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Sesquioxide characterization of some pedons derived from the basement complex parent material of Northwest Nigeria

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Abstract

Content of organically bound pyrophosphate extractable iron (Fe_p), amorphous form of iron oxide (Fe_{ox}) and total free iron oxide (Fe_d) were studied in five different soil individuals (namely: SI1, SI2, SI3, SI4 and SI5) developed on the basement complex to evaluate their pedogenic characteristics. Their values obtained were subjected to statistical analysis to ascertain differences and correlation among the soil individuals. Content of Fe_p progressively decreased in concentration down the profile in all the soils (except pedons SI2P1 – BCt horizon and SI3P1 - Bg_2 horizon) and was generally observed to be in the lowest proportion the three forms of iron examined. The percent mean values of Fe_p content of the surface soils (e.g. SI1 = 0.36 %) were higher than those recorded for the subsurface soils (e.g. SI1 = 0.24 %); the Fe_p correlated negatively with clay (r = -0.01467) and silt (r = -0.03224) and correlated positively with sand (r = 0.03592). The Fe_{ox} contents were generally higher (by 0.64 % and above) than those reported for Fe_p among the soil individuals. The significant difference (P < 0.05) between percentages of Fe_p and those of Fe_{ox} (Fe_p negatively correlated with Fe_{ox}, r = -0.48628**) and Fe_d (Fe_p negatively correlated with Fe_d, r = -0.08477) surmised a shift towards inorganic, pedogenic phases, at the expense of organically bound phase. Contents of Fe_d distribution pattern in the soil individuals generally showed an increase in content with pedal depth. The mean ratio of oxalate to dithionite sequence (SI2<SI3<SI1<SI4<SI5) indicate that SI5 had the highest amount of poorly ordered iron compounds than in crystalline showing the direction of pedogenic age of the soils. Clay/Fe_d ratios indicate that the soils had accumulated appreciable clay content with reduced surface area as the crystallization of iron oxide is significantly high in the basement complex soils.

1.0 Introduction

Iron primarily originates from chemical weathering of parent materials. The majority of iron deposits are formed in rocks beneath the earth's surface (Adiele *et al*., 2015). Iron is a significant constituent of the lithosphere and occurs in several mineralogical forms as discrete particles or associated with other minerals' surfaces (Maniyunda *et al*., 2014). Another source of iron-rich soil is magma flow from erupted volcanoes (Gao *et al*., 2008). Iron exists in different forms, and the nature and amount of various forms of iron depend on soil texture, pH, organic matter content and other soil characteristics (Jiang *et al*., 2009; Adiele *et al*., 2015).

Oxides of iron are variable in structure, composition and degree of crystallinity. The forms in which they exist depend substantially on physical soil conditions and the forms and transformations of soil organic matter. Even at low concentrations, iron oxides within soils have high pigmenting power and determine the colour of soils under well-drained condition. This colour and distribution of iron oxides within a profile help explain soil genesis and are used widely in soil classification (Sherwan, 2010).

Different forms of iron oxide [i.e. total free iron oxides or citrate–bicarbonate–dithionite (CBD) extractable iron (Fe_d), the organically bound pyrophosphate extractable iron (Fe_p) and the amorphous forms of iron oxide, (oxalate extractable iron – Fe_{ox})] crystallize as they age (Schwertmann, 1964). The ratio of oxalate extractable Fe to dithionite extractable forms, which is a measure of the reactivity of the sesquioxide (Blume and Schwertmann, 1969), has also been used to evaluate soil development weathering (Omenihu *et al.,* 1994). Similarly, percentages of iron oxides have also been used as aids in distinguishing

soil types, differentiating soil horizons and determining soil age or degree of soil development (Akinbola *et al.*, 2013). Although sesquioxides studies have already been advanced; however, they still need further consideration to understand better the dynamics of soil development on the basement complex soils, especially agricultural practices.

2.0. Materials and Methods

2.1. Study site

The study area lies between $11°25'N$ to $11°34'N$ and $7°16'E$ to $7°22'E$, located in Funtua, Funtua Local Government Area (LGA) of Katsina State, Nigeria. Faskari LGA borders it to the north, Bakori and Danja LGAs to the east

and Dandume LGA to the west (Fig. 1). The area has land coverage of 10,000 ha. The study area is underlain by crystalline rocks of the basement complex, (Katsina Diary, 1989). It has three geological formation types: the migmatite, granite gneiss and undifferentiated schist (Shobayo *et al.*, 2019). The undifferentiated schist has a limited occurrence. The study area's climate is tropical and typical of that of the northern guinea savanna of Nigeria. It is characterized by a long dry season and a shorter but very conspicuous wet season (Fig. 2). It has total annual rainfall figures ranging from 1000 mm to over 800 mm (Abaje *et al.*, 2016). The mean monthly maximum range of temperature was between 35.40 and 28.70 °C; while the minimum range between 16.89 °C and 32.70 °C (Fig. 2).
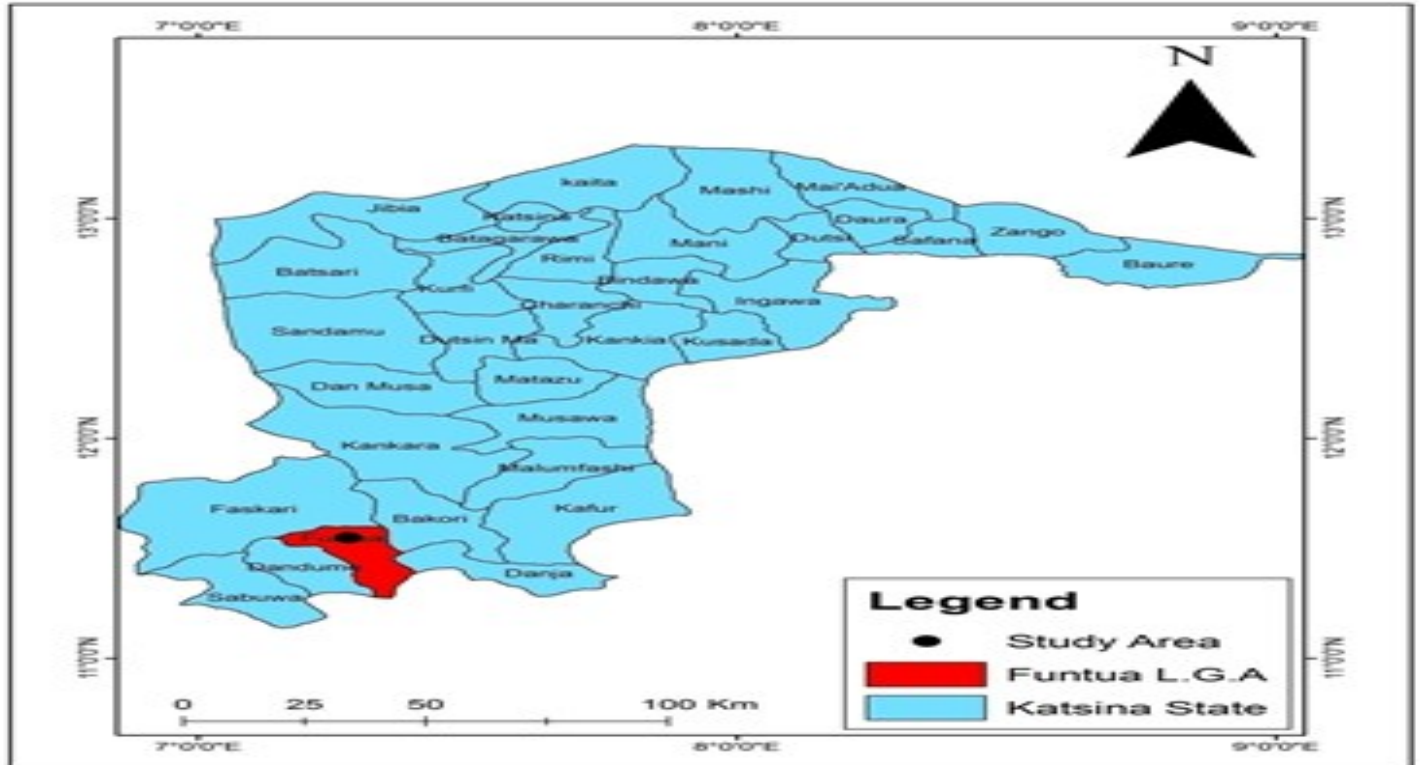

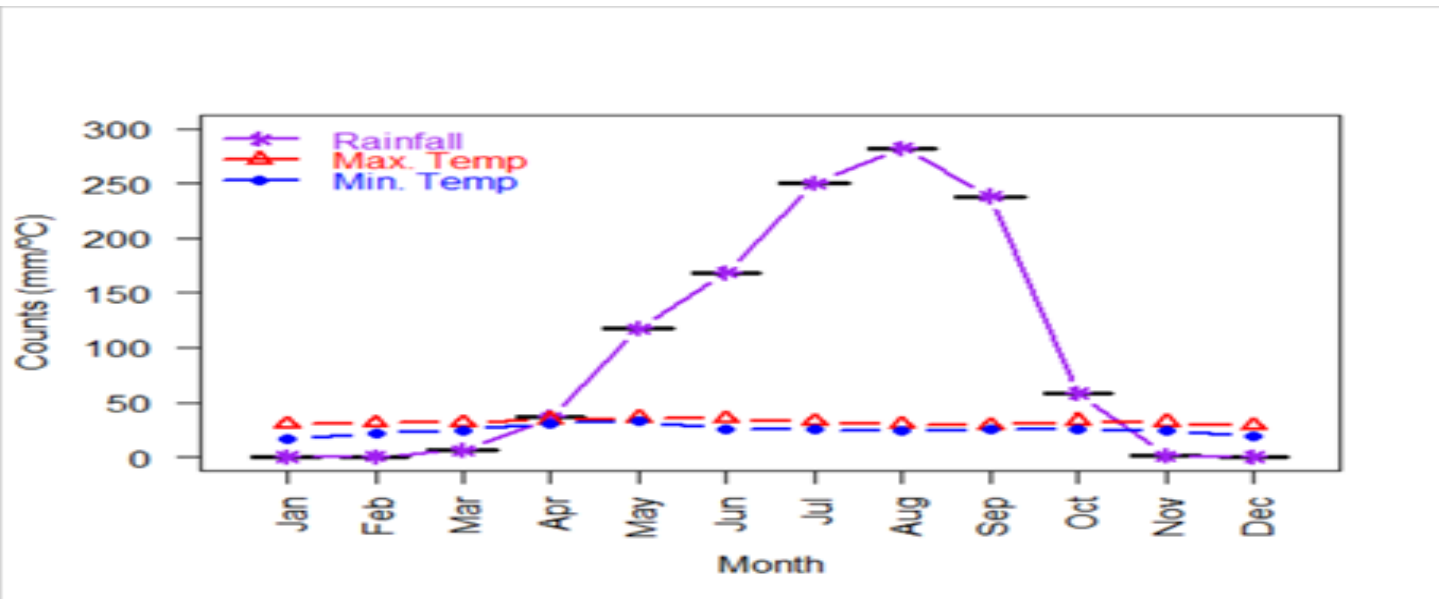Fig. 1: Location map of the study area

Fig. 1: Climatic data of the study area

2.2. Method of sample collection

A GPS assisted detailed soil survey was carried out in the study area, according to the Soil Science Division Staff (2017). Afterwards, five soil individuals, namely: SI1, SI2, SI3, SI4 and SI5, were identified. The soil individuals' concept was based on soils that shared similar morphological, topographical and physical characteristics of depth, drainage, the colour of soil matrix and mottles, texture and structure identified. Two soil profile pits were dug on each soil individual, described and sampled from the genetic horizon. Soil samples were air-dried in the laboratory, crushed with porcelain pestle and mortar and sieved to remove materials greater than 2 mm (gravel). The less than 2 mm of soil separates were subjected to laboratory analysis.

2.3. Laboratory analyses

Bulk density was determined by the method described by Blake and Hartge (1986). The particle size distribution of soils was determined by the hydrometer method described by Gee and Or (2002). Soil reaction (pH) was determined in water in a 1:2.5 soil solution ratio, using a Pye Unicam model 290 MK pH meter. The acid dichromate wet oxidation method of Walkley and Black as described by Nelson and Sommers (1986) was used to determine organic carbon. Total nitrogen was determined by the regular Macro Kjeldahl method (Bremmer and Mulvaney, 1982). Available phosphorus was determined by the Bray – 1 method (Bray and Kurtz, 1945). Exchangeable bases (Ca, Mg, K and Na) were determined by neutral (pH 7.0) ammonium acetate (NH_4OAc) solution as described by Anderson and Ingram (1993). Available cationic micronutrients were extracted with 0.1M HCl solution as described by IITA (1979). Base saturation was calculated by dividing the total exchangeable bases (Ca, Mg, K and Na) by the CEC obtained by the NH_4OAc procedure as follows:

% Base saturation = Total exchangeable bases/CEC ×100

McKeague (1967) method was used for the determination of the organic bound form of iron oxide in the soils. Two grams of the soil passed through a 250 μm sieve were transferred to a 500 cm3 bottle to which 200 ml 0.1M $Na_4P_2O_7$ solution was added through a pipette. This was closed and shaken overnight. Then 25 ml of the suspension was transferred to each of two 50 cm^3 centrifuge tubes and centrifuged. AAS determined the Fe content in the clear supernatant solution after dilution. The amorphous form of iron was extracted using the method of Schwertmann (1964). Approximately 0.5 g of soil was weighed into a 50 cm^3 centrifuge tube to which 25 cm^3 of acidified ammonium oxalate extraction solution was added. The tube was closed with a stopper and shaken in darkness for four hours. A portion of the extract was diluted and Fe content determined by the AAS.

Total free iron oxides in the soils were determined by Mehra and Jackson (1960). One gram of the 0.02 mm fraction of the soil sample was weighed into a 50 cm^3 plastic centrifuge tube to which 40 cm^3 of sodium citrate solution and 5 cm^3 of sodium bicarbonate solution were added. The tube with its content was heated on a water bath to 70 – 80 °C. One gram of sodium dithionite salt was added to the centrifuge tube's content, stirred continuously for 1 minute and occasionally for 15 minutes. The treatment with CBD was repeated till the reddish colour of the sample had dis-

appeared. The suspension was then centrifuged, and the extract decanted into a 200 cm^3 volumetric flask. The soil was washed twice with 40 cm^3 sodium citrate, centrifuged and the clear supernatant solution added to the extract in the 200 cm^3 volumetric flask. A portion of this extract was diluted and Fe content determined by the AAS.

Statistical Analysis

The data generated were analyzed statistically using the Student *t* test and was run by Statistical Analysis for Sciences (SAS) programme on the computer. The t-test results were used to compare the surface and subsurface horizons and between soil individuals. Data generated was also subjected to Pearson correlation analysis to determine the relationships between parameters studied.

Results and Discussion

Three forms of iron oxides were examined in all the soil individuals (SI1, SI2, SI3, SI4 and SI5) (Table 1) identified in the study area. Content of organic bound pyrophosphate extractable iron (Fe_p) was found to vary between 0.31 and 0.41 (mean, 0.36), 0.48 and 0.50 (mean, 0.49), 0.62 and 0.68 (mean, 0.65), 0.32 and 0.38 (mean, 0.35), 0.32 and 0.47 (mean, 0.40) % in the surface horizons of SI1, SI2, SI3, SI4 and SI5 respectively. The corresponding subsoil horizon values varied between 0.22 and 0.29 (mean, 0.24), 0.31 and 0.46 (mean, 0.38), 0.24 and 0.45 (mean, 0.33), 0.19 and 0.19 (mean, 0.19), 0.10 and 0.35 (mean, 0.25) %.

Content of Fe_p progressively decreased in concentration down the profile in all the soil individuals (except pedons SI2P1 – BCt horizon and SI3P1 - Bg_2 horizon) and was generally observed to be in the lowest proportion the three forms of iron studied (Table 1). This observation is suggestive of the Fe_p constituting a very small fraction of the free iron oxides. This occurrence may be attributed to the study area's sparse vegetative nature (Northern Guinea Savanna). The relatively higher value observed in SI3 (surface soils) compared to other soil individuals could be attributed to the reductimorphic property of the soil matrix; which implies that drainage and moisture regime of soils influences Fe_p formation, translocation and accumulation processes (Juo *et al.,* 1974; Udo, 1980; Maniyunda *et al.* 2014).

The percent mean values of Fe_p content of the surface soils were higher than those recorded for the subsurface soils; as buttressed by the Fe_p correlating negatively (Table 2) with clay (r = -0.01467) and silt (r = -0.03224) and correlated positively with sand (r = 0.03592) indicating decrease with increase in silt and clay content as the surface soils were highest in the sand. However, the differences were statistically not significant. Also, when mean values between soil individuals were compared, soil individuals did not vary significantly. Positive correlation values (Table 2) obtained between Fe_p with exchangeable calcium (r = 0.02043), potassium (r = 0.10563), sodium (r = 0.07578), organic carbon (r = 0.38349), total nitrogen (r = 0.23386), available phosphorus (r = 0.4171*) and microelements: copper (r = 0.15153*), manganese (r = 0.16805), zinc (r = 0.07872) and boron (r = 0.20185) implies crystallization will be inhibited by organo complexes dominating the surface soils.

The amorphous forms of iron oxide (oxalate extractable iron – Fe_{ox}) which crystallize as they age (Schwertmann, 1964) were examined in all the soil individuals and had their Fe_{ox} contents generally higher than those reported for Fe_p. This implies that an appreciable percentage of Fe's

oxides were in the amorphous form than in the organically complexed form. Content of amorphous forms of iron oxide (Fe_{ox}) was found to vary between 1.05 and 1.06 (mean, 1.06), 0.37 and 0.05 (mean, 0.21), 0.05 and 0.41 (mean, 0.23), 0.14 and 0.52 (mean, 0.33), 0.40 and 0.70 (mean, 0.55) % in the surface horizons of SI1, SI2, SI3, SI4 and SI5 respectively. The corresponding subsoil horizons values varied between 0.09 and 1.23 (mean, 0.96), 0.12 and 0.50 (mean, 0.29), 0.18 and 0.61 (mean, 0.39), 1.00 and 1.00 (mean, 1.00), 0.93 and 1.11 (mean, 1.03) %. Their values generally decreased with an increase in pedal depth (Table 1).

The significant difference (Table 2) between percentages of Fe_p and those of Fe_{ox} (Fe_p negatively correlated with Fe_{ox}, r = -0.48628**) and Fe_d (Fe_p negatively correlated with Fe_d, r = -0.08477) suggested a shift towards inorganic, pedogenic phases, at the expense of organically bound phase (Jersak et al., 1992). However, Seal et al. (2006) submitted that there is probably no precise differentiation between crystalline and non-crystalline material. Content of Fe_{ox} was lower than those of Fed in their corresponding horizons in soil individuals SI1, SI2 and SI3 and could be attributed to the well-developed soils subjected to continuous cultivation, which promoted soil Fed production and retarded the formation of Fe_{ox} (Chi et al., 2010). However, the content of Fe_{ox} was higher than those recorded for Fe_d in their corresponding horizons in SI4 and SI5 (Table 1). This could imply that Fe_{ox} in SI4 and SI5 were aged, crystallized and influenced petroplinthite formation in these soils.

The percent mean values of Fe_{ox} content of the surface soils were lower than those obtained at the subsurface soils (except soil individual SI1 soils), and the differences were not significant at 5 % level of probability. Percent mean values between soil individuals when compared showed the proportion of Fe_{ox} in SI1 to be significantly higher than that in soils of SI2 (p < 0.01) and SI3 (p < 0.05); and SI5 also varied significantly with SI2 (p < 0.05). Soils of SI2, SI3 and SI4 were statistically at par. The observed order SI2 < SI3 < SI4 < SI5 < SI1 implies the soil individuals' pedogenic advancement. The significantly positive correlation values obtained between Fe_{ox} with pH $CaCl_2$ (r = 0.37093*) implies that Fe_{ox} contributed more to the soil's acidity more at the colloidal fraction and its consequent inverse proportional distribution with base saturation (r = -0.10112) is suggestive of the amorphous form being low in inherent fertility and indicating the soils are in their advanced stage.

Total free iron oxide or citrate–bicarbonate–dithionite (CBD) extractable iron (Fe_d) was found to vary between 5.60 and 8.34 (mean, 6.97), 0.44 and 0.81 (mean, 0.63), 0.75 and 0.76 (mean, 0.76), 0.20 and 0.71 (mean, 0.45), 0.25 and 0.26 (mean, 0.25) % in the surface horizons of SI1, SI2, SI3, SI4 and SI5 respectively. The corresponding subsoil horizon values varied between 0.88 and 8.14 (mean, 3.26), 0.53 and 1.07 (mean, 0.73), 0.73 and 0.90 (mean, 0.83), 0.44 and 0.44 (mean, 0.44), 0.31 and 0.56 (mean, 0.40) % (Table 1). Proportion of Fe_d in the surface (Ap) horizons were found to be statistically similar (P > 0.05) to the subsoil horizons in all the soil individuals. However, proportion of Fe_d in SI1 was significantly higher (P < 0.001) than those of SI2, SI3, SI4 and SI5. There was no significant difference between the means of soil individuals SI2, SI3, SI4 and SI5, though the mean percentages varied in the decreasing order of SI3 (mean, 0.81 %) > SI2 (0.70 %) > SI4 (0.45 %) > SI5 (0.35 %).

Contents of the Fe_d were higher than those of the Fe_p and Fe_{ox} contents, implying that total free iron oxide constitutes the largest proportion of Fe's three forms of oxides. It indicates Fe present in the soil are free discrete bodies (i.e. crystalline) and not part of the structure of silicate minerals (Obi et al., 2009). However, Olatunji et al., (2015) opined that free discrete bodies collectively referred to as uncombined or pedogenic free forms of the element could either be mobile (amorphous) or immobile (crystalline). Its distribution pattern in all the soil individuals generally showed an increase in content with pedal depth. Its values were mostly highest in the B horizons (except SI4 and SI5) of the profiles, suggesting intense weathering or illuvial accumulation. Similar distribution pattern with clay and positive correlation (Table 2) with clay (r = 0.12732) and silt (r = 0.05542) fractions was noticed in most of the soil profiles, implying an association of Fe_d with finer fraction in the soils as buttressed by its negative correlation values obtained between Fe_d with sand (r = -0.13258, p > 0.05), bulk density (r = -0.12288, p > 0.05) and Fe_p (r = -0.08477, p > 0.05). Choudhari (1987) attributed this phenomenon to adsorption of electro-positively charged Fe ions released during weathering under the clay particles' oxidising environment. The significantly negative correlation values (Table 2) obtained between Fe_d with organic carbon (r = -0.47113**), total nitrogen (r = -0.28549*) and available phosphorus (r = -0.29232) may reflect inhibitory effect of soil organic matter on Fe oxide (Samndi et al., 2006).

However, higher mean values of Fe_{ox} were observed in the subsurface horizons of SI4 and SI5, and this could be a reflection of the corresponding horizon higher values of Fe_d recorded because Fe_d significantly correlated positively with Fe_{ox} (r = 0.44915*); implying the free iron oxides were more in the amorphous form (Olatunji et al., 2015) and consequently hardened and contributed significantly to the petroplinthic nature of the soil individuals. The highest value recorded was 8.34 % (SI1P1) followed by 8.14 % (SI1P2) implying that the soils were more developed than those of SI2, SI3, SI4 and SI5 as this was buttressed by their deep depth (Table 1). Several workers used these forms of Fe oxides to explain the ageing/development and crystalline characteristics of soils (Huang et al., 1977; Juo, 1981; Agbenin and Tiessen, 1995; Raji et al., 2000; Akinbola, 2001; Maniyuda et al., 2014).

The ratio of oxalate to dithionite – extractable Fe, commonly known as the active Fe ratio, is shown in Table 1. Lowest mean ratio (0.15) was observed in the most intense red coloured soils (SI1P2), implying that soils of this individual were pedogenically aged and exists mainly in the crystalline rather than the amorphous form as the value was less than 0.2 reported by Blume and Schwertmann (1969) as the limit for young soils. The mean ratio sequence (SI2<SI3<SI1<SI4<SI5) indicate that SI5 had the highest amount of poorly ordered iron compounds than in crystalline (Blume and Schwertmann, 1969). This sequence also indicates the direction of pedogenic age of the soils.

Soil individual SI1P1, SI2P2, SI3, SI4 and SI5 active Fe ratios were generally greater than 0.2; suggesting that the soils were pedogenically younger than SI1P2 and SI2P1. Soil individual SI5 (mean, 2.55) appeared to be the youngest compared to other individuals; however, the soil is in the advanced weathering stage. Individuals SI4 (mean, 0.89) and SI1P1 (mean, 0.66) recorded ratios greater than 0.5; a value of active iron ratio Maniyunda et al. (2014)

Table 1: Pyrophosphate (Fe_p), Oxalate (Fe_{ox}) and Dithionite (Fe_d) extractable iron oxides, active Fe/dithionite extractable and Clay/Fe_d ratios

Horizon	Depth (cm)	Fe_p	Fe_{ox} %	Fe_d	Clay/Fe_d	Fe_{ox}/Fe_d	Sand	Silt g Kg⁻¹	Clay	BD Mgm⁻³	pH CaCl₂	BS %	Ca	Mg	K cmol Kg⁻¹	Na	TN	OC g Kg⁻¹	AP	Cu	Mn mg Kg⁻¹	Zn	B
Soil Unit SI1 (Pedon P1) Location: Lat.: 11°32'40.9" Long.: 7°16'41.6" Altitude: 699m																							
Ap	0-9	0.41	1.05	8.34	2.88	0.13	480	280	240	1.36	5.36	60.72	3.71	0.19	0.17	0.12	0.28	9.58	1.05	0.36	0.47	0.75	0.21
BA	9-50	0.24	1.13	1.18	20.39	0.96	420	340	240	1.41	5.45	57.31	3.75	0.20	0.34	0.18	0.21	2.59	0.88	0.29	4.65	1.12	0.16
B	50-84	0.22	1.15	1.36	16.16	0.85	440	340	220	1.33	5.95	63.12	3.80	0.20	0.13	0.10	0.14	2.39	0.10	0.25	4.08	0.56	0.23
Bt	84-200	0.21	1.23	1.76	13.64	0.70	510	250	240		5.66	65.76	3.65	0.29	0.26	0.14	0.07	2.39	0.10	0.18	4.07	0.62	Trace
Soil Unit SI1 (Pedon P2) Location: Lat.: 11°25'8.3" Long.: 7° 19'54.4" Altitude: 693m																							
Ap	0-29	0.31	1.06	5.60	3.57	0.19	300	500	200	1.34	6.00	65.74	4.53	0.99	0.97	0.61	0.07	4.99	1.58	0.21	1.92	2.14	0.12
B	29-65	0.29	1.07	6.22	1.61	0.17	460	440	100	1.40	5.24	48.67	2.58	0.55	0.48	0.43	0.07	2.39	1.40	0.23	5.66	3.54	0.21
Bt	65-110	0.24	1.08	8.14	3.44	0.13	340	380	280	1.31	5.93	68.08	2.41	0.55	0.31	0.27	0.07	1.40	1.23	0.23	0.54	0.83	0.22
BCt	110-165	0.24	0.09	0.88	40.81	0.10	320	320	360		5.52	62.97	2.80	0.52	0.48	0.23	0.07	0.40	1.05	0.21	0.78	0.57	Trace
Soil Unit SI2 (Pedon P1) Location: Lat.:11°25'15.3" Long.: 7°21'11.6" Altitude: 680m																							
Ap	0-22	0.48	0.05	0.44	68.65	0.11	280	420	300	1.40	5.14	77.30	2.14	0.19	0.30	0.23	0.14	4.79	2.45	0.25	4.38	1.05	0.38
B	22-60	0.37	0.14	0.53	34.22	0.26	400	420	180	1.40	5.52	56.80	1.06	0.17	0.13	0.06	0.14	3.39	1.58	0.21	4.48	2.33	0.41
Btg	60–109	0.31	0.18	0.59	54.46	0.31	320	360	320	1.37	5.14	62.00	2.37	0.19	0.13	0.10	0.07	3.19	1.05	0.19	2.38	1.16	0.32
BCtg	109-143	0.35	0.12	0.63	47.71	0.20	320	380	300		5.43	57.36	2.56	0.20	0.15	0.13	0.07	2.59	1.05	0.28	4.53	1.60	Trace
Soil Unit SI2 (Pedon P2) Location: Lat.:11°27'15.9" Long.: 7°20'16.8" Altitude: 692m																							
Ap	0-26	0.50	0.37	0.81	22.12	0.46	420	400	180	1.36	5.70	71.41	3.80	0.20	0.34	0.23	0.14	5.99	1.58	0.24	2.88	0.77	0.20
Bt	26–74	0.46	0.50	1.07	28.11	0.47	320	380	300	1.40	5.94	58.45	3.17	1.21	0.43	0.10	0.07	2.99	1.40	0.19	2.65	1.80	0.23
Bg	74–106	0.43	0.49	0.82	24.37	0.61	300	500	200	1.44	5.90	59.26	3.21	1.21	0.26	0.12	0.14	1.20	0.53	0.20	2.37	1.63	0.18
Soil Unit SI3 (Pedon P1) Location: Lat.:11°26'14.7" Long.: 7°20'13.0" Altitude: 680m																							
Ap	0-17	0.62	0.05	0.76	15.81	0.06	620	260	120	1.37	5.80	56.27	2.07	0.17	0.42	0.21	0.14	3.79	2.98	0.21	3.10	0.68	0.25
Bg₁	17–40	0.24	0.25	0.83	21.58	0.30	420	400	180	1.33	5.65	50.86	2.33	0.17	0.35	0.10	0.14	2.79	1.23	0.26	2.89	0.98	0.15
Bg₂	40–82	0.25	0.18	0.73	19.14	0.24	400	460	140	1.31	5.81	50.28	2.57	0.18	0.60	0.27	0.14	2.00	0.53	0.29	2.69	1.28	0.14
Soil Unit SI3 (Pedon P2) Location: Lat.: 11°26'10.8" Long.: 7°19'26.3" Altitude: 673m																							
Ap	0-29	0.68	0.41	0.75	18.62	0.55	640	220	140	1.36	5.94	49.00	2.23	0.19	0.62	0.29	6.98	2.10	3.68	0.25	2.31	0.79	0.22
B	29-66	0.45	0.46	0.90	19.94	0.51	300	520	180	1.53	5.80	59.38	2.33	0.18	0.83	0.52	4.39	1.40	2.98	0.28	4.20	1.07	0.20
Bg₁	66-98	0.41	0.47	0.84	21.40	0.55	260	560	180	1.66	5.90	14.39	1.07	0.19	0.12	0.26	2.99	1.05	2.80	0.33	3.74	1.06	0.15
Bg₂	98-147	0.31	0.61	0.86	18.57	0.70	280	560	160		5.90	30.66	1.46	0.19	0.70	0.44	0.28	0.53	1.23	0.29	3.97	1.01	0.14
Soil Unit SI4 (Pedon P1) Location: Lat.:11°28'8.3" Long, 7°21'38.5" Altitude: 704m																							
Ap	0-25	0.32	0.14	0.71	11.25	0.20	600	320	80	1.31	5.80	49.52	2.33	0.18	0.46	0.10	0.53	1.79	2.36	0.33	2.59	0.95	0.21
C	25-43																	Stony					

Table 1 cont.: Pyrophosphate (Fe$_p$), Oxalate (Fe$_{ox}$) and Dithionite (Fe$_d$) extractable iron oxides, active Fe/dithionite extractable and Clay/Fe$_d$ ratios

Horizon	Depth (cm)	Fe$_p$	Fe$_{ox}$ %	Fe$_d$	Fe$_{ox}$/Fe$_d$	Clay/Fe$_d$	Sand	Silt (g Kg^{-1})	Clay	BD Mgm^{-3}	pH CaCl$_2$	BS %	Ca	Mg (cmol Kg^{-1})	K	Na	TN	OC (g Kg^{-1})	AP	Cu	Mn (mg Kg^{-1})	Zn	B
Soil Unit SI4 (Pedon P2) — Location: Lat.:11°26'10.8" Long.: 7°17'45.5" Altitude: 700m																							
Ap	0-31	0.38	0.52	0.20	2.65	91.28	480	340	180	1.34	6.00	58.55	2.45	0.17	0.62	0.39	0.53	1.30	2.98	0.32	3.86	0.83	0.22
CBt	31-50	0.19	1.00	0.44	2.29	54.87	470	290	240	1.40	6.80	41.09	1.15	0.16	0.30	0.28	0.18	0.20	2.63	0.15	1.82	1.15	0.20
Soil Unit SI5 (Pedon P1) — Location: Lat.:11°26'10.8" Long.: 7°17'45.5" Altitude: 700m																							
Ap	0-13	0.32	0.40	0.25	1.63	32.63	560	360	80	1.34	5.80	51.94	2.40	0.46	0.32	0.04	6.78	2.10	3.85	0.18	1.26	0.83	0.40
B	13-54	0.23	1.11	0.31	3.60	19.56	520	420	60	1.40	6.40	50.00	1.65	0.46	0.41	0.03	5.59	0.88	3.68	0.18	1.07	0.72	0.25
Cv	54 – 71	0.14	1.10	0.56	1.96	24.90	520	340	140	1.31	7.20	49.10	1.95	0.43	0.52	0.39	3.19	0.88	2.28	0.17	1.08	0.76	0.21
Soil Unit SI5 (Pedon P2) — Location: Lat.:11°27'59.9" Long.: 7°20'6.5" Altitude: 701m																							
Ap	0-25	0.47	0.70	0.26	2.69	46.33	580	300	120	1.34	6.00	51.23	2.45	0.47	0.21	0.20	7.20	2.79	2.98	0.18	2.24	1.00	0.32
Bt	25-56	0.35	0.99	0.32	3.09	93.57	460	240	300	1.36	5.40	29.56	2.45	0.66	0.16	0.10	4.28	1.28	2.71	0.14	2.00	0.70	0.30
CRv	56-80	0.10	0.93	0.40	2.31	24.88	600	300	100	1.31	6.20	43.39	1.95	0.46	0.18	0.10	2.16	0.88	1.11	Trace	1.98	0.17	0.22

Table 2: Correlation matrix of iron oxides VS soil physical and chemical properties

	Ca	Mg	K	Na	TN	OC	AP	Cu	Mn	Zn	Fe	B	Fe$_p$	Fe$_{ox}$	Fe$_d$	Fe$_{ox}$/Fe$_d$
Mg	0.34753 *															
K	0.14497	0.13422 *														
Na_	0.06711 **	0.02164	0.78612 ***													
TN	-0.27803 ***	0.01555	0.04725 *	-0.06151												
OC	0.51463 ***	-0.0866 *	-0.11928 *	0.07961	-0.23911 ***											
AP	-0.48853 ***	-0.12865 ***	0.20993 *	0.1072 *	0.73583 ***	-0.16815 *										
Cu	0.06236	-0.45707 **	0.12786	0.15532 *	-0.24166 **	0.27028 **	-0.13562 *									
Mn	-0.02531	-0.29998 ***	0.00546 *	0.17774 **	-0.29013 **	-0.02210	-0.19414 *	0.29249								
Zn	0.04167 **	0.32169 *	0.17553 *	0.29153 *	-0.27234	0.11492	-0.15393	-0.05419	0.45817 ***							
Fe	0.27079 **	-0.12346 *	-0.21094 ***	-0.16983 ***	-0.09295	0.02073	-0.30543 ***	0.09107 ***	0.23262	-0.13775						
B	-0.2697	-0.06203	-0.46938 ***	-0.48294	0.32907 *	0.11796 ***	0.36571 ***	-0.43138 *	-0.01829 *	-0.00536	0.20185 **					
Fe$_p$	0.02043 **	-0.01548 *	0.10563	0.07578 *	0.23386	0.38349 ***	0.4171 *	0.15153 *	0.16805 *	0.07872	0.36571 ***	0.16805 *				
Fe$_{ox}$	0.29248 ***	0.23607 *	-0.01405	0.15025 **	0.10155 **	-0.05098 ***	-0.14971 **	-0.21808 *	-0.1655 *	-0.031 **	-0.21808 *	-0.28273 **	-0.48628 ***			
Fe$_d$	0.39163 **	0.19614 *	0.09966 *	0.27976 *	-0.28549 ***	-0.47113 ***	-0.29232 ***	0.20456 ***	-0.20144 **	0.31208 ***		-0.24284 *	-0.08477 **	0.44915 ***		
Fe$_{ox}$/Fe$_d$	-0.27451 **	0.08067	-0.11723	-0.15385	0.56954 ***	-0.40722 *	0.47179 **	-0.39079 *	-0.27943 *	-0.33936 *		0.19615 ***	-0.27445 ***	0.43662 **	-0.36829 ***	
Clay/Fe$_d$	-0.26421	-0.07653	-0.23052	-0.13928	0.1221	-0.21070	0.29607	-0.22376	0.0578	-0.17402		0.46486 ***	0.08314	-0.23974	-0.51232 ***	0.4815 ***

LOS (P): NS > 0.05, * ≤ 0.05, ** ≤ 0.01, *** ≤ 0.001

Table 2. cont.: Correlation matrix of iron oxides VS soil physical and chemical properties

	Sand	Silt	Clay	BD	pH_CaCl₂	BS	Fe$_p$	Fe$_{ox}$	Fe$_d$	Fe$_{ox}$/Fe$_d$
Silt	-0.72395 ***									
Clay	-0.60843 ***	-0.10701 ***								
BD	-0.5125 ***	0.57123 ***	0.11431 *							
pH_CaCl2	0.30486	-0.03755	-0.39619	-0.11929						
BS	-0.10978	-0.14060	0.31997	-0.40178 **	-0.27488 **					
Fe$_p$	0.03592 *	-0.03224 *	-0.01467	0.28736 *	-0.3084 ***	0.11064				
Fe$_{ox}$	0.18199 *	-0.16117	-0.07687 *	-0.11961 *	0.37093 *	-0.10112 **	-0.48628 ***			
Fe$_d$	-0.13258 ***	0.05542 **	0.12732 **	-0.12288 *	-0.19227 ***	0.25106 ***	-0.08477 **	0.44915 ***		
Fe$_{ox}$/Fe$_d$	0.42763 ***	-0.27981 **	-0.29442 ***	-0.1271	0.51248 ***	-0.37224 ***	-0.27445 **	0.43662 *	-0.36829 ***	
Clay/Fe$_d$	-0.06731	-0.24549	0.37941	-0.01858	-0.10706	-0.08739	0.08314	-0.23974	-0.51232 ***	0.4815 ***

LOS (P): NS > 0.05, * ≤ 0.05, ** ≤ 0.01, *** ≤ 0.001

defined as old age or a high degree of weathering. Thus, soils from this individual suggest their Fe oxide ageing and leading to some relatively moderate degrees of crystallinity.

Higher iron reactivity indicates a lower degree of aging of the minerals, suggesting that the release of iron from the primary mineral lattice exceeded the crystallization of iron. The ratios were higher than those reported for red soils of different origins (0.01-0.08) in Southwest of Nigeria (Okusami et al., 1997) and this can be attributed to the red soils being highly weathered in their advanced stage. Therefore, the distinct variation in ratios between the individuals was attributed to the influence of varying mineralogical composition of the parent material.

The Clay/Fe_d ratio is presented in Table 1. The ratios (mostly > 18) observed for the soil individuals (SI1, SI2, SI3, SI4 and SI5) were generally higher than those (mean, 17.97) reported by Maniyunda et al. (2014) on the Older granites basement complex soils of Kaduna State, implying the latter were pedogenically older. The high ratios (mean, > 20) indicate that the soils had accumulated appreciable clay content with reduced surface area as the crystallization of iron oxide was significantly high in the basement complex soils. Clay/Fe_d ratio was highest in SI5 (93.57) and SI4 (91.28), indicating a seeming additional diagnostic property for clay accumulation zones (Okusami et al., 1997). Soil individual SI3 (mean ratio, < 20) recorded low ratios that suggest that free Fe oxides dominated the soils' clay sized particles.

4.0. Conclusion

Content of Fe_p progressively decreases in concentration down the profile in most of the pedons. Appreciable content of the oxides of Fe was in the amorphous form than in the organically complexed form. Contents of Fe_d were higher than those of the Fe_p and Fe_{ox} contents indicating Fe present in the soil are in free discrete bodies (i.e. crystalline). The lowest mean ratio of oxalate to dithionite – extractable Fe (0.1494) was observed in the most intense red coloured soils (SI1P2), implying that soils of this individual were pedogenically aged and exists mainly in the crystalline form. The Clay/Fe_d ratios (mostly > 18) observed for the soil individuals (SI1, SI2, SI3, SI4 and SI5) were generally high, indicating that the soils had accumulated appreciable content of clay with the reduced surface area.

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