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Pedogenic forms of iron and manganese and its implication on soil genesis over a lithosequence in Nigeria

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ABSTRACT

The citrate-bicarbonate-dithionite extractable iron and manganese oxides (Fed and Mnd), oxalate extractable iron and manganese oxides (Feox and Mnox), sodium pyrophosphate extractable iron and manganese oxides (Fep and Mnp), active iron and manganese oxide ratios (Feox/d and Mn ox/d) and Clay/dithionite iron ratio (clay/ Fed) were evaluated in soils derived from schist and older granite in two agroecological zones to evaluate the influence of parent materials on soil development and identify major pedogenic processes in the study area. Significant differences were observed in means of most of the properties studied between the parent materials except for means of Fed and Mn ox/d that were not significant. There were higher values of Fed, Feox, Fep, Mnd, Mnox and Mnp (2.276, 0.511, 0.350, 0.085, 0.017 and 0.016% respectively) in soils formed on schist. There was a correlation between the forms of iron and manganese with gravel, clay, pH and exchangeable cations. the major pedogenic processes in the soils are; co-translocation of Fe with clay by elluviation and illuviation, plinthization and co-migration of clay with Mnd. This study revealed that parent materials influence pedogenesis in the soils studied and the extent of pedogenesis varied on the lithosequence.

1.0. Introduction

Oxides, hydroxides, and oxy-hydroxides of iron (Fe), manganese (Mn), aluminium (Al) and titanium (Ti) are referred to as sesquioxides. Manganese (Mn) and iron (Fe) are important plant nutrients and are involved in redox phenomena and heavy metal dynamics in soils. In soil environments, Mn and Fe exist predominantly as oxides (including oxyhydroxides and hydrated oxides). Mn oxide minerals such as birnessite, vernadite, and lithiophorite scavenge heavy metals in soils by adsorbing them on the mineral surface or incorporating them into the crystal lattice by isomorphic substitution (Miyata et al., 2007). Iron (Fe) and Aluminum (Al) found in soils are released during soil weathering and soil development. They are re-precipitated as amorphous or crystalline oxides, hydroxides or oxyhydroxides (Guertal, 1994; Obi et al., 2009).

Pedogenetic processes and physicochemical properties have been reported to be influenced by the nature, content, and distribution of sesquioxides and this knowledge has been used in the evaluation of the type, rate and extent of pedogenesis (Durn *et al*., 2001; Igwe, 2001; Kurihara *et al*., 2002; Osodeke *et al.,* 2005; Jelic *et al*., 2011; Maniyunda *et al*., 2015) and soil classification (Ibia, 2002; Essoka and Esu, 2003). The rates of Fe crystallization of Fe released during the weathering of soils have been assessed as Fe crystallinity index (CI) and used to grade pedogenetic development and soil classification (Durn *et al*., 2001; Kurihara *et al*., 2002).

Soil physicochemical properties such as phosphate retention, surface charge, ion adsorption, specific surface area, aggregate formation, and stabilization have been reported to be influenced by nature, amount and distribution (Duiker et al., 2003; Obi *et al.,* 2009).

There have been several pedogenic examining morphologic, physical, chemical and mineralogical properties of soils developed on different parent materials in Nigeria (Adegbite *et al.,* 1994; Ogunwale *et al.,* 2000; Olowolafe, 2002; Ajiboye *et al.,* 2008; Elias and Gbadegesin, 2012; Orimoloye and Akinbola, 2013). There have also been many studies on the distribution of sesquioxides and their uses in interpreting pedogenic processes and soil properties in Nigeria (Obi, *et al.,* 2009; Osayande, *et al.,* 2013; Maniyunda, *et al.,* 2015). There are reports on the classification of some soils in the study area however; there are no studies on the pedogenesis of the soils. The knowledge of pedogenesis of soil is important in the identification of the nature, properties, response of soils to use and management. This study was carried out to:

- Evaluate the forms of iron and manganese in the soils of the study areas
- To identify major pedogenic processes in the study area using the nature, form, and distribution of iron and manganese.
- To evaluate the relationship between forms of iron and manganese and some soil physicochemical properties.

2.0. Materials and Methods

Description of the study areas: Ado-Ekiti: The soils of the study site at Ado-Ekiti are formed from older granite. It lies between latitude 7.710802N and 7.713800N and longitude 5.243230E and 5.246470E. The area belongs to the upland Tropical Rain Forest zone.

Kabba: The soils of the study site at Kabba are formed from schist. It lies between latitude 7.860376N and 7.862225N and longitude 6.069576E and 6.074468E within the southern guinea savanna zone of Nigeria.

The study areas have distinct wet and dry seasons with a typical humid tropics climate.

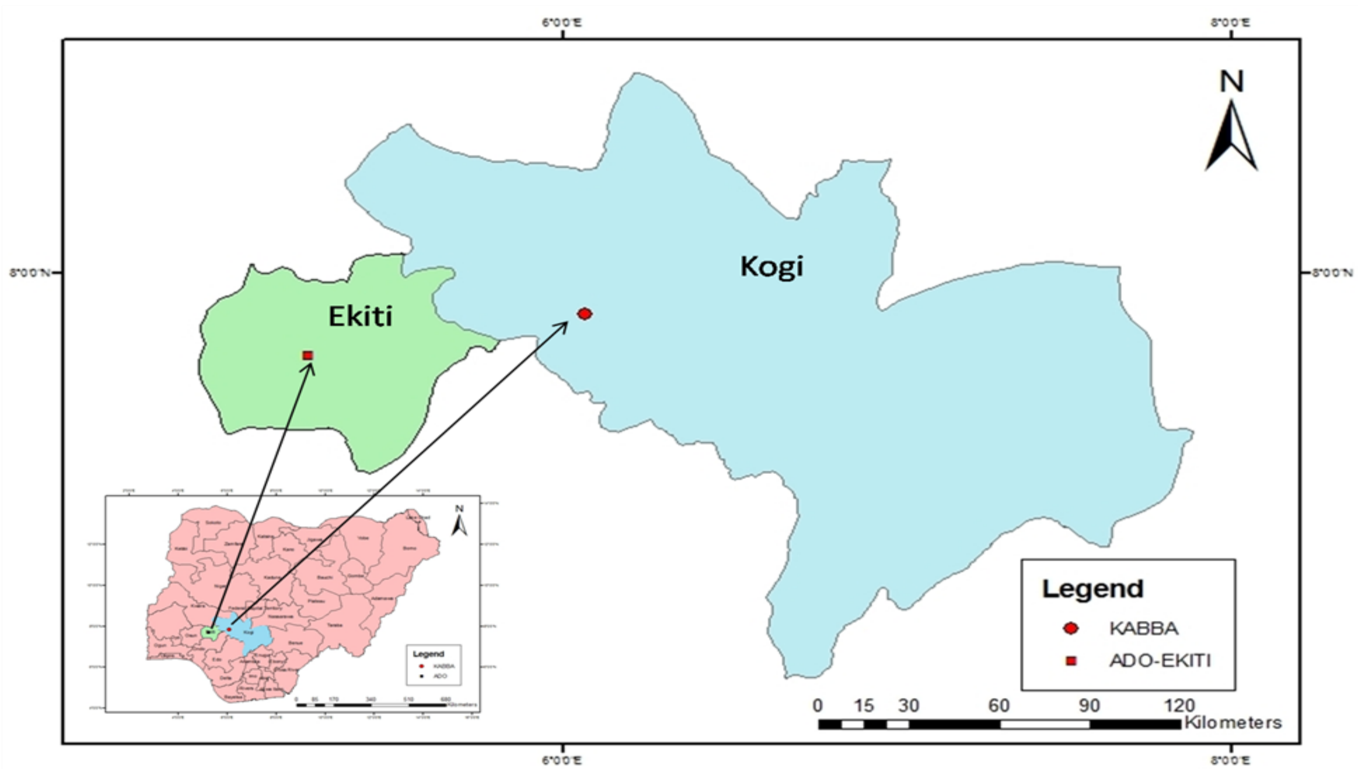

Figure 1: Map of Nigeria Showing the Location of the Two Sites

Soil Survey and Sampling: The conventional method of soil survey involving a rigid grid procedure was used to map each of the study sites. Observations were made along traverses of 50 m apart with a soil auger. The Global Positioning System (GPS) was used for locating points. Augering was made to a depth of 125 cm or to an impenetrable layer whichever is deeper. At each observation point, the local relief, soil erosion or deposition hazard, rock outcrops, surface characteristics, vegetation, and land use were recorded. Soil morphological properties were described in the field following the procedure described in the USDA Soil Survey manual (Soil Survey Staff, 2014). The following features were observed and described; soil depth, colour, mottling, structure, texture, consistency, horizon boundary, roots, concretions, and pores.

Areas with the same soil type were mapped together and plotted on a base map. An area of 12.4395 and 12.1841 hectares of land were mapped in Ado Ekiti and Kabba respectively. Soil boundary lines were drawn to delineate soil mapping units.

Laboratory analysis: Laboratory analyses of < 2 mm samples were carried out using standard laboratory methods. Particle size analysis was determined using hydrometer method (Bouyoucos, 1951), bulk density as described by Blake and Hartge (1986a), particle density as described by Blake and Hartge (1986b), total porosity was calculated mathematically (Danielson and Sutherland, 1986) from the particle density (pd) and bulk density (bd) of the soils using the formula: Porosity (%) = (1-(pd/db) x 100, available water capacity by calculating the difference in moisture content at field capacity (33kpa) and permanent wilting point (1500KPa) pressure (USDA, NRCS, 2004) using pressure plate method as described by Klute from the formula: Available Water Capacity (%) = Field capacity (%) – Permanent wilting point (%), Soil pH was determined in a 1:1 soil/ water. Exchangeable bases (Ca, Mg, K, Na) were determined using NH_4OAc saturation method and exchange acidity was obtained as described by Thomas (1982). Effective cation exchange capacity (ECEC) was calculated by the addition of exchangeable bases and acidity, ECEC of clay fraction was calculated. Organic carbon was determined by the Walkley-Black dichromate wet oxidation method (Nelson and Sommer, 1982), total nitrogen (TN) by micro-Kjeldahl technique as described by Bremner and Mulvaney (1982) and available phosphorus (AP) as described in IITA (1979) laboratory manual. Base saturation (BS) percentage and Exchangeable sodium percentage (ESP) were calculated. Electrical conductivity was determined at a 1:2.5 soil/water ratio using a Wheatstone bridge at 25°C, Calcium carbonate ($CaCO_3$) using the titration method of Rowell (1994).

Total iron oxide: soils were extracted with a combination of reducing and complexing solutions (Sodium Hydrosulphite and Sodium Citrate) by shaking overnight (16hrs) at ambient temperature (Mehra and Jackson, 1960). The Fe in the filtrate was determined using Atomic Absorption Spectrophotometer (AAS).

0.1 M HCI Extractable cationic Micronutrients (Cu, Fe, Mn, and Zn): available cationic micronutrients were extracted with 0.1M HCI solution by Shaking soil paste for 4 hours and then centrifuged at 10,000pm. The Cu, Fe, Mn and Zn content in the extract was determined on the AAS at 325, 373.9, 280 and 214m wavelengths respectively.

Total Cationic Micronutrients (Cu, Fe, Mn, and Zn) by the Aqua-Regia Acids: the soil samples were digested using aqua-regia acid (a mixture of 3 parts of HCI to1 part of HNO3) but not allowed to dry completely. The digests were transferred using deionized water and filled to mark (USDA NRCS, 2004). The cations (Cu, Fe, Mn, and Zn) were determined in the solution on the AAS AT 325, 373.9, 280 and 214 nm wavelengths respectively.

Citrate – Bicarbonate – Dithionite (CBD) Extractable Iron and Manganese (Fed & Mnd): free iron and manganese were extracted following the method of Mehra and Jackson (1960) as described by IITA (1979). The content of Fe and Mn in the extracts was determined after ten times dilution on a Pye Unicam model SP 192 atomic absorption spectrophotometer (AAS) at 280nm and 373.9nm wavelengths respectively.

Acid Oxalate Extractable Iron Manganese (Feox and Mnox): amorphous inorganic form Fe and Mn oxides were extracted using ammonium oxalate (PH3) in the dark (Mckeague and Day, 1966) using the modified Tamn's method as described by IITA (1979). Iron and Mn in the extract were determined on the AAS at 325, 373.9, 280 and 214m wavelengths respectively

Pyrophosphate Extractable Iron and Manganese (Fep and Mnp): amorphous organic form of Fe and Mn oxides were extracted using pyrophosphate solution as described by Mckeague (1967). Iron and Mn in the extract were deter-

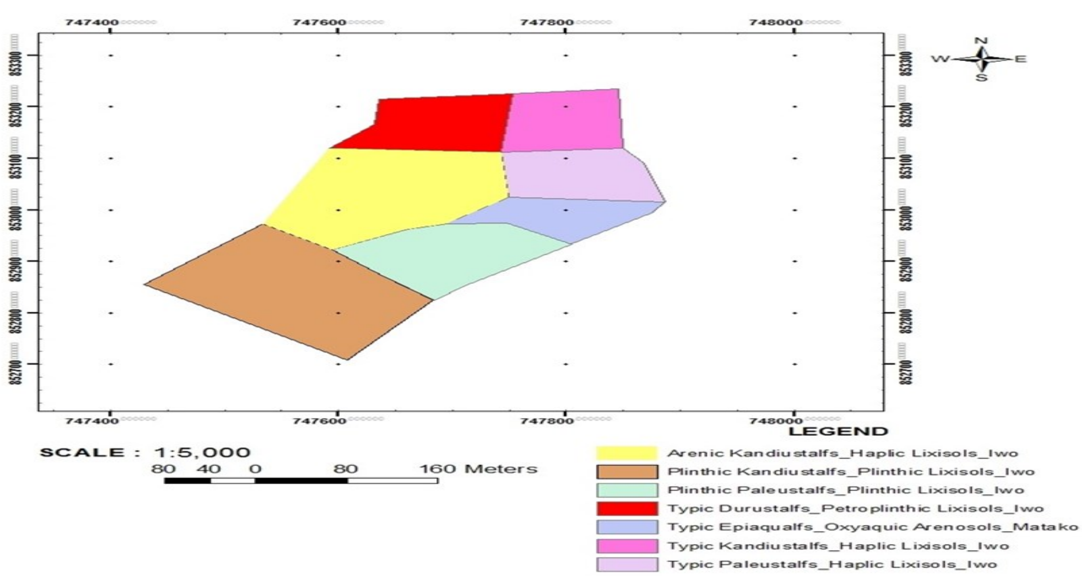

Figure 1: Soil map of Ado-Ekiti study site

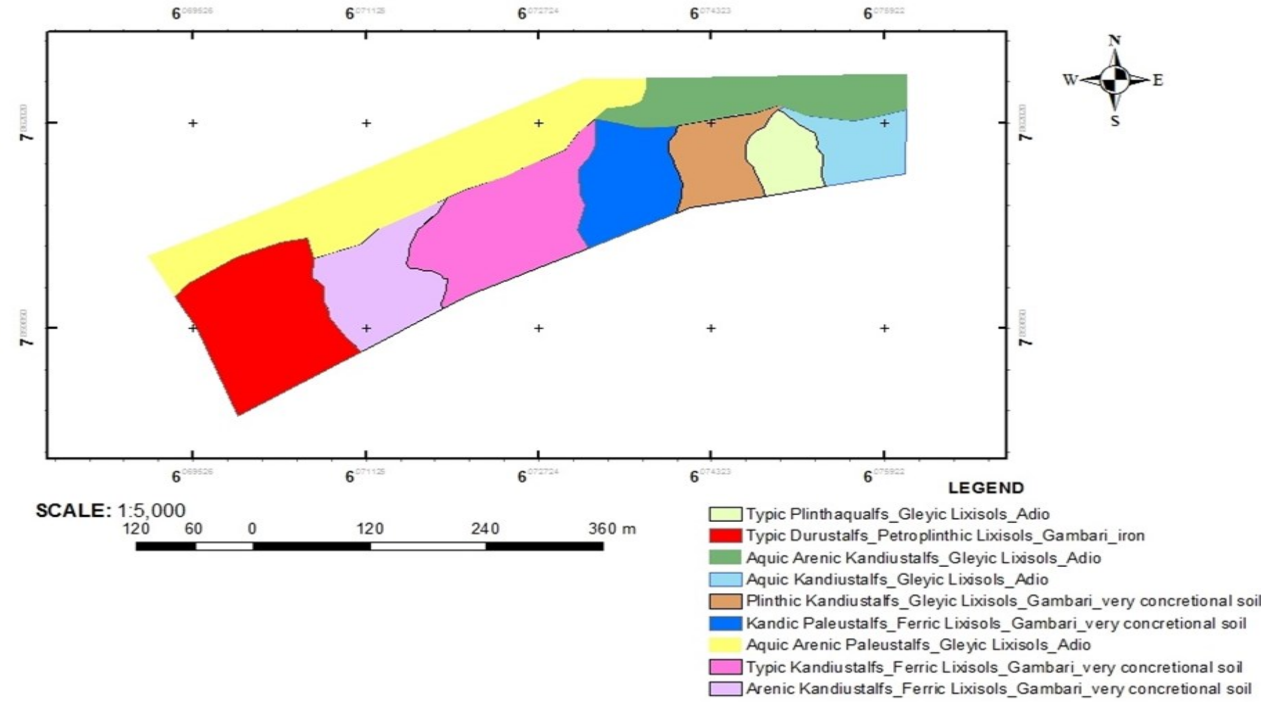

Figure 2: Soil map of Kabba study site

mined on the AAS at 325, 373.9, 280 and 214m wavelengths respectively. Statistical analysis: T-test was used to compare differences between the soils on schist and older granite and between surface and subsurface horizons. Linear correlation analysis was used to determine the relationship between the soil properties. All the statistical analyses were carried out at 95% confidence level. The analysis was carried out using statistical package for social science (SPSS IBM Statistics 19.0).

3.0. Results

Means of the physical and chemical properties, micro and macronutrients of soils at both locations are presented in Tables 1-3. The forms of iron and manganese are presented in Tables 4-7. The relationship of the soil properties is presented in 8 to 11.

The Citrate-bicarbonate-dithionite extractable Iron oxide (Fed- total free iron oxides) values (Tables 4-5) ranged from 1.336 to 2.826% and 0.750 to 1.531% in the surface horizons of schists and older granite soils respectively. Subsurface horizons values ranged from 1.151 to 2.997% and 0.924 to 2.706% in soils on schist and older granite respectively. There was no significant difference between parent materials (Table 6). There was a significant difference ($P \leq 0.05$) in the horizons (Table 7). A significant correlation of total free iron oxides was observed (Table 9 and 11) with sand (0.600*), Clay (-0.525*), PWP (0.526*), AWC (0.633**) and OC and Fed (-0.256).

Oxalate extractable iron oxide (Feox) (amorphous form) values (Tables 4-5) ranged from 0.423 to 0.711% and 0.171 to 0.349% in the surface horizon of schist and older granite soils respectively. At the corresponding subsurface horizons values ranged from 0.358 to 0.568% and 0.284 to 0.453%. Parent materials significantly ($P \leq 0.05$) influenced Feox in soils studied (Table 6). There was no significant difference in the horizons (Table 7) and distribution patterns were irregular in the soils on older granite but decreases down the soil depth in soils on schist. Clay (0.628**), Exchangeable Ca (0.682**), Mg (0.844**), K (0.780**) and Na (0.732**), TEB (0.771**), ECEC (0.756**), BS (0.800**), total nitrogen (0.623**), available copper (-0.826**) and available zinc (-0.678**) were significantly correlated with Feox (Table 8-11).

Sodium pyrophosphate extractable (Fep) (organo-complexed form) values (Table 4-5) at the surface horizon ranged from 0.238 to 0.500% and 0.222 to 0.369% in soils derived schist and older granite respectively. At the corresponding subsurface horizon Fep values ranged from 0.142 to 0.590% and 0.84 to 0.369%. Parent materials significantly ($P \leq 0.05$) influenced variation in Fep of soils (Table 6). Fep was highly significantly correlated (Table 33) with Md (0.694**), Mnox (0.784**) and Mnp (0.862**) (Table 8). It also correlates significantly with pH (0.794**), Exchangeable Ca (0.576*), Mg (0.650**), K (0.821**) and Na (0.685**), TEB (0.571*), ECEC (0.585*) BS (0.576*) $CaCO_3$ (0.621**), TP (0.515*), PWP (0.500*), TN (0.820*), FeHCl (0.503*), available P (0.515*), FeTotal (0.806**) and ZnTotal (0.509*) (Table 9 -11).

The active iron oxide ratio (Feox/d) values (Tables 4-5) in the surface horizons ranged from 0.197 to 0.514 and 0.307 to 3.291 in soils on schist and older granite respectively. The corresponding subsurface horizon values ranged from 0.135 to 0.409 and 0.359 to 4.903. Parent materials and horizons significantly ($P \leq 0.05$) influence the variation of Feox/d in the soils (Tables 6-7). Feox/d correlated significantly with Fed (-0.532), silt (-0.653**) and clay (-0.621**), Organic carbon (-0.556*) (Tables 8-11).

Clay/dithionite iron ratio (clay/ Fed) values (Tables 4-5) ranged from 8.660 to 23.353 and 16.223 to 33.375 in soils on schist and older granite. At the corresponding subsurface horizon values ranged from 9.143 to 23.632 and 3.696 to 33.375. Parent materials significantly ($P \leq 0.05$) influence variation of clay/ Fed (Table 6). There was significant correlation of Clay/ Fed with Fed (-0.856**), Fep (-0.541*), Mnp (-0.553), Feox/d (0.632*), clay (0.686**), silt/clay ratio (0.579*), CaCO3 (-0.533*), TN (-0.670**), CuHCl (0.568*), CuTotal (-0.553), (Tables 8-11).

The citrate-bicarbonate-dithionate extractable manganese oxide (Mnd) (total free manganese oxide) values (Tables 4 -5) ranged from 0.044 to 0.090% and 0.051 to 0.064% at the surface horizons of soils on schist and older granite respectively. At the corresponding subsurface horizon, the values ranged from 0.440 to 0.114% and 0.051 to 0.078%. There was significant difference ($P \leq 0.05$) between the parent materials (Table 6). There was significant relationship with sand (-0.579*), clay (0.572*), BD (-0.541*), Silt/Clay ratio (-0.595*), pH(H2O) (0.639*), exchangeable Mg (0.624**) and K (0.625**), BS (0.553*), CaCO (0.621**), OC (0.539*), TN (0.894**), FeTotal (0.799**), CuTotal (0.745**), MnHCl (-0.653*) and ZnHCl (-0.561) Tables 8 and 11).

Oxalate extractable manganese (Mnox) (amorphous form) values (Tables 4-5) ranged from 0.010 to 0.016% and 0.005 to 0.010% in the surface horizon of soils on schist and older granite respectively. The corresponding subsurface horizon values ranged from 0.006 to 0.019% and 0.005 to 0.013%. There was significant difference ($P \leq 0.05$) between the parent materials (Table 6). pH (0.639*), exchangeable Ca (0.786**), Mg (0.726**), K (0.807**) and Na (0.755**), TEB (0.751**), ECEC (0.712**), BS (0.811**), CaCO3 (0.656*), PWP (0.743**), MnTotal (0.700**) and ZnTotal (0.517*) EA (-0.778*), AP (-0.599*), CuHCl (-0.605) and ZnHCl (-0.704**) all correlated significantly with Mnox (Table 8 and 11).

Pyrophosphate extractable manganese oxide (Mnp) (Organo-complexed form) values (Tables 4-5) in the surface horizons ranged from 0.011 to 0.020% and 0.007 to 0.010% in soils on schist and older granite respectively. The corresponding subsurface horizon values ranged from 0.006 to 0.019% and 0.007 to 0.013%. Parent materials and horizons significantly ($P \leq 0.05$) influence variation of Mnp (Tables 6-7). Mnp correlates with OC (0.539*), available Mn, Mnd and Mnox (0.602**, 0.627** and 0.706** respectively), TN (0.894**), FeTotal (0.791**), CuHCl (-0.882**), CuTotal (0.745**), ZnHCl (-0.720**), BD (-0.568*), TP (0.556*), FC (0.575*), PWP (0.539*), AWC (0.541*), pH (0.619**) exchangeable Ca (0.612*), Mg (0.820**), K (0.630**) and Na (0.587*), TEB (-0.752**), EA (0.596*), ECEC (0.690**) EC (0.720**) and CaCO3 (0.640**) (Tables 8-11).

The active manganese oxide ratio (Mnox/d) values (Table 4-5) ranged from 0.135 to 1.299 and 0.008 to 1.960 in soils on schist and older granite respectively. At the corresponding subsurface horizon, the values ranged from 0.010 to 1.053 and 0.078 to 1.961. There was no significant difference in parent materials. Sand (-0.691*) have an

Table 1: Means of soil physical properties.

Parameter	Unit	Schists	Older Granite
Gravel	%	13.779	1.042
Sand	%	57.526	63.667
Silt	%	12.875	7.728
Clay	%	29.599	28.605
Bulk density (BD)	g/cm^3	1.697	1.414
Particle density (PD)	g/cm^3	2.646	2.029
Total porosity (TP)	%	42.889	31.198
Field capacity (FC)	%	19.691	14.177
Permanent wilting point (PWP)	%	11.834	7.637
Available water content (AWC)	%	7.857	6.523
Silt/Clay ratio		0.363	0.299

Table 2: Means of soil chemical properties

Parameters	Unit	Schists	Older Granite
pH(H_20)		6.374	4.783
Exchangeable Calcium	Cmol/kg	3.069	1.317
Exchangeable Magnesium	Cmol/kg	1.440	0.210
Exchangeable Potassium	Cmol/kg	0.392	0.142
Exchangeable Sodium	Cmol/kg	0.167	0.088
Total Exchangeable Bases	Cmol/kg	5.064	1.795
Exchange Acidity (EA)	Cmol/kg	0.438	0.899
Effective Cation Exchange Capacity (ECEC)	Cmol/kg	5.502	2.695
Effective Cation Exchange Capacity Clay (ECEC Clay)	Cmol/kgclay	9.437	11.323
Base Saturation (BS)	%	91.850	66.991
Exchangeable Sodium Percentage (ESP)	%	3.094	3.376
Electrical Conductivity (EC)	dS/m	0.143	0.026
Calcium Carbonate ($CaCO_3$)	%	0.590	0.372

Table 3: Means of soil macronutrients and micronutrients

Parameters	Unit	Schist	Older Granite
Organic Carbon (OC)	%	0.668	0.452
Organic Matter (OM)	%	1.151	0.783
Total Nitrogen (TN)	%	0.241	0.039
Available Phosphorus (AP)	Ppm	6.653	7.575
Available Iron (FeHCl)	mg/kg	29.052	14.399
Total Iron (FeTotal)	%	5.510	3.979
Available Manganese (MnHCl)	mg/kg	7.071	5.017
Total Manganese (MnTotal)	mg/kg	304.872	222.361
Available Copper (CuHCl)	mg/kg	0.088	0.578
Total Copper (CuTotal)	mg/kg	27.00	17.207
Available Zinc (ZnHCl)	mg/kg	5.942	6.245
Total Zinc (ZnTotal)	mg/kg	49.475	40.462

Table 4: Iron and Manganese Oxides and their active ratios of Kabba study area (Schists Belt)

Horizon	Depth (cm)	Fe_d (%)	Fe_{ox} (%)	Fe_P (%)	Mn_d (%)	Mn_{ox} (%)	Mn_p (%)	$Fe_{ox/d}$	$Mn_{ox/d}$	$Clay/Fe_d$
Profile KA 7.859302N 6.069769E										
Ap	0 – 9	1.892	0.647	0.500	0.077	0.010	0.020	0.342	1.299	13.319
Bv	9 – 20	2.412	0.539	0.331	0.089	0.008	0.020	0.223	0.090	12.521
Bx	20 – 40	2.975	0.543	0.373	0.089	0.008	0.020	0.183	0.090	9.143
Profile KB 7.859440N 6.070209N										
Ap	0 – 18	2.825	0.555	0.352	0.090	0.017	0.018	0.197	0.189	9.628
Bc	18 – 39	2.530	0.535	0.413	0.086	0.006	0.015	0.212	0.070	11.482
Bcg1	39 – 69	2.835	0.540	0.590	0.101	0.006	0.015	0.190	0.059	10.200
Bcg2	69 – 130	2.835	0.478	0.590	0.082	0.017	0.017	0.169	0.207	13.416
Bgx	130 – 200	2.835	0.493	0.368	0.082	0.017	0.011	0.174	0.207	13.123
Profile KC 7.860822N 6.069576E										
Ap	0 – 20	1.969	0.423	0.251	0.084	0.015	0.020	0.215	0.178	8.669
Bt	20 – 46	2.848	0.409	0.451	0.069	0.010	0.018	0.144	0.145	6.696
Btcg1	46 – 70	2.965	0.512	0.351	0.087	0.010	0.018	0.173	0.115	8.162
Btcg2	70 – 110	2.034	0.475	0.397	0.104	0.008	0.020	0.234	0.077	13.373
Btg	110 – 200	2.521	0.494	0.336	0.087	0.010	0.008	0.960	0.115	12.935
Profile KD 7.860376N 6.072108E										
Ap	0 – 20	1.336	0.541	0.291	0.044	0.016	0.019	0.405	0.364	23.353
Btcg1	20 – 74	1.382	0.565	0.238	0.044	0.007	0.019	0.409	0.159	19.682
Btcg2	74 – 102	2.100	0.509	0.214	0.059	0.010	0.010	0.242	0.170	16.762
Btcg3	102 – 145	2.021	0.483	0.390	0.084	0.006	0.010	0.239	0.071	19.520
Profile KE 7.860811N 6.072108E										
Ap	0 – 24	2.271	0.486	0.395	0.071	0.015	0.018	0.214	0.211	12.109
Btc1	24 – 47	2.296	0.375	0.443	0.112	0.007	0.018	0.289	0.063	10.105
Btc2	47 – 67	2.492	0.517	0.482	0.102	0.015	0.010	0.208	0.147	15.329
Btc3	67 – 99	2.651	0.359	0.338	0.095	0.019	0.018	0.135	1.053	14.772
Btgx	99 – 150	2.700	0.375	0.276	0.095	0.019	0.012	0.139	1.053	14.630

Table 4: Iron and Manganese Oxides and their active ratios of Kabba study area (Schists Belt)

Horizon	Depth (cm)	Fe_d (%)	Fe_{ox} (%)	Fe_P (%)	Mn_d (%)	Mn_{ox} (%)	Mn_p (%)	$Fe_{ox/d}$	$Mn_{ox/d}$	$Clay/Fe_d$
Profile AA 7.711121N 5.243230E										
Ap	0 – 13	0.863	0.284	0.222	0.064	0.005	0.007	3.291	0.078	30.127
Bt	13 – 36	1.618	0.453	0.222	0.051	0.008	0.010	2.800	1.569	21.632
Btv1	36 – 84	2.525	0.453	0.369	0.078	0.008	0.013	1.794	1.026	15.842
Btv2	84 – 118	2.525	0.296	0.222	0.078	0.010	0.008	1.172	1.282	16.634
Btcx	118 – 130	2.706	0.319	0.222	0.064	0.008	0.007	1.179	0.125	17.369
Profile AB 7.710876N 5.245183E										
Ap	0 – 15	0.750	0.296	0.222	0.064	0.005	0.008	3.947	0.008	26.667
Bt1	15 – 38	0.924	0.453	0.222	0.051	0.010	0.007	4.903	1.961	21.645
Bt2	38 – 69	1.618	0.319	0.184	0.051	0.010	0.013	1.972	1.961	24.722
Btc	69 – 100	1.618	0.453	0.184	0.064	0.005	0.007	2.800	1.008	35.229
Btx	100 – 114	2.525	0.581	0.184	0.064	0.005	0.007	2.580	1.008	22.970
Profile AC 7.712567N 5.244153E										
Ap	0 – 19	1.531	0.284	0.222	0.051	0.010	0.010	1.855	1.960	13.717
Bh1	19 – 35	1.531	0.453	0.369	0.051	0.008	0.013	2.959	1.569	13.063
Bh2	35 – 60	1.618	0.453	0.184	0.064	0.008	0.007	2.800	0.125	21.632
Bh3	60 -94	2.706	0.349	0.184	0.078	0.008	0.007	1.290	1.026	14.043
Profile AD 7.713800N 5.244635E										
Ap	0 – 18	0.863	0.171	0.369	0.064	0.008	0.007	1.198	0.125	22.016
B	18 – 34	0.924	0.453	0.222	0.078	0.005	0.007	0.490	0.064	20.563
Btx	34 – 64	1.618	0.581	0.222	0.051	0.005	0.013	0.359	0.098	32.756
Profile AE 7.713694N 5.245869E										
Ap	0 – 35	0.750	0.349	0.369	0.051	0.010	0.008	0.379	0.196	24.000
Bh	35 – 79	2.706	0.453	0.222	0.051	0.005	0.007	0.167	0.098	14.043
Bhx	79 – 120	2.700	0.581	0.184	0.064	0.008	0.007	0.215	0.125	20.741

Horizon	Depth	Fe_d	Fe_{ox}	Fe_P	Mn_d	Mn_{ox}	Mn_p	$Fe_{ox/d}$	$Mn_{ox/d}$	Clay/Fe_d
	(cm)	(%)	(%)	(%)	(%)	(%)	(%)			
Profile AF 7.712131N 5.246052E										
Ap	0 – 20	0.924	0.284	0.222	0.051	0.010	0.010	0.307	0.196	16.234
B	20 – 49	1.531	0.453	0.222	0.064	0.008	0.007	0.296	0.125	10.451
Bt	49 – 85	1.618	0.319	0.222	0.078	0.008	0.017	0.197	0.103	22.250
Btx	85 – 105	1.618	0.319	0.184	0.078	0.005	0.007	0.197	0.064	33.375
Profile AG 7.710802N 5.246470E										
Ap	0 – 9	0.863	0.171	0.222	0.051	0.005	0.008	0.198	0.098	16.223
Bw1	9 – 20	2.706	0.284	0.222	0.064	0.005	0.007	0.105	0.078	3.696
Bw2	20 – 60	2.706	0.453	0.222	0.064	0.005	0.013	0.167	0.078	4.065

Table 6: T-test for Iron and Manganese Oxides and their active ratios of parent materials

Parameter	Unit	Schists	Older Granite	t-test value	P(two tailed)
Fe_d	%	2.276	1.290	4.252	NS
Fe_{ox}	%	0.511	0.295	3.945	0.044
Fe_p	%	0.350	0.182	5.230	0.021
Mn_d	%	0.085	0.049	3.599	0.047
Mn_{ox}	%	0.017	0.006	2.686	0.028
Mn_p	%	0.016	0.006	7.868	0.030
$Fe_{ox/d}$		0.251	0.993	-1.848	0.046
$Mn_{ox/d}$		0.235	0.402	-0.939	NS
Clay/Fe_d		13.631	15.365	-0.471	0.039

P ≤0.05 level, NS>0.05

Table 8: Correlation matrix for Iron and Manganese Oxides and their active ratios

	Fe_d	Fe_{ox}	Fe_p	Mn_d	Mn_{ox}	Mn_p	$Fe_{ox/d}$	$Mn_{ox/d}$
Fe_{ox}	0.376							
Fe_p	0.706**	0.724**						
Mn_d	0.565*	0.494	0.694**					
Mn_{ox}	0.602*	0.690**	0.784**	0.745**				
Mn_p	0.640**	0.724**	0.862**	0.627**	0.706**			
$Fe_{ox/d}$	-0.532*	-0.124	-0.418	-0.376	-0.377	-0.399		
$Mn_{ox/d}$	0.079	0.024	0.076	-0.141	0.184	0.015	0.397	
Clay/Fe_d	-0.856**	-0.306	-0.541*	-0.485	-0.409	-0.661**	0.632**	0.300

* Correlation is significant at 0.05 level (two tailed)
** Correlation is significant at 0.01 level (two tailed)

Table 9: Correlation matrix of Physical Properties versus Iron and Manganese Oxides and their active ratios

	Gravel	Sand	Silt	Clay	BD	PD	TP	FC	PWP	AWC	Silt/Clay
Fe_d	0.658**	0.600*	-0,275	-0.525*	-0.247	-0.259	0.218	0.191	0.526*	0.633**	-0.614**
Fe_{ox}	0.701**	0.112	0.106	0.628**	-0.224	0.350	0.285	0.329	0.676**	0.035	0.323
Fe_p	0.789**	0.147	-0.053	-0.121	-0.521*	0.041	0.515*	0.041	0.500*	0.062	-0.157
Mn_d	0.530*	-0.579*	-0.106	0.572**	-0.541**	0.088	0.479	0.139	0.482	-0.032	-0.595*
Mn_{ox}	0.767**	0.010	-0.015	0.052	-0.193	-0.072	0.210	0.181	0.743**	-0.006	-0.127
Mn_p	0.746**	0.629*	0.003	-0.339	-0.568	0.262	0.556*	0.575*	0.539*	0.541*	-0.221
$Fe_{ox/d}$	0.433	-0.585*	0.653*	-0.621**	0.074	0.450	0.015	-0.238	0.068	-0.353	0.511*
$Mn_{ox/d}$	0.216	-0.691**	0.432	0.518*	0.002	-0.097	0.041	-0.141	0.053	-0.109	0.269
Clay/Fe_d	-0.453	-0.635	0.309	0.689**	0.385	0.059	-0.324	-0.444	-0.318	-0.371	0.579*

Table 10: Correlation matrix of Chemical Properties versus Iron and Manganese Oxides and their active ratios

	pH	Exch. Ca	Exch. Mg	Exch. K	Exch. Na	TEB	EA	ECEC	BS	ESP	EC	$CaCO_3$
Fe_d	0.474	0.394	0.468	0.456	0.526*	0.365	-0.316	0.379	0.288	-0.079	-0.300	0.544*
Fe_{ox}	0.382	0.682**	0.844**	0.780**	0.732**	0.771**	-0.793**	0.756**	0.800**	-0.300	0.056	0.562*
Fe_p	0.794**	0.576*	0.650**	0.821**	0.685**	0.571*	-0.627**	0.585*	0.576*	-0.188	0.365	0.621*
Mn_d	0.639*	0.462	0.624**	0.625**	0.488	0.459	-0.618**	0.479	0.553*	-0.347	0.082	0.621*
Mn_{ox}	0.640**	0.786*	0.726**	0.807**	0.755**	0.751**	-0.778**	0.712**	0.811**	-0.350	0.099	0.656**
Mn_p	0.619*	0.612*	0.820**	0.630**	0.587*	-0.752**	0.596*	0.690))	-0.139	0.171	0.720**	0.640**
$Fe_{ox/d}$	-0.229	-0.259	-0.324	-0.263	-0.276	-0.238	0.253	-0.226	0.238	0.065	0.074	-0.624*
$Mn_{ox/d}$	0.218	0.135	-0.118	0.082	0.012	0.059	0.169	0.071	-0.024	-0.118	0.279	-0.232
Clay/Fe_d	-0.268	-0.232	-0.335	-0.352	-0.321	-0.247	0.333	-0.247	-0.265	0.059	-0.065	-0.535*

* Correlation is significant at 0.05 level (two tailed)
** Correlation is significant at 0.01 level (two tailed)

Table 11: Correlation matrix of iron and manganese oxides versus macronutrients and micronutrients

	Fe_d	Fe_{ox}	Fe_p	Mn_d	Mn_{ox}	Mn_p	$Fe_{ox/d}$	$Mn_{ox/d}$	Clay/Fe_d
OC	-0.256	0.021	-0.303	-0.153	-0.311	0.539*	-0.532*	-0.077	-0.402
TN	0.681**	0.623**	0.820**	0.664**	0.852**	0.894**	-0.611*	-0.032	-0.670**
AP	-0.468	-0.347	-0.515*	-0.309	-0.599*	-0.330	0.279	0.076	0.253
FeHCl	0.097	0.321	0.503*	0.379	0.390	0.328	0.124	0.203	0.038
FeTotal	0.332	0.888**	0.806**	0.559*	0.745**	0.791**	-0.603	0.506*	0.262
MnHCl	-0.638**	0.426	0.218	-0.653**	0.700	0.602**	0.047	-0.656**	0.050
MnTotal	0.217	0.302	0.199	0.029	0.426	0.084	0.009	0.239	0.112
CuHCl	-0.541*	-0.826**	-0.794**	-0.388	-0.603	0.882**	0.368	0.097	0.568*
CuTotal	0.600**	0.579*	0.632**	0.735**	0.674**	0.745**	-0.479	0.124	-0.553*
ZnHCl	-0.400	-0.678**	-0.571*	-0.561*	-0.704**	-0.720**	0.518*	0.193	0.461
ZnTotal	0.350	0.371	0.509*	0.247	0.517*	0.322	-0.221	0.026	-0.071

* Correlation is significant at 0.05 level (two tailed)
** Correlation is significant at 0.01 level (two tailed)

inverse relationship with Mnox/d, on the other hand, there was a positive relationship with clay (0.518*) (Table 9).

4.0. **Discussion**

Soils on schist have higher values of Fed than older granite soils. The lower values in the older granite soils can be attributed to the intensity of weathering and leaching in the area (Maniyunda, 2012). The subsurface horizons appeared to have higher values of Fed than the surface horizons, similar result was reported by Maniyunda (2012) in soils on basement complex geology and it was attributed to co-translocation of Fe with clay from the surface to subsurface horizons through alluviation-illuviation processes (Blume and Schwertmann, 1969; Juo et al., 1974). According to Fanning and Fanning (1989), the process was triggered by the redox process. The highest values were within the horizons that contain iron-manganese concretions and plinthites. The values in this study are in agreement with the findings of Aghimien *et al.*, (1988), Maniyunda (1999), Raji *et al.,* (2000), Ibia (2002) and Essoka and Esu (2003). Correlation of total free iron observed with sand, Clay, PWP, and AWC establishes the fact that drainage and moisture regime of soils influenced Fed formation, translocation and accumulation processes (redox process) (Udo, 1980; Perkins and Lawrence, 1982; Aghimien *et al.,* 1988).

Higher Feox values were observed in soils on schist and it indicates that the soils on schist are pedogenically younger than soils on older granite. Exchangeable Ca, Mg, K, and Na, TEB, ECEC, and BS correlate with Feox. This implies that an increase in all these properties will lead to an increase in Feox.

Differences in parent materials in Fep of soils can be attributed to the amount of organic matter generated by vegetation in the different ecological zones of this study. Different values of Fep had been reported for different agroecological zones in Nigeria (Raji *et al.,* 2000; Abdourahamane and Yaro, 2007; Olaleye *et al*., 2000; Samundi *et al.,* 2006). pH, Exchangeable Ca, Mg, K and Na, TEB, ECEC, BS, $CaCO_3$, TP, PWP, TN, Fe, HCl, Available P, FeTotal and Zn Total have similar distribution pattern with Fep and may contribute to the content of organically complexed iron in the soils studied. Fe-phosphorus interactions commonly occur in both plant metabolism and soil media. The affinity between Fe(III) and H_2PO_4 is known to be great and therefore the precipitation of $FePO_4.2H_2O$ can easily occur under favourable conditions (Kabata-Pendias and Pendias, 1989) in the soils studied. Fep was highly significantly correlated Md (0.694**), Mnox, Mnp. A similar trend was observed for Feox and Fed, this signifies that their availability is controlled by similar pedogenic processes or factors.

Results of Feox/d indicate that parent materials influenced crystallization in the soils. The highest value was observed in soils on older granite and it relates to their pedogenic age. The surface horizon values were higher. This signifies that there is more crystallization of iron oxide at the surface horizon than the subsurface (Blume and Schwertmann, 1969; Lekwa and Whiteside, 1986). Feox/d correlated significantly with silt and clay this indicates that an increase in silt weathering to clay increases active iron co-migration and coating of a clay surface, which will lead to an increase in iron crystallization (Maniyunda, 2012). The relationship between Feox/d and organic matter indicates that organic matter inhibits crystallization in the soils. There was an indication that Fed significantly contributed to the crystallization of iron in the soils, this was reflected in the significant correlation of Feox/d with Fed.

The pattern of distribution of clay/ Fed within the soil depths was irregular for most of the profiles except for profile AG where it decreases down the depth. This indicates that with the advancement in pedogenic development there is independent migration of clay and Fed. This reflected in the significant correlation with clay.

The lowest values of Mnd were observed in soils on older granite. This can be attributed to the higher sand percentage in the soils which led to leaching and translocation of Mnd. This was established in a significant negative correlation with sand. There are higher values of Mnd at the subsurface than the surface horizons in most of the profiles. This signifies alluviation-illuviation processes and probably the release of Mn oxides from silicates (Blume and Schwertmann, 1969; Naho *et al.,* 1989). There is a significant correlation with clay this signifies the co-migration of clay with Mnd. There is an indication that an increase in pH(H_2O) increases Mnd content of soils in this study, this was observed in the significant correlation of Mnd with pH(H_2O). There was a significant correlation with exchangeable Mg and K, BS, $CaCO_3$, OC, TN, FeTotal, CuTotal. This could be due to the similarity in their distribution pattern. Also, the distribution pattern of BD, Silt/Clay ratio, MnHCl, and ZnHCl were in opposite direction with Mnd.

Soils of the schist origin have higher values Mnox than soils of the older granite. The pattern of distribution was observed to be irregular in most of the profiles except for profiles AD, AG and KA where the value decreases down the soil depth. pH, exchangeable Ca, Mg, K and Na, TEB, ECEC, BS and CaCO3 correlated with Mnox. This indicates that an increase in pH and exchangeable cations increase amorphous manganese in the soils studied. An inverse significant relationship was observed with EA, AP, CuHCl, and ZnHCl signify that their increase in soil decreases Mnox. There is a likelihood that PWP, MnTotal and ZnTotal are having similar distribution patterns in soils of this study.

There were higher values of Mnp at the surface horizons than the subsurface horizons. This can be attributed to the contribution of organic matter and this was confirmed by the significant positive correlation of Mnp with OC. Available Mn, Mnd, and Mnox have similar distribution pattern and the major source and reservoir of available Mn might be Mnp in that they are correlated. There were indications that Mnp has a relationship with the following properties; TN, FeTotal, CuHCl, CuTotal, ZnHCl, BD, TP, FC, PWP, AWC, pH, exchangeable Ca, Mg, K and Na, TEB, EA, ECEC, EC, and $CaCO_3$. They might have similar distribution patterns or contribute to Mnp contents in the soils studied.

Higher values of Mnox/d were observed in older granite soils. There was no difference in the values between the parent materials; this may be because both parent materials are of the basement complex geology. The distribution pattern was irregular down the soil depth. This indicates that the crystallization process in the soils was irregular for manganese. Sand (-0.691*) has an inverse relationship with Mnox/d. This implies that an increase in the sand in the soils studied will decrease the crystallization of Mn. On the other hand, clay has a positive relationship with Mnox/d this indicates that an increase in clay favours crystallization of Mn.

5.0. Conclusion

The nature, amount and distribution of sesquioxides in the soils studied are controlled by similar pedogenic processes. The major pedogenic processes in the soils studied are; co-translocation of Fe with clay by alluviation and illuviation, plinthization, leaching and co-migration of clay with Mnd. The study also showed that drainage, moisture, sand, clay and organic matter played a significant role in the formation and distribution of Fe and Mn. The forms Mn influenced the distribution of pH and exchangeable cations in the soils. Furthermore, it was revealed that the soils developed over schist are pedologically younger than soils on older granite.

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