

Sesquioxides Distribution of Soils of Contrasting Land Units in Egbema, Southeastern, Nigeria

B.U.Uzoho

Department of Soil Science and Technology, Federal University of Technology
P.M.B 1526, Owerri, Imo State, Nigeria
betheluzoho@yahoo.com.

Abstract

Sesquioxides provide information about several physicochemical properties of the soil including the age, drainage condition, ion retention amongst others. Duplicate soil samples were collected from three depths (0-15, 15-30 and 30-45 cm) of three land units (natural levee, floodplain and upland) in Egbema, southeastern, Nigeria. and analyzed for dithionate (d) and oxalate (ox) Fe, Al and Mn. Also the Fe_d , Al_d , Mn_d , Fe_{ox} , Al_{ox} and Mn_{ox} were correlated with selected soil properties. Soil Fe_d , Al_d and Mn_d contents ranged from 7800-20400 and 2200-21900 $mg\ kg^{-1}$, 200-300 and 100-400 $mg\ kg^{-1}$ and 12000- 20000 and 6000-18100 $mg\ kg^{-1}$ while Fe_{ox} , Al_{ox} and Mn_{ox} ranged from 10000-20000 and 10100-16600 $mg\ kg^{-1}$, 100-200 and 100- 300 $mg\ kg^{-1}$ and 600-1200 and 10000-14000 $mg\ kg^{-1}$ in the top and sub soils respectively. Whereas, dithionate extractable Al and Mn were higher than the oxalate extractible, the reverse was the case for Fe indicating the prevalence of Fe in the amorphous highly reactive fraction. Active Fe, Al and Mn ranged from 0.98-1.28 and 0.55-4.90, 0.33-0.67 and 0.50-2.00 and 0.30-1.00 and 0.56-1.83 in the top and sub soils respectively indicating that their reactivity was stronger in the sub than the top soil. Mean active Fe was higher than the threshold values of 0.54 signifying that the soils are young and poorly drained with the youthfulness and low drainage conditions degreasing as floodplain > natural levee > upland. Soil properties especially sand, silt, clay, silt/clay ratio, TN, OM, P, Ca, K, Mg, Na, H, ECEC and % BS affected soil sesquioxide concentrations. In general, the soils may support intensive production of such crops as rice that tolerates waterlogging and could also retain large amounts of toxic materials or other pollutants from crude oil pollution into insoluble and non available forms due to their high reactivity.

Keywords: Sesquioxides, Distribution, Soils, Land units and Nigeria

1.0 Introduction

Sesquioxides refer to the oxides and hydroxides of iron, aluminium, titanium, manganese and silicon in the soil (Ojo-Atere and Ajuwon, 1985; Essoka and Esu, 2000). They are crystalline and amorphous in nature, although a small fraction may be present as organic complexes and together they influence several soil physicochemical properties (Hassan et al., 2005). They play significant roles in swelling and aggregate formation, cation exchange capacity, anion adsorption, surface charge, specific surface area, nutrient transformation and pollutant retention in soils (Aghimien et al, 1988; Essoka and Essu, 2000; Hassan et al., 2005). They also play important role in the conferment of 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). Sesquioxides exist as discrete particles or coatings on soils and precipitate P into insoluble forms as Fe-P and Al-P thereby restricting their mobility and availability in soils (Sims and Ellis, 1983). Also, they are important in cementation and aggregate formation processes of tropical soils and as such influences their plasticity and compressibility (Townsend, 1987). Furthermore, sesquioxides are significant in the estimation of the degree of weathering and stage of soil development (Shwertzman, 1992).

Relevance of sesquioxides in soil physicochemical processes vary depending on their crystallinity, with the less crystalline or amorphous fractions more reactive than the highly crystallized forms. For instance, it has been indicated that P and metal sorption is higher with amorphous Fe and Al oxides than the crystalline forms (Uzoho et al., 2005). Crystalline oxides may be extracted using Dithionite-Citrate-Bicarbonate (Mehre and Jackson, 1960) and the amorphous oxides with ammonium oxalate (McKeague and Day, 1966). According to Hassan et al. (2005), the dithionite extractible Fe and Al have been considered to give a reasonable estimate of the total pedogenic free Fe and Al while oxalate extractible forms represent the amorphous Fe and Al in soils. Crystalline (free) or dithionite extractable iron oxide is considered as the total pedogenic iron and occurs in forms such as goethite, lepidocrocite and haematite while aluminium occurs in such form as gibbsite (Brady and Weil, 2002). The extractable dithionite-citrate manganese is termed the easily reducible manganese (NSSC, 1995). Reactivity of sesquioxides depends on the ratio of the oxalate to the dithionite extractible Fe and Al oxides and describes the relative amount of the poorly ordered and crystalline Fe and Al oxides in the soil (Gallez et al., 1975; Omenihu et al., 1994). Poorly drained soils are more reactive with higher ratios than well-drained soils (Aghimien et al 1988, Ibia,2001).

Distribution of sesquioxides in the tropics and indeed Nigerian soils 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). It has been indicated that the content of different sesquioxides in tropical soils increases as the soils ages, largely due to the influence of weathering (Udo, 1980; Osodeke et al., 2005). Profile distribution of sesquioxides in some Nigerian soils has been reported. These include ranges such as 18.04-19.35 and 6.07-28.70 mg kg⁻¹ oxalate Fe and 98.40-175.46 and 18.04-205.00 mg kg⁻¹ dithionite Fe and 16.07-18.37 and 3.44-106.00 mg kg⁻¹ oxalate Al and 16.40-164.00 and 16.40-162.36 mg kg⁻¹ dithionite Al in the surface and subsurface soils respectively of granitic savanna soils of Bauchi state (Hassan et al., 2005), 4000-10000 and 1100-6000 mg kg⁻¹ dithionate Fe and 1900-7600 and 1900-19300 mg kg⁻¹ dithionate Al in the surface and subsurface depths respectively of some southwestern Nigeria soils (Ojo-Atere and Ajuwon, 1985), 959.0-5838.0 and 1084.0-5838.0 mg kg⁻¹ oxalate Fe and 6255.0-8131 and 5421.0-8131.0mg kg⁻¹ dithionate Fe and 83.30-550.50 and 25.0-33971.0 mg kg dithionate Mn and 41.70-325.00 mg kg⁻¹ oxalate Mn in surface and subsurface depths respectively of the inland valleys of central cross river (Essoka and Esu, 2000). It also includes a range of 300-6600 and 300-11400 mg kg⁻¹ oxalate Fe and 7400-58600 and 4900-40600 mg kg⁻¹ dithionate Fe and 30-1200 and 100-1200 mg kg⁻¹ oxalate Al and 1900-8700 mg kg and 3400- 17800 mg kg⁻¹ dithionate Al in the surface and sub surface depths respectively of soils along a toposequence in Umudike area of southeastern Nigeria (Osodeke et al., 2005).

Soil properties especially clay, sand, silt, pH, OM, ECEC amongst others may affect sesquioxide distribution in soils. None serious relationship has been reported between dithionate Fe and sand, silt, clay, pH, OM, N, P Ca, Mg, K and ECEC but between oxalate Fe and sand, pH and K, dithionate Al with sand and clay and oxalate Al with pH and K (Osodeke et al., 2005).

Egbema lies in the low land area of Southeastern and experiences yearly seasonal flooding between the months of September to November in the raining season. Sediments and organic material transported by this flood water are usually deposited on soils as they make their way into the Atlantic Ocean. These soils are thus usually fertile on the account of these alluvial deposits. However, despite the potentials of these soils for agriculture, only limited information exists about their characteristics especially the sesquioxide distribution. The objectives of this study were therefore to determine the sesquioxide distribution in soils of contrasting land units in Egbema, southeastern, Nigeria and the relationship between the sesquioxide contents and selected soil properties.

2.0 Materials and Methods

2.1 Study Sites, Sample Collection and Preparations

The study location was Egbema in the humid rainforest zone of southeastern Nigeria. Egbema lies in lowland area of southeastern Nigeria and suffers from seasonal annual flooding that occurs between the months of August and November yearly. The geology, climate and climax vegetation of the study site has been reported in another study (Uzoho and Okechukwu, 2014).

Duplicate soil samples were collected from three depths (0-15, 15-30 and 30-45 cm) of three land units (Natural levee, floodplain and upland) and given a total of 18 samples. The samples were air dried and sieved using 2mm diameter mesh and the fine earth fractions subjected to laboratory analysis.

2.2 Laboratory Analysis

Routine and sesquioxides content analyses were conducted on the soils. Particles size (Gee and Or, 2002), soil pH in 1:2:5 soil/water and 1N KCl ratio using glass electrode of the pH meter, organic carbon by modified wet oxidation method of Walkley and Black (Nelson and Sommers, 1996) and OM determined by multiplication with 1.724 (van Bemmelen correction factor), total N Bremner (1996), available P (Olson and Sommers, 1982) and ECEC (Thomas, 1996).

Sesquioxide contents were determined as follows: Free Fe, Al and Mn oxides were determined using the Dithionate Citrate Bicarbonate (DCB) method (Mehre and Jackson, 1960) while the Amorphous Fe, Mn and Al oxides were determined using the ammonium oxalate method (Mckeague and Day, 1966). Iron, aluminium and manganese in the extracts, were measured using Alpha 4 Atomic Absorption spectrophotometer

2.3 Statistical Analysis:

Data generated for the various physical and chemical properties of the soils as well as the sesquioxides were subjected to Analysis of Variance (ANOVA) and treatment means separated using Least Significant difference (LSD) at 15% level of probability. Also correlation between sesquioxides and selected soil properties was determined via correlation analysis. All statistical analyses were run using Genstat statistical package (Buysse 2004).

3.0 Results and Discussion

3.1 Results

3.1.1 Soil Characterization

Sand, silt and clay contents differed significantly (LSD 0.05) with depths in all land units (Table 1). Whereas, sand content was significantly (LSD 0.05) higher in the top than the sub soil the reverse was the case

for clay content in most land units. Distribution of the silt was irregular with depth in the soils. Mean sand, silt and clay contents were 889.66, 576.40 and 808.47, 16.24, 241.80 and 65.97 and 94.10, 181.80 and 125.57 g kg⁻¹ in the natural levee, floodplain and Upland land units respectively, with sand contents much higher than the other soil fractions. Texture of the soils varied between loamy sand and sandy loam indicating that the soils are dominantly sandy. Soil OM, TN, ECEC and available P ranged from 2.30-32.30 g kg⁻¹, 0.30-0.60 g kg⁻¹, 1.55-6.24 Cmol (+) kg⁻¹ and 2.76-14.97 mgkg⁻¹ respectively and decreased seriously (LSD 0.05) with depth in most land units. Mean values of soil OM, TN, ECEC and P in natural levee, floodplain and upland land units were 8.83, 21.87 and 20.63 g kg⁻¹, 0.37, 0.50 and 0.50 g kg⁻¹, 1.55, 5.44 and 2.98 Cmol (+) kg⁻¹ and 3.96, 3.04 and 11.36 mgkg⁻¹ (P) respectively flood plain having the least values but for available P. Soil pH ranged from 5.21-6.67 and decreased distinctly (LSD 0.05) with depths in all land units but floodplain. Mean soil pH increased in the order floodplain (pH = 5.51) < natural levee = upland (pH = 6.61) signifying that floodplain was more acidic relative to others.

3.1.2 Aluminium Oxides

Dithionate aluminium (Al_d) ranged from 200-300 and 100-400 mg kg⁻¹ in the top and sub soil (15-45 cm) depths of the various land units respectively (Table 2). It distinctly (LSD 0.05) decreased and increased but irregular with depth in the upland, floodplain and natural levee respectively. Mean concentrations of the various land units was a decreased order of floodplain > natural levee > upland soils. Amorphous or oxalate aluminium (Al_{ox}) varied as 100-200 mg kg⁻¹ and 100-300 mg kg⁻¹ in the top and sub soils with sub soil concentrations distinctly (LSD 0.05) higher than the top soils of the various land units respectively (Table 2). Mean Al_{ox} concentrations of the various land units varied as the dithionate fraction. Active Al obtained as a ratio of Al_{ox} to Al_d ranged from 0.33-0.67 and 0.50-2.00 in the top and sub soil depths respectively and increased seriously (LSD 0.05) with depths in the various land units. Mean concentrations decreased as Upland > floodplain > natural levee.

3.1.3 Iron Oxides

Distribution of iron oxides in the various land units is presented in Table 3. Dithionate Fe (Fe_d) ranged from 7800-20400 mg kg⁻¹ and 2200-21900 mg kg⁻¹ in the top and sub soils respectively with concentrations in the later significantly (LSD 0.05) better than that in the former for most land units. Mean Fe_d decreased in the order upland > natural levee > floodplain. Oxalate Fe (Fe_{ox}) ranged from 10000-20000 and 10100-16600 mg kg⁻¹ in the top and sub soil depths respectively with pattern of distribution irregular with depth exception being floodplain that increased with soil depth. Mean concentration in the different land units decreased in the order upland > natural levee > floodplain. Active Fe ranged from 0.98-1.28 in the top and 0.55-4.90 in the sub soil depths, with pattern of distributions significantly (LSD 0.05) irregularly with depth in the various land units. Mean concentration amongst land units decreased as floodplain > natural levee > upland.

3.1.4 Manganese Oxides

Free or dithionate manganese (Mn_d) ranged from 12000-20000 and 6000-18100 mg kg⁻¹ in the top and sub soil depths respectively, with pattern of distribution irregular with depth in all land units (Table 4). Mean concentrations varied as 10300, 12700 and 18700 mg kg⁻¹ for natural levee, floodplain and upland land units respectively being better in the upland than the other land units. Oxalate manganese (Mn_{ox}) ranged from 600-1200 in the top and 10000-14000 mg kg⁻¹ in the sub soil with the later better relative to the former. In each land unit Mn_{ox} increased distinctly (LSD 0.05) with soil depth and with mean concentrations varying as 10300, 11300 and 11700 mg kg⁻¹ for natural levee, floodplain and upland signifying a decreasing sequence of natural levee > floodplain > upland. Active Mn ranged from 0.30-1.00 and 0.56-1.83 in the top and sub soil depths respectively. Besides upland which increased distinctly (LSD 0.05) with depth, pattern for the other land units was irregular. Mean active Mn varied as upland < floodplain < natural levee land units.

3.1.5 Relationship between Clay Content and Dithionate Iron

Ratio of soil clay to dithionate Fe (Fe_d) is presented in Table 5 and ranged from 6.17-9.04 (mean = 7.65), 16.38-85.73 (mean = 25.97) and 5.30-6.97 (mean = 6.22) in natural levee, floodplain and upland land units respectively. Pattern of distribution with soil depth was inconsistent but with mean values amongst the land units decreasing as floodplain > natural levee > upland

3.1.6 Correlation between Sesquioxide Contents and selected Soil Properties

Correlation between sesquioxide contents and selected soil properties of the land units are shown in Table 6. Dithionate Fe correlated significantly (P < 0.05) with clay (r = -0.42), Al (r = 0.85), silt/clay ratio (r = -0.44), available phosphorus (r = -0.73) and base saturation (r = 0.51) but not with OM (r = -0.25), silt (r = -0.35), sand (r = 0.38), pH (r = 0.03), ECEC (r = -0.37), Ca (r = -0.19), Na (-0.03), TN (r = -0.23), C/N ratio (r = -0.14), K (r = -0.09) and Mg (r = -0.05). Also, correlation between Fe_{ox} with %BS (r = 0.44) and K (r = -0.73) were significant while that with OM (r = 0.08), clay (r = 0.04), silt (r = 0.06), sand (r = -0.06), pH (r = 0.03), ECEC (r = -0.07), Al (-0.20), silt/clay ratio (r = -0.02), Ca (r = -0.01), Na (r = 0.14), TN (r = -0.06), available P (r = -0.07), C/N ratio (r = 0.07) and Mg (r = 0.14) was not significant (P < 0.05). Besides available P, active Fe was not distinctly (P < 0.05) correlated with OM (r = -0.01), clay (r = 0.12), silt (r = 0.02), sand (r = -0.05), pH (r =

0.22), ECEC ($r = -0.05$), Al ($r = 0.38$), silt/clay ratio ($r = 0.06$), Ca ($r = -0.20$), Na ($r = 0.08$), TN ($r = -0.03$), C/N ratio ($r = 0.003$), BS ($r = -0.25$), K ($r = -0.22$) and Mg ($r = -0.08$). There was serious ($P < 0.05$) relationship between Al_d with Al ($r = 0.65$), TN ($r = 0.57$), available P ($r = 0.52$) and BS ($r = -0.45$) but not with OM ($r = 0.34$), clay ($r = 0.35$), silt ($r = 0.28$), sand ($r = -0.30$), pH ($r = -0.16$), ECEC ($r = 0.37$), silt/clay ratio ($r = 0.33$), Ca ($r = 0.18$), Na ($r = -0.20$), C/N ratio ($r = -0.10$), K ($r = -0.09$) and Mg ($r = 0.07$). Equally, the relationship between Al_{ox} with Al ($r = 0.44$), available P ($r = 0.54$) and BS ($r = -0.65$) were distinct ($P < 0.05$) while those with OM ($r = 0.21$), clay ($r = 0.20$), silt ($r = -0.01$), sand ($r = -0.04$), pH ($r = 0.14$), ECEC ($r = -0.003$), Al ($r = 0.44$), silt/clay ratio ($r = -0.03$), Ca ($r = -0.32$), Na ($r = 0.29$), TN ($r = 0.28$), C/N ratio ($r = -0.03$) and K ($r = -0.30$) were non distinct ($P < 0.05$). Active Al was significantly correlated with Ca ($r = -0.47$) only but not with OM ($r = -0.26$), clay ($r = -0.12$), silt ($r = -0.26$), sand ($r = 0.25$), pH ($r = 0.20$), ECEC ($r = -0.33$), Al ($r = -0.28$), silt/clay ratio ($r = -0.35$), Na ($r = 0.22$), TN ($r = -0.26$), available P ($r = -0.12$), C/N ratio ($r = -0.17$), BS ($r = -0.09$), K ($r = -0.12$) and Mg ($r = -0.23$). Furthermore, correlation between Mn_d with OM ($r = -0.54$), clay ($r = -0.73$), silt ($r = -0.65$), sand ($r = 0.69$), pH ($r = 0.44$), Al ($r = -0.81$), silt/clay ratio ($r = -0.65$), Ca ($r = -0.45$), TN ($r = -0.53$) and %BS ($r = 0.45$) was serious while those with ECEC ($r = 0.19$), Na ($r = 0.05$), available P ($r = 0.0004$), C/N ratio ($r = -0.15$), K ($r = 0.07$) and Mg ($r = -0.34$) were not serious. There was distinct correlation between Mn_{ox} with clay ($r = 0.42$) and C/N ratio ($r = -0.51$) but not with OM ($r = -0.35$), silt ($r = 0.17$), sand ($r = -0.25$), pH ($r = -0.28$), ECEC ($r = 0.19$), Al ($r = 0.23$), silt/clay ratio ($r = 0.12$), Ca ($r = -0.24$), Na ($r = 0.38$), TN ($r = -0.04$), available P ($r = 0.13$), %BS ($r = -0.38$), K ($r = -0.36$) and Mg ($r = 0.16$). Finally, active Mn correlated significantly ($P < 0.05$) with OM ($r = 0.48$), clay ($r = 0.78$), silt ($r = 0.64$), sand ($r = -0.68$), pH ($r = -0.41$), ECEC ($r = 0.63$), Al ($r = 0.68$), silt/clay ratio ($r = 0.57$), TN ($r = 0.47$) and not with Mg ($r = 0.34$), K ($r = -0.33$), %BS ($r = -0.41$), C/N ratio ($r = 0.08$), available P ($r = -0.04$), Na ($r = -0.03$) and Ca ($r = 0.24$).

3.2 Discussion

Dominance of soil texture of the land units as sandy could be ascribed to the nature of their parent materials. According to Orajiaka (1975), geology of the area has been characterized as quaternary, alluvium, meander belt, wooded back swamp, fresh water swamps and Sombreiro-Warri Deltaic plains. Increased clay content with soil depth could be due to clay eluviation from the surface horizon. Soils were acidic with a moderate pH value of 6 and beyond in some land units probably due to complexation of soluble aluminium from organic matter decomposition of the deposited organic sediments (Aluko and Fagbenro, 2000). Much acidity (mean pH value < 5.50) in the floodplain relative to the other land units could be due to depletion of bases from leaching and flood erosion, probably more severe in the land unit. Except upland soils with high available P, concentration of OM and other nutrients were low and below critical limits for southeastern Nigerian soils (Enwezor et al., 1990). The less than 16 cmol (+)kg⁻¹ of soil ECEC in the land units, indicate that they are of low clay activity (Opara-Nadi et al., 2000).

Ranges of Fe_{ox} (10,000-20,000 and 10,100-16,600 mg kg⁻¹) and Fe_d (7800-20400 and 2200-21900 mg kg⁻¹) and those of Al_{ox} (100-200 and 100-300 mg kg⁻¹) and Al_d (200-300 and 100-400 mg kg⁻¹) in the top and sub soils respectively of the various land units studied were high relative to ranges of Fe_{ox} (18.04-19.35 and 6.07-41.66 mg kg⁻¹) and Fe_d (98.40-175.46 and 8.56-205 mg kg⁻¹) and those of Al_{ox} (16.07-18.37 and 3.44-106.60 mg kg⁻¹) and Al_d (16.40-164.00 and 16.40-162.36 mg kg⁻¹) in the top and sub soils respectively of granitic savanna soils of Bauchi State, Nigeria (Hassan et al, 2005). Also ranges of Fe_d in the land units studied were high relative to those of 4000-10,000 and 1100-6000 mg kg⁻¹ Fe_d while those of Al_d were low compared to ranges of 1900-7600 and 1900-19300 mg kg⁻¹ Al_d in the top and sub soils respectively of some southwestern Nigerian soils (Ojo-Atere and Ajuwon, 1985). However, ranges of Fe_{ox} and Fe_d in the present study were comparable to those of 959-5838 and 1084-5838 mg kg⁻¹ Fe_{ox} and 6255-8131 and 5421-8131 mg kg⁻¹ Fe_d in the top and sub soils respectively of inland valley soils of Central Cross River State, Nigeria (Essoka and Esu, 2000). They were also comparable to ranges of 300-6600 and 300-11,400 mg kg⁻¹ Fe_{ox} and 7400-58600 mg kg⁻¹ and 4900-40600 mg kg⁻¹ Fe_d and those of 30-1200 and 100-1200 mg kg⁻¹ Al_{ox} and 1900-8700 and 3400-17800 mg kg⁻¹ Al_d in the top and sub soil depths respectively along a toposquence in Umudike area of southeastern Nigeria (Osodeke et al., 2005). Furthermore, ranges of Mn_{ox} (600-1200 and 10000-14000 mg kg⁻¹) and Mn_d (12000-20000 and 6000-18100 mg kg⁻¹) in the top and sub soils respectively in the present study were higher than those of 41.70-325.0 and 20.85-1583.35 mg kg⁻¹ Mn_{ox} and 83.30-550.00 and 25.00-3391.70 mg kg⁻¹ Mn_d reported in the top and sub soils respectively of inland valley soils of Central Cross River State, Nigeria (Essoka and Essu, 2000). Values of Al_d and Mn_d were higher than Al_{ox} and Mn_{ox} while the reverse was the case for Fe_d and Fe_{ox} for most land units indicating the prevalence of crystalline Al and Mn and amorphous Fe in the soils. It has been reported that P and metal sorptivity are higher with amorphous than crystalline oxides (Uzoho et al., 2005). This indicates that ion sorption will be controlled by amorphous Fe rather than Al and Mn in the land units especially in natural levee and floodplains soils. Other workers have however reported high dithionate than oxalate Fe concentrations (Udo, 1980; Essoka and Esu, 2000; Hassan et al., 2005; Osodeke et al., 2005). In the land units, values of Fe_{ox} was higher in the sub than topsoils of the floodplain and natural levee as has been reported for sub soils of soil profiles (Ibia 2001, Osodeke et al., 2005; Hassan et al., 2005). Udo (1980) attributed the high values of Fe_{ox} to

the poor drainage conditions. These high values and the apparent confinement in the subsoil of these landscapes suggests that gleziation is one of the major pedogenic processes and induces the alteration, mobilization and fixation of iron following water movement (Khan et al., 1997). Mean dithionate iron (Fe_d) content of the soils varied as 7000, 12,300 and 20200 $mg\ kg^{-1}$ for floodplain, natural levee and upland landscapes respectively; with upland higher relative to others and indicative of its old age (Hassan et al., 2005).

Mean Al_d concentration equivalent to 277.78 $mg\ kg^{-1}$ (166.67, 366.67 and 300.00 $mg\ kg^{-1}$ for upland, floodplain and natural levee respectively) was greater than mean Al_{ox} equivalent to 188.89 $mg\ kg^{-1}$ (133.33, 266.67 and 166.67 $mg\ kg^{-1}$ for upland, floodplain and natural levee respectively), attributable to the neoformation process of clay silicates (Hassan et al., 2005) and to the increase in the alteration products with time, thus serving as an index of the stage and degree of soil development (Blume and Swertzmann, 1969; Dolui and Mustafi, 1997).

Ratios of Fe_{ox} , Al_{ox} and Mn_{ox} to Fe_d , Al_d and Mn_d have been used to measure the reactivity of sesquioxides and indicate the relative amounts of the amorphous and the ordered or crystalline oxides in a soil (Gallez et al., 1975; Omenihu et al., 1994). Active Fe ratios defined as oxalate extractable divided by dithionate extractable Fe has been used in classifying soils into well drained and poorly drainage conditions (Udo, 1980), evaluate soil development and weathering (Omenihu et al., 1994) and indicate the amount of crystalline and amorphous free oxides (Blume and Schwertmann, 1969). Active Fe (range of 0.98-1.28 and mean =1.09) on the top soil and (range of 0.55-4.91 and mean = 1.61) in the sub soil were high compared to ranges reported for most Nigerian soils (Essoka and Esu, 2000; Hassan et al., 2005; Osodeke et al., 2005) probably due to variation in the land unit architecture. Mean active Fe in the top and sub soils of the land units were 0.98 and 0.66, 1.28 and 2.34 and 1.02 and 1.31 respectively in the upland, floodplain and natural levee respectively. It has been reported that values of active iron greater than 0.35 represent poorly drained while lower values signify well drained conditions (Udo, 1980; Essoka and Esu, 2000). As postulated by Dolui and Mustafi, (1997) soils with ratios of 0.65 will be younger than those with ratios of 0.55 or 0.45. On the basis of this observation, soils of the land units studied could be said to be poorly drained and young since their ratios were greater than 0.35 and 0.65 respectively. Extent of drainage and youthfulness decreased in the order floodplain > natural levee > upland land units. This showed that upland soils were older, more drained and crystalline than the other land units. Mckeague and Day (1966) obtained ratios not greater than 0.33 for well drained soils.

Ratio of clay to dithionate Fe has been used to indicate the comigration of clay and iron oxides from the A horizon to the B horizon (Agbenin, 2003; Enya et al., 2011). According to Udo (1980), the pedogenic parameters expected of well drained soils is the co-migration of percent clay and dithionate citrate bicarbonate iron (Fe_d). It has also been noted that Fe oxide is related to the clay content where the clay content is more than 40% in the B horizon and closely to the silt content in soils with less than 40% clay (Udo, 1980 and Ibia, 2001). The inconstancy in the pattern of distribution of the clay to Fe_d ratio with soil depth signifies lack of comigration of the clay and iron oxides in the land units. This thus confirms the poor drainage condition of the soils.

Other workers have reported the influence of soil properties on sesquioxide distributions (Omenihu et al., 1994; Ibia, 2001; Osodeke et al., 2005). For instance significant correlation has been reported between oxalate iron with sand, pH and K, dithionate aluminium with sand and clay, oxalate aluminium with pH and K but with non distinct correlation ($P \leq 0.05$) between oxalate Fe, Dithionate Fe, oxalate Al and dithionate Al with OM, N, P, ECEC, Ca and Mg (Osodeke et al., 2005).

4.0 Conclusions

In conclusion, the sesquioxide contents of the soils varied with depth, with subsoil higher than top soil in most land units. Whereas amorphous or Fe_{ox} was dominant, Al_d and Mn_d were in most land units. Soils were poorly drained and young with the extent being a decreasing order of floodplain > natural levee > upland land units. Reactivity of the soils varied with the extent due to active Fe, Mn and Al in the floodplain, natural levee and upland land units respectively. Soil properties especially pH, OM, ECEC, P, TN, sand, silt, clay, silt/clay ratio, Ca, Mg, K, Na, H, C/N ratio and % BS influenced sesquioxide contents of the land units. In general, soils of the land units could sustain intensive agriculture due to their youthfulness but requires liming and OM to reduce nutrient sorption and adaptable to poor drainage conditions. Reactivity of the soils qualify them as suitable sinks for retention of toxic and hazardous materials especially those from crude oil exploitation that is prevalent in the area.

5.0 References

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Table 1. Selected Physicochemical Properties of Soils of the various Land units

Depth cm	Sand	Silt	Clay g kg ⁻¹	OM	TN	ECEC Cmol (+) kg ⁻¹	P mgkg ⁻¹	pH	TC
Natural Levee									
0-15	907.00a	14.60a	78.40a	15.80b	0.50ab	1.81a	4.55a	6.70a	S
15-30	873.77b	30.43b	95.80b	8.40c	0.30a	1.55c	4.22b	6.62a	LS
30-45	888.20c	3.70c	108.10c	2.30a	0.30b	1.29b	3.10c	6.52b	LS
Mean	889.66	16.24	94.1	8.83	0.37	1.55	3.96	6.61	
Floodplain									
0-15	633.20a	208.20a	158.60a	8.70a	0.40ab	6.24a	3.19a	5.21a	SI
15-30	528.40b	273.40b	198.20b	32.30b	0.50a	5.20b	3.16a	5.97b	SI
30-45	567.60c	243.80c	188.60c	24.60c	0.60b	4.89c	2.76b	5.34c	SI
Mean	576.4	241.8	181.8	21.87	0.5	5.44	3.04	5.51	
Upland									
0-15	828.40a	63.40a	108.20a	25.00b	0.70b	3.38b	14.79c	6.75a	LS
15-30	828.40a	43.40b	128.20b	19.30a	0.40a	2.79a	10.36b	6.44b	LS
30-45	768.60b	91.10c	140.30c	17.60c	0.40a	2.77a	8.92a	6.64a	LS
Mean	808.47	65.97	125.57	20.63	0.5	2.98	11.36	6.61	

Means followed by different letters are significantly different at LSD 0.05, OM = Organic matter, TN = Total nitrogen, S Sand, LS =Loamy sand, SL = Sandy loan and TC = Textural class

Table 2. Dithionate(d), Oxalate(ox) and Active Aluminium Oxides in Soils of the various Land units

Soil Depths cm	Al _d mg kg ⁻¹	Al _{ox}	Active Al
Natural levee			
0-15	300.00a	100.00b	0.33b
15-30	300.00a	200.00a	0.67a
30-45	300.00a	200.00a	0.67a
Mean	300	166.67	0.56
Flood plain			
0-15	300.00b	200.00b	0.67b
15-30	400.00a	300.00a	0.75a
30-45	400.00a	300.00a	0.75a
Mean	366.67	266.67	0.73
Upland			
0-15	200.00a	100.00b	0.50b
15-30	200.00a	100.00b	0.50b
30-45	100.00b	200.00a	2.00a
Mean	166.67	133.33	1.02

Means followed by similar letters are not significantly different using LSD 0.05

Table 3. Dithionate (d), Oxalate (ox) and Active Fe in soils of the various Land units

Soil depth cm	Fe _d mg kg ⁻¹	Fe _{ox}	Active Fe
Natural levee			
0-15	12700.00b	13000.00c	1.02c
15-30	10600.00c	16000.00a	1.51a
30-45	13500.00a	15000.00b	1.11b
Mean	12300	14700	1.2
Flood plain			
0-15	7800.00b	10000.00c	1.28b
15-30	12100.00a	10100.00b	0.83c
30-45	2200.00c	10800.00a	4.91a
Mean	7000	12700	2.34
Upland			
0-15	20400.00b	20000.00a	0.98a
15-30	18400.00c	10200.00c	0.55c
30-45	21900.00a	16600.00b	0.76b
Mean	20200	15600	0.77

Means followed by similar letters are not significantly different at LSD 0.05

Table 4: Dithionate(d), Oxalate (ox) and Active Mn in soils of the various land units

Soil depth cm	Mn _d mg kg ⁻¹	Mn _{ox}	Active Mn
Natural Levee			
0-15	12000.00b	12000.00a	1.00b
15-30	6000.00c	11000.00b	1.83a
30-45	13000.00a	12200.00a	0.94b
Mean	10300	11700	1.14
Floodplain			
0-15	12600.00b	8000.00c	0.63c
15-30	8800.00c	12000.00b	1.36a
30-45	16600.00a	14000.00a	0.84b
Mean	12700	11300	0.89
Upland			
0-15	20000.00a	6000.00c	0.30c
15-30	18000.00b	10000.00b	0.56b
30-45	18100.00b	15000.00a	0.83a
Mean	18700	10300	0.55

Means followed by similar letters are not significantly different using LSD 0.05

Table 5. Ratio of Clay to Dithionate Extractable Fe (Fe_d) in the various Land units

Land units	Soil Depth (cm)	Clay/F _d ratio
Natural Levee	0-15	6.17
	15-30	9.04
	30-45	8.01
	Mean	7.65
Floodplain	0-15	20.33
	15-30	16.38
	30-45	85.73
	Mean	25.97
Upland	0-15	5.30
	15-30	6.97
	30-45	6.41
	Mean	6.22

Table 6. Simple Correlation between Sesquioxides and selected Soil Properties

Parameters	Fe _d	Fe _{ox}	Active Fe	Al _d	Al _{ox}	Active Al	Mn _d	Mn _{ox}	Active Mn
OM	-0.25	0.08	-0.01	0.34	0.21	-0.26	-0.54	-0.35	0.48
Clay	-0.42	0.04	0.12	0.35	0.20	-0.12	-0.73	0.42	0.78
Silt	-0.35	0.06	0.02	0.28	-0.01	-0.26	-0.67	0.17	0.64
Sand	0.38	-0.06	-0.05	-0.30	-0.04	0.25	0.69	-0.25	-0.68
pH	0.03	0.03	0.22	-0.16	0.14	0.20	0.44	-0.28	-0.41
ECEC	-0.37	-0.07	-0.05	0.37	-0.003	-0.33	0.19	0.19	0.63
Al	-0.85	-0.20	0.38	0.65	0.44	-0.28	-0.81	0.23	0.68
Silt/clay ratio	-0.44	-0.02	0.06	0.33	-0.03	-0.35	-0.65	0.12	0.57
Ca	-0.19	-0.01	-0.20	0.18	-0.32	-0.47	-0.45	-0.24	0.24
Na	-0.03	0.14	0.08	-0.02	0.29	0.22	0.05	0.38	-0.03
TN	-0.23	-0.06	-0.03	0.57	0.28	-0.26	-0.53	-0.04	0.47
Avail. P	-0.73	-0.07	0.76	0.52	0.54	-0.12	0.0004	0.13	-0.04
C/N ratio	-0.14	0.07	0.003	-0.1	-0.03	-0.17	-0.15	-0.51	0.08
%BS	0.51	0.44	-0.25	-0.45	-0.65	-0.09	0.45	-0.38	-0.41
K	-0.09	-0.73	-0.22	-0.09	-0.14	-0.12	0.07	-0.36	-0.33
Mg	-0.05	0.14	-0.08	0.07	-0.30	-0.23	-0.34	0.16	0.34