DIFFERENTIAL SPECIATION AND AVAILABILITY OF COPPER IN SOILS DERIVED FROM DIFFERENT PARENT MATERIALS IN IMO STATE, SOUTHEASTERN NIGERIA

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ABSTRACT

Effective and efficient management of copper (Cu) in soils for optimum crop production and environmental conservation depends on proper knowledge of the various copper forms and fractions in soils as well as parent material. The distribution of forms of Cu in soils of different parent materials (coastal plain sands, alluvium, false-bedded sandstones and Imo clay shale) in Imo State, Southeastern Nigeria was evaluated using sequential extraction procedure, comprising of six fractions; water soluble (WS), exchangeable (EX), specifically sorbed/CO_3 bound (SSC), Fe-Mn bound (Fe-Mn), organic matter bound (OMB) and residual bound (RE) fractions. Soil was sampled at 0-15, 15-30, 30-45, 45-60 and 60-75 cm depths from each soil. Data obtained were subjected to analysis of variance and means separation was done by the procedure of Least Significant Difference at 5% probability level. Correlation analysis of the various Cu forms and some soil properties was also carried out. Results showed that the water soluble, specifically sorbed/carbonate bound, Fe-Mn bound, organic matter bound (OMB) and residual bound (RE Cu fractions differed significantly among the soils of the different parent materials. The Fe-Mn bound copper was the dominant fraction in most of the soils, contributing 41.53-46.63% to the total Cu, being highest in the alluvial soil (6.389 mg kg^{-1}) and lowest in the Imo clay shale soil (2.231 mg kg^{-1}). Moderate concentrations of available Cu (0.694-1.456 mg kg^{-1}) were observed and significant differences were observed among the soils. Correlations among the different Cu forms (WS vs EX r - 0.48; EX vs Fe-Mn r −0.46) and some soil properties (OM vs Fe-Mn r −0.86; Ca vs RE r −0.59; Clay Vs Fe-Mn r −0.53) were determined.

Key words: copper fractions, copper availability, parent materials, soil properties, southeastern Nigeria

INTRODUCTION

Copper is a micronutrient element which acts as a medium for electron transport in enzyme systems responsible for oxidation-reduction processes in photosynthesis (Brady and Weil, 2010). Halvin *et al*. (2012) noted that copper is necessary in plants for photosynthesis, respiration, lignin formation in cell walls, carbohydrate metabolism and lipid metabolism. Copper is immobile in plant system, hence its deficiency in plants first appears in younger leaves, showing chlorosis, withering and usually distortion of terminal leaves and subsequently premature death of the apex resulting in the production of several auxiliary buds (Singh, 2011). Copper present in soils appears in several forms that are partitioned between the solution and the solid phases. Its bioavailability and phytotoxicity are closely related to its distribution in the different chemical forms (Lagomarsino *et al.*,

2010). These chemical forms include soluble and exchangeable form, organic matter bound, carbonate bound, Mn-oxide, amorphous Fe-oxide, crystalline Fe-oxide associated metal forms, and residual fraction or metal ions fixed to silicate structures (Fathi *et al.*, 2014). The water soluble and exchangeable forms are considered readily mobile and available to plants; while metal incorporated into crystalline lattices of clays appear relatively inactive. The other forms-precipitated as carbonate, occluded in Fe, Mn and Al oxides or complexed with organic matter could be considered relatively active or firmly bound, depending upon the actual combination of physical and chemical properties of soil (Kabata-Pendias, 2011). Parent materials tend to govern the initial status of copper fractions in soils (Melo, 2006). It has been reported that soils derived from alluvium are richer in

organic matter bound copper than soils derived from coastal plain sands (Ideriah *et al.*, 2013; Oviasogie *et al*., 2011) Also, higher concentration of water soluble copper has been observed in soils derived from sandstones relative to soils derived from highly weathered quaternary red earths (Yu *et al*., 2004). An evaluation of total metal levels following a strong acid digestion of soil may be useful as a general indicator of contamination, but it provides little indication of metal's bioavailability, mobility, and reactivity in soils (Baltrenaite *et al.,* 2009). Due to the significant impact of parent material on soil chemical properties, the knowledge of influence of parent materials on chemical speciation of metals in the soil environment is important. This will provide land managers managing soils derived from different parent materials with useful guide necessary for proper management of land resources. Thus, there is the need to evaluate the chemical fractions of metals in soils from different parent materials. Although there have been a lot of studies on chemical fractionation of copper in soils, there is dearth of information on the influence of parent materials on the chemical fractions of copper in the soils of Imo State, Southeastern Nigeria. Therefore, the objective of this study was to examine the chemical fractions and availability of copper in soils from different parent materials in Imo State, Southeastern Nigeria.

MATERIALS AND METHODS

Study Area

The study was conducted in four different locations in Imo State, Southeastern Nigeria. The soils were derived from four different parent materials namely coastal plain sands, alluvium, Imo clay shale and false bedded sandstones (Orajaka, 1975). The study locations were Ihiagwa (Coastal plain sands) located between Latitudes $5^{o}21^{'}$ and $5^{o}27'$ N and longitudes $7^{o}02^{'}$ and $7^{o}15'$ E, Egwe (Alluvium) located between Latitudes $5^{o}42^{'}$ and $5^{o}46'$ N and Longitudes $6^{o}47^{'}$ and $6^{o}49^{'}$ E, Amauro (Imo clay shale) located between latitudes $5^{o}48'$ and $5^{o}53^{'}$ N and Longitudes $7^{o}20'$ and $7^{o}25^{'}$ E and Mbato (False-bedded sandstones) located between Latitudes $5^{o}55^{'}$ and $5^{o}58^{'}$ N and Longitudes $7^{o}02^{'}$ and $7^{o}08'$ E. Imo State lies between Latitudes $4^{o}40^{'}$ and $8^{o}15^{'}$ N and Longitudes $6^{o}40^{'}$ and $8^{o}15'$ E. (Federal Department of Agricultural Land Resources, 1985) and it is within the humid tropics. Temperatures are high and change slightly during the year. Mean daily temperature is about 27°C. The average annual rainfall is about 2400 mm and there is a distinct dry season of about 3 months usually from December-February (Okoli *et al*., 2016). The vegetation is characterized by multiple tree species such as oil bean tree (*Pentaclethra macrophyllum*), oil palm tree (*Elaeis guineensis*), mango

(*Mangifera indica*), etc. (Onweremadu *et al*., 2007b, Onweremadu and Peter, 2016). Agriculture and cottage industries are the major socio-economic activities in Imo State. Crops mostly cultivated in the study area include yam (*Dioscorea* spp), cassava (*Manihot* spp), oil palm (*Elaies guineensis*) and maize (*Zea mays*) while cottage industries are Cassava processing, Oil palm processing, block molding, etc.

Soil Sampling and Laboratory Analyses

A profile pit was dug at each location, guided by the geological map of the study area. Triplicate samples were collected from 0-15, 15-30, 30-45, 45-60 and 60-75 cm depths from each profile pit. The soil samples were air-dried, sieved through a 2-mm sieve and subjected to laboratory analyses. The analyses conducted included particle size distribution (Gee and Or, 2002) and pH (1: 2.5 soil/water) using glass electrode pH meter (Thomas, 1996). Exchangeable cations (Ca^{2+}, Mg^{2+}, K^{+}, Na^{+}) were extracted with NH_4OAc buffered at pH 7.0 (Thomas, 1982). The exchangeable K^{+} and Na^{+} were determined using the flame photometer while exchangeable Ca^{2+} and Mg^{2+} were determined using the ICE 3300 atomic absorption spectrophotometer. Exchangeable acidity (Al^{3+} and H^{+}) was extracted with 1 N KCl (Thomas, 1982) and determined by titrating with 0.5 N NaOH, using phenolphthalin as an indicator. Effective cation exchange capacity (ECEC) was obtained by summation of basic and acidic cations. Organic matter content of the soils was determined by the wet oxidation method (Nelson and Sommers, 1982) while available P was determined using Bray II solution (Olsen and Sommers, 1982).

Copper Sequential Fractionation Procedures

Water soluble, exchangeable, specifically sorbed/carbonate bound, Fe-Mn oxide bound, organic matter bound and residual bound Cu fractions were determined using the sequential extraction procedure described by Salbu *et al.* (1998). The procedure is outlined as follows:

Water Soluble Fraction (F1):

Two grams of soil sample were weighed into a 50-mL polycarbonate centrifuge tube and extracted using 20 mL of de-ionised water for 1 h at 20°C on a rolling table.

Exchangeable Fraction (F2):

The residue obtained from water soluble extraction was washed with 10 mL de-ionised water and the supernatant discarded. The residue was transferred into a 50 mL polycarbonate centrifuge tube and extracted with 20 mL of 1M NH_4OAc solution buffered at pH 7 for 2 h.

Specifically Sorbed and Carbonate Bound Fraction (F3):
The residue obtained from the extraction of exchangeable form was washed with 10 mL de-ionised water and the supernatant discarded. The residue was transferred into a 50-mL polycarbonate tube and extracted with 20 mL of 1M NH_4OAc solution buffered at pH 5 for 2 h.

Fe-Mn Oxide Bound Fraction (F4):
The residue obtained from the extraction of specifically sorbed and carbonate bound form was washed with 10 mL de-ionised water and the supernatant discarded. The residue was transferred into a 50-mL polycarbonate tube and extracted with 20 mL of 0.04 M $NH_2OH.HCl$ in 25% HOAc for 6 h in a water bath at 60^oC .

Organic Matter Bound Fraction (F5):
 In this procedure, residue obtained from the extraction of Fe-Mn oxide bound form was washed with 10 mL deionised water and transferred into a 50-mL polycarbonate tube and extracted with 15 mL of 30% H_2O_2 at pH 2 (adjusted with HNO_3) for 5.5 h in a water bath at 80^oC. The content was allowed to cool and 5 mL of 3.2 M NH_4OAc in 20% HNO_3 was added and diluted to 20 mL with deionised water.

Residual Fraction (F6):
 In this method, 1 g of the residue obtained from the extraction of organic matter bound form was dried after which it was digested in a conical flask with 10 mL of 7 M HNO_3 on a hot plate for 6 h. After evaporation, 1 mL of 2 M HNO_3 was added and the residue dissolved. Thereafter, it was diluted using 10 mL de-ionised water. After each successive extraction, the mixture of soil sample and extractant was centrifuged at 1000 rpm for 30 min and the supernatant decanted into polyethylene bottles, acidified to pH < 2 and stored for analysis. The various chemical fractions of Cu were determined using ICE 3300 atomic absorption spectrophotometer at 324.8 nm wavelength.

Available and Total Copper Determination
Available copper was calculated as sum of water soluble (F1) and exchangeable (F2) fractions (F1+F2) while total copper was calculated as sum of all the fractions (F1+F2+F3+F4+F5+F6) determined (Ramzan *et al.*, 2014).

Statistical Analysis
Data obtained from selected phyisco-chemical properties and copper fractions determined were subjected to Analysis of Variance (ANOVA) and means were separated using Least Significant Differences (LSD) at 5% level of Probability. Correlations between selected soil properties and copper forms and amongst copper fractions were determined. All statistical analyses were done using GenStat statistical package described by Buysse *et al.* (2004)

RESULTS AND DISCUSSION
Physico-chemical Properties of the Soils of Different Parent Materials
The results of the physico-chemical properties of the soils studied are presented in Table 1. Particle size distribution varied significantly (p < 0.05) among the soils of the different parent materials. Three textural classes comprising sand, loamy sand and sandy loam were observed in the soils of the coastal plain sands. For the alluvial soils, the texture was sand all through the profile. The texture of the false-bedded sand-stone soils varied from sandy loam to sandy clay loam while the variation was from clay loam to clay in the soils derived from Imo clay shale. The results showed decreasing sand fraction with depth whereas clay fraction increased with depth. The increasing clay content with depth could be attributed to the illuviation process that has taken place, leading to accumulation of clay in the lower horizons (Esu, 2005). The high sand fraction observed in the soils derived from coastal plain sands could be due to the sandy nature of the parent material (Onweremadu *et al.*, 2007a). Similarly, significant (p < 0.05) higher clay fraction observed in the soils of Imo clay shale could be attributed to the clayey nature of the parent material (Anenyeonwu, 2016). The high values of sand fraction in soils derived from alluvium were similar to the report of Onweremadu *et al*. (2007b) for soils of the same study area derived from alluvium. These authors attributed the results to the presence of old deltaic, lacustrine and fluvial deposits in the area.
The soils derived from the Imo clay shale and the surface soil derived from the false-bedded sandstones contained moderate amounts of organic matter. The organic matter content of the other soils was low (FAO, 2004) and varied significantly (p < 0.05). Similar results were reported for some soils of the same area by Uzoho *et al.* (2014). The low organic matter content of most of the soils was attributed to high temperature and rainfall in the area which encourages rapid mineralization, erosion and leaching of organic matter (Nwagbara and Ibe, 2015). The soils generally contained very low to low amounts exchangeable calcium (FAO, 2004). Similar results were reported for some soils in the area derived from coastal plain sands and alluvium by Onweremadu *et al.* (2011). They attributed the observation to the sandy texture and the leaching prone characteristics of the soils. Acidity (pH) differed significantly (p < 0.05) among the soils, ranging from 4.28 to 5.63 in coastal plain sands soils, 5.31 to 5.62 in alluvial soils, 5.12 to 5.41 in false bedded sandstone soils and 5.55 to 5.98 in Imo clay shale soils. These values varied from extremely acidic to moderately acidic (FAO, 2004).

The generally low pH of the soils could be due to the high amounts of rainfall in the study area and the associated leaching out of the basic cations (Ca^{2+}, K^+, Na^+ and Mg^{2+}), leading to the dominance of acidic cations (Al^{3+}, H^+) on the exchange complex of the soils. Similar pH results have been reported by Ahukaemere *et al*. (2016) for some soils of southeastern Nigeria. Also, differences in the pH of some soils from southeastern Nigeria derived from different parent materials had been reported (Obalum and Chibuike, 2017). The soils contained very low levels of available P (0.23-3.36 mg kg^{-1}) which were far lower than the critical limit of 10 mg kg^{-1} recommended by Esu (1999) for arable crop production. However, the soils derived from the alluvium contained relatively higher levels of available P. The low levels of available P in the soils could be due to fixation by sesquioxides in the low pH soil environments (Havlin *et al*., 2012). The exchangeable properties are presented in Table 1. Comparatively, the Imo clay shale soils had the highest ECEC of 5.28 cmol$_c$ kg^{-1} which may be attributed to its higher clay content while the alluvial soils had the lowest value 4.16 cmol$_c$ kg^{-1}.

However, these values are low when compared with the critical limit of 6 cmol$_c$ kg^{-1} recommended by Esu (1991) for arable crop production. The ECEC of soil is a reflection of its metal retention capacity and is an important parameter in the prediction of metal retention, movement and extractability (Udom *et al*., 2004: Rieuwerts *et al*., 2005). The low ECEC of the soils could be attributed to parent materials, climate and land use interactions (Onweremadu *et al*., 2011).

Fractions and Distribution of Copper in the Soils
The results of the distribution of the copper forms in the soils are presented in Table 2. The concentration of water soluble copper was low in the soils and differed significantly (p < 0.05) among the soils with the highest mean value of 0.795 mg kg^{-1} equivalent to 12.93% of total copper recorded in the soils of the false bedded sandstones and the lowest mean value of 0.269 mg kg^{-1} equivalent to 3.85% of total copper observed in the soils of the coastal plain sands. Apart from the False-bedded sandstones soils, the water-soluble Cu form was the smallest in the soils.

Table 1: Physico-chemical properties of the sampled soils

Soil depth (cm)	Sand	Silt (%)	Clay	TC	OM (g kg^{-1})	Ca (cmol$_c$ kg^{-1})	pH-H$_2$O	Avail. P (mg kg^{-1})	ECEC (cmol$_c$ kg^{-1})
				Coastal plain sands					
0-15	90	4	6	S	13.99	1.22	4.28	0.86	4.14
15-30	88	4	8	S	1.28	1.61	4.89	0.66	4.7
30-45	86	2	12	LS	1.28	1.22	5.63	0.73	3.75
45-60	84	4	12	LS	6.41	2.03	4.91	0.47	5.11
60-75	80	4	6	SL	1.56	1.81	5.26	0.56	5.09
Mean	**85.6**	**3.6**	**10.8**		**4.90**	**1.58**	**4.99**	**0.66**	**4.56**
				Alluvium					
0-15	95	2	4	S	2.27	1.22	5.36	2.19	4.03
15-30	94	0	4	S	2.22	1.42	5.49	2.38	3.93
30-45	96	1	4	S	1.91	1.61	5.62	1.44	5.81
45-60	96	2	4	S	1.91	1.80	5.32	1.73	4.36
60-75	94	2	4	S	1.73	2.01	5.31	2.56	4.67
Mean	**95**	**1.4**	**4.0**		**2.01**	**1.61**	**5.42**	**2.06**	**4.16**
				False-bedded sandstones					
0-15	68	14	18	SL	38.51	3.41	5.41	0.92	6.47
15-30	50	20	30	SCL	5.72	1.4	5.41	0.76	4.14
30-45	52	18	30	SCL	13.63	1.83	5.21	0.36	4.69
45-60	52	16	32	SCL	2.24	1.61	5.12	0.27	4.88
60-75	49	19	32	SCL	1.91	1.61	5.31	0.23	5.14
Mean	**54.2**	**17.4**	**28.4**		**12.40**	**1.97**	**5.29**	**0.51**	**5.06**
				Imo Clay Shale					
0-15	44	28	28	CL	48.87	2.04	5.56	3.36	5.37
15-30	30	26	44	C	2.95	1.02	5.56	0.29	2.89
30-45	26	24	50	C	47.78	3.23	5.55	0.23	6.59
45-60	28	12	60	C	43.28	2.00	5.98	0.96	4.79
60-75	42	26	32	CL	46.03	2.61	5.85	1.56	6.78
Mean	**34**	**23.2**	**42.8**		**31.98**	**2.18**	**5.70**	**1.30**	**5.28**
LSD$_{(0.05)}$	18.7	8.1	11.7		8.99	1.25	0.20	0.47	2.87

OM - organic matter, Avail P - Available phosphorus, ECEC - effective cation exchange capacity, TC - textural class, S - sand, LS - loamy sand, SL - sandy loam, SCL - sandy clay loam, CL - clay loam, C – clay

The low concentration of water soluble copper when compared with the other fractions in the soils could be due to losses from leaching and plant uptake, since this represents the fraction that is most bioavailable and mobile in soils (Filgueiras *et al.*, 2002) or as a result of poor extractive strength of water (Mbila *et al.*, 2001). Low level of water soluble fraction of metals is natural for forest and unpolluted soils. Kabata-Pendias *et al.* (2011) noted that copper in soil solution ranges from 0.0005 to 0.135 mgkg^{-1}, depending on the techniques used and on soil types. The results obtained in this study were higher than the range reported by Kabata-Pendias *et al.* (2011) for soil solutions. Probably, the low pH of the soils might have contributed to the high solubility of copper in the soil solutions (Havlin *et al.*, 2012). It may as well be due to low organic matter content of the soils (< 50 g/kg) which agreed with the reports of Havlin *et al*. (2012) who observed that copper is more strongly bound to organic matter than any other micronutrient, an indication that decreasing OM in soils, increases copper solubility. The values obtained for soils derived from coastal plain sands were similar to results obtained by Koka *et al*. (2011) who reported a mean value of 0.265 mg kg^{-1} in the topsoils of some cocoa growing areas of the Central Region of Ghana. The values obtained in the soils derived from false bedded sandstones were similar to those reported for some Inceptisols derived from sandstones by Yu *et al*. (2004).

Furthermore, with the exception of the soils derived from false bedded sandstones, other soils showed highest accumulation of water soluble Cu at the surface horizon perhaps due to anthropogenic activities (Kabata-Pendias and Pendias, 2001). The water soluble Cu content of the soils was in the order; false-bedded sandstones > Imo clay shale > alluvium > coastal plain sands. Apart from soils derived from false bedded sandstones, exchangeable copper fraction in the soil profiles was higher than the water soluble fraction in the soils, but there was no significance difference (p < 0.05) among the different soils. The results showed that the highest mean value 0.661 mg kg^{-1} was observed in the soils of false-bedded sandstones whereas soils of alluvium had the least mean of 0.354 mg kg^{-1}. Apart from the water-soluble, organic matter bound and residual fractions, the exchangeable Cu fraction was the smallest of the total Cu content of the soils and constituted about 7.09, 2.58, 10.75 and 11.22% of total copper concentration in the soils derived from coastal plain sands, alluvium, false bedded sandstones and Imo clay shale, respectively. The exchangeable copper levels were lower than the 20 mg kg^{-1} reported for some soils from a former vineyard of Torino, Italy (Lagomarsino *et al*., 2010) and the 20.08 mg kg^{-1} reported for some Inceptisols derived from sandstones (Yu *et al*., 2004). The low

levels of exchangeable Cu in the soils may be due to the low organic matter content of the soils which may have reduced the exchange sites (Brady and Weil, 2010). In addition, the low pH of the soils may have reduced the number exchange sites (Havlin *et al*., 2012). The specifically sorbed/carbonate bound copper fraction was higher than water soluble and exchangeable copper fractions in the soils and varied significantly (p < 0.05) among the soils. However, the values were lower than the Fe-Mn bound Cu fraction in the soils. The highest Mean value of 5.483 mg kg^{-1} equivalent to 40.02% of total copper was observed in the soils derived from alluvium whereas least mean value of 1.736 mg kg^{-1}equivalent to 28.24% of total copper was recorded in the soils derived from false-bedded sandstones (Table 2). The specifically sorbed/carbonate Cu content of the soils based on their parent materials was in a decreasing order of alluvium > coastal plain sands > Imo clay shale > false bedded sandstones. The values obtained for the soils of the alluvium and falsebedded sandstones were similar to those the reported by Oviasogie *et al*. (2011) in the wetland (Alluvium) soils of the Niger Delta, Nigeria and those reported by Yu *et al*. (2004) for some Inceptisols derived from sandstones in China, respectively. The results further showed decreasing concentration of the specifically sorbed/carbonate with depth in the soil derived from the alluvium but the distribution in the other soils did not follow any well-defined pattern. The Fe-Mn bound copper fraction differed significantly (p < 0.05) among the soils of different parent materials. The highest mean value of 6.389 mgkg-^{1} equivalent to 46.63% of the total copper concentration was observed in the soils derived from alluvium while the lowest mean value of 2.231 mg kg^{-1} equivalent to 45.42% of the total Copper concentration was recorded in the soils derived from the Imo clay shale. A comparison with the other copper fractions showed that the Fe-Mn bound copper was the most dominant fraction which is consistent with the reports of Kabat-Pendias and Pendias (2001) and that of Oviasogie *et al*. (2011) for alluvial soils of the Niger Delta, Nigeria. Kabata-Pendias (2011) had reported that the greatest amounts of adsorbed Cu have always been found in Fe and Mn oxides (hematite, goethite, birnessite), amorphous Fe and Al hydroxides, and clays (Kabata-Pendias, 2011) which could be due to adsorption mechanism of copper onto metal oxides. Copper forms strong surface bonds with metal oxides such as Cu-O-Al, Cu-O-Mn or Cu-O-Fe which do not break easily (Halvin *et al*., 2012). The organic matter bound copper fraction in the soils was very low and in many cases, particularly in soils derived from Imo clay shale, was not detectable.

Table 2: Fractions and distribution of copper (mg kg^{-1}) in the soils

Depth (cm)	Water Soluble (mg kg^{-1})	Exchangeable	Available	Specifically sorbed/CO$_3$ bound	Fe-Mn bound	OM bound	Residual Bound	Total
	Coastal plain sands							
0-15	0.603	0.739	1.342	0.943	2.320	ND	ND	4.605
15-30	0.149	0.733	0.882	0.454	4.441	0.413	ND	6.190
30-45	0.138	0.112	0.250	5.931	3.144	0.543	ND	9.868
45-60	0.067	0.239	0.306	1.007	3.855	ND	ND	5.168
60-75	0.386	0.650	1.036	5.243	2.151	0.639	ND	9.069
Mean	**0.269**	**0.495**	**0.764**	**2.716**	**3.182**	**0.319**	**ND**	**6.980**
%Total	3.85%	7.09%	10.95%	38.91%	45.58%	4.57%		
	Alluvium							
0-15	0.403	0.795	1.198	7.104	1.373	ND	ND	10.873
15-30	0.342	0.001	0.343	6.153	5.201	0.611	ND	12.651
30-45	0.280	0.398	0.678	5.202	6.223	0.993	ND	13.774
45-60	0.272	0.283	0.555	4.569	8.103	0.331	ND	14.113
60-75	0.337	0.295	0.620	4.385	11.049	0.277	ND	16.963
Mean	**0.340**	**0.354**	**0.694**	**5.483**	**6.389**	**0.442**	**ND**	**13.702**
%Total	2.48%	2.58%	5.06%	40.02%	46.63%	3.23%		
	False-bedded Sandstones							
0-15	0.365	0.663	1.028	1.476	7.604	ND	1.125	11.232
15-30	0.550	0.372	0.922	0.892	2.299	ND	ND	4.113
30-45	2.205	0.997	3.202	1.425	1.363	ND	ND	5.990
45-60	0.546	0.690	1.236	2.562	0.061	ND	ND	3.859
60-75	0.308	0.583	0.891	2.327	1.441	0.883	ND	5.542
Mean	**0.795**	**0.661**	**1.456**	**1.736**	**2.553**	**0.177**	**0.225**	**6.147**
%Total	12.93%	1O.75%	23.69%	28.24%	41.53%	2.88%	3.66%	
	Imo Clay Shale							
0-15	0.360	0.507	0.867	1.632	4.260	ND	ND	6.759
15-30	0.310	0.426	0.736	0.477	1.947	ND	ND	3.160
30-45	0.354	0.490	0.844	0.490	2.713	ND	ND	4.047
45-60	0.175	0.885	1.060	2.001	0.582	ND	ND	3.643
60-75	0.631	0.448	1.079	4.217	1.655	ND	ND	6.951
Mean	**0.366**	**0.551**	**0.917**	**1.763**	**2.231**	**ND**	**ND**	**4.912**
%Total	7.45%	11.22%	18.67%	35.89%	45.42%			
LSD$_{(0.05)}$	0.159	0.313	0.229	1.200	1.266	0.122	0.075	2.414

ND – not detected

Table 3: Simple linear correlation among copper fractions and between copper fractions and selected soil properties ($n = 20$)

	Exch. Cu	W-S Cu	Specifically sorbed/CO$_3$ bound Cu	Fe/Mn bound Cu	OM bound Cu	Residual bound Cu
Exch. Cu	-	-	-	-	-	-
W-S Cu	0.48*	-	-	-	-	-
Specifically sorbed/CO$_3$ bound Cu	-0.26	-0.13	-	-	-	-
Fe/Mn bound Cu	-.46*	-0.24	0.10	-	-	-
OM bound Cu	-0.41	0.25	0.43	0.21	-	-
Residual bond Cu	0.12	-0.05	-0.14	0.39	-0.15	-
Avail. P.	0.16	-0.14	0.38	0.46*	-0.10	-0.03
Ca	0.06	-0.12	0.22	0.31	0.24	-0.59*
Clay	0.30	0.11	-0.49*	-0.55*	-0.36	-0.08
ECEC	0.18	0.04	-0.16	0.08	-0.22	-0.40
OM	0.24	0.06	-0.27	-0.86**	-0.41	0.35
P^H(H$_2$0)	0.23	-0.13	-0.30	0.03	0.06	0.04

W-S- water soluble, Avail. P-available phosphorus, ECEC – effective cation exchange capacity, OM - organic matter, *-Significant at 5% probability level, **- significant at 1% probability level

The mean values of organic matter bound copper fraction significantly ($p < 0.05$) decreased in the order of alluvium (0.442 mg kg^{-1}) > coastal plain sands (0.319 mg kg^{-1}) > false bedded sandstones (0.177 mg kg^{-1}) > Imo clay shale (not detected). Halvin *et al.* (2012) observed that at ≤ 8% soil OM, both organic and mineral surfaces are involved in Cu adsorption, while at > 8% OM, binding of Cu takes place mostly on organic surfaces. Thus, it is possible that the low values observed in the soils could be due to their low organic matter contents (< 5%). Apart from the 1.125 mg kg^{-1} residual Cu contained in the surface of the soil derived from the False-bedded sandstones, residual Cu was not detectable in the soils. The results were similar tothose of Oviasogie *et al.* (2011) in the wetland

(Alluvium) soils of the Niger Delta, Nigeria but far below mean value of 30.03 mg kg^{-1} reported by Fathi *et al*. (2014) in some soils of Iran. The low level of residual bound Cu in the soils could be due to high weathering of Cu-bound rocks and minerals and the transformation of other Cu forms. (Kabata-Pendias, 2011). Generally, the concentrations of copper fractions differed in each of the soil profiles. The fractions decreased in the order; Coastal Plain Sands: F4 > F3 > F2 > F5 > F1 > F6 Alluvium: F4 > F3 > F5 > F2 > F1 > F6 False Bedded Sandstones: F4 > F3 > F1 > F2 > F6 > F5 Imo Clay Shale: F4 > F3 > F2 > F1 > F5 - F6 This clearly shows the dominance of the Fe-Mn oxide bound Cu in the soils which is consistent with the report of Oviasogie *et al.* (2011) in the wetland (Alluvium) soils of the Niger Delta, Nigeria.

Distribution of Available and Total Copper in the Soils
There was significant (p < 0.05) difference in the distribution of available copper among the soils. The mean values ranged from 0.694 mg kg^{-1} to 1.456 mg kg^{-1}. The values fell within the medium range (i.e., 0.2-2.0 mg kg^{-1}) of fertility ratings of available copper for arable crop production recommended by Esu (1991), which indicated that plants growing in the area were not likely to suffer copper deficiency. Adiele *et al*. (2015) and Verma *et al.* (2005) also reported medium concentrations of available copper in some soils of coastal plain sands (0.8 mg kg^{-1}) in the farm of National Root Crop Research Institute, Abia State, Southeastern Nigeria and the alluvial soils (0.26-1.90 mg kg^{-1}) of Punjab, India, respectively. The available Cu levels obtained in the soils derived from False-bedded sandstones were higher than average value of 0.18 mg kg^{-1} obtained from some soils derived from sandstones in the Akko Local Government Area of Gombe State, Nigeria (Mustapha *et al*., 2011). This result could be due to the fact the soils derived from the False bedded sandstones had lower pH than those soils used by Mustapha *et al*. (2011). Havlin *et al*. (2012) have shown that low pH increases Cu availability in soils. The total copper concentration also differed significantly (p < 0.05) among the soils. It was highest in the alluvial soil with a mean value of 13.702 mg kg^{-1} and lowest in soil derived from Imo clay shale with a mean value of 4.912 mg kg^{-1}. Havlin *et al*. (2012) noted that total copper concentration in soils varies between 1-40 mg kg^{-1} with an average value of about 9 mg kg^{-1} and it may be 1 to 2 mg kg^{-1} in deficient soils. Thus, apart from the alluvial soil, the soils used in this study could be considered as low in total Cu. The source of total Cu contents of the soils is speculated to be of lithogenic and pedogenic origin since there is no history of anthropogenic activity in the area that could result to accumulation of Cu in the soils. Iwegbue (2011) and Iyaka and Kakulu

(2009) had also reported low concentrations of total Cu in the coastal plain sands soils of Southeastern Nigeria and the sandstones soils of Bida, north central Nigeria, respectively. Similarly, the values obtained in the alluvial soils were consistent with the report of Oviasogie *et al*. (2011) in the wetland (Alluvium) soils of the Niger Delta, Nigeria. Furthermore, the total Cu concentrations in the soils were below the maximum permissible agricultural soil concentration of 100 mg kg^{-1} recommended by Kabata-Pendias and Pendias (2001).

Relationships among Copper Fractions and Between Copper Fractions and Selected Soil Properties
Few significant correlations existed among copper forms and between copper forms and selected soil properties (Table 3). Exchangeable copper had significant positive correlation with water soluble Cu (r = 0.48). On the contrary, exchangeable Cu significantly (p < 0.05) and negatively correlated with Fe-Mn bound Cu (r = −0.46). Available phosphorous had significant (p < 0.05) positive correlation with Fe-Mn bound Cu (r = 0.46) whereas Ca had a significant negative correlation with residual bound Cu (r = −0.59). Furthermore, clay had significant (p < 0.05) negative correlation with Fe-Mn bound Cu (r = −0.53) and specifically sorbed/carbonate bound copper (r = −0.49). Thus, increases in clay content would be associated with significant decreases in Fe-Mn bound and specifically sorbed/carbonate bound copper forms. Organic matter content of the soils had a highly significant negative (p < 0.01) correlation with Fe-Mn bound Cu (r = −0.86) which implies that increases in organic matter content of the soils would be associated with decreases in Fe-Mn bound Cu (Table 3).

CONCLUSIONS
The results of this study have shown that water soluble, specifically sorbed/carbonate bound, Fe-Mn bound, organic matter bound and residual bound copper fractions differed significantly among the soils of the different parent materials investigated. The Fe-Mn bound was the dominant copper fraction in the soils whereas residual bound copper was not detectable in majority of the soils probably because of high weathering of most of the Cu-bearing rocks and minerals in the study area. All the soils had moderate concentrations of available copper, although the levels were significantly different. Significant correlations were obtained between exchangeable and water soluble Cu forms, exchangeable and Fe-Mn bound Cu forms, available P and Fe-Mn bound Cu, Clay and Fe-Mn bound Cu, Ca and residual bound Cu, Clay and Specifically sorbed/carbonate bound Cu and between organic matter and Fe-Mn bound Cu.

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