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Distribution of Free Iron and Aluminium Oxides in Selected Soils on Basement Complex Parent Rocks from South West Nigeria

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Abstract

Twenty (20) soil samples from soils of basement complex parent rocks origin were collected to investigate the distribution of free iron and aluminium oxides and their influence on soil chemical and physical properties. Distribution of total free Fe and Al oxides of the soils samples were determined by ammonium oxalate and citrate bicarbonate dithionite methods. The Fed was higher than Feo in all the locations. The soil samples from Oyo State (Barrack) had the highest amount of Feo (1.6 g kg⁻¹) while Ekiti (Ado Ekiti) recorded the highest total free iron oxide (Fed) content (2.8 g kg⁻¹). Both Crystalline aluminium oxide (Al₀) and amorphous aluminium oxide (Ald) were high in soil from Oyo state (Barrack). The highest ratio of iron oxide (Feo/Fed) was obtained for soil from Oke oya (Oyo State). Significant correlation were obtained between Fed and crystalline iron (Feo) (r = 0.788, P<0.01); Feo and Al₀ (r = 0.691, P< 0.01); pH and organic carbon (r² = 0.599, P<0.01); Fed and Ald (r² = 0.585, P< 0.01) ; Al₀ and organic matter (r² = -0.57, P<0.01); cFe and exchangeable acidity (r= 0.510, P< 0.05); Fed and Al₀ (r=0.494, P<0.01) ; Feo and pH (r =- 0.487, P<0.05); CFe and organic carbon (r = 0.471, P< 0.05); Organic carbon and organic matter (r = 0.459, P< 0.01) ; Feo and Fed at (r = 0.453, P< 0.05) and Al₀ and available P (r = 0.446, P<0.05).

This result shows that both Fed and Al_o were extracting from the same pool and the soils were highly weathered with little minerals as revealed by the low values of Fe_o. The low quantity of the crystalline oxides in these soils is an indication of lack of accumulation of concretions, nodules and plinthites which can make the soil unproductive. Organic matter, pH, exchangeable acidity, organic carbon and available P had strong influence on the distribution of iron and aluminium oxides in the study soil.

Keywords: Charnockites, soil properties, dithionite extractable iron and aluminium oxides.

Introduction

The hydroxides and oxides of iron (Fe), aluminium (Al), manganese (Mn), silicon (Si) and titanium (Ti) are categorized as sesquioxides and are usually formed in the soils by the process of weathering. (Ojo-Atere and Ajunwon, 1985; Essoka and Esu, 2000, Obi *et al.*, 2008). In nature, sesquioxides occur in the crystalline and amorphous forms while a small fraction can be found as organic complexes (Hassan *et al.*, 2005) such that these are significant in predicting the degree of weathering and stage of soil development (Schwertmann, 1992). The sesquioxides influence soil chemical and physical

properties through the prominent roles played in soil swelling, aggregates formation, cation exchange capacity, anion adsorption, surface charge, specific surface area. nutrient transformation and pollutant retention in soils (Aghimien et al., 1988; Essoka and Esu, 2000; Hassan et al., 2005). The influence on soil plasticity and compressibility is attributed to the roles in cementation and aggregate formation processes in tropical soil (Townsend, 1987). The presence of sesquioxides confers on the soil tints, especially the reddish, yellowish or brownish colours in well-drained and the reddish, yellowish or brownish mottles in poorly-drained soils (Ojo-Atere and Ajuwon, 1985). The importance of sesquioxides in soil physico-chemical processes depends on the degree of crystallinity, with the less crystalline or amorphous fractions being more reactive than the highly crystallized forms. The sesquioxides are found as coats on soils and as discrete particles that precipitate insoluble phosphorus (P) as Fe-P and Al-P limiting their movement and availability in soils (Sims and Ellis, 1983). Uzoho et al. (2005) observed higher P and metal sorption by amorphous Fe and Al-oxides than the crystalline forms. The distribution of sesquioxides in soils of the tropics and indeed Nigeria has been widely studied (Sims and Elis, 1983; Ojo-Atere and Ajuwon, 1985; Aghimien et al., 1988: Essoka and Esu, 2000: Hassan et al., 2005; Osodeke et al., 2005). From the various studies it had been revealed that the different content of sesquoxides in tropical soils increases with soils age and this was due to the influence of weathering (Udo, 1980: Osodeke et al., 2005). Balagopalan and Rugmini (1989) studied the effects of Tectona grandis plantation on soil characteristics and observed high Fe2O3 and Al2O3 values which were attributed to the effects of hydrolytic breakdown of soil minerals and their interaction with the humic constituents. Alekseeva et al. (2010) reported high Fed and Ald with low Feo, Fe2O3 and Al2O3 in soils under tea plantation. After 40 to 50 years establishment of Laurophyllous spp. Zanellis et al. (2007) recorded little changes in Fe and Al content with high Feo/Fed ratio which was attributed to intensive weathering processes.

The chemical and physical properties of soils greatly influence the amount and the nature of amorphous and crystalline inorganic oxides of Fe and Al such that the distribution can be used to determine soil forming processes, direction, extent of pedogenic processes and soil age (Mckeaque *et al.,* 1971; Alexander, 1974. Therefore, the objective of this study was to investigate the status and distribution of Fe and Al oxides in some selected soils formed on basement complex rocks in Ekiti and Oyo States and to evaluate their relationship with soil chemical and physical properties. This becomes necessary for predicting the pedogenic process in some selected soils formed on basement complex rocks

Materials and Methods

Description of the study sites:

The study was conducted in areas where charnockites are found in Ekiti and Oyo States,

south-west Nigeria. The five areas chosen as study sites in Ekiti State are Ado-Ekiti, Ikere-Ekiti, Ijan-Ekiti, Ijesa-isu Ekiti and Ire-Ekiti while the areas chosen in Iseyin (Oyo State) are Barracks, Oke-oja, Ladogan, Total Area, Oja Ila area. The coordinates of areas chosen in Ekiti State are Ado Ekiti: $7^{\circ}31'N$ and $5^{\circ}7'E$; Ikere-Ekiti: $7^{\circ}29'N$ and $5^{\circ}13' E$; Ijan-Ekiti: $7^{\circ}38' N$ and $5^{\circ}23' E$; Ijesaisu: $7^{\circ}45' N$ and $5^{\circ}35'E$ while the coordinates of areas chosen in Iseyin are Barracks: 7° 95', $3^{\circ}61'E$; Oke-oja 7° 92'N, $3^{\circ}59'E$; Ladogan area 7° 97N, 3° 58 ' E; Total area 8° 01'N, 3° 56'E; Oja Ila area 7° 97 'N, 3° 59 'E.

Routine analysis

Soil samples were air-dried, crushed gently with pestle and mortar, sieved using 2 mm sieve and the procedures described in Udo and Ogunwale (1986) followed for the analysis: particle size distribution using the hydrometer method; pH with a glass electrode pH meter in 1:1 soil solution in distilled water; exchangeable bases extracted with neutral normal ammonium acetate and Ca, Mg and K read off atomic absorption spectrophotometer and Na with a flame photometer; exchangeable acidity extracted with 1N KCl and titrated with 0.01N NaOH (using phenolphthalein as an indicator); and effective cation exchangeable capacity (ECEC) taken as the sum of exchangeable cations and exchangeable acidity. The percentage base saturation was calculated as thus:

<u>Ca +Mg + K + Na</u> X 100 ECEC

Soil organic carbon was analyzed by dichromate oxidation and organic matter obtained from organic carbon by multiplication with the 'Broadbent factor' of 1.724. Available P was extracted with Bray P-1 extractant and determined by colorimetry. Total nitrogen was determined by the macro-Kjeldahl method.

The citrate-bicarbonate-dithionite (CBD) procedure developed by Mehra and Jackson (1960) was used to determine the total free Fe and Al oxides with Fe and Al in the extracts read off the atomic absorption spectrophotometer (AAS). The ammonium oxalate method was used to determine the amorphous free Fe and Al oxides by the procedure of Schwertmann (1964). The statistical tools used for analysis were the ranges and arithmetic means of the soil properties and correlation analysis of the relationships between the free Fe and Al oxides and the soil physical and chemical properties.

Results and Discussion

Physical and chemical properties of the soil samples

The properties of the soils used for the study are shown in Table 1. The particle size distribution show that the sand content ranged from 338-778 g kg-1 with a mean value of 666 g kg-1 ; silt ranged from 54-1 94 g kg-1 with a mean value of 125 g kg-1 while the clay ranged from 108-228 g kg-1 and a mean value of 173 g kg-1. Thus, the soils were generally light textured and varied from sandy loam to sandy clay loam. This corroborates the findings of Shittu (2014) that soils formed on charnockite were generally coarse in texture and ranged from loamy sand to sand.

These soils were slightly acid to neutral in nature with pH values ranging from 5.7 to 7.5 and a mean value of 6.6 and-would be-suitable for arable crops in the savannah (Ayodele and Omotoso 2008). The soil organic carbon ranged from 3.3 to 15 g kg-1 with a mean value of 7.33 g kg-1. The distribution showed that only two (2) soil samples contained 10 to 14 g kg-1 and belong to the high organic carbon content class (FFD, 2012). The total N content ranged from 0.4 to 2.2 g kgwith a mean value of 1.18 g kg-1 1 but with seven (7) of the soils selected from Ekiti State below the critical level of 0.6-1 .0 g kg-1 while the others are moderate with values ranging between 1.1 g kg-1 and 1.5 g kg-1 1. All the soils selected from Iseyin had total N values above the critical level of 0.6-1 .0 g kg-1 proposed by FFD (2012). This is an indication that the soils varied from moderately low to moderately high in total N.

The organic matter contents of the soils ranged from 0.9 g kg-1 in sub-soil from Ijesha-Isu to 25.9 g kg-1 in top soil from Ire in Ekiti State with a mean value of 11.8 g kg-1. These values fall below the critical levels of 2.0 g kg-1 (FMANR 1990)

The available P in the soils varied from 6 mg kg-1 in Ikere-Ekiti and Oja-ila to 41 mg kg⁻¹ in Ado-Ekiti with a mean value of 13.6 mg kg⁻¹. Only the sub-soils from Ikere-Ekiti, Ijan Ekiti, Ire Oke-Oja and Oja-ila had P levels lower than the critical level for maize production. Other soils had P values well above critical levels proposed for most crops, so that the soils had moderate to high P values (FFD, 2012).

Exchangeable Mg ranged from 0.2 to 3.6 cmol kg¹ and had a mean value of 1.23 cmol kg-1. Magnesium level in some of the soils (about ten soil

samples) were higher than the critical level of 0.28 cmol kg⁻¹ suggested for soils in south western zone of Nigeria. Exchangeable K ranged from 0.05 - 0.92 cmol kg⁻¹ with a mean value of 0.31 cmol kg⁻¹ which is consider high on the fertility class of nutrient elements for soils from the region (FMANR, 1990). Exchangeable Na ranged from 0.01 - 0.6 cmol kg⁻¹ with a mean value of 0.22 cmol kg⁻¹. The order of abundance of the exchangeable bases was Ca >Mg > K > Na.

Exchangeable Ca ranged from 1.72 - 6.4 cmol kg⁻¹ with a mean value of 2.61 cmol kg⁻¹. Calcium values in soils were below the critical level of 2 cmol kg⁻¹ reported by Aduayi *et al.*, 2002; Havlin *et al.*, 2005). Exchangeable acidity had values that ranged from 0.04 – 0.8 cmol kg⁻¹ with a mean value of 0.37 cmol kg-1.

The effective cation exchange capacity (ECEC) ranged from 3.18 - 8.02 cmol kg⁻¹ with a mean value of 4.72 cmo lkg⁻¹. There is no criterion for the interpretation of ECEC, but the low values in the soils is due to the coarse textue and dominant type of low activity clays (1:1 Laolinite, and low specific surface oxide (Juo and Fox, 1977)

Distribution of free Fe and Al oxides in the soil samples

Table 2 shows the distribution of Fe and Al oxides in the soils. Feo (amorphous) ranged from 0.2 to 1.6 g kg-1 with a mean value of 0.81 g kg-1 and Fed (total free Fe oxide) values varied from 0.9 and 2.8 g kg-1 with a mean value of 1.83 g kg-1. The crystalline Fe (CFe) calculated as the difference between Feo and Fed ranged from 0.3 to 2.2 g kg-1 with a mean value of 1.04 g kg^{-1} . The Al_o ranged from 0.01 to 0.19 g kg-1 with a mean value of 0.067 g kg-1 while Ald ranged from 0.14to 0.38 g kg-1 with a mean value of 0.22 g kg-1. The higher values of dithionite extractable (Fed) than the oxalate extractable iron (Feo) are an indication that the crystalline form of Fe oxide dominated the free sesquoxides. A similar observation was made by Olatunji et al. (2015) in Southwestern soils. The low oxalate extractable value can be attributed to strong weathering and crystallization of Fe in the study area where the soils occur under well-drained conditions (Raji et al., 2000; Hassan et al., 2004 and Kparmwang, 1993).

	Location	Depth (cm)	pH H2O	O.C	Total N	O.M	Available P	E.A	Mg	К	Na	Ca	ECEC	B.S	Sand	Silt	Clay	Class
					g kg-1 		mg kg-1			Cmol	kg-1			%		g kg-1 -		
1	Ado-Ekiti	0-20	6.7	9.2	1.4	15.6	41	0.24	1.0	0.14	0.04	3.4	4.82	77	698	134	168	SL
2	Ado-Ekiti	20-40	6.4	4.8	0.9	8.3	11	0.48	1.0	0.05	0.10	6.4	8.03	88	696	132	158	SL
3	Ikere-Ekiti	0-20	6.6	8.7	1.1	15.0	40	0.44	2.0	0.23	0.02	2.6	3.49	81	699	114	188	SL
4	Ikere-Ekiti	20-40	6.2	5.0	0.7	8.6	6	0.48	3.6	0.1	0.23	3.2	7.61	74	538	74	108	SCL
5	Ijan	0-20	6.1	7.9	0.8	13.6	12	0.2	1.0	0.2	0.01	2	3.41	68	578	154	168	SL
6	Ijan	20-40	6.0	4.3	0.4	7.4	09	0.44	1.4	0.09	0.10	2.6	4.63	56	568	134	158	SCL
7	Ijesha-Isu	0-20	7.2	6.2	0.8	10.7	13	0.2	1.0	0.14	0.10	2.6	4.04	82	698	114	187	SL
8	Ijesha-Isu	20-40	6.8	4.5	0.5	0.9	10	0.36	1.8	0.19	0.10	4.1	6.55	93	697	94	108	SCL
9	Ire	0-20	7.5	15.0	1.2	25.9	12	0.04	1.6	0.14	0.13	2.2	4.11	77	778	84	185	SL
10	Ire	20-40	7.3	9.7	0.6	16.7	08	0.12	1.2	0.12	0.20	3.8	5.44	90	718	54	168	SL
11	Barracks	0-20	6.1	6.9	1.7	11.9	18	0.30	1.01	0.42	0.40	1.92	4.05	83	658	174	188	SL
12	Barracks	20-40	5.7	3.3	1.1	5.7	15	0.10	0.91	0.22	0.20	1.72	3.15	89	656	154	168	SL
13	Oke-Oja	0-20	6.3	7.6	1.6	13.1	10	0.40	1.31	0.52	0.20	1.82	4.25	84	658	114	228	SCL
14	Oke-Oja	20-40	6.0	7.2	1.5	12.4	08	0.20	0.91	0.22	0.20	1.72	3.25	85	638	94	218	SCL
15	Ladogan	0-20	7.2	7.5	2.2	12.9	14	0.80	1.41	0.82	0.50	2.22	5.75	79	698	194	208	SL
16	Ladogan	20-40	7.1	5.8	1.7	1.0	12	0.50	0.81	0.32	0.30	1.72	3.65	72	678	154	168	SL
17	Total area	0-20	6.9	8.3	1.3	14.3	10	0.60	1.11	0.62	0.30	2.02	4.65	78	718	111	228	SCL
18	Total area	20-40	6.5	6.7	1.1	11.6	07	0.81	0.12	0.1	1.82	3.25	0.81	67	658	93	188	SL
19	Oja-Ila	0-20	7.0	10	1.5	17.2	11	1.51	0.92	0.6	2.32	5.95	1.51	85	657	174	168	SL
20	Oja Ila	20-40	6.5	7.9	1.4	13.6	06	0.91	0.52	0.5	1.92	4.35	0.91	77	638	154	108	SCL
	Mean	6.61	7.33	1.18	11.8	13.65	6.61	0.37	1.23	0.31	0.22	2.61	4.72	79	666	125	173	
	Max	7.5	15	2.2	25.9	41.0	7.5	0.80	3.6	0.92	0.6	6.4	8.03	93	778	194	228	
	Min	5.7	3.3	0.4	0.9	6.0	5.7	0.04	0.2	0.05	0.01	1.72	3.15	56	538	54	108	

Table 1: Some physical and chemical properties of the soil samples used for the study

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O.C = Organic carbon, O.M = Organic matter, E.A = Exchangeable acidity, Avail. P = Available phosphorus, ECEC = Effective Cation Exchange Capacity, B.S = Base Saturation, Total N = Total Nitrogen, SL = Sandy loam, SCL = Sandy clay loam

S/N	Soil Location	Soil Depth	Feo	Fed	Fed-Feo	Alo	Ald	Feo/Fed
		(cm)		g kg	3-1			
1.	Ado-Ekiti	0 - 20	1.3	2.8	1.5	0.16	0.19	0.5
2.	Ado-Ekiti	20 - 40	1.1	2.1	1.0	0.08	0.18	0.5
3.	Ikere-Ekiti	0 - 20	0.9	1.4	0.5	0.04	0.20	0.6
4.	Ikere-Ekiti	20 - 40	0.4	1.0	0.6	0.03	0.15	0.4
5.	Ijan	0 - 20	0.6	2.8	2.2	0.06	0.23	0.2
6.	Ijan	20 - 40	0.5	2.2	1.7	0.05	0.20	0.2
7.	Ijesha-Isu	0 - 20	0.7	1.3	0.6	0.09	0.18	0.5
8.	Ijesha-Isu	20 - 40	0.4	1.2	0.8	0.07	0.14	0.3
9.	Ire	0 - 20	0.3	2.5	2.2	0.02	0.25	0.1
10.	Ire	20 - 40	0.2	1.1	0.9	0.01	0.19	0.2
11.	Barracks	0 - 20	1.6	2.5	0.9	0.19	0.34	0.6
12.	Barracks	20 - 40	1.5	2.3	0.8	0.10	0.23	0.7
13.	Oke-Oja	0 - 20	1.3	1.6	0.3	0.03	0.19	0.8
14.	Oke-Oja	20 - 40	0.9	1.4	0.5	0.02	0.17	0.6
15.	Ladogan	0 - 20	0.7	1.7	1.0	0.08	0.16	0.4
16.	Ladogan	20 - 40	0.4	0.9	0.5	0.05	0.14	0.4
17.	Agip	0 - 20	1.1	1.6	0.5	0.09	0.28	0.7
18.	Agip	20 - 40	0.5	1.3	0.8	0.04	0.26	0.4
19.	Ojude-Oba	0 - 20	0.9	2.6	1.7	0.07	0.38	0.3
20.	Ojude-Oba	20 - 40	0.8	2.3	1.5	0.06	0.31	0.3
	Mean		0.81	1.83	1.03	0.07	0.22	0.44
	Max		1.6	2.8	2.2	0.19	0.38	0.8
	Min		0.2	0.9	0.3	0.01	0.14	0.1

Table 2: Distribution free Fe and Al oxides of the soil samples from Ekiti and Oyo States

Table 3: Correlation co-efficient ()	r) between i	free Fe and	Al oxides and	l some soil p	properties c	of the soil sam	ples
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Parameter	Feo	Fed	CFe	Alo	Ald	pН	0.C	Total N	Avail.P	E.A	O.M
Feo		0.453^{*}	-0.187	0.691**	0.357	-	-0.182	0.431	0.391	-0.341	-0.422
						0.487^{*}					
Fed			0.788^{**}	0.494^{*}	0.585**	-0.232	0.300	0.145	0.261	0.252	-0.010
CFe				0.083	0.374	0.094	0.471^{*}	-0.138	0.084	0.510^{*}	0.259
Alo					0.323	-0.169	-0.184	0.285	0.446*	-0.133	-0.57**
Ald						-0.048	0.366	0.245	-0.061	0.103	0.065
pН							0.599**	0.154	0.034	0.311	0.336
O.C								0.266	0.198	0.362	0.459*
Total N									0.169	0.046	-0.122
Avail.P										0.031	-0.430
E.A											0.055
ОM											

*, ** Significant (P < 0.05, 0.01 respectively), CFe = Crystalline Fe

Summary and Conclusion

Free iron and aluminium oxides (amorphous) extracted by ammonium oxalate (Fe₀, Al₀) and free iron oxide extracted by citrate-bicarbonate-dithionite (Fed) were all extracting from the same pool. As the soil pH increases, the free iron oxides in the soil becomes less active. The low quality of the

crystalline oxides in these soils showed lack of accumulation of concretions, nodules and plinthites which can affect the physical and chemical properties of the soil negatively and unproductive. Soil pH significantly contributes to the availability of free Fe and Al oxides and oxy-hydroxides of soils. Soil Organic Matter (SOM), Soil Organic Carbon (SOC) and Exchangeable Acidity seem to play a significant role in the relationship between free iron and aluminium oxides and their distribution in the

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tropics. Soil managements that favours a buildup of the organic matter reserves could ameliorate the negative effects of both active and reserved soil acidity in these soils.

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