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Forms and content of sesquioxides in soils on basement complexes of northern Guinea savanna of Nigeria

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The forms and content of sesquioxides (Fe and Mn) were studied in soils developed on basement complex rocks within Northern Guinea Savanna of Nigeria. The study showed that variation in parent materials and pedogenetic development significantly influenced content of dithionite, oxalate extractable forms of iron and active iron ratio in these soils. The mean values of active sesquioxides (Fe and Mn) ratios between the soils varied in the order of soils on mica schists > quartzites > older granites > migmatite gneiss suggesting that the soils pedogenic development was lowest in soils on mica schist and highest in soils on migmatite gneiss. Increase in pedogenetic development increased sesquioxides crystallization and was indicated by the highly significant correlation between active Fe ratio and iron crystallinity index ($r = - 0.507^{**}$). Pedogenetic development and sesquioxides crystallization were significantly higher in the subsoil compared to surface horizons. Clay and organic matter had strong influence on movement and distribution of the forms of sesquioxides in the soils.

Key words: Sesquioxides, basement complex, iron oxide, manganese oxide, crystallinity index.

INTRODUCTION

Oxides, hydroxides and oxy-hydroxides of iron (Fe), manganese (Mn), aluminium (Al) and titanium (Ti) are referred to as sesquioxides. They occur in soils mainly as amorphous and crystalline inorganic compounds. A small fraction may be present in the organic complexes. The amorphous oxides are extracted with ammonium oxalate solution (Mckeague and Day, 1966) while total free oxides constituting both amorphous and crystalline sesquioxides are extracted with citrate bicarbonate

dithionite solution (Mehra and Jackson, 1960). The amorphous organically- complexed sesquioxides are extracted with pyrophosphate solution (Mckeague, 1967).

The nature, content and distribution of sesquioxides influence pedogenetic processes and physicochemical properties of soils (Blume and Schwertmann, 1969; Juo, 1981; Schwertmann and Taylor, 1989; Jelic et al., 2011). The nature and contents of sesquioxides (Fe, Mn, Al and Ti) in soils have been used to make predictions with

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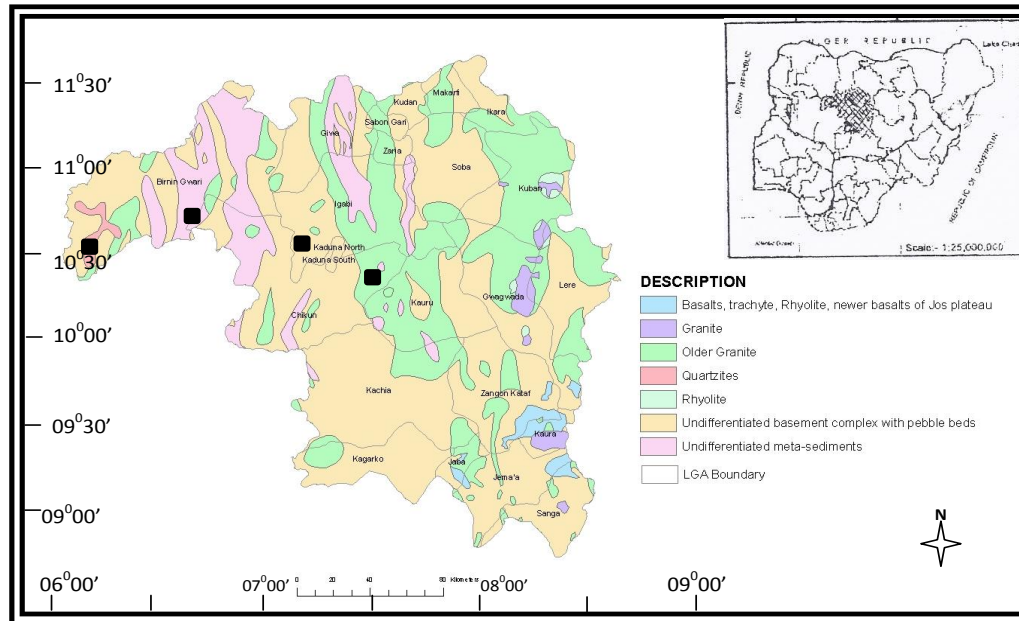


Figure 1. Geological Map of Kaduna State, Nigeria indicating Project Sites (■) Adopted from National Bureau of Statistics (2009).

regard to type, direction, degree and stage of pedogenesis (Blume and Schwertmann, 1969; Alexander, 1974; Schwertmann and Taylor, 1989; Durn et al., 2001; Igwe, 2001; Kurihara et al., 2002; Osodeke et al., 2005). Predictions have also been made of soil types (classification), types of soil horizons and soil drainage (Juo et al., 1974; Udo, 1980; Schwertmann and Taylor, 1989; Ibia, 2002; Essoka and Esu, 2003). During weathering of soils, iron released from primary minerals crystallizes into secondary iron minerals under dry condition. The rates of Fe crystallization have been assessed as Fe crystallinity index (CI) and used to grade pedogenetic development (age) and soils classification (Nagatsuka, 1975; Durn et al., 2001; Kurihara et al., 2002).

The form and content of the oxides influence soil physicochemical properties such as phosphate retention making it unavailable in highly weathered tropical soils, surface charge, specific surface area, aggregate formation and stabilization (Juo, 1981; Igwe, 2001; Duiker et al., 2003). Although, there are several studies on forms and distribution of sesquioxides and their uses in interpreting pedogenic processes and soil properties in Nigeria (Juo et al., 1974; Udo, 1980; Raji et al., 2000; Ibia, 2002; Yaro, 2005), there is dirt of information on their distribution and their effect on soils developed on different basement complex rocks. Therefore, the objective of this study was to examine the content and forms of Fe and Mn oxides in soils developed on different basement complex rocks in Northern Guinea Savanna of

Kaduna State Nigeria, as a basis of making predictions on pedogenic processes in the soils.

MATERIALS AND METHODS

Description of study area

The locations for the study were situated within older granite (OG), quartzite (QZ), mica schist (MS) and migmatite gneiss (MG) basement complexes parent material area, within Northern Guinea Savanna zone of Kaduna State, Nigeria. The underlying geology is the Precambrian era Basement Complex of metamorphic and igneous rocks (Kogbe, 1976). The sites lie within latitude 10°27'55.7"N to 10°43'43.2"N and longitude 06°11'14.0"E to 07°39'27.3"E (Figure 1). The mean amount of rainfall of the study areas ranged between 1,180 and 1,286 mm/annum. Mean annual evaporation record ranged between 2194 to 2822 mm/ annum. Rainfall was in excess of evaporation in the month of July to September. The mean annual temperature ranged between 24.8 and 28.7°C and the mean monthly temperature consecutively from February to October is less than 5°C. Therefore, the soil temperature regime is considered as isohyperthermic.

Field studies

Exploratory survey was used to identify suitable sites on crestal position using geological map of Kaduna State (Figure 1), ecoclimatological zones map and Topo map sheets (1:50,000). Three soil profile pits were sited and dug on cultivated fields on each of the four parent material locations. The morphological properties observed in field were described based on procedures in the USDA Soil Survey Manual (Soil Survey Division Staff, 1993). Soils were sampled within pedogenic horizons.

Laboratory analysis

Laboratory analyses of the fine earth (< 2 mm) samples were carried out using standard laboratory methods. Particle size was determined by hydrometer method (Gee and Bauder, 1986). 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). Cation exchange capacity (CEC) was determined by neutral (pH 7.0) NH_4OAc saturation method (Rhoades, 1982). Organic carbon was determined by 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.

Total free iron (Fe_d) and manganese (Mn_d) oxides were extracted following the method of Mehra and Jackson (1960) as described by IITA (1979) using citrate-bicarbonate-dithionite mixtures. Amorphous inorganic form of Fe (Fe_{ox}) and Mn (Mn_{ox}) oxides was extracted using ammonium oxalate (pH 3) in the dark (McKeague and Day, 1966) using the modified Tamm's method (IITA, 1979). Amorphous organic form of Fe (Fe_p) and Mn (Mn_p) oxides was extracted using pyrophosphate solution (McKeague, 1967). Total iron (Fe_t) was extracted with double acid (mixture of 3 parts of HCl to 1 part of HNO_3) through digestion process (USDA, NRCS, 2004). Content of Fe and Mn in the respective extracts were determined with atomic absorption spectrophotometer (AAS) at 280 and 373.9 nm wavelengths respectively. Iron crystallinity index (CI) was obtained from the equation:

$$CI = \frac{(\text{Fe}_d - \text{Fe}_{ox})}{\text{Fe}_t}$$

Statistical analysis

The data obtained from the study were subjected to descriptive statistics to assess the soil properties. Mean differences in properties between soils developed on the four parent materials and between horizons were analyzed using two way analysis of variance (ANOVA). Correlation analysis was used to determine relationship between the free oxides and soil properties (SPSS Statistics 17.0).

RESULTS AND DISCUSSION

Soil physicochemical properties

The soils were generally deep to very deep (135 to 190 cm). The depth of some soils on quartzites (QZ1) and mica schist (MS2 and MS3) were restricted due to parent materials encountered between 14 and 72 cm. Plinthite was encountered in all the pedons on migmatite gneiss within the depth of 48 to 172 cm and were within range reported by Osher and Buol (1998) and Yaro (2005) on soils developed on landscape position in eastern Madre de Dios, Peru and on upper slope to crest positions on plinthite landscape at Samaru, Zaria respectively. Earlier studies (Raji, 1995; Idoga et al., 2007) attributed extent of soil depth to parent material, erosion and slope of area. All surface horizons of soils in this study were sandy loam

with the subsoil horizons characterized by clay, sandy clay to sandy clay loam in the deeper horizons. The finer textured subsoil may be attributed to illuviation of clay (argilluviation).

Sand dominated the particle size fraction of the fine earth (< 2 mm) portion in all the soils formed from the different parent materials (Table 1). This agrees with studies on soils formed on basement complex rocks in different regions of Nigeria (Malgwi et al., 2000; Odunze, 2006; Fasina et al., 2007; Obi and Akinbola, 2009; Ande, 2010). Total sand fraction of all the soils varied between 271 and 771 gkg^{-1} and variation in parent material did not significantly influence total sand content of the soils. The mean clay content in subsurface horizon was three times greater than the mean surface value (128.8 gkg^{-1}). The increase in clay with soil depth had been attributed to clay translocation and erosion in surface horizon (Kparmwang, 1993; Raji, 1995; Obi and Akinbola, 2009). The difference in parent materials did not significantly influence clay particle of the soils. The mean values of silt/ clay ratio of all the soils were higher than the 0.15 critical value considered to be highly or intensively weathered (Van Wambeke, 1962; Yakubu and Ojanuga, 2009), hence the soils were considered to be moderately weathered. Weathering intensity significantly increased in order of soils on MS < OG < QZ < MG (Table 1).

The soils chemical properties indicated strongly acid to neutral pH (H_2O) (5.30 - 6.90) and were within range reported on soils on basement complexes in different parts of Nigeria (Raji and Mohammed, 2000; Fasina et al., 2007; Law-Ogbomo and Nwachokor, 2010). The soils were rated low to high in CEC (NH_4OAc) with moderate base saturation and were classified as Alfisols (Soil Survey Staff, 2010). Parent materials significantly influenced forms of CECs and base saturation, with the least significant means in soils on MG indicating more leaching of exchangeable bases in soils on MG (Table 1). This may be attributed to high degree of weathering in soils on MG compared to the other soils as indicated by the Si/C ratio.

The soils were generally low in organic carbon (range 0.40 and 11.57 gkg^{-1}) and total nitrogen (range 0.18 and 0.70 gkg^{-1}). Available phosphorus varied between 1.40 and 35.00 mgkg^{-1} in content and rated low to high. The low content of organic carbon (OC), total nitrogen and available phosphorus in these soils were attributed to continuous cultivation, bush burning, high rate of mineralization, and crop removal without incorporating back to soils (Bowman et al., 1990; Raji, 1995; Odunze, 2006).

Mean values of OC, TN and AP contents of surface soils were significantly higher than subsoils ($P < 0.01$). This may be attributed to accumulation and decomposition of organic matter on surface horizon. Similar content and trend was reported by Esu et al. (1987) on soils on basement complexes. Total nitrogen and AP significantly correlated with OC ($r = 0.747^{***}$ and

Table 1. Range and means of selected physical and chemical properties of soils of the studied areas.

Parameter unit	Older granite		Quartzites		Mica- Schists		Migmatite-Gneisses	
	Range	Mean	Range	Mean	Range	Mean	Range	Mean
Sand g kg ⁻¹	271 – 651	482	371 – 771	547	398 – 691	515	271 – 771	511
Silt g kg ⁻¹	147 – 327	229	107 – 227	156	187 – 367	248	107 – 367	204
Clay g kg ⁻¹	122 – 442	289	82 – 462	298	102 – 329	237	109 – 449	311
Si/C -	0.44 – 2.30	0.97	0.27 – 2.77	0.82	0.69 – 3.60	1.25	0.39 – 2.50	0.79
pH(H ₂ O) -	5.49 – 6.29	5.83	5.78 – 6.27	6.02	5.84 – 6.44	6.09	5.30 – 6.90	6.05
pH(CaCl ₂) -	4.90 – 5.80	5.19	4.77 – 5.51	5.25	4.76 – 5.93	5.30	4.60 – 5.66	5.26
TEB Cmol(+) ⁻¹ kg	3.27 – 7.60	5.94	3.70 – 6.72	5.52	3.05 - 10.42	6.25	2.92 – 5.41	4.20
EA “	0.6 -1.0	0.76	0.3 – 1.2	0.72	0.3 – 0.8	0.47	0.3 – 1.2	0.69
CEC (OAc) “	5.6 – 9.9	7.90	4.8 – 15.3	8.97	5.4 – 14.3	8.33	5.4 – 7.9	6.46
Base Sat. %	39.4 – 86.2	75.2	26.9 – 89.9	65.6	47.8 – 95.4	73.1	44.2 – 91.7	66.2
OC g kg ⁻¹	1.20 -8.78	5.66	0.40 – 11.57	4.56	0.80 – 7.98	3.51	0.60 – 7.78	3.37
TN g kg ⁻¹	0.18 – 0.70	0.37	0.18 – 1.05	0.37	0.18 – 0.70	0.37	0.18 – 0.70	0.45
AP mg kg ⁻¹	1.75 – 21.00	12.89	1.75 – 15.75	6.44	1.40 – 8.75	4.07	3.50 – 35.00	9.92

0.347*), thus implies that organic matter is a main reservoir of TN and AP.

Forms of iron and manganese oxides

The content of total free iron oxide (Fe_d) varied between 5.71 and 34.86 gkg⁻¹ (Table 2) with mean values of 17.48, 17.66, 21.30 and 22.95 gkg⁻¹ (Table 3) were obtained in the respective soils on older granites, quartzites, mica schists and migmatite gneisses. Parent materials significantly influenced the distribution of Fe_d. Mean values of Fe_d in soils on MG and MS were statistically similar, however significantly higher content of Fe_d was obtained in soils on MG compared to those on QZ and OG (Table 3). These higher values of Fe_d may be attributed to higher amount of ferromagnesian minerals in these soils (MG and MS). Udo (1980) observed that parent material influenced relative distribution of free iron oxides.

Total free iron oxide values were significantly higher in subsoil than the surface horizons, and was attributed to co-translocation of Fe with clay through eluviation - illuviation processes (Blume and Schwertmann, 1969; Juo et al., 1974; Agbenin, 2003; Jelic et al., 2011). The significant correlation between Fe_d and clay ($r = 0.617^{***}$) further buttressed the co-migration of Fe and clay. All the soils on the different parent materials increased in Fe_d content with increase in depth of soil. The highest values (31.00 to 34.86 gkg⁻¹) were recorded within plinthite horizons (Bt_{cv}) of soils on migmatite gneiss. The values of Fe_d were higher than those reported by Ibia (2002) and Essoka et al. (2007), but lower than values reported in lateritic basaltic soils (Kpamwang, 1993). The variation was attributed to the poor drainage in soils studied by Ibia (2002) and Essoka et al. (2007), and good drainage condition with higher Fe content in lateritic basalts studied by Kpamwang (1993). Citrate-bicarbonate-dithionite

extractable manganese oxide (Mn_d) in the soils varied between 0.41 and 4.07 gkg⁻¹, with mean values of 0.70, 0.92, 0.81 and 1.43 gkg⁻¹ respectively in soils on older granites, quartzites, mica schists and migmatite gneisses. There was no significant difference in the mean values of soils formed on the different parent materials, but mean values ranked in the order of OG < MS < QZ < MG. All the soils increased in Mn_d content with increase in depth of soil, but decreased in the lowest horizon of soils on QZ, MG and MS. The mean value of Mn_d in subsurface horizon was significantly higher than the surface soil (Table 4). The relative accumulation of Mn_d in the subsurface (Bt) horizons was attributed to eluviation-illuviation processes, and probably related to release of Mn oxides from silicates (Blume and Schwertmann, 1969; Nahon et al., 1989). The illuviation and accumulation of total free manganese oxide in subsurface horizons may be significantly influenced by clay content.

Table 2. Iron and manganese oxides, active ratios and crystallinity index of soils of the studied areas.

Pedon	Basal depth (cm)	Fe_d	Fe_{ox}	Fe_p	Mn_d	Mn_{ox}	Mn_p	Fe_t	Cl	Fe_{ox/d}	Mn_{ox/d}	Clay/Fe_d
gkg⁻¹%												
Soils on Older Granites												
Pedon OG 1												
Ap	26	7.14	1.43	3.43	0.41	0.10	0.12	2.90	0.20	0.20	0.25	17.09
Bt1	75	14.29	2.14	3.43	0.41	0.05	0.06	5.98	0.20	0.15	0.12	29.53
Bt2	119	11.40	4.29	1.72	0.61	0.05	0.06	9.96	0.13	0.25	0.08	16.45
BC	183	17.14	3.57	1.72	0.61	0.15	0.12	3.98	0.34	0.21	0.25	14.12
Pedon OG 2												
Ap	17	8.00	2.86	2.57	0.61	0.10	0.18	2.98	0.17	0.36	0.17	20.25
Bt	70	17.14	2.86	2.57	0.81	0.05	0.12	3.98	0.36	0.17	0.06	23.45
Btc	190	28.57	3.57	3.43	1.22	0.10	0.06	7.97	0.31	0.13	0.08	8.47
Pedon OG 3												
Ap	23	8.57	2.86	2.57	0.41	0.05	0.06	7.97	0.07	0.33	0.12	16.57
Bt	57	22.86	5.00	2.57	0.81	0.05	0.06	9.96	0.18	0.22	0.06	14.96
Btc1	121	28.57	5.71	3.43	1.02	0.10	0.12	11.95	0.19	0.20	0.10	13.37
Btc2	160	22.86	4.29	1.72	0.81	0.05	0.06	9.96	0.19	0.19	0.06	19.34
Soils on Quartzites												
Pedon QZ 1												
Ap	14	5.71	2.14	3.43	0.81	0.10	0.12	1.99	0.18	0.38	0.13	14.36
AC	40	7.14	2.86	4.28	1.02	0.05	0.12	3.98	0.48	0.40	0.05	19.89
C1	98	14.29	4.29	4.28	1.63	0.15	0.06	2.90	0.29	0.30	0.09	29.53
C2	135	22.86	5.00	1.72	0/81	0.10	0.06	1.99	0.24	0.22	0.13	14.09
Pedon QZ 2												
Ap	19	5.86	2.14	1.72	1.02	0.15	0.10	5.98	0.18	0.37	0.15	13.99
Bt1	51	25.71	3.57	0.86	1.22	0.20	0.24	3.98	0.54	0.14	0.17	14.08
Bt2	84	20.00	4.29	3.43	0.81	0.10	0.18	7.97	0.11	0.22	0.13	23.10
Bt3	139	17.14	3.57	2.57	1.22	0.10	0.12	9.96	0.35	0.21	0.08	22.29
Btcv	187	28.57	4.29	2.57	0.61	0.10	0.12	5.98	0.90	0.15	0.17	11.97
Pedon QZ 3												
Ap	19	5.71	2.14	4.28	0.61	0.10	0.12	1.99	0.06	0.38	0.17	17.86
AB	40	22.86	3.57	2.57	0.61	0.31	0.36	3.98	0.56	0.16	0.50	8.84

Table 2. Contd.

Bt1	63	25.71	2.86	2.57	1.02	0.15	0.18	7.97	0.20	0.11	0.15	16.41
Bt2	97	20.00	5.71	3.43	0.81	0.05	0.06	5.98	0.14	0.29	0.06	23.10
BC	167	25.71	2.86	2.57	0.61	0.10	0.06	3.98	0.41	0.17	0.17	14.86
Soils on Mica Schists												
Pedon MS 1												
Ap	18	12.86	6.43	2.57	0.41	0.10	0.18	1.99	0.22	0.50	0.25	12.60
Bt	54	28.57	5.71	5.14	0.61	0.05	0.12	7.97	0.19	0.20	0.08	10.57
Btc	177	22.86	4.29	3.43	1.02	0.15	0.06	5.98	0.24	0.19	0.15	13.21
Pedon MS 2												
Ap	16	17.14	5.71	3.43	0.81	0.15	0.18	3.98	0.32	0.33	0.19	7.12
Bt	37	22.86	4.29	1.72	0.81	0.10	0.18	3.98	0.26	0.19	0.13	12.34
BC	72	25.71	5.71	3.43	1.22	0.15	0.12	5.98	0.29	0.22	0.13	12.52
C	143	28.57	3.57	3.43	1.02	0.10	0.12	3.98	0.31	0.13	0.10	11.52
Pedon MS 3												
Ap	19	12.86	6.43	0.86	0.61	0.10	0.18	2.90	0.29	0.50	0.17	7.93
Bt1	42	17.14	5.71	1.72	0.81	0.15	0.12	5.98	0.47	0.33	0.19	14.12
Bt2	96	25.71	6.43	4.28	1.02	0.05	0.06	7.97	0.34	0.25	0.05	8.63
BC	168	20.00	4.29	3.43	0.61	1.02	0.12	5.98	0.63	0.21	0.17	11.10
Soils on Migmatite Gneisses												
Pedon MG 1												
Ap	15	12.86	3.57	4.28	0.61	0.05	0.18	5.98	0.16	0.28	0.08	11.59
Bt	47	25.71	4.29	4.28	1.02	0.10	0.12	3.98	0.54	0.17	0.10	12.80
Btcv1	103	31.00	2.86	5.14	1.43	0.05	0.12	3.98	0.71	0.09	0.04	11.90
Btcv2	147	27.24	2.86	1.72	0.81	0.10	0.06	3.98	0.61	0.11	0.13	10.61
Pedon MG 2												
Ap	18	20.00	2.86	2.57	0.61	0.10	0.24	3.98	0.43	0.14	0.17	5.45
AB	44	22.86	2.14	1.72	0.81	0.10	0.18	5.98	0.38	0.09	0.13	15.27
Bt1	78	14.29	2.14	1.72	1.02	0.15	0.18	5.98	0.20	0.15	0.15	30.02
Bt2	123	31.43	2.14	5.14	4.07	0.15	0.12	7.97	0.37	0.07	0.04	12.38
BCcv	167	17.14	4.29	1.72	1.02	0.10	0.12	3.98	0.32	0.25	0.10	16.86
Pedon MG 3												
Ap	25	13.86	2.14	2.57	1.02	0.05	0.31	2.90	0.40	0.15	0.05	15.08
Bt1	47	20.00	2.14	4.28	0.61	0.15	0.12	3.98	0.45	0.11	0.25	17.45
Bt2	89	34.86	2.86	2.57	4.07	0.26	0.12	5.98	0.54	0.08	0.06	12.88
BCcv	162	27.14	1.43	3.43	1.43	0.05	0.06	7.97	0.32	0.05	0.04	12.12

Table 3. Ranking of means of iron and manganese oxides of parent materials.

Parameter	Unit	Older	Quartzite	Mica	Migmatite	SE±	LOS
		Granites		Schist	Gneiss		
Fe _d	gkg ⁻¹	17.48 ^b	17.66 ^b	21.30 ^{ab}	22.95 ^a	0.15	*
Fe _{ox}	gkg ⁻¹	3.51 ^b	3.62 ^b	5.32 ^a	2.75 ^c	0.03	***
Fe _p	gkg ⁻¹	2.65	2.87	3.04	3.16	0.46	NS
Mn _d	gkg ⁻¹	0.70	0.92	0.81	1.43	0.42	NS
Mn _{ox}	gkg ⁻¹	0.07	0.13	0.11	0.11	0.39	NS
Mn _p	gkg ⁻¹	0.09	0.14	0.13	0.15	0.46	NS
Fe _t	%	6.29	4.33	4.47	4.83	0.73	NS
Cl	-	0.19	0.26	0.31	0.39	0.05	NS
Fe _{ox/d}	-	0.22 ^b	0.25 ^{ab}	0.28 ^a	0.13 ^c	0.01	**
Mn _{ox/d}	-	0.12	0.15	0.15	0.10	0.48	NS
Clay/Fe _d	-	17.60 ^a	17.46 ^a	11.06 ^b	14.19 ^b	0.55	*

LOS (P): NS (Not Significant) > 0.05, * ≤ 0.05, ** ≤ 0.01, *** ≤ 0.001. Means followed by the same letters in the same rows are not significantly different at 5% LOS.

The co-migration of Fe and clay was also indicated by the significant correlation between clay and Mn_d ($r = 0.398^{**}$). This is contrary to the findings of Agbenin (2003) that Mn movement and distribution in Savanna Alfisol was independent of clay movement and distribution.

Generally, the mean values of oxalate extractable and pyrophosphate extractable Fe and Mn were low (Table 2). The values of Fe_{ox} ranged between 1.43 and 6.43 gkg⁻¹ while pyrophosphate forms varied between 0.86 and 5.14 gkg⁻¹ in all the soils. For MnO₂, the values ranged from 0.05 to 0.31 gkg⁻¹ for oxalate extractable forms, and from 0.06 to 0.36 gkg⁻¹ for the pyrophosphate extractable forms. The generally low extractable values of the various forms of sesquioxides have been attributed to well drained condition of the soils which promote strong weathering and crystallization of sesquioxide Fe and Mn in these soils (Kparmwang, 1993; Hassan et al., 2004). Raji et al. (2000) attributed low values of pyrophosphate sesquioxides to low organic matter contents of the soils (< 20 gkg⁻¹). The values of Fe_{ox} were higher than those reported on the floodplains of Southeastern Nigeria (Ibia, 2002; Essoka et al., 2007). Ibia (2002) suggested that poor drainage condition of the floodplains prevent strong weathering and subsequent formation of sesquioxides in the soils. Oxalate forms of Mn were irregularly distributed in the soils and the values were within range reported on plinthitic landscape in Zaria, Nigeria by Yaro (2005).

Active iron and manganese oxides and clay /Dithionite iron ratio

The ratios of oxalate extractable Fe and Mn to dithionite extractable form which is a measure of the reactivity of sesquioxides indicates the pedogenic development (age) of the soils (Blume and Schwertmann, 1969; Dolui and Mustafi, 1997; Alamdari et al., 2010). The active

sesquioxide ratios varied between 0.05 and 0.50 for Fe and between 0.05 and 0.25 for Mn in the soils developed from the different parent materials (Table 2). The mean active ratio was only significantly different for Fe. The mean values of active Fe and Mn ratios showed similar trend of variation in the order of soils on MS < QZ < OG < MG (Table 3). The trend indicated the increasing degree of pedogenic development of the soils. The values of Fe_{ox/d} were less than 0.5 indicating high degree of weathering as rated by Alexander (1974). Active sesquioxide (Fe and Mn) ratios decreased with increase in depth of soils and mean value of surface soil was significantly greater than subsoil (Table 4), thus implies that pedogenic development occurred more in subsoil compared to surface soil (Lekwa and Whiteside, 1986; Durn et al., 2001; Yaro, 2005; Samndi et al., 2006).

Iron crystallinity index defined as (Fe_d - Fe_{ox})/Fe_t have been used as a pedogenetic criteria to grade Fe crystallization and classification of soils (Nagatsuka, 1975; Durn et al., 2001; Kurihara et al., 2002). Sesquioxides crystallization progresses by pedogenesis with the alternation of dryness and wetness of soils (Blume and Schwertmann, 1969; Schwertmann and Taylor, 1989; Ibia, 2002; Kurihara et al., 2002; Alamdari et al., 2010). The crystallinity index for the soils ranged between 0.072 and 0.897 (Table 2). The values of CI generally increased irregularly with increase in soil depth and the higher values were observed in the plinthitic subsurface horizons. The mean value of CI was significantly higher in the subsoil compared to the surface horizons (Table 4). This affirms previous reports that crystallization and pedogenetic development is more pronounce in subsoil than surface soils (Lekwa and Whiteside, 1986; Yaro, 2005; Samndi et al., 2006) and organic matter inhibits Fe oxide crystallization in surface soils compared to subsoils (Blume and Schwertmann, 1969; Yaro, 2005; Samndi et al., 2006). This is further

Table 4. Ranking of means of iron and manganese oxides of horizons.

Parameter	Unit	Surface	Subsurface	SE±	LOS
		Horizon	Horizon		
Fe _d	gkg ⁻¹	10.88 ^b	22.75 ^a	0.18	**
Fe _{ox}	gkg ⁻¹	3.39	3.86	0.03	NS
Fe _p	gkg ⁻¹	2.86	2.97	0.04	NS
Mn _d	gkg ⁻¹	0.66 ^b	1.06 ^a	0.02	**
Mn _{ox}	gkg ⁻¹	0.10	0.11	0.00	NS
Mn _p	gkg ⁻¹	0.17 ^a	0.12 ^b	0.00	**
Fe _t	%	3.80 ^b	6.16 ^a	0.73	**
Cl	-	0.22 ^b	0.35 ^a	0.05	*
Fe _{ox/d}	-	0.33 ^a	0.18 ^b	0.02	***
Mn _{ox/d}	-	0.16 ^a	0.12 ^b	0.03	*
Clay/Fe _d	-	13.32	15.79	0.75	NS

LOS (P):NS (Not Significant) > 0.05, * ≤ 0.05, ** ≤ 0.01, Means followed by the same letters in the same rows are not significantly different at 5% LOS.

buttressed by the significant negative correlation between Cl and organic carbon ($r = -0.436^*$). The mean values of Cl were not significantly different but varied in the order of soils on OG < QZ < MS < MG. The highest mean value of Cl in soils on MG may be associated to the high content of ferromagnesian minerals and to more pedogenetic development of the soil. Similarly Fe crystallization have reported to be associated with parent materials and pedogenetic age of soils (Kurihara et al., 2002; Alamdari et al., 2010). The highly significant correlation between Cl and Fe_{ox/d} ($r = 0.507^{**}$) further indicated that as pedogenetic development increases, sesquioxides crystallization increases in soils.

Clay / dithionite iron ratio in the soils ranged between 5.45 and 29.53. Clay/ dithionite ratio for soils on QZ and MS were irregularly distributed in their profiles, whereas, clay/ dithionite ratio for soils on OG and MG decreased regularly with depth in some portion of their profiles except for Pedon MG 2 which had an irregular distribution. This indicates that with advancement in pedogenetic development in these soils, independent migration of clay and Fe_d (QZ and MS) shift towards partial co-migration (OG and MG) (Juo et al., 1974). The mean of clay/ dithionite Fe ratios of surface and subsoil were not significantly different. This indicates that there was partial co migration between clay and iron in these soils and more clay seems to be illuviated into the subsoil than Fe oxide. Similarly, the strong bearing of clay on the distribution of forms of Fe have been reported by Sharma et al. (2000), Alamdari et al. (2010) and Jelic et al. (2011).

Conclusion

The study of forms and content of sesquioxides shows

that variation in parent materials and pedogenetic processes significantly influenced mean values of dithionite, oxalate forms of iron and active iron ratio in these soils. Active sesquioxides (Fe and Mn) ratios varied in the order of soils on MS > QZ > OG > MG suggesting that the soils pedogenetic development was lowest in soils on mica schist and highest in soils on migmatite gneiss. Increase in pedogenetic development increased sesquioxides crystallization and was indicated by the highly significant correlation between active Fe ratio and iron crystallinity index ($r = -0.507^{**}$). The study showed that clay significantly influenced movement and distributions of the sesquioxides through the soil profiles. Crystallization occurred more in subsoil compared to surface soil horizons as the mean crystallinity index was significantly greater in subsoil (0.35) compared to the surface horizon (0.22) and was attributed to inhibitory effect of soil organic matter on crystallization. Forms of manganese oxides were significantly influenced by horizons, thus affirming effect of organic matter on manganese content in soils.

Conflict of Interest

The authors have not declared any conflict of interest.

REFERENCES

- Agbenin JO (2003). The distribution and transformation of iron and manganese in soil fractions in a Savanna Alfisol under continuous cultivation. *Nutr. Cycl. Agroecosyst.* 66:259-270.
- Alexander EB (1974). Extractable iron in relation to soil ash on Terraces along the Truckee River. *Soil Sci. Soc. Am. Proceed.* 38:121-124.
- Alamdari P, Jafarzadeh AA, Oustan S, Toomanian N (2010). Iron oxide forms and distribution in a transect of Dasht-e-Tabriz soils,

- Northwest Iran. *J. Food, Agric. Environ.* 8(3-4):976-979.
- Ande OT (2010). Morphogenetic characterization of soils formed from basement complex rock in the humid tropical rainforest of Nigeria. *J. Soil Sci. Environ. Manage.* 1(6):122-126.
- Blume HP, Schwertmann U (1969). Genetic evaluation of profile distribution of Aluminium, Iron and Manganese oxides. *Soil Sci. Soc. Am. J.* 33:438-444.
- Bowman RA Reeder JD, Lober RW (1990). Changes in soil properties in a central plain rangeland soil after 3, 20 and 60 years of cultivation. *Soil Sci.* 150:851-857.
- Bremner JM, Mulvaney CS (1982). Nitrogen-Total. In Page AL, Miller RH and Keeney DR (eds). *Methods of Soil Analysis. Part 2 Agron 9.* Madison WI. pp. 595-624.
- Dolui AK, Mustafi SC (1997). Forms of extractable Iron in relation to soil characteristics of some Alfisols. *J. Indian Soil Sci. Soc.* 45:192-194.
- Duiker SW, Rhoton FE, Torrent J, Smeck NE, Lal R (2003). Iron (hydro) oxide crystallinity effects on soil aggregation. *Soil Sci. Soc. Am. J.* 67:606-611.
- Durn G, Slovenec D, Covic M (2001). Distribution of iron and manganese in Terra Rossa from Istria and its genetic implications. *Geologia Croatica* 54(1):27-36.
- Essoka AN, Esu EI (2003). Profile distribution of sesquioxides in the inland valley soils of Central Cross River State, Nigeria. *Nig. J. Soil Res.* 4:41-49.
- Essoka PA, Jayeoba IA, Essoka AN (2007). A toposequence study of soils developed on gneiss and granodiorite and on the Cross River Rainforest zone. In Uyovbisere EO, Raji BA, Yusuf AA, Ogunwale JO, Aliyu L and Ojeniyi SO (ed). (2007). *Soil and Water Management for Poverty Alleviation and Sustainable Environment. Proceedings of the 31st Annual Conference of the Soil Science Society of Nigeria held at Ahmadu Bello University Zaria, Nigeria. Nov. 13-17, 2006, pp. 43-51.*
- Esu IE, Ibangi IJ, Ojanuga AG (1987). Soil-landscape relationships in Keffi plains of northern Nigeria. *Sam. J. Agric. Res.* 5(1&2):109-123.
- Fasina AS, Omolayo OS, Faladun AA, Ajayi OS (2007). Granitic derived soils in humid forest of southwestern Nigeria. Genesis, classification and sustainable management. *American-Eurasian J. Agric. Environ. Sci.* 2(2):189-195.
- Gee GW, Bauder JW (1986). Particle size analysis. In Klute A (eds). *Methods of soil analysis, Part 1: Physical and Mineralogical methods.* 2nd Ed. ASA, SSSA. Madison, WI. pp. 320-376.
- Hassan AM, Singh BR, Alkali M (2004). Profile distribution of sesquioxides in a granitic soil in Bauchi Nigeria. *Proceedings of the 29th Annual Conference of the Soil Science Society of Nigeria, December 6-10, 2004, pp. 93-96.*
- Ibia TO (2002). Forms of Fe and Al in soil profiles of inland flood plains of South Eastern Nigeria. *Nig. J. Soil Res.* 3:72-77.
- Idoga S, Ibangi IJ, Malgwi WB (2007). Variation in soil morphological and physical properties and their management implication on a toposequence in Samaru area, Nigeria. In Uyovbisere EO, Raji BA, Yusuf AA, Ogunwale JO, Aliyu L and Ojeniyi SO (ed) (2007). *Soil and Water Management for Poverty Alleviation and Sustainable Environment. Proceedings of the 31th Annual Conference of the Soil Science Society of Nigeria held at Ahmadu Bello University Zaria, Nigeria. Nov. 13-17, 2006, pp. 19-26.*
- Igwe CA (2001). Free oxide distribution in Niger flood plain soils in relation to their total and available phosphorus. *Proceed. Soil Sci. Soc. Nig.* pp. 196-201.
- IITA (1979). Selected methods for soil and plant analysis. International Institute of Tropical Agriculture. Manual series pp. 1-70.
- Jelic MZ, Milivojevic JZ, Trifunovic SR, Dalovic IG, Milosev DS, Seremesic SI (2011). Distribution and forms of iron in the Vertisols of Serbia. *J. Serbian Chem. Soc.* 76(5):781-794.
- Juo ASR (1981). Chemical characteristics. In Greenland DJ *Characterisation of soils in relation to their classification and management for crop production.* Oxford University Press. NY USA, pp. 51-79.
- Juo ASR, Moormann FR, Maduakor HO (1974). Forms and pedogenic distribution of extractable iron and aluminium in selected soils of Nigeria. *Geoderma* 11:167-179.
- Kogbe CA (1976). *Geology of Nigeria.* Elizabethan Publishing Company. Nigeria, P. 436.
- Kparmwang TT (1993). Characterization and classification of Basaltic soils in the northern guinea savanna zone of Nigeria. Ph.D thesis (unpublished). Ahmadu Bello University Zaria, Nigeria. P. 176.
- Kurihara H, Kitagawa Y, Nagatsuka S (2002). Characteristics of free sesquioxides and humic acids in soil distributed under Warm-temperate forest climate in Nyu mountains, Fukui Prefecture, Central Japan. *Soil Sci. Plant Nutr.* 48(6):833-839.
- Law-Ogbomo KE, Nwachokor MA (2010). Variability in selected soil physico-chemical properties of five soils formed on different parent materials in Southeastern Nigeria. *Res. J. Agric. Biol. Sci.* 6(1):14-19.
- Lekwa G, Whiteside EP (1986). Coastal plain soils of Southeastern Nigeria: II. Forms of extractable iron, aluminium and phosphorus. *Soil Sci. Soc. Am. J.* 50:160-166.
- Malgwi WB, Ojanuga AG, Chude VO, Kparmwang T, Raji BA (2000). Morphological and physical properties of some soils at Samaru, Zaria, Nigeria. *Nig. J. Soil Environ. Res.* 1:58-64.
- McKeague IA (1967). An evaluation of 0.1M pyrophosphate-dithionite in comparison with oxalate as extractants. *Canad. J. Soil Sci.* 47:95-99.
- McKeague IA, Day JH (1966). Dithionite and oxalate extractable Fe and Al as aid in differentiating various classes of soils. *Can. J. Soil Sci.* 46:13-20.
- Mehra OP, Jackson ML (1960). Iron oxide removal from soils and clays by dithionite citrate system buffered with sodium bicarbonate. *Clays Clay Minerals* 7:317-327.
- Nagatsuka S (1975). Genesis and classification of Yellow-brown forest soils in Southwest Japan. *Bulletin Nat. Instit. Agric. Sci.* 26:133-257.
- Nahon DB, Herbillon AJ, Beauvais A (1989). The epigenetic replacement of kaolinite by lithiophorite in a manganese – laterite profile, Brazil. *Geoderma* 44:247-259.
- Nelson DW, Sommers LE (1982). Organic carbon. In Page AL, Miller RH and Keeney DR (eds). *Methods of Soil Analysis. Part 2 Agron 9.* Madison WI. pp. 538-580.
- Obi JC, Akinbola GE (2009). Texture contrast in some basement complex soils of southwestern Nigeria. In Fasina AS, Ayodele OJ, Salami AE and Ojeniyi SO (ed). (2007). *Management of Nigeria soil resources for enhanced agricultural productivity. Proceedings of the 33rd Annual Conference of the Soil Science Society of Nigeria held at University of Ado-Ekiti, Ado-Ekiti, Ekiti State, Nigeria. March 9-13, 2009, pp. 38-44.*
- Oduzue AC (2006). Soil properties and management strategies for some sub-humid savanna zone Alfisols in Kaduna State, Nigeria. *Sam. J. Agric. Res.* 22:3-14.
- Osher LJ, Buol SW (1998). Relationship of soil properties to parent materials and landscape position in Eastern Madre de Dios, Peru. *Geoderma* 83:143-166.
- Osodeke VE, Nwotiti IL, Nuga BO (2005). Sesquioxides distribution along a toposequence in Umudike area of Southeastern Nigeria. *Electr. J. Environ. Agric. Food Chem.* 4(6):1117-1124.
- Raji BA (1995). Pedogenesis of ancient dune soils in the Sokoto sedimentary basin, North Western Nigeria, unpublished. Ph.D thesis Ahmadu Bello University Zaria, Nigeria, P. 194.
- Raji BA, Mohammed K (2000). The nature of acidity in Nigerian savanna soils. *Sam. J. Agric. Res.* 16:15-24.
- Raji BA, Esu EI, Chude VO (2000). Status and profile distribution of free oxides in Haplustults and Quartzipsamments developed on ancient dunes in NW Nigeria. *Sam. J. Agric. Res.* 16:41-51.
- Rhoades JD (1982). Cation exchange capacity. In Page AL, Miller RH and Keeney DR (eds). *Methods of Soil Analysis. Part 2 Agron 9.* Madison WI, pp. 149-157.
- Samndi MA, Raji BA, Kparmwang T (2006). Long-term effects of fast-growing tree species (*Tectona grandis* Linn. F.) on the distribution of pedogenic forms of iron and aluminium in some soils of Southern Guinea Savanna of Nigeria. *Savan. J. Agric.* 1(1):39-45.
- Schwertmann U, Taylor RM (1989). Iron oxides. In Dixon JB et al., (eds). *Minerals in Soil Environments.* ASA, Madison, USA. pp. 379-438.
- Sharma BD, Mukhopadhyay SS, Sidhu PS, Katyal JC (2000). Pedospheric attributes in distribution of total and DTPA extractable Zn, Cu, Mn and Fe in Indo-Giangatic Plains. *Geoderma* 96:131-151.
- Soil Survey Division Staff (1993). *Soil Survey Manual. Agric. Handbook.* No 18. U.S. Gov. Print. Office. Washington, DC.
- Soil Survey Staff (2010). *Soil Taxonomy. A basic system of soil*

- classification for making and interpreting soil surveys. 2nd Edition. Agric. Handbook. P. 436. U.S. Gov. Print., Office. Washington, DC.
- SPSS. Statistical Package for Social Sciences. SPSS Statistics 17.0. (<http://www.spss.com>).
- Thomas GW (1982). Exchangeable cations. In Page AL, Miller RH and Keeney DR (eds). Methods of Soil Analysis. Part 2 Agron 9. Madison WI. pp. 159-165.
- Udo EJ (1980). Profile distribution of iron sesquioxide contents in selected Nigerian soils. J. Agric. Sci. 95:191-198.
- USDA NRCS (United States Department of Agriculture, Natural Resources Conservation Service), (2004). Soil survey laboratory methods manual, Burt, R. (ed.). Soil Survey Laboratory Lincoln, Nebraska. Soil Survey Investigation Report No. 42 version 4.0 November 2004, P. 735.
- Van Wambeke AR (1962). Criteria for classifying tropical soils by age. J. Soil Sci. 13:124-132.
- Yakubu M, Ojanuga AG (2009). Pedogenesis, weathering status and mineralogy of the soils on ironstone plateau (laterites), Sokoto, Nigeria. In Fasina AS, Ayodele OJ, Salami AE and Ojeniyi SO (ed). (2009). Management of Nigeria soil resources for enhanced agricultural productivity. Proceedings of the 33rd Annual Conference of the Soil Science Society of Nigeria held at University of Ado-Ekiti, Ado-Ekiti, Ekiti State, Nigeria. March 9-13, 2009, pp. 26-37.
- Yaro DT (2005). The position of plinthite in a landscape and its effects on soil properties. Ph.D thesis (unpublished). Ahmadu Bello University, Zaria. Nigeria. P. 225.