Free iron and aluminum oxides in soils derived from coastal plain and beach sands in Akwa Ibom State, Nigeria

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Abstract
The status and distribution of free iron (Fe) and aluminum (Al) oxides in some soils derived from coastal plain sand (CPS) and beach sand (BHS) in Akwa Ibom State, Nigeria, were investigated in view of the roles the metallic oxides play in aggregate stability, pH buffering, carbon sequestration and anions (nutrients and toxicants) adsorption. Twenty four samples obtained from the different genetic horizons of six representative soils were analyzed using the dithionite-citrate-bicarbonate (DCB) and ammonium oxalate extraction methods. Results showed low status of free Fe and Al oxides in all the soils. DCB-extractable Fe oxides (Fe_d), oxalate-extractable Fe (Fe_o), definite crystalline Fe oxides (Fe_p), DCB-extractable Al oxides (Al_d), oxalate-extractable Al oxides (Al_o) and definite crystalline Al oxides (Al_p) ranged0.92-1.59, 0.44-1.03, 0.40-0.65, 0.37-0.86, 0.19-0.47 and 0.18-0.46 gkg^{-1} in the CPS-derived soils but ranged 1.06-1.50, 0.47-0.93, 0.5-0.62, 0.45-0.70, 0.25-0.40 and 0.17-0.33 gkg^{-1} in the BHS-derived soils, respectively. The proportions of Fe_p and Al_p were less than those of Fe_o and Al_o in most horizons of the soils indicating the predominance of amorphous iron and aluminum oxides in the CPS/BHS soils. The Fe_d, Fe_o, Al_d and Al_o as well as clay/Fe_d and clay/Al_d ratios increased down the profiles suggesting co-migration of the free oxides with clay. Fe_d and Fe_o correlated positively with clay but negatively with organic matter in the CPS and BHS soils. Although their status were low, the oxides could still play great roles in the adsorption of anionic nutrients and pollutants.

Keywords: Free iron/aluminum oxides, coastal plain sands, beach sands, anionic nutrients

Introduction

Iron (Fe) and aluminum (Al) oxides are minerals that occur in virtually all soils (Dixon and Weed, 1977, 1989, Bera *et al*., 2005; Berhe *et al*., 2015). They are mostly formed from the weathering of primary silicate minerals that are rich in iron and aluminum(Olatunji *et al.*, 2015). As the ferrous and aluminum ions (Fe^2 and Al^{3+}) are released from silicates during weathering, they hydrolyze and precipitate almost exclusively as oxide minerals and their mineral phase, composition and distribution are continually modified by soil environmental conditions (Schwertmann and Taylor, 1989; Cornell and Schwertmann, 1996; Rampazzo *et al*., 1999; Scheinost, 2005; Havlin *et al*., 2009). Soil pH, organic matter content, drainage and temperature are among these environmental factors (Rampazzo *et al*., 1999; Scheinost, 2005; Havlin *et al*., 2009; Bortoluzzi *et al*., 2015).

For instance, extreme soil acidification or low pH provides conditions for neoformation and accumulation of crystalline and amorphous Fe oxides and lowering of Al oxides in extremely acidic soils (Rampazzo *et al*., 1999). Low soil temperatures, coupled with high organic matter content, are less favourable to the formation of Fe oxides (Dixon and Weed, 1977; Cornell and Schwertmann,

1996).Lesser proportions of free Fe and Al oxides are reportedly incorporated into the structures of silicate clay minerals or complexes by organic matter, while greater proportions are free and extractable (Olatunji *et al*., 2015). These free oxides are usually less than 0.001 mm in diameter size and exist in crystalline and non crystalline/amorphous forms (Brady and Weil, 2012). Highly weathered soils may contain as much as 50% (by weight) of these metal oxides (Sadusky and Sparks, 1991; Berhe *et al*., 2015).

Crystalline Fe and Al oxides usually exist as discrete minute particles increasing in amounts with soil age and indicating an advanced stage of weathering if strongly accumulated under well-drained soil conditions (Dixon and Weed, 1977; Udo *et al*., 2009; Olatunji *et al*., 2015). However, the non crystalline or amorphous counterparts exist mostly as coatings on the particles of clay minerals decreasing in amounts with soil age and indicating low weathering if they are predominant (Dixon and Weed, 1977; Udo *et al*., 2009; Maniyunda *et al*., 2015). These forms are more reactive because of their larger specific surface area and greater magnitude of net surface charge (Dixon and Weed, 1977; Brady and Weil, 2012). Iron oxides are reportedly the most abundant metallic oxides in soils (Cornell and Schwertmann, 1996; Bigham *et al.*, 2002) and goethite, hematite, maghemite and magnetite are the various crystalline forms, whereas ferrihydrite, lepidocrocite and ferroxite are the short-range-ordered crystalline/non crystalline counterparts (Schwertmann 1985; Cornell and Schwertmann 2003; Brady and Weil, 2012; Wang *et al*., 2013).Goethite and hematite appear to be the most abundant in well-drained soils, whereas lepidocrocite, maghemite and magnetite may occur in abundance in poorly drained soils (Schwertmann 1985; Cornell and Schwertmann 2003). In spite of their lower stability, lepidocrocite and ferrihydrite (metastable forms) often occur in manysoils, particularly in younger or less weathered soils (Schwertmann 1988). Gibbsite, boehmite, bayerite, corundum and diaspore are known aluminum oxides in soils (Dixon and Weed, 1989; Brady and Weil, 2012).

Apart from contributing to the formation of soil structure, bulk density, colour, acidification, pH buffering and carbon sequestration and stabilization (Esu, 2010; Brady and Weil, 2012), free Fe and Al oxides also influence soil surface charge characteristics and ion adsorption/exchange (Dixon and Wed, 1977; Schwertmann and Taylor, 1989; Wagai and Mayer, 2007; Maniyunda *et al*., 2015; Osayande *et al*., 2016). The high densities of positive electrical charge on their surfaces under soil acidic conditions play a great role in the non-specific adsorption of anionsby the metallic oxides in acidic soils (Dixon and Weed, 1989; Shamshuddin and Anda, 2008).

By this adsorption, native and applied anionic nutrients (including nitrate and chloride) are gradually removed from soil solution and loosely retained on the surfaces of the metallic oxides for use by higher plants and microorganisms, while anionic toxicants are removed and sequestered thus preventing them from contaminating groundwater (Brady and Weil, 2012). Moreover, the status and distribution of free Fe and Al in soils also

provide a useful tool for evaluating the stages of weathering and development in soils (Osayande *et al*., 2016), differentiating genetic horizons (Akpan *et al*., 2009) and classifying soils at the family level of USDA Taxonomy (Schwertmann and Taylor, 1989). The Fe_o/Fe_d and clay/Fe_d ratios are useful for predicting soil drainage conditions (Agbenin, 2003; Akpan *et al*., 2009; Ibia, 2012) and co-migration of clay and the metallic oxides down the profile of a soil (Udo, 1980; Akpan *et al*., 2009).

However, free Fe and Al oxides in soils have been associated with fixation of some essential plant nutrients including phosphate/sulphate through specific adsorption or chemisorption making the nutrient(s) become temporarily unavailable to plants and microorganisms (Dixon and Weed, 1977; Thompson and Goyne, 2012; Brady and Weil, 2012; Mehmood *et al*., 2015).

Soils in Nigeria reportedly contain varied amounts of free iron aluminum oxides (Osayande *et al*. (2016) reported low contentsand predominance of the crystalline forms of the oxides for some well-drained CPS-soils in Benin, Edo to the researchers, the contents of DCB-extractable iron (Fe_d), oxalate extractable iron oxides (Fe_o), DCB-extractable aluminum (Al_d) and oxalate extractable aluminum oxides (Al_o) ranged 11.13-34.16, 7.47-15.45, 5.01 – 10.98 and 2.64 – 9.59 $mgkg^{-1}$, respectively. Olatunji *et al*. (2015) reported Fe_d, Fe_o, Al_d and Al_o values of 7.18 – 444.3, 2.74 – 10.86, 2.88 – 43.31 and 1.30 – 8.66 gkg^{-1} for a toposequence at Ejioku in southwestern Nigeria respectively. Maniyunda *et al*.(2015) reported Fe_d and Fe_o contents of 5.71 – 28.57 and 1.43 – 5.71$gkg^{-1}$for some basement complex soils in the northern Guinea Savanna zone of Kaduna State respectively. The Fe_d and Fe_o contents were observed by the researchers to increase with soil depth. Akpan *et al*. (2009) reported mean Fe_d, Fe_o, Al_d and Al_o values of 0.06 - 0.20, 0.05 - 0.90, 0.006 - 0.120 and 0.005 - 0.130 % respectively for some soils derived from beach sands in Akwa Ibom State.

According to the report, the quantities of the amorphous forms of Fe and Al oxides in all the soils studied were greater than those of their crystalline counterparts. Ajiboye *et al*. (2015) reported higher Fe_d and Al_d than Fe_o and Al_o for some talc overburden soils in Kogi State. Igwe *et al*. (2010) reported greater quantities of the crystalline forms for some coastal plain soils (Ultisols and Inceptisols) of southeastern Nigeria. Udo (1980) reported higher contents of crystalline iron oxides for some for some coastal plain soils in southeastern Nigeria.

Although similar studies have been conducted before in the present study area, this study was necessary because it might provide an update needed for effective management of anionic nutrients/control of environmental pollution caused by anionic toxicants in the soils for improved food productivity and enhanced environmental safety. Its objective was, therefore, to determine the status and distribution of free iron and aluminum oxides in selected soils derived from coastal plain sands and beach ridge sands in Akwa Ibom State, Nigeria, in view of the roles the metallic oxides play in aggregate stability, pH buffering, carbon sequestration and anion adsorption.

Materials and methods

Study area

The study was conducted in Akwa Ibom State, Nigeria. Samples of soils derived

from coastal plain sands (CPS) were obtained at Utu Etim Ekpo (Etim Ekpo), Ikot Ekan (Etinan) and Ikot Akpan Udo 1 (Oruk Anam); while samples of soils derived from beach sands (BHS) were obtained at Utaewa (Ikot Abasi), Ntak Inyang (Esit Eket) and Esit Urua (Eket). All these locations lie between latitudes 4^0 32^1 and $5^0 33^1$ N and longitudes $7^0 25^1$ and 8^0 25^1 E and have a tropical moist climate, which is characterized by a wet season (April - November) and a short dry season (December - March) (Fig. 1). The topography of the locations is generally low varying from 20 to 62m above the sea level (Petters *et al*., 1989). Soils derived from coastal plain sands cover about 70 percent of Akwa Ibom State (NGSA, 2009; Ibia, 2012) and are mostly classified as Ultisols (Udoh and Lekwa, 2014), while those derived from BHS cover about 5 percent of the state and are generally classified either as Entisols or Inceptisols depending on the stage of weathering (Udoh and Akpan, 2015).

Soil sample size, sampling technique and laboratory analyses

A total of twenty four (24) soil samples were used for the study. They were collected from the different genetic (B and A) horizons of six soil profiles using freshly dug soil pits at the various study locations. The geographical position of each soil pit was determined with a geographical positioning system (GPS). All the soil samples were air-dried, crushed and passed through relevant sieves before laboratory analyses. Soil physicochemical properties were determined by routine methods (Udo *et al*., 2009). A combination of the crystalline and amorphous forms (Fe_d/Al_d) of each of the metallic oxides was determined by the dithionite-citrate-bicarbonate (DCB) extraction method, while the amorphous form (Fe_o/Al_o) alone was determined by the ammonium oxalate extraction method (Bera *et al*., 2005; Udo *et al*., 2009). The definite crystalline form (Fe_p/Al_p) of each metallic oxide was determined by finding the difference between the values obtained by the two methods (Ajiboye *et al.,* 2015).

Statistical analysis

All the data generated from the study were analyzed using descriptive statistical tools (mean and range) and the relationships between free iron/aluminum oxides and selected physicochemical properties of the soils were assessed using Pearson Product Moment Correlation analysis at 5% level of significance.

Results and discussion

Physicochemical properties of the soils

The physicochemical properties of the soils are shown in Tables 1 - 5. The proportions of sand particles (61.20 – 85.70%) were the highest in all the horizons of the CPS/BHS-derived soils, while the proportions of silt particles were the least (0.50 – 10.80%) (Tables 1 and 2). Clay contents of the CPS-derived soils ranged from 10.80 to 33.80%, while those of the BHS-derived soils ranged between 10.00 and 28.00%. Sand contents decreased with depth, clay contents increased with depth. while silt distribution was irregular. Most surface horizons of the soils had loamy sand texture, while most subsurface horizons had sandy clay loam texture. The silt/clay ratios recorded for most horizons of the CPS and BHS-derived soils were above 0.15 indicating low degree of weathering (Ojetade and Amusan, 2014).

The surface horizons of the CPS and BHS-derived soils were extremely acidic (pH 4.1 -

4.3), whereas the subsurface horizons were extremely to very strongly acidic (4.2 - 4.9) (Tables 3, 4 and 5).The status of organic matter (0.70 - 2.31%), total N (0.01 - 0.20%), exchangeable bases [Ca (0.20 - 2.80 $cmolkg^{-1}$), Mg (0.08 - 2.00 $cmolkg^{-1}$), K (0.02 - 0.78 $cmolkg^{-1}$) and Na (0.02 - 0.14 $cmolkg^{-1}$)] and ECEC (2.71 - 5.99 $cmolkg^{-1}$) was low; whereas the status of available P(4.60 - 16.93 $mgkg^{-1}$) was low to moderate in all the surface and subsurface horizons of the CPS and BHS-derived soils (Metson, 1961; FPDD, 1990).The exchangeable acidity (0.16 - 1.08 $cmolkg^{-1}$) was high indicating high potential acidity, while base saturation was medium to high (58.33 - 91.30%) in all the CPS and BHS-derived soils.

The results were in agreement with those reported by earlier researchers (Udoh *et al*., 2013; Udoh and Lekwa, 2014; Udoh and Akpan, 2015). The high active acidity of the soils could be due to the acidic nature of the parent materials and excessive leaching among other factors (Havlin*et al*., 2009). The low status of organic matter and essential plant nutrients could be due to leaching, erosion and low inputs. The low ECEC of the soils could be due to low organic matter contents, high proportions of sand and coating of clay mineral surfaces by the amorphous oxides of iron and aluminum (Shamshuddin and Anda, 2008) and might have negative implications on ion adsorption and exchange in the soils. Soils like these need regular and effective nutrient management for improved fertility and productivity.

Status and distribution of extractable iron and aluminum oxides in the soils

As shown in Table 6, the contents of DCB-extractable iron (Fe_d), oxalate-extractable iron oxides (Fe_o) and definite crystalline iron oxides (Fe_p) in the CPS-derived soils ranged 1.13 - 1.59, 0.44 - 1.03 and 0.40 - 0.65 gkg^{-1} and averaged 1.38, 0.85 and 0.55 gkg^{-1}, while Al_d, Al_o and Al_p ranged 0.37 - 0.86, 0.19 - 0.47 and0.18 - 0.46 $gkg^{-1}$and averaged 0.64, 0.33 and 0.31 gkg^{-1}, respectively.

In contrast, Fe_d, Fe_o and Fe_p in the BHS-derived soils (Table 7) ranged 1.06 - 1.50, 0.47 - 0.93 and 0.51 - 0.62 gkg^{-1} and averaged 1.28, 0.72 and 0.57 gkg^{-1}, while Al_d, Al_o and Al_p ranged 0.45 - 0.70, 0.25 - 0.40 and 0.17 - 0.33 gkg^{-1} and averaged 0.55, 0.32 and 0.23 gkg^{-1}, respectively (Table 7). Fe_d, Fe_o and Fe_p were all greater than their Al counterparts in each of the studied soils. Based on earlier reports (Dixon and Weed, 1977; Berhe *et al*., 2015; Osayande *et al*., 2016), the status of free Fe and Al oxides in all the CPS/BHS-soils studied was rated low. The Fe_d, Fe_o, Al_d and Al_o contents of the CPS/BHS-derived soils were found to increase with depth down to the third horizon of each of the soils and Fe_p and Al_p contents were less than those of Fe_o and Al_o in virtually all the soil horizons except those in the first two layers of the Ikot Ekan soil which were greater than Fe_o and Al_o. The Fe_o/Fe_d (0.44 – 0.64) and Al_o/Al_d (0 43 – 0.65) of the CPS-derived soil horizons as well as the Fe_o/Fe_d (0.44 – 0.64) and Al_o/Al_d (0.46 – 0.70) values recorded for the BHS-derived soil horizons were greater than 0.35. The clay/Fe_d values increased with depth down to the third horizon in all the CPS and BHS-derived soils.

Regarding their relationships with selected physicochemical properties of the soils, the Fe_d and Fe_o contents of the CPS-derived soils (Table 8) correlated positively with clay (r = 0.2611 vs0.2327) and pH (r = 0.4437 vs 0.3957), but negatively with organic matter (r = -0.2128 vs -0.3107) and

available P (r = -0.0034 vs0.1814). The Al_d and Al_o contents of the soils correlated positively with pH (r = 0.1906 vs 0.2865) and available P (r = 0.0508 vs 0.0427), but negatively with organic matter (r = -0.1161 vs -0.1604) and ECEC (r = -0.153 vs -0.0123). Fe_p correlated positively with pH (r = 0.2067), organic matter (r = 0.1455) and available P (r = 0.1497), but negatively with clay (-0.1734) (Table 9). Al_p correlated positively with organic matter (r = 0.4646), but negatively with clay (r = -0.8370*), available P (R = -0.2310) and ECEC (r = -0.2126) (Table 8).

Given the magnitudes of the correlation coefficients recorded (Table 8), Fe_o appeared to exert more influence on virtually all the selected physicochemical properties (clay percentage, organic matter, and available P) of the CPS-derived soils than $Ee_p/Al_p/Al_o$. Osayande *et al*. (2016) observed similar relationships between Fe_o/Al_o and clay/organic carbon in the CPS-derived soils they studied in Benin, Edo State, Nigeria. The Fe_d and Fe_o contents of the BHS-derived soils (Table 9) correlated positively with clay (r = 0.4979 vs0.1349), pH (r = 0.2738 vs 0.3286) and ECEC (r = 0.0774 vs0.1289), but negatively with organic matter (r = -0.1213 vs -0.1788); whereas the $Al_d$and Al_o contents of the soils correlated negatively with clay (r = -0.0653 vs -0.1811), organic matter (r = -0.0337 vs -0.1841) and available P (r = -0.1886 vs -0.4318). Fe_o appeared to exert more influence on the ECEC of the soils, whereas Al_oappeared to exert more influence on the available P contents, as indicated by their coefficients of determination.

Some of the results agreed with earlier reports (Udo, 1980; Bera *et al*., 2005; Akpan *et al*., 2009; Osayande *et al*., 2016). For instance, most Fe_d and Fe_o values recorded in the present study for the coastal plain soils were much lower than those reported by Udo (1980) for similar soils in the present study fell within the ranges reported by Osayande *et al*. (2016) for similar soils in Benin, Edo State, Nigeria. The higher status of free Fe oxides compared to their Al counterparts in all the CPS/BHS-derived soils in the present study agreed with reports by Akpan *et al*. (2009) and Osayande *et al*. (2016), while the higher status of the amorphous forms of the metallic oxides in the BHS-derived soils agreed with the earlier report by Akpan *et al*. (2009).Osayande *et al*. (2016) reported higher status of the definite crystalline forms of Fe and Al oxides in some CPS-derived soils. The preponderance of the amorphous forms of the two metallic oxides in the BHS-derived soils agreed with the findings of Akpan *et al*. (2009), though virtually all the Fe_d, Fe_o, Al_d and Al_o values recorded in the present study were greater than those reported by these earlier researchers. The variations between some of the present and past results could be due to spatial and procedural differences, while the low status of the metallic oxides and the preponderance of the amorphous forms in the studied soils could be due to the highly sandy nature and low degree of weathering/weak development of the soils. According to Bortoluzzi *et al*. (2015), the presence and abundance of Fe and Al oxides in soils depend on the evolution conditions of the soils, as dictated by parent materials, climate, biota, relief and time. These factors determine soil properties, such as pH, organic matter content, drainage and temperature, which are known to influence the presence and abundance of Fe and Al oxides in soils (Rampazzo *et al*., 1999; Scheinost, 2005; Havlin *et al*., 2009;

Bortoluzzi *et al*., 2015). Extreme soil acidification, for instance, provides conditions for neoformation and accumulation of crystalline and amorphous Fe oxides and lowering of Al oxides in soils (Rampazzo *et al*., 1999; Havlin *et al*., 2009). Moreover, the crystalline forms of free Fe and Al oxides increase in amounts with soil age or as the degree of weathering increases. This explains why they are predominant in highly weathered soils (Ultisols and Oxisols) of the tropics (Dixon and Weil, 1977, 1989; Udo *et al*., 2009; Esu, 2010; Brady and Weil, 2012; Maniyunda *et al*., 2015; Olatunji *et al*., 2015; Bortoluzzi *et al*., 2015).

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Conclusion

The status of free Fe and Al oxides, as estimated by the dithionite and oxalate extraction methods, was low in all the studied soils and this could be due to the highly sandy nature of the two parent materials and weak development of most horizons of the soils. The contents of the amorphous forms were greater than those of the definite crystalline counterparts in all the BHS-derived soils; whereas the crystalline forms were higher in contents than the amorphous forms in about a third of the CPS-derived soils. Although their status is low, the metallic oxides can still play great roles in the retention of anions and sorption of pollutants, organic matter stabilization and aggregate stability in the soils.Adequate and regular applications of manure in combination with appropriate inorganic fertilizers should be practiced for improved nitrogen, phosphorus and sulfur fertility of the soils. Regular applications of manure improve soil organic matter levels and these may help reduce fixation of anionic nutrients. Split applications of anionic nutrients should be adopted to reduce losses through leaching.

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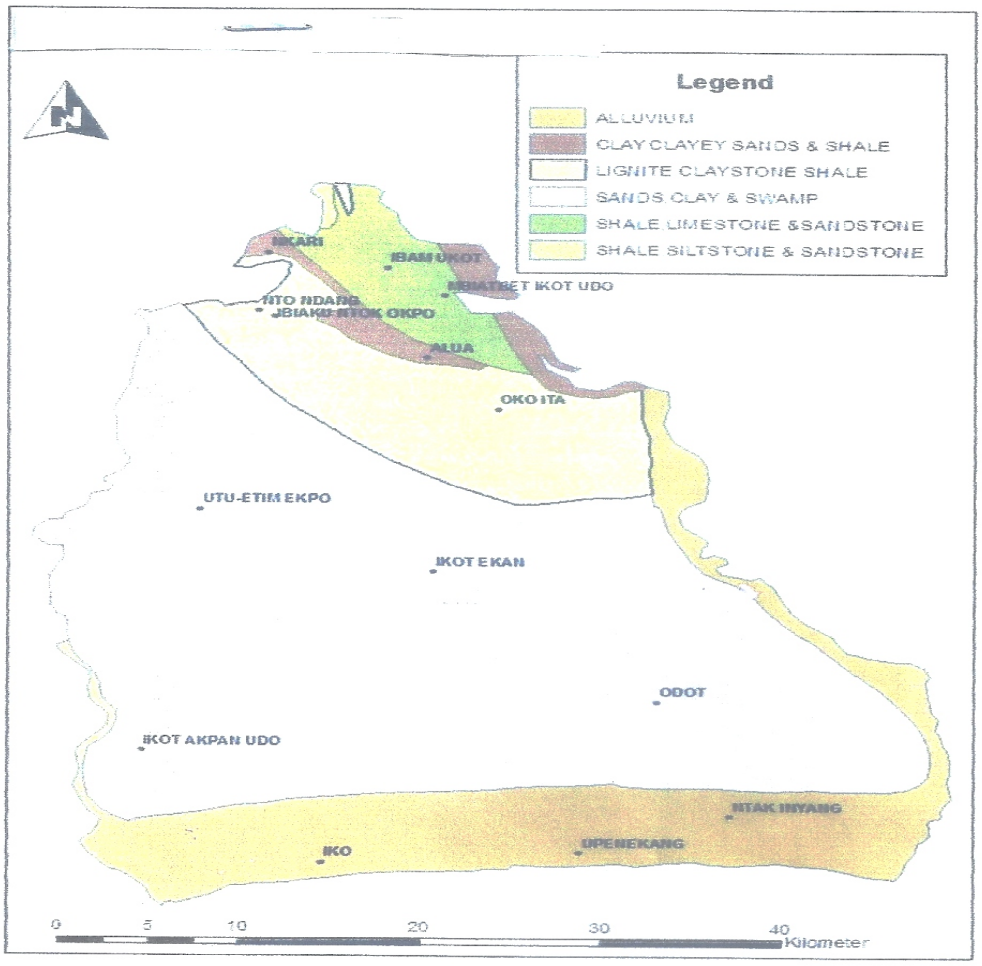


Fig. 1: Map of study area showing sampling points

Table 1: Particle size distribution of soils derived from coastal plain sands (CPS)

Soil	Depth (cm)	Particle Size (%)			Texture	Silt/ clay
		Sand	Silt	Clay		
Utu Etim Ekpo	0 – 20	84.70	2.50	12.80	LS	0.20
	20 – 72	69.20	2.80	28.00	SCL	0.10
	72 – 143	66.70	0.50	32.80	SCL	0.02
	143 – 200	65.20	6.80	28.00	SCL	0.24
	Mean	71.45	3.15	25.40		0.14
Ikot Ekan	0 – 18	85.70	4.50	10.80	LS	0.42
	18 – 74	68.20	4.80	16.00	SL	0.36
	74 – 121	65.70	2.50	31.70	SCL	0.08
	121 – 200	62.20	2.80	30.00	SCL	0.26
	Mean	70.28	5.15	22.13		0.28
Ikot Akpan Udo I	0 – 12	78.70	4.50	16.80	SL	0.27
	12 – 51	65.20	4.80	30.00	SCL	0.16
	51 – 110	64.70	1.50	33.80	SCL	0.04
	110 – 200	61.20	8.80	30.00	SCL	0.29
	Mean	67.45	4.90	27.65		0.19

LS = Loamy sand, SL = Sandy loam, SCL = Sandy clay loam

Table 2: Particle size distribution of soils derived from beach ridge sands (BHS)

Soil	Depth (cm)	Particle Size (%)			Texture	Silt/ clay
		Sand	Silt	Clay		
Utaewa	0 – 15	84.70	3.50	11.80	LS	0.23
	15 – 50	79.20	3.80	17.00	SL	0.18
	50 – 102	78.70	0.50	20.80	SCL	0.02
	102 – 200	75.20	9.80	15.00	SL	0.40
	Mean	79.45	4.40	16.15		0.21
Esit Urua Eket	0 – 20	83.20	6.00	10.80	LS	0.49
	20 – 75	73.20	10.80	16.00	SL	0.45
	75 – 110	71.20	4.00	24.80	SCL	0.38
	110 – 200	70.20	8.80	21.00	SCL	0.36
	Mean	74.45	7.40	18.15		0.42
Ntak Inyang	0 – 20	75.20	14.80	10.00	SL	0.60
	20 – 75	75.20	8.80	16.00	SL	0.35
	75 – 120	75.20	2.80	22.00	SCL	0.11
	120 – 200	69.20	2.80	28.00	SCL	0.09
	Mean	73.30	7.30	19.00		0.29

LS = Loamy sand, SL = Sandy loam, SCL = Sandy clay loam

Table 3: Chemical properties of the soils derived from coastal plain sands (CPS)

Soil	Depth (cm)	Ph		OM (%)	Total N (%)	Av.P (mgk g^{-1})	Exchangeable bases ($cmolkg^{-1}$)				H (cmol kg^{-1})	Al (cmol kg^{-1})	EA (cmol kg^{-1})	ECEC (cmol kg^{-1})	BS (%)
		H_2O	KCl				Ca	Mg	K	Na					
Utu Etim Ekpo	0-20	4.3	3.6	2.26	0.03	16.68	2.00	1.60	0.13	0.02	1.50	0.30	1.80	5.55	67.57
	20-72	4.8	3.7	2.08	0.09	8.60	2.40	0.08	0.03	0.09	0.48	0.32	0.80	3.40	76.47
	72-143	4.8	3.6	2.03	0.01	13.10	2.40	1.60	0.06	0.09	1.53	0.31	1.84	5.99	69.28
	143-200	4.6	3.5	1.98	0.08	7.60	1.60	1.20	0.06	0.10	0.36	0.36	0.72	3.68	80.43
	Mean	4.6	3.6	2.09	0.05	11.50	2.10	1.30	0.71	0.08	0.97	0.32	1.29	4.66	73.44
Ikot Ekan	0-18	4.3	3.6	2.10	0.02	11.20	2.10	1.50	0.07	0.03	0.58	0.32	0.90	4.47	79.87
	18-74	4.5	3.5	1.98	0.02	8.50	2.20	0.70	0.03	0.05	0.41	0.31	0.72	3.70	80.54
	74-121	4.4	3.6	1.72	0.01	7.30	1.97	1.40	0.06	0.08	1.50	0.30	1.80	5.31	66.10
	121-200	4.3	3.4	1.54	0.01	6.30	1.53	0.60	0.04	0.11	0.31	0.32	0.63	2.91	78.35
	Mean	4.4	3.5	1.84	0.02	8.30	1.95	1.05	0.05	0.08	0.70	0.31	0.01	4.10	76.22
Ikot Akpan Udo 1	0-12	4.2	3.6	2.31	0.01	14.70	2.40	1.60	0.06	0.03	1.29	0.31	1.60	5.69	71.88
	12-51	4.6	3.8	2.13	0.11	7.10	2.40	0.40	0.03	0.04	0.18	0.22	0.40	3.27	87.77
	51-110	4.3	3.7	1.28	0.03	4.60	2.00	1.20	0.05	0.05	1.48	0.28	1.76	5.06	65.22
	110-200	4.4	3.5	1.86	0.10	6.50	2.80	0.40	0.02	0.14	0.14	0.18	0.32	3.68	91.30
	Mean	4.4	3.7	1.90	0.06	8.23	2.40	0.90	0.04	0.07	0.77	0.25	1.02	4.43	79.04

OM = Organic matter, Av. P = Available phosphorus, EA = Exchangeable acidity, ECEC = Effective cation exchange capacity, BS = Base saturation

Table 4: Chemical properties of the soils derived from beach, ridge sand (BHS)

Soil	Depth (cm)	pH		OM (%)	Tot al N (%)	Av.P (mgk g^{-1})	Exchangeable bases ($cmolkg^{-1}$)				H (cmol kg^{-1})	Al (cmol kg^{-1})	EA (cmol kg^{-1})	ECEC (cmol kg^{-1})	BS (%)
		H_2O	KCl				Ca	Mg	K	Na					
Utaewa	0-15	4.1	3.8	1.48	0.03	10.00	2.80	0.08	0.11	0.09	1.28	0.16	1.14	4.22	72.99
	15-50	4.8	3.6	1.42	0.10	13.33	1.60	0.80	0.03	0.09	0.67	0.21	0.88	3.40	74.12
	50-102	4.6	3.7	1.28	0.01	7.93	2.80	0.08	0.06	0.10	1.24	0.20	1.44	4.48	67.86
	102-200	4.9	3.8	0.95	0.09	11.43	1.60	1.20	0.06	0.10	0.96	0.24	1.20	4.16	71.15
	Mean	4.6	3.7	1.28	0.06	10.67	2.20	0.54	0.06	0.10	1.04	0.20	1.24	4.07	71.51
Ntak Inyang	0-20	4.3	3.5	1.80	0.20	14.27	2.40	0.40	0.07	0.07	0.88	0.32	1.20	4.14	71.01
	20-75	4.7	3.6	1.35	0.14	13.50	1.20	1.60	0.09	0.06	0.77	0.27	1.04	3.99	73.93
	75-120	4.4	3.6	1.28	0.11	15.37	2.00	1.20	0.08	0.04	0.81	0.31	1.12	4.44	74.77
	120-200	4.5	3.5	0.85	0.08	15.83	1.20	2.00	0.02	0.13	0.64	0.24	0.88	4.23	79.20
	Mean	4.5	3.6	1.35	0.13	13.99	1.70	1.30	0.07	0.08	0.78	0.29	1.06	4.20	74.73
Esit Urua Eket	0-20	4.3	3.6	1.36	0.14	16.93	2.00	0.40	0.60	0.04	0.88	0.24	1.12	4.16	73.08
	20-75	4.8	3.7	1.24	0.13	11.37	2.80	0.20	0.53	0.06	1.30	0.30	1.60	5.19	69.92
	75-110	4.2	3.6	0.86	0.10	16.77	2.30	0.40	0.78	0.10	1.52	0.48	2.00	5.58	64.16
	110-200	4.6	3.8	0.70	0.05	6.83	2.10	0.32	0.41	0.11	1.68	0.42	2.10	5.04	58.33
	Mean	4.5	3.7	1.04	0.11	12.98	2.30	0.33	0.58	0.08	1.35	0.36	1.71	5.22	66.37

OM = Organic matter, Av. P = Available phosphorus, E A = Exchangeable acidity, ECEC = Effective cation exchange capacity, BS = Base saturation

Table 5: Means and ranges of the physicochemical properties of the soils

Soil property	CPS		BHS	
	Range	Mean	Range	Mean
Sand (%)	61.20 – 85.70	69.64	69.20 – 84.70	79.07
Silt (%)	0.50 – 8.80	4.40	0.50 – 14.80	6.37
Clay (%)	10.80 – 33.80	20.73	10.00 – 28.00	17.77
pH	4.2 – 4.8	4.50	4.1 – 4.9	4.5
Organic matter (%)	1.86 – 2.31	1.94	0.70 – 1.80	1.22
Total N (%)	0.01 – 0.11	0.04	0.01 – 0.20	0.10
Available P ($mgkg^{-1}$)	4.60 – 16.68	9.34	6.83 – 16.93	12.55
Exch. Ca ($cmolkg^{-1}$)	1.53 – 2.80	2.15	1.20 – 2.80	2.07
Exch. Mg ($cmolkg^{-1}$)	0.08 – 1.60 -	0.81	0.08 – 2.00	0.72
Exch. K ($cmolkg^{-1}$)	0.02 – 0.13	0.27	0.02 – 0.78	0.24
Exch. Na ($cmolkg^{-1}$)	0.02 – 0.14	0.08	0.04 – 0.13	0.09
Exch acidity ($cmolkg^{-1}$)	0.16 – 0.95	0.55	0.40 – 1.08	0.67
ECEC ($cmolkg^{-1}$)	2.71 – 5.99	4.40	3.40 – 5.58	4.50
Base saturation (%)	66.10 – 91.30	76.23	58.33 – 79.20	70.87

Exch. = Exchangeable

Table 6: Dithionite and oxalate forms of iron and aluminum oxides in soils derived from coastal plain sands (CPS)

Soil	Depth (cm)	Fe_d	Fe_o	Fe_p ($Fe_d - Fe_o$) gkg^{-1}	Al_d	Al_o	Al_p ($Al_d - Al_o$)	Fe_o/Fe_d	Al_o/Al_d	$Clay/Fe_d$
Utu Etim Ekpo	0 – 20	1.59	0.94	0.65	0.70	0.39	0.31	0.59	0.65	8.05
	20 – 72	1.56	0.91	0.65	0.70	0.38	0.32	0.58	0.54	17.95
	72 – 143	1.58	0.94	0.64	0.73	0.40	0.33	0.59	0.55	20.76
	143 – 200	1.43	1.03	0.40	0.68	0.39	0.29	0.72	0.57	19.58
	Mean	**1.54**	**1.00**	**0.59**	**0.70**	**0.39**	**0.31**	**0.62**	**0.56**	**16.59**
Ikot Ekan	0 – 18	1.33	0.73	0.60	0.74	0.32	0.42	0.55	0.43	8.12
	18 – 74	1.41	0.94	0.47	0.81	0.35	0.46	0.67	0.43	11.35
	74 – 121	1.50	0.98	0.52	0.86	0.47	0.39	0.65	0.55	21.13
	121 – 200	1.38	0.83	0.55	0.80	0.41	0.39	0.60	0.51	21.74
	Mean	**1.41**	**0.87**	**0.54**	**0.80**	**0.39**	**0.42**	**0.62**	**0.48**	**15.59**
Ikot Akpan Udo 1	0 – 12	0.92	0.44	0.48	0.37	0.19	0.18	0.48	0.51	18.26
	12 – 51	1.13	0.58	0.55	0.39	0.21	0.18	0.51	0.54	26.55
	51 – 110	1.39	0.84	0.55	0.47	0.26	0.21	0.60	0.55	24.32
	110 – 200	1.31	0.81	0.50	0.40	0.22	0.18	0.62	0.55	22.90
	Mean	**1.19**	**0.67**	**0.52**	**0.41**	**0.22**	**0.19**	**0.55**	**0.54**	**23.01**

Table 7: Dithionite and oxalate forms of iron and aluminum oxides in soils derived from beach ridge sands (BHS)

Soil	Depth (cm)	Fe_d	Fe_o	Fe_p ($Fe_d - Fe_o$) gkg^{-1}	Al_d	Al_o	Al_p ($Al_d - Al_o$)	Fe_o/Fe_d	Al_o/Al_d	Clay/Fe_d
Utaewa	0 -15	1.08	0.47	0.61	0.70	0.37	0.33	0.44	0.53	10.93
	15 – 50	1.22	0.61	0.61	0.63	0.35	0.28	0.50	0.56	13.93
	50 – 102	1.46	0.93	0.53	0.56	0.35	0.21	0.64	0.63	14.25
	102 – 200	1.41	0.90	0.51	0.52	0.31	0.18	0.64	0.60	10.64
	Mean	**1.29**	**0.73**	**0.57**	**0.60**	**0.35**	**0.25**	**0.56**	**0.58**	**12.44**
Ntak Inyang	0 – 20	1.29	0.74	0.55	0.45	0.25	0.20	0.57	0.56	7.75
	20 – 75	1.32	0.78	0.54	0.47	0.27	0.20	0.59	0.57	12.12
	75 – 120	1.50	0.91	0.59	0.49	0.30	0.19	0.61	0.61	14.67
	120 – 200	1.41	0.90	0.51	0.48	0.31	0.17	0.64	0.65	19.86
	Mean	**1.38**	**0.83**	**0.55**	**0.47**	**0.28**	**0.19**	**0.60**	**0.60**	**13.60**
EsitUruaEket	0 – 20	1.06	0.54	0.52	0.56	0.26	0.30	0.51	0.46	10.19
	20 -75	1.13	0.57	0.56	0.58	0.31	0.27	0.50	0.53	14.16
	75 – 110	1.26	0.64	0.62	0.61	0.40	0.21	0.51	0.66	19.68
	110 – 200	1.21	0.61	0.60	0.57	0.40	0.17	0.50	0.70	17.36
	Mean	**1.17**	**0.59**	**0.58**	**0.58**	**0.34**	**0.24**	**0.51**	**0.59**	**15.35**

Table 8: Simple correlation between DCB/Oxalate Fe/Al oxides and selected physicochemical properties of the CPS -derived soils

Soil physicochemical property	Fe_d	Fe_o	Fe_p	Al_d	Al_o	Al_p
Clay	0.2611	0.2327	-0.1734	-0.1293	0.1052	-0.1130
pH	0.4437	0.3957	0.2067	0.1906	0.2865	0.0792
Organic matter	-0.2128	-0.3107	0.1455	-0.1161	-0.1604	0.0322
Available P	-0.0034	-0.1814	0.1497	0.0508	0.0427	0.0251
ECEC	0.0759	-0.0338	0.2613	-0.0153	-0.0123	-0.0026

Table 9: Simple correlation between DCB/Oxalate Fe/Al oxides and selected physicochemical properties of the BHS-derived soils

Soil physicochemical Property	Fe_d	Fe_o	Fe_p	Al_d	Al_o	Al_p
Clay	0.4979	0.1349	0.2992	-0.0653	-0.1811	-0.1203
pH	0.2738	0.3286	-0.2208	-0.2208	-0.1144	-0.1206
Organic matter	-0.2013	-0.1788	-0.0043	-0.0337	0.1841	0.0137
Available P	0.1287	-0.0157	0.0008	-0.1886	-0.4318	0.1021
ECEC	0.0774	0.1289	0.5847	0.4345	-0.3581	0.1465

Table 10: Correlation coefficients between DCB/Oxalate Fe/Al oxides and selected physicochemical properties of the BHS-derived soils

Soil physicochemical property	Fe_d	Fe_o	Fe_p	Al_d	Al_o	Al_p
Clay	0.4979	0.1349	0.2992	-0.0653	-0.1811	-0.8370*
pH	0.2738	0.3286	-0.3337	-0.2208		
Organic matter	-0.2013	-0.1788	-0.0043	-0.0337	0.1841	0.4646
Available P	0.1287	-0.0157	0.0008	-0.1886	-0.4318	-0.2310
ECEC	0.0774	0.1289	0.5847	0.4345	-0.3581	-0.2126

*Significant at 5% level

Table 11: Coefficients of determination between DCB/oxalate Fe/Al oxides and selected physicochemical properties of the BHS - derived soils

Soil physicochemical property	Fe_d	Fe_o	Fe_p	Al_d	Al_o	Al_p
Clay	0.2480	0.0182	0.0895	0.0043	0.0328	0.7005
Organic matter	0.0405	0.03197	0.0000	0.0011	0.0339	0.2158
Available P	0.0166	0.0002	0.0000	0.0356	0.1865	0.0533
ECEC	0.0060	0.0166	0.3419	0.1888	0.1282	0.0452