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ASSESSMENT OF DITHIONITE AND OXALATE EXTRACTABLE IRON AND ALUMINIUM OXIDES IN SOILS SUPPORTING RAPHIA PALMS AT NIFOR MAIN STATION

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ABSTRACT:
The oxides of iron and aluminium are known to affect the physical and chemical properties of soils such as ion adsorption, aggregate stability, phosphorus sorption and charge characteristics. This study was conducted to provide information on the status of free oxides in both soils of the Inland Valley and a well drained Upland soil at the NIFOR main station. Twenty four (24) representative samples were obtained from twelve (12) mini pits sunk at the two locations. The samples were air-dried and analyzed for physico-chemical properties including iron and aluminium oxides using standard methods. The results indicated that Fe_d ranged from 5.86mg/kg to 151.38mg/kg at the Inland Valley and ranged from 11.13mg/kg to 34.46mg/kg at the Upland. The Fe_d values were higher than Fe_o values in both locations. The Fe_o/Fe_d ratio (diagnostic index) values clearly distinguished the well drained Upland soil from the poorly drained Inland Valley as the values decreased with increased soil depth at the Inland Valley but increased significantly with increased soil depth at the Upland. There was no evidence of co-migration of clay with Fe_d in both locations though significant correlations were obtained between clay and clay/Fe_d ratio of Inland Valley and Upland with ($r = 0.841$, $P < 0.01$) and ($r = 0.891$, $P < 0.01$) respectively. Significant correlations were also obtained between Fe_d and Fe_d-Fe_o ($r = 0.998$, $P < 0.01$); Fe_d and organic carbon ($r = 0.945$, $P < 0.01$); Fe_d and clay ($r = -0.720$, $P < 0.01$); Fe_d and Clay/Fe_d ratio ($r = -0.719$, $P < 0.01$) Al_d and Al_d-Al_o ($r = 0.922$, $P < 0.01$); Al_d and Fe_o/Fe_d ($r = 0.592$, $P < 0.05$); Al_d and Clay/Fe_d ($r = 0.628$, $P < 0.05$); Al_o and Al_d-Al_o ($r = -0.653$, $P < 0.05$); Fe_d-Fe_o and Clay/Fe_d($r = -0.724$, $P < 0.01$); Fe_d-Fe_o and organic carbon ($r = 0.948$, $P < 0.01$); Fe_d-Fe_o and Clay ($r = -0.736$, P 0.01); Fe_o/Fe_d and Clay/Fe_d ($r = 0.617$, $P < 0.05$) and Fe_o/Fe_d and Clay ($r = 0.705$, $P < 0.01$) at the Inland Valley. This trend of correlation continued at the Upland except that Al_d was not correlated with Fe_o/Fe_d and Clay/Fe_d while Fe_o was correlated with Fe_o/Fe_d of Upland ($r = 0.607$, $P < 0.05$) and was not correlated with Fe_o/Fe_d of the Inland Valley. This study has revealed that the soils of NIFOR main station are highly weathered soils and contained little weatherable minerals as revealed by the low amounts of Fe_o. The low amounts of the crystalline oxides in these soils reveal a lack of accumulation of concretions, nodules and plinthites which lead to deterioration of physical and chemical properties of soils.

Key words: Dithionite, NIFOR, Oxalate, Raphia palms, Sesquioxides

INTRODUCTION

Many soils in Nigeria have been reported to contain sesquioxides in varying proportions (Ogunkunle and Onansaya, 1992; Agbenin, 2003). The crystalline forms of the sesquioxides had been found to dominate in the basement complex soils of Southwestern Nigeria (Ogunkunle and Onansaya, 1992). This is the more advanced stage compared to the amorphous forms that are mobile in the soil and could be associated with organic matter (Obi *et al*., 2009). Percentages of free iron (Fe^{3+}) have long been used as aids in distinguishing soil types and differentiating soil horizons (McKeague *et al.*, 1971). Comparisons of percentages of free iron frequently have been used as aids in determining relative ages of soils (Ogunsola *et al*., 1989). Iron is subject to increase in concentration through soil development processes, as reflected by contents of ten to fifteen percent in many soil colloids (Osodeke *et al.,* 2005). Soils having the high percentages are approaching the iron content of low grade iron ore. High stability of soil aggregates and high soil porosity are usually associated with high iron oxide contents. Two analytical methods are commonly used in estimating percentages of free iron in soils: the acid-ammonium oxalate method first applied to soils by Schwertmann (1964) and the dithionite-citrate-bicarbonate method proposed by Mehra and Jackson (1960). The oxalate extraction is presumed to remove the poorly crystalline iron oxides. The dithionite extraction is presumed to remove finely crystalline iron oxides in addition to the oxalate-soluble fractions. Therefore, the amount of iron released by the dithionite method (Fe_d) should be equal to or greater than the amount of iron released by the oxalate method (Fe_o). The difference between the values obtained by the two methods represents the amount of iron present in definite crystalline forms (Ogunsola *et al.,* 1989) so that with increasing soil age, the crystalline iron oxides increase at the expense of the poorly crystalline forms. This trend is reflected in the ratio of Fe_o to Fe_d (Fe ratio) (Ogunsola *et al.* 1989). Ideally, the Fe ratio has values less than unity that decrease with increasing soil age (Alexander, 1974). Low Fe_o/Fe_d ratio indicates a high degree of crystallinity of Fe oxides (Obi *et al*., 2009). The nature, amount and distribution of dithionite citrate bicarbonate and acid ammonium oxalate extractable Fe and Al oxides in a soil significantly affect its properties, such as charge characteristics and ion adsorption, particularly phosphorus sorption (Obi *et al.,* 2009). The fact that these oxides affect the physico-chemical properties of soils call for their study which would provide information that would be useful in planning, use and management of the soils, especially with respect to raphia palms which predominantly thrive in hydromorphic soils. Thus, the purpose of this study was to determine:

- the forms of Fe and Al oxides at the NIFOR Inland Valley earlier assessed for raphia palms cultivation and compare findings with an Upland soil in NIFOR.
- the interrelationship between Fe and Al oxides in both soils of the NIFOR Inland Valley and Upland.
- the interrelationship between Fe and Al oxides and some selected soil physico-chemical properties of the Inland Valley and Upland soils of NIFOR.

MATERIALS AND METHODS

Field studies

Two locations were chosen; the NIFOR Inland Valley which is close to the Okhuo River located on Lat 6º34′N and longitude 5º43′E representing wetland or hydromorphic or poorly drained soil and the plantation behind chemistry Division, representing well-drained upland agricultural soil. Six (6) mini pits were dug on each location and two samples were collected from each pit, giving a total of twelve pits (12) per location. The mini pits were sunk in the various locations based on differences in vegetation, topography and surface visual soil colour. Thus variations in

the locations were adequately covered through purposive sampling. Samples obtained from the pits were stored in polythene bags and accurately labelled for further processing in the laboratory.

Laboratory study

The samples were taken to the laboratory and air dried. The air dried samples were crushed with the hand and sieved using a 2mm sieve. The samples that did not pass through this sieve were discarded while those that passed through were further analyzed for physico-chemical properties as follows: Particle size analysis was determined using the hydrometer method using Calgon as a dispersing agent. Soil pH was determined in a 1:1soil/water suspension using a pH meter. Organic carbon was determined by the dichromate wet oxidation method of. The crystalline iron and aluminium oxides designated as Fe_d and Al_d respectively were determined by dithionite-citrate buffered with sodium bicarbonate solution. The content of ammonium oxalate soluble iron and aluminium oxides also designated as Fe_o and Al_o respectively were determined by Mckeague and Day (1966) method.

Statistical analysis

Data were subjected to analysis of variance (ANOVA) using Genstat Statistical software. The means between depths were separated using Least Significant Difference (LSD) at 5% level of probability. The Matrix of Correlation Coefficient (r) was run using SPSS version 17.

RESULTS AND DISCUSSION

Morphological Description of NIFOR Soils

The soils of NIFOR are inherently developed on Coastal Plain Sands. Soils formed on Coastal Plain Sands and Sandstones are similar in chemical characteristics, and have the same soil class Aquult in the USDA Soil Taxonomy. These soils are referred to as 'Acid Sands.' They are acidic, have low CEC, low base saturations and low fertility level, usually suffering from multiple nutrient deficiencies. Their prominent clay type is kaolinite. Four soil series of Acid Sands have been classified in NIFOR main station. They are Ahiara, Kulfo, Orlu and Alagba series. Soils of the Inland Valley are Ahiara series while those of the upland soils are Orlu series. Their detailed morphological descriptions are given in Table 1.

Table 1: Field Morphological Descriptions of Typical (Normal) NIFOR Soils

Profile No. And soil series	Horizon	Depth (cm)	Colour (moist)	Boundary *	Structure **	Texture***
5 Ahiara Series	A11	0-11	7,5YR3/4	a,w	1,c,g	Slightly clayey sand (LS)
(normal)	A12	11-36	5YR3/4	c,w	1,m,g	Clayey Sand (SL)
	B21	36-70	5YR3/3	d,w	1,m,g	Slightly clayey sand (LS)
	B22	70-104	5YR3/3	d,w	1,m,g	Slightly clayey sand (LS)
	B23	104-136	5YR3/3	d,w	1,m,g	Slightly clayey sand (LS)
	B24	136-174	2,5YR3/6	d,w	1,m,g	Clayey Sand (SL)
	B25	174-200	25YR3/6	d,w	1,m,g	Slightly clayey sand (LS)
10 Kulfo	A11	0-12	10YR3/2	c,w	1,c,g	Slightly clayey sand (LS)
Series(normal)	A12	12-40	7.5YR3/4	d,s	1,m,g	Slightly clayey sand (LS)
	A13	40-78	7.5YR3/4	d,s	1,m,g	Slightly clayey sand (LS)
	B21	78-105	5YR3/4	d,s	1,m,g	Clayey Sand (SL)
	B22	105-135	5YR4/6	d,s	1,m,g	Clayey Sand (SL)
	B23	135-163	5YR5/6	d,s	1,m,g	Clayey Sand (SL)
	B24	163-200	2.5YR5/6	-	2,m,sb	Clayey Sand (SL)
12 Orlu Series	A11	0-24	7.5YR3/4	c,s	1,m,g	Slightly clayey sand (LS)
(normal)	A12	24-55	2.5YR3/4	c,s	2,m,g	Clayey Sand (SL)
	B21t	55-88	2.5YR3/6	c,s	2,m,sb	Very clayey Sand (SCIL)
	B22t	88-126	2.5YR3/6	d,s	2,m,sb	Very clayey Sand (SCIL)
	B24t	126-154	2.5YR3/6	d,s	2,m,sb	Very clayey Sand (SCIL)
	B24t	154-200	2.5YR3/6	-	2,m,sb	Very clayey Sand (SCIL)
6 Alagba	A11	0-7	7.5YR3/4	c,s	1,m,g	Slightly clayey sand (LS)
Series	A12	7-21	5YR3/4	d,s	2,m,g	Clayey Sand (SL)
(normal)	B21t	21-40	2.5YR4/4	d,s	2,m,sb	Very clayey Sand (SCIL)
	B22t	40-67	2,5YR3/6	d,s	2,m,sb	Very clayey Sand (SCIL)
	B23t	67-105	2,5YR3/6	d,s	2,m,sb	Sandy clay (SCI)
	B24t	105-136	2,5YR3/6	d,s	1,c,sb	Sandy clay (SCI)
	B25t	136-200	2,5YR3/6	-	1,c,sb	Sandy clay (SCI)

*a = abrupt, w = wavy, c = clear, d = diffuse, s = smooth

** 1 = weak, 2 = Moderate, c = coarse, m = medium, g = granular, sb = subangular blocky

*** LS = Loamy sand, SL = Sandy loam, SCIL = Sandy clay loam, SCl = Sandy clay

Source: NIFOR 1982

The soil physico-chemical properties:

Some physical and chemical properties of the soils of both locations are shown in Tables 2 and 3. Soil pH and organic carbon at the Inland Valley increased with increased soil depth. In comparison with the upland soil, soil pH followed the same trend though it was slightly higher at the Upland. Soil pH was slightly acidic at the Inland Valley and moderately acidic at the Upland (Tables 2 and 3). Organic carbon was different in comparison with the Upland and decreased with increased soil depth. The increase in organic carbon with increased soil depth at the Inland Valley could be due to the inefficient breakdown of organic matter by facultative anaerobes. This is consistent with the findings of Aghimien *et al*., (1988) who called it lithological discontinuity. Comparatively, clay decreased with increased soil depth at the Inland Valley but increased significantly with increased soil depth at the Upland. Silt and sand followed the same trend in both locations.

Distribution of dithionite and oxalate extractable forms of Fe and Al oxides in the soils

The citrate-bicarbonate dithionite extractable only indicate the Fe and Al that are present in the soil as free discrete bodies (i.e. crystalline and amorphous) but not those that are part of the structure of silicate minerals. These free discrete bodies are collectively referred to as uncombined or pedogenic free forms of the element and could either be mobile (amorphous) or immobile (crystalline).Tables 4 and 5 show the distribution of crystalline, definite crystalline and poorly crystalline form of Fe and Al oxides in soils of the Inland Valley and Upland. Fe_d ranged from 5.86 mg/kg to 151.38 mg/kg at the Inland Valley and increased with increased soil depth. In comparison with the Upland soil, it ranged from 11.13 mg/kg to 23.71 mg/kg and increased significantly with increased soil depth. Fe_d values were higher at the Inland Valley than the Upland soil values and were generally higher than Fe_o values of both locations. Fe_o values of the Inland valley were lower than those of Upland which was probably due to the influence of water, a condition which inhibits weathering of minerals. The increase in Fe_d with increased soil depth was consistent with the findings of Juo and Maduakor (1974). They reported that dithionite Fe (total free Fe oxides) content increases with the increase of depth and added that the oxalate extractable Fe (amorphous Fe oxides) constitutes less than 10% of the total free Fe oxides throughout the profiles. Fe_o ranged from 0.66 mg/kg to 9.64 mg/kg at the Inland Valley and also increased with increased soil depth. Fe_o of Upland soil ranged from 5.01 mg/kg to 10.98 mg/kg and also increased with increased soil depth. Al_d of the Inland Valley ranged from 8.20 mg/kg to 19.47 mg/kg and decreased with increased soil depth while Al_o and Fe_d-Fe_o ranged from 0.32 mg/kg to 4.61 mg/kg and 2.34 mg/kg to 141.74 mg/kg respectively and both increased with increased soil depth. Al_d-Al_o, Fe_o/Fe_d and clay/Fe_d ratios decreased with increased soil depth at the Inland Valley (Table 4). In Upland soil, Al_d and Al_o increased with increased soil depth and ranged from 7.28 mg/kg to 15.45 mg/kg and 2.64 mg/kg to 9.59 mg/kg respectively while the definite crystalline form (Fe_d-Fe_o) decreased significantly with increased soil depth. (Al_d-Al_o) decreased with increased soil depth.

Table 2: Physico-Chemical Properties of Nifor Inland Valley

S/No	Location/ Depth (cm) Inland V	pH (H2O)	O.C. (g/kg)	Clay (g/kg)	Silt (g/kg)	Sand (g/kg)	Textural Class
1	0-60	5.69	5.40	56.00	14.00	930.00	Sand
2	0-60	6.02	30.40	10.00	25.00	965.00	Sand
3	0-60	5.42	8.30	46.00	19.00	935.00	Sand
4	0-60	5.44	15.00	36.00	19.00	945.00	Sand
5	0-60	5.48	6.40	41.00	14.00	945.00	Sand
6	0-60	5.75	14.10	10.00	25.00	965.00	Sand
Mean	**Mean**	**5.63**	**13.30**	**33.20**	**19.30**	**947.50**	
7	60-120	6.31	8.00	36.00	24.00	940.00	Sand
8	60-120	5.39	25.30	20.00	35.00	945.00	Sand
9	60-120	5.85	3.50	41.00	14.00	945.00	Sand
10	60-120	5.79	35.50	20.00	25.00	955.00	Sand
11	60-120	5.48	6.40	41.00	14.00	945.00	Sand
12	60-120	5.35	18.90	20.00	30.00	950.00	Sand
	Mean	**5.70**	**16.30**	**29.70**	**23.70**	**946.70**	
	Range	5.35-6.31	3.50-35.50	10.0-56.0	14.0-35.0	930.0-965.0	
	LSD (0.05)	NS	NS	NS	NS	NS	

NS = Non-significant.

Table 3: Physico-Chemical Properties of Upland Soils of Nifor

S/No	Location/ Depth (cm) Upland	pH (H2O)	O.C. (g/kg)	Clay (g/kg)	Silt (g/kg)	Sand (g/kg)	Textural Class
1	0-60	5.87	8.0	36.0	19.0	945.0	Sand
2	0-60	6.12	7.0	36.0	14.0	950.0	Sand
3	0-60	5.99	8.0	41.0	24.0	935.0	Sand
4	0-60	6.18	8.0	41.0	29.0	930.0	Sand
5	0-60	6.28	8.6	36.0	29.0	935.0	Sand
6	0-60	6.35	7.4	31.0	9.0	960.0	Sand
	Mean	**6.13**	**7.83**	**36.80**	**20.70**	**942.50**	
7	0-60	6.27	6.1	56	24.0	920.0	Sand
8	0-60	6.21	5.1	86	24.0	890.0	Sand
9	0-60	6.19	5.4	76	19.0	905.0	Sand
10	0-60	6.2	5.1	61	24.0	915.0	Sand
11	0-60	6.32	5.4	86	24.0	890.0	Sand
12	0-60	6.37	4.5	36	24.0	940.0	Sand
	Mean	**6.26**	**5.27**	**66.80**	**23.20**	**910.00**	
	Ranges	5.87-6.37	4.5-8.6	31-86	14-29	945-890	
	LSD(0.05)	NS	NS	19.06	NS	17.79	

NS = Non-significant

Table 4: Dithionite and Ammonium Oxalate Iron and Aluminium Oxides of the Inland Valley of Nifor

S/No	Location/ Depth (cm)	Fe_d (mg/kg)	Fe_o (mg/kg)	Al_d (mg/kg)	Al_o (mg/kg)	Fe_d-Fe_o (mg/kg)	Al_d-Al_o (mg/kg)	Fe_o/Fe_d	Clay/Fe_d
1	0-60	10.01	7.67	19.47	0.55	2.34	18.92	0.77	0.56
2	0-60	111.57	0.66	13.25	2.42	110.91	10.83	0.01	0.01
3	0-60	10.5	3.92	11.05	1.21	6.58	9.84	0.37	0.44
4	0-60	27.49	0.8	8.97	1.76	26.69	7.21	0.03	0.13
5	0-60	6.66	1.17	15.12	2.86	5.49	12.26	0.18	0.62
6	0-60	39.93	5.69	9.19	5.6	34.24	3.59	0.14	0.03
	Mean	**34.00**	**3.30**	**12.84**	**2.40**	**31.00**	**10.40**	**0.25**	**0.30**
7	60-120	15.04	1.34	12.59	0.32	13.7	12.27	0.09	0.24
8	60-120	48.99	3.8	11.49	1.32	45.19	10.17	0.08	0.04
9	60-120	5.86	1.17	14.46	3.22	4.69	11.24	0.20	0.70
10	60-120	151.38	9.64	12.7	3.51	141.74	9.19	0.06	0.01
11	60-120	12.58	5.35	10.25	4.61	7.23	5.64	0.43	0.33
12	60-120	74.65	2.97	8.20	1.65	71.68	6.55	0.04	0.03
	Mean	**51.00**	**4.00**	**11.61**	**2.44**	**47.00**	**9.20**	**0.15**	**0.23**
	LSD(0.05)	NS	NS	NS	NS	NS	NS	NS	NS

NS = Non-significant.

Table 5: Dithionite and Ammonium Oxalate Iron and Aluminium Oxides of Nifor Upland Soil

S/No	Location/ Depth (cm)	Fe_d (mg/kg)	Fe_o (mg/kg)	Al_d (mg/kg)	Al_o (mg/kg)	Fe_d-Fe_o (mg/kg)	Al_d-Al_o (mg/kg)	Fe_o/Fe_d	Clay/Fe_d
1	0-60	23.71	5.72	15.45	5.82	17.99	9.63	0.24	0.15
2	0-60	18.45	5.01	7.28	3.18	13.44	4.1	0.27	0.20
3	0-60	20.05	7.12	11.57	3.62	12.93	7.95	0.36	0.21
4	0-60	34.46	7.47	9.59	4.61	26.99	4.98	0.22	0.12
5	0-60	19.19	7.04	7.47	5.49	12.15	1.98	0.37	0.19
6	0-60	20.39	8.98	10.92	3.18	11.41	7.74	0.44	0.15
	Mean	**22.70**	**6.89**	**10.38**	**4.32**	**15.00**	**6.06**	**0.32**	**0.17**
7	60-120	15.76	8.98	10.07	5.38	6.78	4.69	0.57	0.36
8	60-120	13.81	6.55	10.91	2.64	7.26	8.27	0.47	0.62
9	60-120	14.3	8.24	9.92	6.04	6.06	3.88	0.58	0.53
10	60-120	19.56	8.01	11.24	9.59	11.55	1.65	0.41	0.31
11	60-120	20.54	10.98	9.15	5.82	9.56	3.33	0.53	0.42
12	60-120	11.13	8.24	13.91	5.71	2.89	8.2	0.74	0.32
	Mean	**15.80**	**8.50**	**10.87**	**5.86**	**7.30**	**5.00**	**0.55**	**0.43**
	LSD(0.05)	5.65	NS	NS	NS	6.05	NS	0.13	0.12

NS = Non-significant.

Table 6: Correlation Matrix of Physico-Chemical Properties, Iron and Aluminium Oxides of inland valley soils of nifor

	Fe_d	**Fe_o**	**Al_d**	**Al_o**	**Fe_d-Fe_o**	**Al_d-Al_o**	**Fe_o/Fe_d**	**Clay/Fe_d**	**Oc**	**Clay**
Fed	-									
Fe_o	0.340	-								
Al_d	-0.178	0.171	-							
Al^o	0.162	0.249	-0.309	-						
Fe_d-Fe_o	0.998**	0.284	-0.192	0.150	-					
Al_d-Al_o	-0.208	0.035	0.922**	-0.653*	-0.214	-				
Fe_o/Fe_d	-0.511	0.448	0.592*	-0.132	-0.549	0.525	-			
Clay/Fe_d	-0.71**	-4.153	0.628*	-0.124	-0.724**	0.551	0.617*	-		
Oc	0.945**	0.248	-0.252	0.075	0.948**	-0.231	-0.586*	-0.808*	-	
Clay	-0.720**	0.012	0.523	-0.389	-0.736**	0.575	0.750**	0.841**	-0.773**	-

**Correlation is significant at the 0.01 level, *Correlation is significant at the 0.05 level, OC = Organic carbon.

Table 7: Correlation Matrix of Physico-Chemical Properties, Iron and Aluminium Oxides of Upland Soil in NIFOR

	Fe_d	**Fe_o**	**Al_d**	**Al_o**	**Fe_d-Fe_o**	**Al_d-Al_o**	**Fe_o/Fe_d**	**Clay/Fe_d**	**Oc**	**Clay**
Fed	-									
Fe_o	-0.097	-								
Al_d	-0.096	-0.065	-							
Al^o	-0.008	0.297	0.194	-						
Fe_d-Fe_o	0.968**	-0.345	-0.074	-0.083	-					
Al_d-Al_o	-0.078	-0.263	0.734**	-0.523	-0.007	-				
Fe_o/Fe_d	-0.770**	0.607*	0.162	0.184	-0.880**	0.013	-			
Clay/Fe_d	-0.637*	0.278	-0.047	0.042	-0.671*	-0.070	0.614*	-		
Oc	0.640*	-0.412	-0.165	-0.329	0.708**	0.084	-0.769**	-0.774**	-	
Clay	-0.296	0.419	-0.159	0.169	-0.385	-0.252	0.375	0.891**	-0.647**	-

Correlation is significant at the 0.01 level, *Correlation is significant at the 0.05 level, Oc = Organic carbon.

Fe_o/Fe_d and clay/Fe_d ratios increased significantly with increased soil depth and ranged from 0.22 mg/kg to 0.74 mg/kg and 0.15 mg/kg to 0.62 mg/kg respectively. The Fe_o/Fe_d ratios were less than unity in both locations. It can be said that Fe_d dominated the Inland Valley of NIFOR which is largely due to the migration of reduced components towards oxidized zones in the profile while Fe_o dominated the Upland soils of NIFOR. The diagnostic index Fe_o/Fe_d clearly distinguished the poorly drained Inland Valley from the well drained upland soil. The fact that Fe_d dominated the Inland Valley soils of NIFOR is further buttressed by the Fe_o/Fe_d ratio which decreased with increased soil depth. Juo *et al*., (1974) reported a Fe_o/Fe_d ratio that decreased with profile depth and suggested that larger proportions of Fe oxides were present as crystalline forms in the lower horizons of the well drained soils that they studied. In both locations Fe_d was significantly correlated with Fe_d-Fe_o as was also observed by (Obi *et al*., 2009). The significant correlation between FED and Fe_o/Fe_d of both locations showed that most of the free fE oxides are present in crystalline forms. The significant correlation of Fe_d with organic carbon of both locations suggest that Fe_d was strongly associated with organic matter of both locations though the association was stronger at the Inland Valley as revealed in the high correlation value of 0.945**. Fe_o had no correlation with Fe_o/Fe_d at the Inland Valley but was significantly correlated with Fe_o/Fe_d of Upland which again suggests the dominance of Fe_o (amorphous Fe oxides) in Upland soils of NIFOR. Al_d was significantly correlated with Al_d-Al_o of both locations which was consistent with the findings of Obi *et al*., (2009). This indicated that most of the free Al oxides are in the crystalline forms Al_d was significantly correlated with Fe_o/Fe_d and Clay/Fe_d ratios of the Inland Valley but not with the Upland soils of NIFOR. There was no replacement of the crystalline Fe by Al as revealed by the lack of correlation between Fe_d and Al_d of both locations. Like Fe_d (total free Fe oxides), the definite crystalline Fe (Fe_d-Fe_o) also had significant correlations with organic carbon of both locations. Fe_o/Fe_d was significantly correlated with clay at the Inland Valley ($r = 0.705$, $P < 0.01$) but was not correlated with clay of Upland soils. There was a lack of correlation between Fe_o/Fe_d and clay. There was no evidence of a co-migration of clay with Fe_d in both locations though the negative correlation between Fe_d and clay seemed to suggest a co-migration in Upland soils at the lower concentration of Fe_d. The low mean values of Fe_o of both locations indicate that the soils are highly weathered and contained very little weatherable minerals.

Soils Supporting Raphia Palms

Raphia palms thrive best in deep soils, free of gravels or concretionary materials, of high moisture retention, preferably of shallow water table, coarse to medium texture and flat to gentle undulating topography to enhance less run-off and possible water logging (FMNAR, 1990). Alluvial and marine soils and the Acid Sands (Coastal plain sands, shale and sandstones) constitute the most important soils for raphia palm cultivation (FMANR, 1990; Aghimien 1982). These soils are widespread in Southern Nigeria where the palms play a major role in the traditional lives of the people. Their ability to support raphia palms stem from the fact that these soils are low in sesquioxide contents. Aghimien (1982) in his study of hydromorphic soils supporting raphia palms in Southern Nigeria reported that the low amount of P in occluded forms was partly attributed to the low contents of sesquioxides which were responsible for occluding P fractions under water logged and reduced conditions. This present study has revealed that soils of NIFOR can adequately support raphia palms cultivation as the dithionite and oxalate extractable sesquioxides contents are low and may not sufficiently occlude those nutrients needed by raphia palms in high amounts.

CONCLUSION

Crystalline forms as compared to the amorphous form dominate the free sesquioxides in soils of NIFOR main station as Fe_d, Fe_d-Fe_o, Al_d and Al_d-Al_o contained

38.91%, 35.57%, 11.90% and 8.90% of the total sesquioxide contents of NIFOR Inland Valley respectively. Fe_o and Al_o contained 3.34% and 2.20% of the total sesquioxide content respectively. This trend continued with the Upland soils. These amounts are however not high enough to cause a distortion of the physical property such as hardness of the soils but high enough to influence chemical properties of the soils such as ion adsorption and aggregate stability. Furthermore, the high significance of these crystalline forms of Fe with organic carbon in both locations suggests that organic matter can help mitigate their effects on the physical and chemical properties of the soils. Also significant is that Fe_o/Fe_d ratio clearly distinguished the well drained Upland soil from the poorly drained Inland Valley. There was no evidence of co-migration of clay with Fe_d as revealed by the lack of correlation between Fe_d and clay of both locations. Further studies are needed to study the association of these oxides with nutrients such as N, P, K, Mg and Zn which are highly needed by raphia palms.

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