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FORMS AND PEDOGENETIC DISTRIBUTION OF EXTRACTABLE IRON AND ALUMINUM IN SELECTED SOILS OF NIGERIA*

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ABSTRACT

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The content of various forms of Fe and Al in six well-drained soil profiles sampled from different parts of Nigeria was determined by selective extraction methods. Dithionite-Fe (total free Fe oxides) content increases with the increase of depth. The oxalate-extractable Fe (amorphous Fe oxides) constitutes less than 10% of the total free Fe oxides throughout the profiles. The active Fe ratio decreases with the increase of profile depth, suggesting that larger proportions of Fe oxides are present as crystalline forms in the lower horizons of these well-drained profiles. Little or no relationships were found in the case of Al.

The constant clay/dithionite—Fe ratio within the four profiles from the wetter southern part of Nigeria indicates the co-migration of clay and Fe oxides from the A horizon into the B horizon (lessivage). However, this relationship was not observed in the two soil profiles sampled from the drier northern part of the country.

The need for expansion or alteration of the present U.S.D.A. system of soil classification is emphasized.

INTRODUCTION

The oxides and hydrous oxides of iron and aluminum are among the major components of soils in the tropics. These oxides exist in soil in the forms of amorphous and crystalline inorganic oxides. A small portion of Fe and Al is also present in soils in the form of organic complexes. Approximate differentiation among these three forms of Fe and Al in soil can be made by selective extraction methods. The acid ammonium-oxalate method of Schwertmann (1964) extracts mainly the amorphous forms of inorganic Fe and Al. The alkali Na-pyrophosphate extraction (Aleksandrova, 1960; McKeague, 1967) dissolves the fractions of Fe and Al in the forms of organic complexes. Total

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free oxides as well as the major portion of organic complexes can be determined by the method of Mehra and Jackson (1960) using a dithionite-citrate-bicarbonate system. However, these procedures have proved more successful in differentiating Fe than Al in soils (Bascomb, 1968; McKeague et al., 1971).

The profile distribution of the various forms of Fe and Al has been used as a criterion in interpreting soil formation processes in the temperate region (McKeague and Day, 1966; Blume and Schwertmann, 1969). Ashaye (1969) studied the relationships between clay content and the acid-oxalate-extractable Fe and Al in some soils in Nigeria derived from sandstones and found that the relationships were not significant. On the other hand, the amount and nature of the various forms of Fe and Al oxides and organic complexes may also greatly influence the physical and chemical properties of the soil. Soil properties such as anion sorption, surface charge, specific surface area, swelling and aggregate formation may be significantly modified by the presence of amorphous Fe and Al oxides (McIntyre, 1956; Sumner, 1963; Sherman et al., 1964; Acra and Weed, 1966; Deshpande et al., 1968; and Greenland et al., 1968).

This paper examines the forms and pedogenetic distribution of the various forms of Fe and Al in six well-drained upland soil profiles sampled from various parts of Nigeria.

MATERIALS AND METHODS

Soil samples

Genetic soil horizons of six upland soil profiles were sampled. The soils were classified at the great group level of the U.S.D.A. system (Soil Survey Staff, 1973). According to data presently available, all soils would belong to Oxic subgroups. Soil series were determined in accordance with series descriptions by Irving (1957), Moss (1957), Obihara et al. (1964) and Smyth and Montgomery (1962).

The locations of the sampling sites of the six soil profiles are shown in Fig.1. These profiles represent soils on dominant parent materials in characteristic agro-climatic zones of Nigeria. A summary of the environmental data of the soils is given in Table I. The sedimentary parent material is either Pleistocene to Oligocene, deeply weathered coastal-plain sediments (both Alagba series) or weathered soft, coarse-grained Cretaceous sandstones (Nkpologu and Danggappe series). In the Egbeda profile, the upper horizons are developed in colluvial material with pediment gravels, whereas the lower part of the profile is developed in material weathered in situ.

Horizon designations and general properties of the soils are given in Table II.

A sample profile description of the most common subgroup (Oxic Paleustalf) encountered in this study is given below.

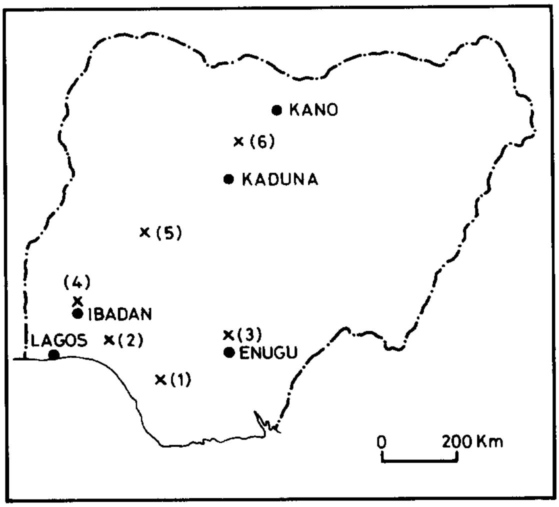

Fig.1. Map of Nigeria showing sampling sites: (1) Alagba Benin, (2) Alagba Shagamu, (3) Nkpologu, (4) Egbeda, (5) Danggappe and (6) Funtua.

Alagba series

Location: Shagamu 6°34′N 3° 42′E.

Classification: Oxic Paleustalf; clayey, kaolinitic, isohyperthermic family.

The soil is very deep over coastal-plain sediment; the profile site is gently undulating with a slope of 2—3%. The present vegetation is bushy regrowth with Eupatorium odoratum after several years of cultivation.

Ap	0—13 cm	Dark reddish-brown moist (5 YR 3/3) fine sandy loam; moderate fine crumb structure; very friable, non-sticky, non-plastic; many fine and medium interstitial pores, common fine and very fine tubular pores; many fine and medium roots; gradual, smooth boundary.
A3	13—36 cm	Dark reddish-brown moist (5 YR 4/3) sandy clay loam; weak medium subangular blocky structure, fine crumb in spots; very friable, non sticky, slightly plastic; common fine and medium interstitial pores, many fine and very fine random inped tubular pores; some faunal voids (termite chambers); many fine, common medium roots; gradual, smooth boundary.
B1	36—68 cm	Dark reddish-brown moist (2.5 YR 3/4) sandy clay; moderate fine subangular blocky structure; friable, non-sticky, slightly plastic; thin, patchy cutans on

TABLE I

Classification and environmental data of the soils used in this study

Location	Series	Great group	Parent material	Topography	Rainfall (mm)	Natural vegetation*
Shagamu	Alagba	Paleustalf	sedimentary	undulating	1700	rain forest
Benin	Alagba	Paleudult	sedimentary	undulating	1800	rain forest
Nsukka	Nkpologu	Paleustult	sedimentary	undulating	1740	Guinean savannah
Ibadan	Egbeda	Paleustalf	metamorphic gneiss	rolling	1200	rain forest—savannah boundary
Mokwa	Danggappe	Paleustalf	sedimentary	flat	1150	Guinean savannah
Zaria	Funtua	Paleustalf	eolian drift	undulating	1100	Guinean savannah

* Papadakis (1966)

		some ped surfaces, clearer in pores and root channels; some fine interstitial pores, many very fine and fine, common medium random inped tubular pores; some faunal voids; common fine, some medium roots; gradual, smooth boundary.
B21t	68—120 cm	Dark red moist (2.5 YR 3/6) sandy clay; moderate, fine subangular blocky structure; firm, slightly sticky, slightly plastic; thin, broken cutans on most peds, locally moderately thick, especially in pores; many fine and very fine, common medium random inped tubular pores; some faunal voids and channels; common fine, some medium roots; diffuse, smooth boundary.
B22t	122—183 cm+	Dark red moist (2.5 YR 3/6) clay; moderate fine subangular blocky structure; firm, slightly sticky, slightly plastic, distinctly more compact than previous horizon; broken thin, locally continuous moderately thick cutans on peds and in pores; common fine and very fine random inped tubular pores; few faunal channels; few fine roots. (No change detected by boring to 300 cm.)

Analytical methods

Soil samples were air-dried and passed through a 2-mm sieve prior to chemical analysis. Organic C content was determined by the dichromate oxidation method (Black, 1967). Cation-exchange capacity was measured by the summation of all exchangeable cations (Black, 1967). Particle-size distribution was determined by Bouyoucos' (1951) hydrometer method. Soil pH was determined in soil paste in water and 1*N* KCl using the Beckman Expandometric pH meter.

Pyrophosphate-extractable Fe and Al were determined by the procedure described by McKeague (1967). The dispersed pyrophosphate soil suspensions were separated on a superspeed centrifuge (Sorvall SS-1). Oxalate-extractable Fe and Al were determined by the photo-chemical extraction procedure developed by Schwertmann (1964). Dithionite-extractable Fe and Al were measured by the method of Mehra and Jackson (1960) using the dithionite-citrate system buffered with sodium bicarbonate.

Fe and Al in the extracting solution were determined colorimetrically on a Bausch and Lomb Spectronic-70 Electrophotometer using the 0-phenanthroline method for Fe (Jackson, 1969) and the modified aluminon method for Al (Hsu, 1964).

RESULTS AND DISCUSSION

Diagnostic analytical data of the soils used in this study are given in Table II. In all cases, a distinct increase in clay content from the A horizon downward is observed. Silt content is low (2—15%), except in the Funtua soil, formed from relatively recent eolian sediments. Delta pH values (pH KCl— pH H_2O) are negative for all horizons, indicating that the soil colloid possesses a net negative surface charge. Organic-carbon content of the surface soils is distinctly lower for the two drier locations, Danggappe and Funtua, which are situated in the northern Guinea and the Sudan savannah, respectively. Cation-exchange capacity of all soils is low, mostly well below 15 mequiv./100 g clay. Base saturation is low for the Nkpologu series and for the lower horizons of the Alagba series from Benin. Both series have a higher annual rainfall and a less pronounced dry season than the other series. The low base saturation of the Nkpologu series is probably related to the fact that it is situated on an old land surface.

The contents of the various forms of extractable Fe and Al in the soil are given in Table III and the distributions of clay content and dithionite-extractable Fe and Al as a function of profile depth are illustrated in Fig.2.

Dithionite-extractable Fe content (total free iron oxides) generally increases with the increase of depth for the six profiles studied. The Egbeda and Nkpologu soils contain the largest amount of free Fe oxides throughout the profile (2950—7184, and 2826—4256 mg Fe/100 g, respectively). The amount of free Fe oxides seems to follow the same distribution pattern as the clay content within the same profile (Fig.2). As also shown in Fig.3, the clay/dithionite-Fe ratios in the Egbeda, Nkpologu, and the two Alagba profiles remain fairly constant as a function of depth. This clearly indicates the combined movement of Fe and clay into the subsoil. Nevertheless, the clay/dithionite-Fe ratios of the Funtua and Danggappe profiles from northern Nigeria decrease with the increase of depth. This suggests that the Fe movement is partially independent of the clay movement in these two soil profiles developed under climatic conditions with a more pronounced dry season. There is little relationship between the content of dithionite-Al and profile depth (Fig.2). The amounts of dithionite-Al present in these profiles are relatively much less than the amount of dithionite-Fe in the profiles studied, except in uppermost horizons of the Danggappe, Alagba/Benin and Funtua profiles where the amount of the dithionite-Al is either greater than or equal to the amount of dithionite-Fe.

The oxalate-extractable Fe (amorphous Fe oxides) remains fairly constant throughout the profiles of Egbeda, Alagba (Shagamu), Alagba (Benin) and Nkpologu. The oxalate-Fe decreases with depth in the Funtua profile and increases with depth in the Danggappe profile. With the exception of Nkpologu soil, the amount of pyrophosphate-extractable Fe (organo-Fe complexes) is the lowest among the three forms and is mostly concentrated in the surface horizons of the profile. In the Nkpologu profile, the amount of pyrophosphate-

TABLE II

General properties of the soils used in this study

Depth (cm)	Horizon	Mech. analysis (%)			pH, soil paste		Organic C (%)	C.E.C. (mequiv./ 100 g)	Base saturation (%)
		Sand	Silt	Clay	H_2O	KCl			
Alagba/Shagamu									
0—13	A1	75	8	17	6.1	5.5	1.41	5.67	94
13—36	A3	71	7	22	6.5	5.6	0.43	3.15	89
36—68	B1	57	5	38	6.1	5.5	0.32	3.42	95
68—122	B21t	47	5	48	6.2	5.4	0.28	3.12	94
122—183	B22t	45	3	53	5.9	5.0	0.20	2.73	94
Alagba/Benin									
0—14	Ap	73	5	21	5.5	4.7	1.50	2.29	90
14—34	AB	60	2	38	5.1	4.2	1.47	2.23	79
34—75	B21t	46	4	50	4.7	3.8	0.27	1.50	29
75—125	B22t	50	2	48	4.8	3.8	0.33	1.35	35
125—175	B23t	50	3	47	4.9	3.9	0.30	1.34	41
Nkpologu/Nsukka									
0—6	Ap	67	7	26	4.6	3.9	1.23	1.87	20
6—43	A3p	65	9	26	4.6	3.9	0.94	1.74	17
43—70	B1	64	7	29	4.7	3.9	0.61	1.78	16
70—93	B21t	58	6	36	4.8	3.9	0.43	2.32	14
93—170	B22t	54	5	41	4.9	3.9	0.32	2.15	16
*Egbeda/Ibadan**									
0—5	A1p	67	12	21	6.6	5.7	1.54	5.45	95
5—15	A3	58	17	25	6.4	5.5	1.50	6.99	96
15—45	B1	49	14	37	6.5	5.8	0.76	5.26	96
45—65	B2t	30	14	56	5.6	5.3	0.28	4.33	96
65—95	IIB2t	30	6	64	5.7	5.3	0.26	4.06	95
95—110	IIB3	20	15	65	5.6	5.4	0.18	4.47	96
Danggappe/Mokwa									
0—8	Ap	66	14	20	6.4	6.1	0.59	3.93	87
8—28	A3	72	9	19	6.1	5.8	0.40	3.11	87
28—53	B1	56	13	31	5.3	5.1	0.23	2.45	80
53—170	B2t	44	11	45	4.7	4.5	0.13	2.48	85
Funtua/Zaria									
0—27	Ap	26	50	24	5.4	4.6	0.68	4.41	93
27—75	B21t	16	43	41	5.3	4.4	0.38	6.45	94
75—166	B22t	13	42	45	5.3	4.6	0.13	8.44	97

* Profile contains moderate amount of quartzite gravels between 0 and 65 cm of depth.

TABLE III

Extractable Fe and Al in soils

Depth (cm)	Extractable Fe (mg/100 g)			Extractable Al (mg/100 g)		Active Fe ratio (× 10^3)	Active Al ratio (× 10^3)
	Pyro-phosphate	Oxalate	Dithionite	Oxalate	Dithionite		
Alagba/Shagamu							
0–13	34	177	1284	95	955	138	99
13–36	25	181	1621	105	840	112	125
36–68	24	190	3018	156	1269	63	123
68–122	5	121	3423	170	902	35	188
122–183	3	122	3716	112	1532	33	73
Alagba/Benin							
0–14	28	72	1115	96	1600	65	60
14–34	122	121	2083	157	1703	58	92
34–75	13	136	2916	195	2023	47	96
75–125	2	120	2567	168	1600	47	105
125–175	3	106	2601	192	1635	41	117
Nkpologu/Nsukka							
0–6	230	147	2826	205	1840	52	111
6–43	199	135	3006	206	1703	45	121
43–70	201	162	3806	225	1634	43	138
70–93	197	162	4256	222	1703	38	130
Egbeda/Ibadan							
0–5	53	190	2950	168	1166	64	144
5–15	41	162	3423	194	1303	47	149
15–45	51	152	4954	208	1109	31	188
45–65	15	149	7139	259	2217	21	117
65–95	13	145	6779	263	2297	21	114
95–110	6	145	7184	246	1989	20	124
Danggappe/Mokwa							
0–8	13	44	614	71	754	72	94
8–28	10	57	682	71	686	84	103
28–53	13	89	1523	110	812	58	135
53–170	25	100	2636	136	1138	38	120
Funtua/Zaria							
0–27	71	185	754	52	781	248	67
27–75	71	110	1441	93	746	76	125
75–166	39	99	1779	114	1119	56	102

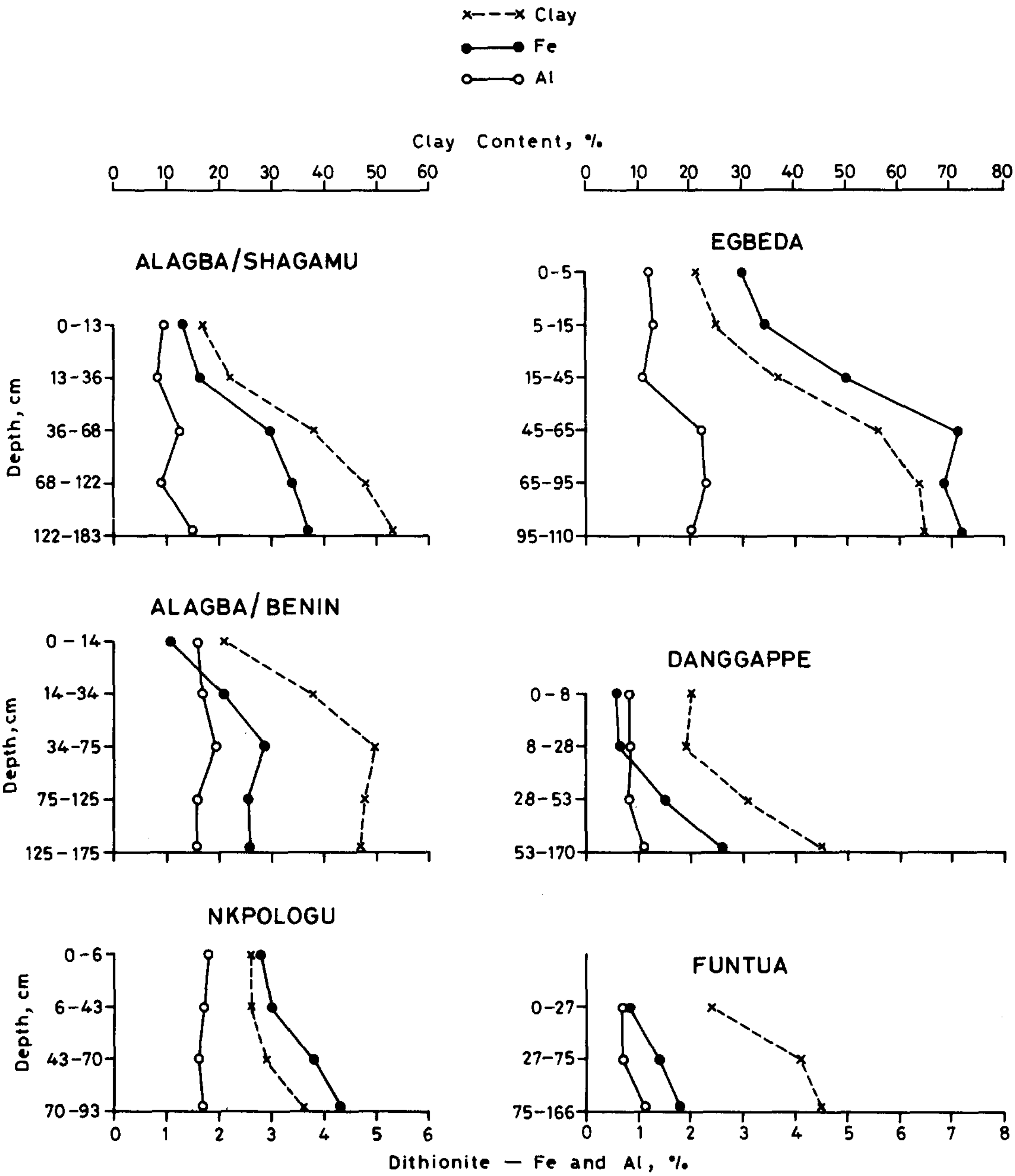

Fig.2. Profile distribution of dithionite-extractable Fe, Al and clay content in soils.

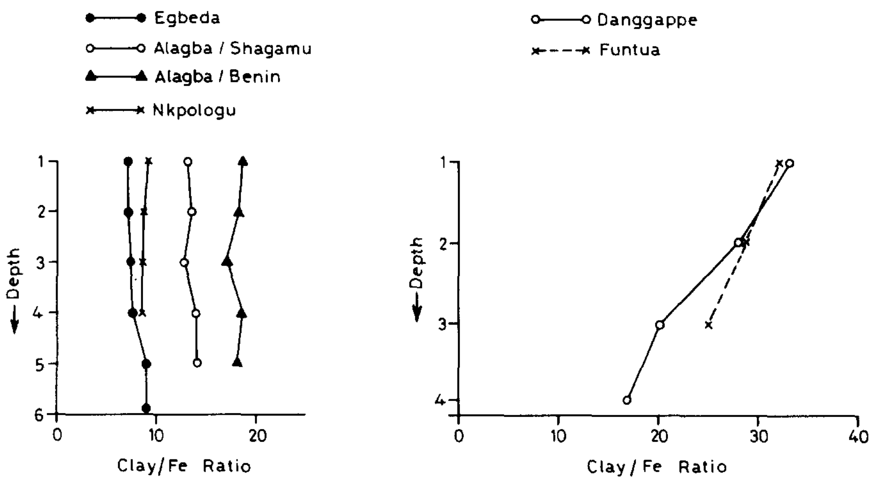

Fig.3. Relationship between clay/dithionite-Fe ratio and profile depth.

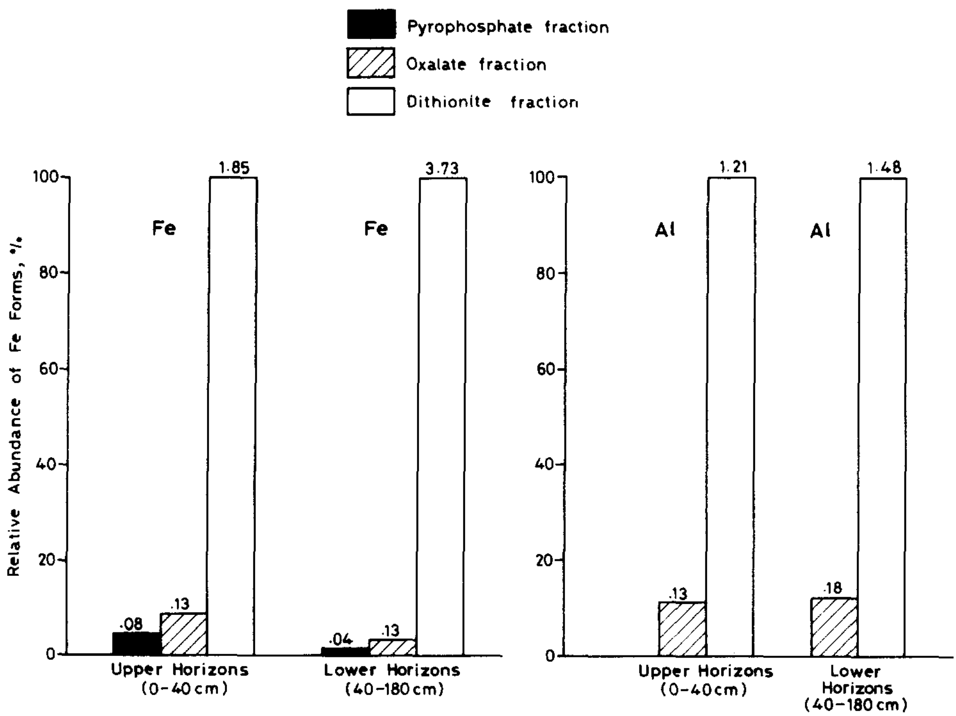

Fig.4. The average percentage of relative abundance of the various forms of Fe and Al in upper and lower horizons of the soil profile samples used in this study. Figures appearing on top of the bars are the actual average percentage of each form of Fe and Al present in the soil.

Fe is slightly higher than the oxalate-Fe throughout the profile. Bascomb (1968) indicated that pyrophosphate extracts amorphous "gel" hydrous oxides in addition to organo-Fe complexes. Thus, the relatively high amount of pyrophosphate-Fe throughout the Nkpologu profile may be due to the presence of a moderate amount of gel-from-Fe hydrous oxides, particularly in the lower horizons.

The relative abundance of the three fractions of Fe and the two fractions of Al in the upper and lower horizons of the six profiles is summarized in Fig.4. Oxalate-Fe and pyrophosphate-Fe constitute approximately 8% and 4%, respectively, of the total dithionite-Fe in the surface soils of the six profiles studied. Much lower proportions were found in the lower horizons of the profiles. Oxalate-Al comprises about 11% of the dithionite-Al both in the surface and the lower horizons of the profiles.

The relative abundance of Fe and Al in the amorphous and organic complex forms is much less in the tropical soils used in this study when compared with the results obtained by McKeague and Day (1966) and McKeague et al. (1971) on soils of a temperate region. They found that the oxalate-Fe constitutes 30—60% of the dithionite-Fe in the soils used in their study (Podzols, Gleysols and Brown Forest soils). Oxalate-Al in these soils in most cases consists of more than 60% of the dithionite-Al.

The high-temperature condition and the prolonged dry season (4—5 months annually) may be responsible for the low content of amorphous Fe and Al fractions in these well-drained soils. As pointed out by Sherman et al. (1964), drying at elevated temperature causes the amorphous Fe and Al oxides to dehydrate and subsequently shifts to a system of greater crystallinity. They also reported evidence showing that the loss of amorphous materials in tropical soils as a result of dehydration and crystallization resulted in significant changes in certain chemical and physical properties of the soil, such as, the decrease in cation-exchange capacity and the increase in both bulk density and particle density of the soil.

The relative distribution of amorphous to total free Fe oxides within each profile can be conveniently expressed as "active Fe ratio", which is obtained as follows:

$$\text{active Fe ratio} = \frac{\text{oxalate-Fe}}{\text{dithionite-Fe}}\,.$$

Results are also given in Table III. The active Fe ratio in all the soils decreases with the increase in depth within the profile. This clearly indicates that higher proportions of Fe oxides are present as crystallized forms in the lower horizons of these well-drained profiles. Nevertheless, the same relationship does not hold true in the case of Al where the active Al ratios are calculated in the same manner as for Fe. In view of the fact that the actual chemical and physical forms of Al in soil extracted by the oxalate and dithionite reagents are poorly understood, therefore no interpretation of results can be made at this point.

The co-migration of clay and dithionite-extractable Fe indicates the mechanical migration of small mineral particles from the A to the B horizons of the soils studied (lessivage). The diagnosis of the B horizon as an argillic horizon is moreover based on the fact that the ratio of the clay content of the eluvial horizon to the illuvial horizon is larger than 1.2. Field observations indicate the presence of cutans on most peds in the B horizons of the profiles sampled. Therefore, these soils are excluded from the order of Oxisols (Soil Survey Staff, U.S.D.A., 1970).

According to degree of base saturation, two soils can be classified as Ultisols (Alagba series, Benin and Nkpologu series), whereas the other four profiles (Alagba/Shagamu, Egbeda, Danggappe and Funtua) with a base saturation of more than 35% in the argillic horizon would classify as Alfisols. The relative enrichment of clay in the B horizon leading to the formation of an argillic horizon is, however, not clear in most of these profiles. Only in the Funtua and Egbeda series a macro- and micro-morphologically distinct argillic horizon, characterized by abundant clay cutans on peds and in pores was observed. In the other four profiles, derived from parent materials poor in weatherable minerals, and situated on older land surfaces, the argillic horizon is attenuated. These soils are thus transitional to the order of Oxisols. Aubert and Segalen (1966) also observed that the process of elimination of clay and Fe from the surface soil without a corresponding formation of a distinct argillic horizon occurred in some West African soils and called the process "impoverishment". This process may well be dominant in the two Alagba soils, the Nkpologu soil and the Danggappe soil. It appears that the classification in the U.S.D.A. system of most of the soils studied here will require further research and may well lead to certain alterations of the classification system for soil conditions in the more humid parts of West Africa.

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