

FORMS AND CONTENTS OF IRON AND ALUMINUM IN INLAND FLOOD PLAINS OF SOUTH-EASTERN NIGERIA

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ABSTRACT

Fourteen representative soils from inland flood plains in Southeastern Nigeria were studied to characterise forms (crystalline and amorphous) contents in iron and aluminium oxides. Total iron and aluminium, extracted using HCl after fusion with Na_2CO_3 , ranged from 1.25 to 7.74 % by weight of dry soil, with a mean of 3.29 % for total Fe_2O_3 and from 9.75 to 44.67 % with a mean of 26.04 % for total Al_2O_3 . Broad textural grouping of the soils showed mean total contents of Fe_2O_3 and Al_2O_3 comparable to fine-textured soil, medium-textured soil, and coarse-textured soil. On the basis of drainage, mean contents of total iron and aluminum are, in a decreasing order : very poorly drained, poorly drained and imperfectly drained soil. Total free oxides (DCB extractable forms) averaged 0.59 and 0.16 %, for DCB Fe_2O_3 and DCB Al_2O_3 , respectively. The fine texture soil gave the highest mean value (0.90 %) for DCB Fe_2O_3 , as compared to medium and coarse texture soils. Generally, values of oxalate extractable and pyrophosphate extractable Fe_2O_3 were relatively low. The reactivity of the sesquioxides, measured using the ratio of oxalate extractable-to dithionite extractable iron and aluminum, tended to be high, indicating that much of the total free oxides exists mainly in the form of amorphous oxides and, which, impeded drainage. Active ratios of Al_2O_3 were generally higher than those of Fe_2O_3 . The extractability of total free iron ranged from 8.50 to 25.3 % while that of aluminum ranged from 0.26 to 1.84 %, suggesting a relatively less weathering of these inland plain soils (Wetland soils).

Key-words : Aluminum, iron, soil, inland flood plains, Nigeria.

RESUME

FORMES ET TENEURS EN FER ET EN ALUMINIUM DES PLAINES DES BAS-FONDS DU SUD-EST DU NIGERIA

Quatorze sols représentatifs des bas-fonds du Sud-Est du Nigeria ont été utilisés dans cette étude. Des échantillons de sols ont été caractérisés au laboratoire pour déterminer les formes et les teneurs en oxydes, fer et aluminium libres. La teneur en fer et aluminium extractible par HCl, après fusion, avec Na_2CO_3 , a varié de 1,25 à 7,74 % par poids de sol sec, avec une moyenne de 3,29 % pour Fe_2O_3 total et de 9,75 à 44,67 % avec une moyenne de 26,04 % pour Al_2O_3 total. Une classification approximative des sols montre des teneurs moyennes de Fe_2O_3 et Al_2O_3 de l'ordre de sol à texture fine, sol à texture moyenne et sol à texture grossière. Sur la base du drainage, la teneur moyenne en fer total et en aluminium est par ordre décroissant : très faiblement drainé, faiblement drainé, anormalement drainé. Les teneurs totales en oxydes (formes extractible au DCB) ont été en moyenne de 0,59 et 0,16 %, pour DCB Fe_2O_3 et DCB Al_2O_3 , respectivement. Les sols à texture fine ont présenté les moyennes les plus élevées (0,90 %) pour DCB Fe_2O_3 , par rapport aux sols à texture moyenne et grossière. De façon générale, les teneurs en Fe_2O_3 extractibles à l'oxalate et au pyrophosphate ont été relativement faibles. La réactivité des sesquioxydes mesurée par la fraction de fer et d'aluminium extractible à l'oxalate, d'une part, et au dithionite d'autre part, tend à être élevée. Ce qui est la preuve qu'une bonne partie des oxydes libres existe sous forme amorphe, à cause du mauvais drainage. Les ratios de Al_2O_3 actif ont été généralement plus élevés que ceux de Fe_2O_3 . L'extractibilité du fer libre total a varié de 8,80 à 25,3 % tandis que celle de l'Aluminium varie de 0,26 à 1,84 % témoignant ainsi d'une altération relativement faible de ces sols de bas-fonds (sols humides).

Mots clés : Aluminium, fer, sol, bas-fonds, Nigeria.

INTRODUCTION

Inland flood plains occupy a sizeable portion of South-eastern Nigeria. The area is drained by Cross River, Enyong Creek, and Ikpa River. The soils are mainly hydromorphic, occurring in fresh water swamps, flood plains and catchments. These soils have not been adequately studied.

Forms of iron and aluminum are important parameters for a proper understanding of these soils. The content and distribution in the soils are known to influence some soil properties such as anions adsorption, surface charges, specific surface area, swelling and aggregate formation, nutrient transformation and pollutants retention (Aghimien *et al.*, 1988 ; Deshpande *et al.*, 1968 ; Greenland *et al.*, 1968). The various forms have been extracted using different reagents (Mc Keague and Day, 1966 ; Blume and Schwertman, 1969). Dithionite extractable iron has been widely considered to give a reasonable estimate of pedogenic free iron in soils while oxalate extractable represents amorphous forms of iron and aluminum and the differences between the two chemical forms give a measure of crystalline iron and aluminum oxides in soils.

These amorphous and crystalline oxides occurring in soils could be used in the understanding of the genesis, properties and classification of the soils, particularly in the tropics. They have been used to identify diagnostic horizons (McKeague and Day, 1966), while Alexander (1974) used the same

parameter to estimate the age of soils he studied. A constant dithionite extractable Fe_2O_3 to clay ratio with depth reported by Juo (1981) indicates a downward migration of iron oxides and clays (Omenihu *et al.*, 1984).

The reactivity of these sesquioxides are usually assessed by the value of the active ratios. Soils with poor drainage conditions have been reported to have high active ratios and therefore, more reactive (Aghimien *et al.*, 1988).

The objectives of this study are to examine the content and forms (Crystalline or amorphous) of iron and aluminum in the soils of some inland flood plains in South eastern Nigeria to and relate these forms to drainage conditions as well as the broad textural grouping of the soils using fourteen representative soil pedons.

MATERIAL AND METHODS

Fourteen soil profiles located in the flood plains of the Cross River, Southeastern Nigeria, were studied. The area is in the rain forest zone with a mean annual rainfall of over 3000 mm. The soils are formed from coastal plain sand, alluvial and shale-rich sediments. Their broad classification and physical characteristics are given in Table 1 (Ibia, 1995).

The profiles were dug and sampled. The soil samples were air-dried and sieved through a 2 mm-sieve. Sub-samples were crushed and further sieved through a 100 mesh-sieve for the determination of the various forms of iron and aluminum.

Table 1 : Some physical characteristics of soils from the inland floodplains of South-Eastern Nigeria.

Quelques caractéristiques physiques des sols de bas-fonds au Sud-Est du Nigeria.

Soil sample	Profile Depth (Cm)	Drainage	Particle Size Distribution (%)			Texture
			Sand	Silt	Clay	
EN31	0 - 36	Imperfectly drained	48.8	16.2	35.0	Sandy clay
EN32	0 - 46	Imperfectly drained	53.1	22.4	24.5	Sandy clay loam
EN33	0 - 45	Imperfectly drained	64.2	17.2	18.6	Sandy loam
EN51	0 - 42	Poorly drained	25.0	16.0	59.0	Clay
EN52	0 - 50	Poorly drained	50.0	26.4	23.6	Sandy clay loam
EN53	0 - 40	Poorly drained	41.0	27.6	31.4	Clay loam
EN54	0 - 30	Poorly drained	43.0	24.2	32.8	Clay loam
EN61	0 - 50	Poorly drained	86.2	5.8	8.0	Loamy sand
EN71	0 - 50	Very poorly drained	4.2	31.0	64.8	Clay
EN72	0 - 50	Very poorly drained	46.8	16.6	36.6	Sandy clay
EN73	0 - 50	Very poorly drained	28.4	35.6	36.0	Clay loam
EN74	0 - 51	Very poorly drained	75.8	6.0	18.2	Sandy loam
EN75	0 - 40	Very poorly drained	53.2	32.0	14.8	Loam
EN81	0 - 40	Very poorly drained	14.2	38.8	47.0	Clay

Adapted from: Ibia, 1995.

EN 31 - EN 81 = Soil Code used in field sampling

ANALYTICAL PROCEDURE

Particle size was determined using the hydrometer method with Calgon (Sodium hexametaphosphate) as the dispersing agent (IITA, 1979). Forms of iron and aluminum were first extracted using various methods. Free oxides (dithionite Fe_2O_3 and Al_2O_3) were extracted with the dithionite-citrate-bicarbonate (DCB) solution. (Mehra and Jackson, 1960). The amorphous oxides (oxalate Fe_2O_3 and Al_2O_3) were extracted using conc. ammonium oxalate solution (McKeague and Day, 1966). The procedure using pyrophosphate solution described by McKeague (1967), was employed to extract organic forms of iron and aluminum.

Total iron and aluminum in the soils were extracted with dilute HCl after fusion with Na_2CO_3 . All forms of iron and aluminum (DCB-extractable, Oxalate-extractable, pyrophosphate-extractable and HCl-extractable) were measured colorimetrically following extraction using the ortho-phenanthroline method for iron (Jackson, 1969) and the modified aluminon method for aluminum (Black, 1967).

RESULTS AND DISCUSSION

Results on the physico-chemical properties of the soils studied have been published elsewhere (Ibia, 1995). The soils were grouped into three drainage classes namely: Imperfectly drained, poorly drained and very poorly drained soils based on the outline by FAO (1986)

Three broad textural groupings (Soil Survey Staff, 1990) were used as shown in Table 1 and defined as follows:

Fine-textured soils: clays, silty clays, sandy clays, clay loam and silty clay loam, with more than 35 % clay.

Medium-textured soils: sandy loam, loam, sandy clay loam, silt loam, silt, silty clay loam and clay loam with less than 35 % clay and less than 65 % sand. The sand fraction may be as high as 82 % when a minimum of 18 % clay is present.

coarse-textured soils: sand, loamy sand and sandy loam with less than 18 % clay and more than 65 % sand.

The soils were shown to be generally acidic (pH 4.72- 5.67), with possible iron and aluminum

toxicity problems and low contents of available P and exchangeable K.

Table 2 shows profile contents of the various forms of iron and aluminum. Contents of total iron ranged from 1.35 to 7.74 % and total aluminum from 9.75 to 44.67 % in the samples. These ranges fell within the limits obtained by Aghimien *et al.*, (1988) in some hydromorphic soils in Nigeria. The values were however, relatively lower than those obtained by Udo (1980) in well drained profiles.

When data were grouped into textural classes (Table 3), mean total iron contents ranged from 2.61 to 4.49 %, the trend being, content in fine textured soils, medium textured soils, coarse textured soils. This trend was also observed for total aluminum contents which ranged from 19.93 % in coarse textured soil to 33.39 % in the fine textured soils. Aghimien *et al.*, (1988) showed that total iron content in the soils they studied tended to be influenced largely by clay and silt fractions. On the basis of drainage class (Table 4), very poorly drained profiles gave highest mean values for total iron and aluminum (3.74 and 32.68) contents followed by poorly drained profiles (3.36 and 23.86) followed by imperfectly drained soils (2.48 and 19.36).

Dithionite Citric Bicarbonate extractable, oxalate extractable and pyrophosphate extractable forms of iron and aluminum are presented in table 2. For dithionite extractable Fe_2O_3 , the mean values ranged from 0.14 to 1.46 and for Al_2O_3 it ranged from 0.10 to 0.24. Content Fe_2O_3 appeared to be higher in fine textured soils with a mean of 0.90 % than in medium and coarse textured class. Higher mean value were also recorded for very poorly drained and imperfectly drained soil classes.

Generally the mean values of oxalate extractable and pyrophosphate extractable Fe_2O_3 and Al_2O_3 were low. Oxalate Fe_2O_3 ranged from 0.08 to 0.32, while pyrophosphate forms ranged from 0.03 to 0.18. For Al_2O_3 , the values ranged from 0.02 to 0.09 % for oxalate extractable forms and from 0.14 to 0.63 for pyrophosphate extractable forms. The generally low extractable values of the various forms of the sesquioxides have been attributed to the poor drainage conditions of the soils which prevent strong weathering and subsequent formation of sesquioxides in these soils (Aghimien *et al.*, 1988).

Table 2 : Mean values of iron and aluminum contents in soils from inland flood plains of South eastern Nigeria.

Valeurs moyennes de la teneur en fer et aluminium des sols de bas-fonds au Sud-Est du Nigeria.

Soil sample	Drainage Class	Extractable Fe			Active Ratio	Extractability (%)	Total	DCB	Extractable Al		Active Ratio	Extractability (%)
		Total	DCB	Oxalate % Fe ₂ O ₃					Oxalate % Al ₂ O ₃	Pyrophosphate		
EN31	Imperfectly Drained	1.89	0.46	0.12	0.26	24.3	14.80	0.11	0.03	0.25	0.27	0.74
EN32	*	3.46	0.44	0.12	0.27	12.7	32.40	0.13	0.10	0.27	0.7	0.40
EN33	*	1.99	0.31	0.11	0.35	15.6	10.89	0.20	0.05	0.26	0.25	1.83
EN51	Poorly drained	7.74	1.46	0.24	0.16	18.9	44.67	0.24	0.06	0.48	0.25	0.53
EN52	*	4.20	0.94	0.32	0.34	22.3	37.50	0.18	0.04	0.44	0.22	0.48
EN53	*	1.35	0.14	0.08	0.57	10.3	9.75	0.18	0.06	0.19	0.33	1.84
EN54	*	2.44	0.52	0.26	0.50	21.3	22.08	0.18	0.04	0.34	0.22	0.81
EN61	*	1.94	0.49	0.31	0.63	25.2	16.78	0.18	0.04	0.34	0.22	0.81
EN71	Very poorly drained	6.06	1.24	0.31	0.25	20.4	50.20	0.20	0.09	0.63	0.45	0.39
EN72	*	2.24	0.67	0.14	0.20	15.8	36.50	0.14	0.02	0.26	0.14	0.38
EN73	*	4.25	0.54	0.16	0.29	12.7	41.60	0.11	0.08	0.48	0.72	0.26
EN74	*	1.89	0.48	0.14	0.29	25.3	10.40	0.10	0.07	0.44	0.70	0.96
EN75	*	2.46	0.21	0.14	0.67	8.5	12.40	0.14	0.04	0.14	0.29	0.11
EN81	*	2.25	0.44	0.11	0.25	19.6	24.70	0.19	0.08	0.38	0.42	0.76
Overall Total		46.16	8.34	0.56	5.03	252.8	364.67	2.22	0.82	4.72	5.53	10.20
Overall Mean		3.29	0.59	0.18	0.31	18.1	26.04	0.16	0.06	0.34	0.38	0.73

* DCB = Dithionite Citrate Bicarbonate

* Active Ratio = Ratio of oxalate/Dithionite extractable Fe or Al.

Oxalate and dithionite extractable iron and aluminum, as well as their various ratios of these cations, have been used to evaluate soil development and weathering (Omenihu *et al.*, 1994). The ratios of oxalate extractable iron and of aluminum to dithionite extractable forms, which are a measure of the reactivity of the sesquioxides, indicate the relative amount of poorly ordered and crystalline iron and aluminium compounds in the soil (Blume and Schwertmann, 1969). Active iron ratios ranged from 0.16 to 0.67 when all the soils studied are pooled together (Table 2). The mean values are comparable to those (0.20 to 0.67) obtained by Aghimien *et al.*, (1988) in some hydromorphic soils of southern Nigeria but relatively higher than values obtained by Omenihu *et al.*, (1994) in well drained coastal plain sand soils of Southern Nigeria. Udo (1980) also obtained values for iron ratio ranging from 0.03 to 0.13 in well-drained Nigerian soils, as compared to values of 0.36 to 0.99 in poorly drained profiles from Nigeria. Generally, the activity of iron is known not to exceed 0.33 in well drained soils (Mc Keague and Day, 1966) whereas, Stonehouse and St. Arnaud (1971) obtained high iron ratios, which were generally above 0.33 in poorly drained soils. Whereas, for these wetland flood plains under study, active iron ratios varied from within the limits to double the limits; particularly in coarse texture soils (Table 3) and poorly-drained profiles (Table 4). According to Schwertmann (1964), a higher iron reactivity indicates lower degree of ageing of the minerals, pointing to the fact that the rate

of iron release from the primary mineral lattices seems to exceed the rate of iron crystallization. The relatively high active iron ratios in these soils show that a large fraction of the total free oxides exists, mainly in the amorphous, rather than the crystalline forms and that, impeded drainage, reduces crystallization of iron minerals.

Active ratios of Al_2O_3 were higher than those of Fe_2O_3 and ranged from 0.22 to 0.77 and were relatively higher than those obtained by Aghimien *et al.*, (1988), which ranged from 0.09 to 0.35. When considered on broad textural grouping, the active aluminum ratio gave a highest mean value of 0.54 in medium-textured soils, as compared to fine-textured soils (Table 3). The relatively higher aluminum ratios indicates the presence of higher amounts of amorphous forms of aluminum oxides than iron oxides in the soils.

Extractability of the various oxides, which is the ratio of the total free oxides (DCB extractable iron or aluminum) to total content of iron and aluminum, is a useful index for evaluating the degree of soils weathering. The extractability of total free iron ranged from 8.50 to 29.2 %, while that of aluminum ranged from 0.26 to 1.84 % in all the soils studied (Table 2).

These results seem to suggest that the soils are relatively less weathered, a feature of most hydromorphic soils. Udo (1980) obtained iron extractability values higher than 50 % in some well drained soils formed on basement complex rocks, whereas for poorly drained ones, average extractability was only 10 %.

Table 3 : Iron and aluminum contents of soils from Inland flood plains of South Eastern Nigeria, as a function of broad textural classes.
Teneurs en fer et en aluminium des sols de plaines alluviales au Sud du Nigéria, en fonction des classes texturales.

Soil sample	Broad Textural Class	Extractable Fe			Active Ratio	Extractability (%)	Extractable Al			Active Ratio	Extractability (%)
		Total	DCB	Oxalate % Fe ₂ O ₃			Pyrophosphate	Total	DCB		
EN31	Fine	1.89	0.46	0.12	0.26	24.3	0.11	0.03	0.25	0.27	0.74
EN51		7.74	1.46	0.24	0.16	18.8	0.24	0.06	0.48	0.25	0.53
EN71		6.06	1.24	0.31	0.25	20.4	0.20	0.09	0.63	0.45	0.39
EN81		2.25	0.44	0.11	0.25	19.6	0.19	0.08	0.38	0.42	0.76
Mean		4.49	0.90	0.20	0.22	20.0	0.19	0.07	0.44	0.37	0.56
EN32	Medium	3.46	0.44	0.12	0.27	12.7	0.13	0.10	0.27	0.77	0.40
EN53		1.35	0.14	0.08	0.57	10.3	0.18	0.06	0.19	0.33	1.84
EN72		4.24	0.67	0.14	0.21	15.8	0.14	0.02	0.26	0.14	0.38
EN73		4.25	0.54	0.16	0.29	12.7	0.11	0.08	0.48	0.72	0.26
EN74		1.89	0.48	0.14	0.29	25.3	0.10	0.07	0.44	0.70	0.96
Mean		3.04	0.48	0.13	0.29	14.8	0.13	0.07	0.33	0.54	0.49
EN33	Coarse	1.99	0.31	0.11	0.36	15.6	0.20	0.05	0.26	0.25	1.83
EN52		4.20	0.94	0.32	0.34	22.3	0.18	0.04	0.44	0.22	0.48
EN54		2.44	0.52	0.26	0.56	21.3	0.18	0.06	0.34	0.22	0.81
EN61		1.94	0.49	0.31	0.63	25.2	0.12	0.06	0.21	0.50	0.71
EN75		2.46	0.21	0.14	0.67	8.50	0.14	0.04	0.14	0.28	1.12
Mean		2.61	0.49	0.23	0.47	18.7	0.16	0.05	0.28	0.31	0.80

Table 4 : Influence of drainage on the content of iron and aluminium in inland flood plains of South Eastern Nigeria
Influence du drainage sur la teneur en fer et aluminium dans les plaines alluviales, au Sud Est de Nigéria.

Soil sample	Drainage Class	Extractable Fe			Extractable Al			Active Ratio	Extractability (%)
		Total	DCB	Oxalate % Fe ₂ O ₃	Total	DCB	Oxalate % Al ₂ O ₃		
EN31	Imperfectly Drained	1.89	0.46	0.12	14.80	0.11	0.03	0.25	0.74
EN32		3.46	0.44	0.12	32.40	0.13	0.10	0.27	0.40
EN33		1.99	0.31	0.11	10.89	0.20	0.05	0.26	1.83
Mean	Poorly drained	2.45	0.40	0.12	19.36	0.15	0.06	0.26	0.77
EN51		7.74	1.46	0.24	44.47	0.24	0.06	0.48	0.53
EN52		4.20	0.94	0.32	37.50	0.18	0.04	0.44	0.48
EN53		1.35	0.14	0.08	9.75	0.18	0.06	0.19	1.84
EN54		2.44	0.52	0.26	22.08	0.18	0.04	0.34	0.81
EN61	Very Poorly drained	1.94	0.49	0.31	16.78	0.12	0.06	0.21	0.71
EN75		2.46	0.21	0.14	12.40	0.14	0.04	0.14	1.12
Mean		3.36	0.63	0.23	23.86	0.17	0.05	0.30	0.71
EN71		6.06	1.24	0.31	50.20	0.20	0.09	0.63	0.39
EN72		4.24	0.67	0.14	36.50	0.14	0.02	0.26	0.38
EN73	Very Poorly drained	4.25	0.54	0.16	41.60	0.11	0.08	0.48	0.26
EN74		1.89	0.48	0.14	10.40	0.10	0.07	0.44	0.96
EN81		2.25	0.44	0.11	24.70	0.19	0.08	0.38	0.76
Mean		3.74	0.67	0.17	32.68	0.15	0.07	0.44	0.45

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