils, high reactivity, high surface charge and more ions adsorption capacity was at the summit, followed by footslope and middle slope had the least. This was so because contents of amorphous Al and Fe were more abundant in the footslope than the summit and middle slope had the least in the study area. Coastal plain sand soils had more abundant of amorphous and

crystalline Al than shale soils. Amorphous Fe was also more abundant in coastal plain sand soils than shale soil. Crystalline Fe was more abundant in shale soils than coastal plain sand soils due to relatively low Al content and the presence of dissolved organic matter, indicating that the two parent materials were not the same. At the summit and middle slope, profile distributions of oxides of Fe and Al indicated high contents of crystalline and amorphous Fe and Al in the B-horizon than other horizons (A and C) in the study area. But at footslope, the contents of crystalline and amorphous Fe and Al were more in the A-horizon than other horizons (A and C) in coastal plain sand and shale soils, indicating little or no depletion of Al and Fe from the A-horizons. Thus, the two parent materials are not the same and should be managed differently.

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