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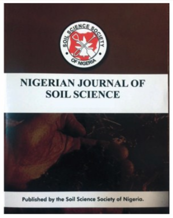

Effects of Parent Material and Land Use on the Variability of Available Cu in a Wetland Soil under Long-Term Farming System

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ABSTRACT

The study was carried out in the dry season to evaluate the variation in available Cu in wetland soil under long-term farming systems. Twenty four surface (0-20 cm) composite soil samples of acidic nature were obtained and analyzed for available Cu in the soils using five extractants (0.01M HCl, Coca-cola, 0.05M EDTA, 0.05M DTPA, and 1N NH_4OAc) respectively. Some important soil characteristics like soil texture, pH, SOM, and ECEC were also determined and correlated with the extractable Cu. The result shows that the content of available Cu varied significantly from 1.72-10.76 mg kg^{-1} by DTPA and Coca-cola methods, and these were rated from low to moderate, respectively. The study further shows that, the comparative extraction capacity of these extractants followed the order: Coca-Cola > O.1N HCl > 0.05M EDTA > NH_4OAc > 0.005M DTPA. The wide variability of the available Cu in the wetland soils under long-term farming suggests that the availability of Cu in the soil are haply influenced by the agricultural locations, type of land use systems and soil parent materials, respectively. Correlation data also indicated that the fractions of Cu by different extractants were in a state of dynamic equilibrium and dependent were on pH, organic matter, ECEC, and clay content. The marginally Cu content of the wetland soils suggests that the use of integrated organo-mineral fertilizer with copper sulphate compound ($CuSO_4.5H_2O$) is required to boost the soil Cu and hence increased crop production.

1. Introduction

Wetland (hydromorphic) soils are those areas that are inundated or soils, which are water-saturated by surface or groundwater during most of the months (Aghimien, 1989, Effiong and Ibia, 2009). These include inland depression (valleys), alluvial plains (floodplains) and coastal plains (swamps) (Ojanuga *et al*., 2003; Ato *et al*., 2012). They constitute soils that are part of land resources available for the cultivation of food crops during the dry season (Ibia and Udo, 2009). In Cross River State, most cultivated soils of floodplain and swamp are derived from parent materials such as; coastal plain sands, basalt, shale, beach ridge sands, sandstone, alluvial deposits and mangrove (Eteng *et al*., 2014).

The characteristics of wetland soils are broad, primarily defined by the original soil parent materials and are influenced by climate, topography and the general agricultural land use pattern and management (Ibia and Udo, 2009). These soils are difficult to use for agriculture due to low fertility level and the need for high inputs. However, under normal circumstances do support, a prevalence of vegetation typically adapted for life in saturated soil conditions (Ato *et al.*, 2012). The soils are marginal, which are generally, ignored or abandoned by farmers and, not necessarily because they are degraded (Onyekwere *et al.*, 2001). This, according to Ogban *et al.* (2011) was due to the potential severe limitations to their uses due to, waterlogging and flooding conditions during the rainy season.

Until recently, farming on these soils has been less attractive due to different land management practices that induce considerable variability and reduction in cationic micronutrients content (Ogban *et al.*, 2011). Among the micronutrient is copper, an essential plant nutrient element (Yruela, 2005), which has been identified to be deficient in wetland soils (Aghimien, 1989; Sakal *et al.*, 1988). Copper (Cu) is an essential redox-active micronutrient that is involved in many physiological processes in plants because it can exist in multiple oxidation states *in vivo* (Kabata-Pendias, 2010). Most Cu in soils is very insoluble and can only be extracted by very strong chemical treatments which dissolve various mineral structures of solubilizing organic matter (Kabata-Pendias, 2010).

The transformation and behavior of micronutrients in submerged soils are entirely different compared to typical soils (Ojanuga *et al.*, 2003). When an acid soil is flooded, the availability of copper decreased due to an increase in soil pH. In most soils, submergence decreases the availability of Cu and thereby creates a deficiency in plants (Effiong and Ibia, 2009). The transformation of Cu in submerged soils is not involved in redox reactions; its behavior is influenced by simple submergence in soils (Ojanuga *et al.*, 2003). It is evident that, Cu exists in soils as different discrete chemical pools which are as follows: (i) water-soluble and exchangeable Cu, (ii) copper associated with clay minerals, (iii) organically bound Cu, (iv) copper associated with different oxides in soils and (v) residual Cu (Scherffer *et al.*, 1990). The amount of each form of Cu in soils depends on soil pH, SOM, Clay content, and CEC (Aghimien, 1989).

Under physiological conditions, copper exists in soils mostly as cupric (Cu^{2+}) and less as cuprous (Cu^{+}) ions. Plants absorb Cu as the Cu^{2+}, but the solution forms are Cu^{2+} in strongly acidic soil, $Cu(OH)^{+}$ in mildly acidic soil and $Cu(OH)_2$ at pH value near neutral and more alkaline (Angelova *et al.*, 2003). It is believed that some available Cu comes from exchangeable forms, some from less exchangeable forms and some from soluble organic complexes or chelates (Norvel, 1984; Angelova *et al.*, 2003). The redox properties that make Cu an essential element also contributes to its inherent toxicity. Nevertheless, either deficient or in excess, Cu can cause disorders in plant growth and development by adversely affecting the critical physiological process in plants. Thus, for healthy plant growth and development, Cu must be acquired from the soil, transported throughout the plant (Menzies *et al.,* 2007).

Copper deficiency in such soil is mostly caused by long-term/continuous cropping with intensive farming, leading to its depletion or nutrient mining (FAO, 2010). However, long -term cropping practices without the fertilization of an important essential plant nutrient element like Cu, often leads to a mineral imbalance in soils and results to a decline in crop productivity (Chude *et al.*, 2012), primarily in soils where Cu deficiency is reported (Sillanpaa, 1990; Kabata-Pendias, 2010). However, primary copper depletion sources from the soil are associated with uptake by crop plants, removal by soil erosion, leaching by rainfall, and immobilization by organic matter and microbial biomass (Kabata-Pendias, 2010).

The availability of copper in the soil is being characterized by the quantity which the plant can access (McBride *et al.*, 2004) and, the amount transgressed from the soil into different extractants (Angelova *et al.*, 2003). Havlin *et al.* (1999) reported that Cu concentration in soil ranges from 1 to 40 mg kg^{-1}, with an average concentration of 9 mg kg^{-1}. An average of 50 % of the Cu in soils is insoluble and unavailable, 30 % is bound by organic sites, 15% is in an oxide form, and 5% is available for plant uptake (Fageria, 2002). The concentration of Cu measured in extractant can provide an estimate of potential nutrient availability for plant uptake (Menzies *et al.,* 2007; Angelova *et al.*, 2003). Previous studies in similar soils (Scherffer *et al* 1990; Udoh *et al.*, 2008; Ogban *et al.*, 2011; Eteng *et al.*, 2014; Essien and Eteng, 2016), showed that the plant availability of micronutrient elements in soil was influenced by several factors such as pH, organic matter content, redox potential, and soil texture.

There is an urgent need for sustainable utilization of the soils of Cross River floodplains and swamps for increased food cultivation. However, the effective and proper management of the wetland soils offers the farmers, an acceptable alternative for sustainable food production, such as; swamp and upland rice, assorted dry season vegetables, cucumber, sweet corn, cassava cultivation, garden egg, pepper, etc. Currently, there is little or no history on the availability of Cu in the wetland soils under long-term farming. The need for information on the Cu fertility of wetland soils has heightened recently. The purpose of this study was to evaluate the variation of extractable Cu in wetland soils of different land use and parent materials under long-term farming systems of Cross River State, Nigeria.

2.0 Materials and Methods

2.1 Location of the study area

The sampling sites represent wetland soils over eight (8) parent materials from eight (8) se-lected long-term farming systems, of Cross River State (Table 1). The State covers, an area of approximately 23, 000 km^2 and span latitudes 4^o 49'- 6^o 56' North and longitudes 7^o49'- 9^o 28 East. The

Table 1: Sampling site of wetland soils in different land use and parent materials under a long-term farming system of Cross River State, Nigeria

Agricultural location	Land use	Parent material	Soil classification
Mbarakom	Cassava production	Coastal plain sand	Typic Paleudults
Nko	Cassava production	Sandstone	Typic Ustifluents
Akpet	Cassava production	Basement complex	Typic Hapludults
Boje	Cocoa production	Basement complex	Typic Psammaquent
Iyamoyoung	Cocoa production	Basalt	Typic Ustpsamments
Ediba	Cocoa production	Shale	Udipsamments
Ndonyam	Maize production	Coastal plain sand	Typic Hapludults
Odukpani	Maize production	Shale	Udic Haplustalfs
Ikom	Maize production	Basalt	Aquic Ustiflurents
Obufa esuk	Mangrove palms	Mangrove soil	Hydraquents
Atimbo creek	Mangrove palms	Mangrove soil	Sulfaquents
Bakassi	Mangrove palms	Mangrove soil	Typichydraquents
Nsidon beach	Natural fallow	Beach ridge soil	Typic Ustifluents
Creek town	Natural fallow	Beach ridge soil	Aquic Hapludults
Ikang	Natural fallow	Beach ridge soil	Typic Psammaquent
Ugep	Sugar cane	Sandstone	Psamment Paleudults
Akamkpa	Sugar cane	Basement complex	Psammentic Paleudults
Ogoja river	Sugar cane	Alluvia deposits	Psammentic Paleudults
Obubra	Swamp rice	Basalt	Aquic Haplustalfs
Ofodua	Swamp rice	Sandstone	Psammentic Paleudults
Adim	Swamp rice	Shale	Typic Paleudults
Anantigha	Vegetable production	Coastal plain sand	Aquic Hapludults
Itigidi beach	Vegetable production	Alluvia deposits	Typic Paleudults
Calabar river	Vegetable production	Alluvia deposits	Udic Haplustalfs

** FDALR (1995); USDA (2006).*

2.2 *Sample Collection and Analysis*

2.2.1 The soil used: Twenty-four surface (0-20 cm) composite soil samples of acidic nature were collected in March 2018 during the dry season from se-lected long-term Agricultural farms known to be deficient in Cu as well as soils where deficiencies were not present but, crops did not respond to Cu fertilization.

2.2.2 Sample preparation and analysis: The soil samples were air-dried under room temperature for seven days, crushed by wooden roller and screened through a 2-mm sieve. The sieved samples were analyzed for mechanical analysis by Bouyoucous hydrometer method (Gee and Bauder, 1986), soil pH (soil: $CaCl_2$ ratio of 1: 2.5) was determined with a combined electrode pH meter (Thomas, 1996). Soil organic carbon was determined by the Walkley-Black method of wet combustion involving oxidation of organic matter with potassium dichromate ($K_2Cr_2O_7$) and sulphuric acid (H_2SO_4) method as described by (Nelson and Sommer, 1996) and the value was converted to organic matter by multiplying the OC values by Van Bremelen factor of 1.724 based on the assumption that SOM contains 58% carbon. The effective cations exchange capacity (ECEC) was determined by the method described by Sumner and Miller (1996) as, a summation of exchangeable bases (Ca^{+2}, Mg^{+2}, $K^{+,}$ and Na^{+}) and exchangeable (H^{+} and Al^{+}).

2.3 *Selection of Extractants*

One of the most important tasks was to find a promising method for the extraction of copper in wetland soils of different land use and parent materials under a long-term farming system which would best estimate the nutrient uptake by plants. Also, this method should be time saving and affordable. The extraction solution should be selected to solubilize the amounts of copper that will be proportional to amounts that will be absorbed by plants during a single growing season (Martens and Lindsay, 1990). Ideally, an extractant that will be effective over a wide range of soil types is preferable.

Generally, soil extractants used for predicting available forms of micronutrients in soils included the weak replacement ion salts ($CaCl_2$, NH_4OAc, etc.) (Whitney, 1988; Kabata-Pendias, 2010); weak acids (acetic acid and hydrochloric acid) (Shittu *et al*., 2010) and weak chelating agents; EDTA and DTPA (Lindsay and Norvel, 1978). The neutral salt solution (NH_4OAc) at different pH is capable of extracting the easily soluble and exchangeable ions, *i.e.,* potentially accessible forms of Cu in soil solution (Gronflaten and Steinnes, 2005) while, the diluted solutions of acids-HCl are used for determining the mobile and available forms of Cu in acid soils. Due to the high active concentration of hydrogen ions in these acids, they extracted not only the mobile but also the steadily bound forms of the elements in the soils (Kabata-Pendias, 2010). The use of acid (HCl and Coca-cola) extractants (Grava, 1980; Schnug *et al.*, 2001) is based on lowering the pH and the consequent solubilization of some compounds containing these elements. Comparatively, Norvel (1984) and Haddad and Evans (1993) reported that, of the commonly used extractants, chelating agents EDTA (ethylenediaminetetraacetic acid) and DPTA (diethylenetriaminepentaacetic acid) have the capacity of reducing the activity of dissolved metals, resulting in the release of more soluble compounds in buffered pH. However, EDTA has been used successfully as an extractant for estimating mobile forms of Cu in soils of different pH whereas, DTPA was observed to be unsuitable for use as an extractant in acid soils (Angelova *et al*., 2003; Menzies *et al*., 2007). Chelating agents can help remove elements from adsorption sites to estimate the “labile pool” and thus, potential bioavailability (Sparks, 1996). Coca-cola (acid group), was chosen for its excellent extractant for Cu, for many soils. Further advantages of Coca-Cola as an acid extractant are its ubiquitous availability, readiness for use, easy and safe handling and, the fact that the procedure has no harmful impacts as compared to the other extracting solutions (Schnug *et al*., 1996; 1998).

Therefore, to test the soil availability Cu, five different extraction methods were selected, representing three main groups of extractants. The selected extractants were hydrochloric acid (0.1 M HCl) and Coca-cola (acid group), ethylenediaminetetraacetic acid (0.005M EDTA) and diethylenetriaminepentaacetic acid (0.05M DTPA) (chelating group) and ammonium acetate (NH_4OAc) (buffered salt group). EDTA and DTPA were chosen due to their ability to form water-soluble and stable complexes with many metal ions and because it has been used extensively in the extraction of micronutrients (Cu, Fe, Mn, and Zn). EDTA is best performing in acid and nonacid soils (Menzies *et al*., 2007; Angelova *et al*., 2003) whereas, DTPA is best in none acid soils (Lindsay and Cox, 1985; Martens and Lindsay, 1990). Ammonium acetate solutions at different pH are widely used to determine exchangeable ions. On the other hand, coca-cola was chosen for its excellent extractant for Cu, for many soils. Further advantages of Coca-Cola as an acid extractant are its ubiquitous availability, readiness for use, easy and safe handling and, the fact that the procedure has no harmful impacts as compared to the other extracting solutions (Schnug *et al*., 1996; 1998).

2.4 *Soil extraction methods used for extracting copper in soil solution*

Table 2: Chemical properties of the extractants used

S/No	Extractant	Soil/solution	Groups	pH	Soil-solution ratio	Shaking time	Reference
1	Coca-cola	1.0g/10 ml	Acid	2.7	1:10	10 mins.	Schnug *et al*. 2001
2	0.01N HCl	5.0g/50 ml	Acid	4.8	1:10	60 min	Eteng *et al.*, 2014
3	0.05M EDTA	5.0g/50 ml	Chelate	7.0	1:2	30 mins.	Eteng *et al.*, 2014
4	1M NH_4OAc	5.0g/50 ml	Salt	7.0	1:10	60 min	Eteng *et al.*, 2014
5	0.005M DTPA	5.0g/50 ml	Chelate	5.0	1:10	60 min	Norvell, 1991

2.5 ***Statistical Analysis***

The data collected were subjected to analysis of variance (ANOVA) procedure, using the general linear model. Significant means were separated using Fisher’s Least Significant Different were appropriate at $P<0.05$ (two-tailed). Also, the Pearson correlation was used to evaluate the association between soil properties and extractable copper in soils under long-term farming systems. The statistical analysis was performed using PASW Statistics software, version 18 for Window 7.0.

Coefficient of variation (CV%) was used to estimate variation in the distribution of extractable Cu in soils under long-term farming systems as influenced by agricultural location, land use, and parent material, respectively, and data were ranked according to the ratings of Wilding et al. (1994) where CV ≤15% (low variation), CV = 16-35% (moderate variation) and CV ≥35≤100% (high variation). For fertility limits, the plant available Cu was rated as low, marginal, and high (Table 2).

Table 3. Particle Size Distribution after Amendment

Extraction method	Limit of fertility rating for Copper (mg kg^{-1}) in the soils		
	Low	Marginal	High
Coco-cola	<1.10	1.21-1.75	>1.75
DTPA	<0.20	0.21-2.00	>2.00
EDTA	<3.50	3.51-6.40	>6.40
HCl	<3.00	3.10-4.97	>4.97
NH_4OAc	<8.00	8.10-13.07	>13.07

Source: Eteng *et al*. (2014)

3.0 Results and Discussion

3.1 *Soil characteristics of the study area*

The texture of the soils varied from SL to SiCL but was dominated by sandy clay loam (SCL) (Table 3). Values of pH in KCl ranged from 3.83 to 5.89, with an average of 4.64, suggesting that the soils were very strongly acidic. The acidic conditions might be due to the acidic nature of the respective parent materials (Onyekwere *et al.*, 2001; Effiong and Ibia, 2009; Ogban *et al*., 2011). Soil organic matter (SOM) contents vary widely from 1.08 to 4.14 gkg^{-1} with a mean of 2.65 gkg^{-1}. At this level, SOM of the soils was rated low as most values are lower than 5 gkg^{-1}. The low OM values might be as a result of high mineralization rate due to intensive farming, which favours rapid mineralization of organic matter. This finding is in agreement with those of Udoh *et al*. (2008) and Ibia and Udo (2009).

Effective cation exchange capacity (ECEC) values ranged between 3.63 and 14.34 Cmol kg^{-1} with an average of 9.87 cmol kg^{-1}. The values are rated moderately low in soil fertility and are considered marginally adequate for crop production in most of the wetland soils. Based on this assessment, and in comparison with the values reported for upland Nigeria soils, the soils of the study area, can sustain crop production for a short cropping season. This condition can conveniently be adequate for the application of Cu fertilizer,

Generally, physical and chemical properties of wetland soils of the tropical rainforest do not for most cases yield easily to generalization. Instead, many of these properties depend on the type of wetland soil, parent materials, and quite often, are site-specific. For instance, wetland soils display ae extensive complexity of textural classes depending on their location and parent materials while, the changes which occur when soil is sub-merged, affect the character of the suitability of the soil for crop production Chude *et al*., 2012). However, the high variation among the soil properties shows that the

Table 3: Characterization of some physical and chemical properties of the soil samples (N=24).

Statistics	Particle size distribution			Texture	Chemical properties		
	Sand	Silt g/kg	Clay		pH (KCl)	Org matter g/kg	ECEC cmol/kg
Mean	488.2	246.1	264.5	SCL	4.64	2.65	9.87
Min	150.2	102.7	141.6		3.83	1.08	3.63
Max	650.2	562.5	433.3		5.89	4.14	14.34
LSD$_{(P<0.05)}$	59.26	17.34	106.73		1.82	1.42	3.61
Probability	0.024	0.015	<0.001		0.012	0.038	0.007
CV %	9.70	6.80	10.80		5.20	7.10	12.00

3.2 *Variation of extractable forms of Cu in soils under long-term farming systems*

Table 4 shows the variability of extractable forms of copper under long-term farming systems. The results revealed that the means of the available Cu content of the soils were determined to be 10.76; 6.80; 1.76; 7.50 and 6.44 mg kg^{-1}, using the extractants; Coca-cola, 0.05M EDTA, 0.05M *DTPA*, 0.01N HCl, and 1N NH_4OAc methods, with percent variations of 32.33%, 22.55%, 20.44%, 19.36% and 5.29%, respectively. Based on the mean values, the relative sequence of the abundance of the extractable Cu in these soils could be arranged in the following order: Coca-Cola > HCl > EDTA > NH_4OAc > DTPA. According to Eteng *et al*. (2014), the means were below the critical values of <0.20 and 8.00 mg kg^{-1} for DTPA and NH_4OAc and, high for Coca-cola (>1.75 mg kg^{-1}), EDTA (>6.40 mg kg^{-1}) and HCl (>4.97mgkg^{-1}), respectively. The wide variability of the extractable Cu in soils under long-term farming suggests that the availability of Cu in the soils depends on the concentration of extraction method used, pH and in fact, the soil parent material (Kataba-Pendias, 2010). Marschner (2012) observed that any deficiency of available Cu in the soils might be due to the variability in the concentration due to the parent materials. However, **Chude** *et al*. (2012) noted that excessive rainfall resulting in leaching, and intensively cultivated soils of this region would sooner or later become deficient in available Cu.

33 Effect of agricultural location on the variability of extractable Cu in soils under long-term farming systems

Concerning the variation due to locational effect, the variability of extractable forms of copper (Table 4) shows that, Coca-cola-extractable Cu varied widely from 2.03 mg kg^{-1} (Itigidi beach) to 4.01 mg kg^{-1} (Obubra) with a variability of 48.4%, EDTA-extractable Cu ranged from 3.57 mg kg^{-1} (Atimbo creek) to 10.38 mg kg^{-1} (Anantigha) with a variability of 56.0%, *DTPA* extractable Cu ranged from 0.82 mg kg^{-1} (Itigidi beach) to 3.35 mg kg^{-1} (Nko) with a variability of 60.2%, HCl-extractable Cu had values variability which ranged from 3.10 mg kg^{-1} (Nsidon beach) to 13.94 mg kg^{-1} (Iyamoyoung) with a of 56.7%, and NH_4OAc extractable Cu ranged from 2.05 mg kg^{1} (Ikang beach) to 12.67 mg kg^{1} (Ofodua) with a variability of 48.7%. According to Wilding *et al*. (1994), the variation of Coca-cola, EDTA, DTPA, HCl, and NH_4OAc-extractable Cu are >50% variability and rated

Table 4: Variation of extractable forms of Cu as influenced by location under long-term farming systems

S/No	Sample location	Coca-Cola	EDTA	DTPA	HCl	NH_4OAc	Mean
		Extractable Copper (mgkg^{-1})					
1	Mbarakom	19.07	9.44	1.05	4.19	3.92	7.53
2	Nko	18.00	10.38	1.02	4.22	4.44	7.61
3	Akpet	20.32	8.75	1.41	5.30	4.53	8.06
4	Boje	17.52	8.33	1.95	7.98	8.52	8.86
5	Iyamoyoung	17.06	9.11	2.32	8.31	8.99	9.16
6	Ediba beach	15.69	9.76	1.64	8.72	9.06	8.97
7	Ndonyam beach	4.01	5.86	0.82	5.33	7.05	4.61
8	Odukpani	5.15	4.78	1.36	3.70	4.33	3.86
9	Ikom	5.31	5.78	1.33	4.78	5.38	4.52
10	Obufa esuk creek	7.13	4.74	2.22	8.38	4.11	5.32
11	Atimbo creek	8.54	6.06	2.12	5.28	4.38	5.28
12	Bakassi beach	8.37	7.30	1.74	5.79	4.62	5.56
13	Nsidon beach	12.05	4.04	2.29	5.64	5.26	5.86
14	Creek town	11.75	3.57	2.14	6.26	5.61	5.87
15	Ikang beach	11.78	5.21	1.84	5.72	5.32	5.97
16	Ugep	11.96	5.93	2.09	8.63	12.67	8.26
17	Akamkpa	11.23	6.79	1.48	8.27	10.51	7.66
18	Ogoja river	12.46	6.25	1.38	7.63	10.67	7.68
19	Obubra	8.49	7.49	2.35	13.75	9.04	8.22
20	Ofodua swamp	7.13	7.77	2.13	13.16	7.70	7.58
21	Adim swamp	7.51	6.87	1.64	13.94	7.63	7.52
22	Anantigha beach	5.76	7.72	1.88	9.09	4.90	5.87
23	Itigidi beach	6.57	5.24	2.28	7.88	4.35	5.26
24	Calabar river	6.38	5.91	1.72	7. 54	2.05	4.72
Mean		10.76	6.80	1.76	7.50	6.44	6.65
Min		4.01	3.57	0.82	3.71	2.05	
Max		20.32	10.38	3.35	13.94	12.67	
CV (%)		58.4	56.0	60.2	58.7	53.8	

3.4 *Effect of land use on the variability of extractable of Cu in soils under long-term farming systems*

The variation due to land use effect (Figure 1), indicates that Coca-cola-extractable Cu varied widely from 2.03 mg kg^{-1} in land use for cassava production to 13.69 mg kg^{-1} in swamp rice production with a variability of 47.4%, EDTA-extractable Cu ranged from 5.71 mg kg^{-1} (sugar cane production) to 9.91 mg kg^{-1} (mangrove palms) with a variability of 55.7%, DTPA extractable Cu ranged from 0.48 mg kg^{-1} (vegetable production) to 4.07 mg kg^{-1} (mangrove palms) with a variability of 66.7%, HCl-extractable Cu had values which ranged from 4.73 mg kg^{-1} (cassava production) to 14.93 mg kg^{-1} (vegetable production) with a variability of 60.9%, and NH_4OAc extractable Cu ranged from 12.47 mg kg^{1} (cocoa production) to 10.76 mg kg^{1} (vegetable production) with a variability of 48.7%.

According to the fertility limits rated by Eteng *et al.* (2014), the soils under long-term farming systems as influenced by land-use effects (Figure 1), reveals that the extractable Cu by coca-cola, EDTA and HCl methods were rated high, DTPA was ranked moderate-to-high while, NH_4OAc methods were rated low-to-moderately in soil fertility. According to the variability (CV %) ratings of Wilding *et al*. (1994), the extractable Cu by all the extraction methods used were rated

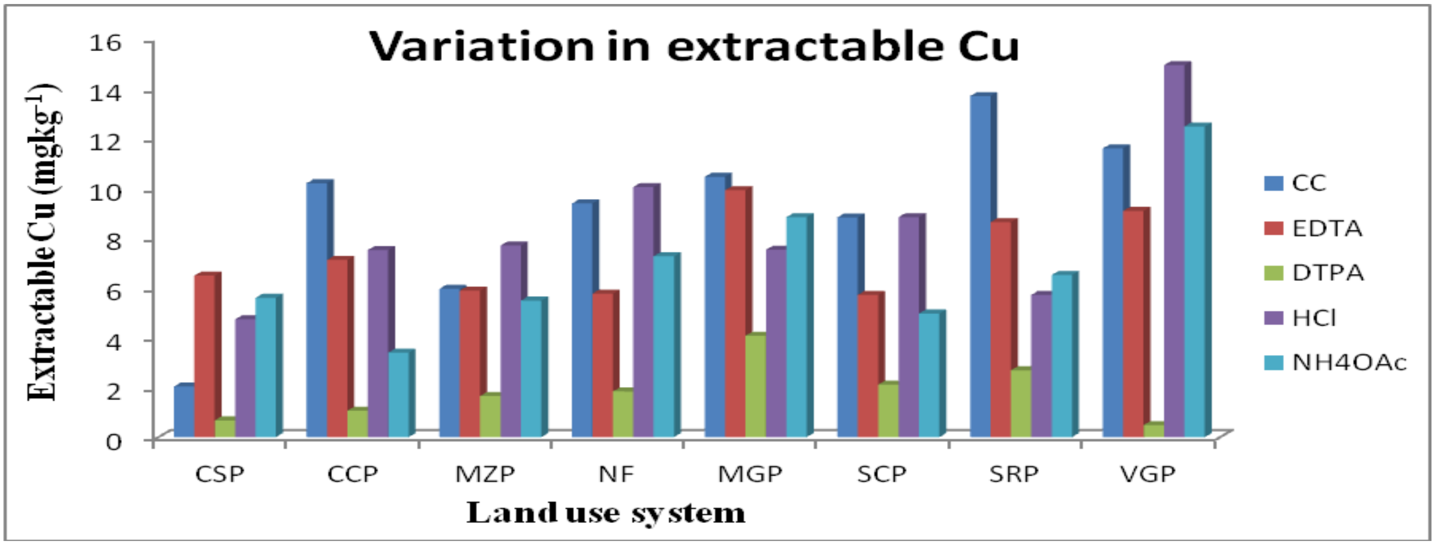

Figure 1: Effect of land use on the variability of extractable Cu under long-term farming systems

CSP=Cassava production, CCP=Cocoa plantation, MZP=Maize production, NF=Natural fallow, MGP=Mangrove palms, SCP=Sugarcane production, SRP=Swamp rice production, and VGP=Vegetable production

3.5 *Effect of parent material on the variability of extractable Cu in soils under long-term farming systems*

The variation of extractable Cu in soils under a long-term farming systems as influenced by parent material (Figure 2), shows that coca-cola-extractable Cu varied widely from 4.85 mg kg-1 (Basement complex) to 18.80 mg kg-1 (Alluvia deposit) with a variability of 26.8%, EDTA-extractable Cu ranged from 4.27 mg kg-1 (Coastal plain sand) to 9.52 mg kg -1 (Alluvia deposit) with a variability of 41.6%. The DTPA extractable Cu ranged from 1.16 mg kg-1 (Alluvia deposit) to 2.39 mg kg-1 (Coastal plain sand) with a variability of 49.8%, HCl-extractable Cu had values which ranged from 4.57 mg kg-1 (Alluvia deposit) to 13.61 mg kg-1 (Sandstones) with a variability of 41.1%, and NH4OAc extractable Cu ranged from 4.10 mg kg1 (Shale) to 10.76 mg kg1 (Mangrove swamp) with a variability of 32.3%. The result is at par with the results published by Ato et al. (2012)

According to the fertility ratings by Eteng et al. 2014, the soils under long-term farming systems as influenced by parent materials (Figure 2), shows that the extractable Cu by coca-cola was rated high, EDTA and HCl methods were rated moderate-to-high while DTPA and NH4OAc methods were rated moderately in soil fertility. Accordingly, the variability (CV %) ratings of Wilding et al. (1994), shows that the extractable Cu were rated medium variation (CV = 16-35%) for coca-cola and NH4OAc methods and, high variation (CV ≥35≤100%) for EDTA, DTPA and HCl methods, respectively.

However, among the soils derived from the parent materials, the content of extractable Cu varied widely and significantly (P<0.001) with higher extractable Cu (4.36 mg kg-1) from the basement complex (Basement complex rock). Lower extractable Cu (9.51 mg kg-1) was obtained from basalt (Basalt) derived soils which could be rated as high in fertility status according to the ratings reported in Okoli et al. (2017).

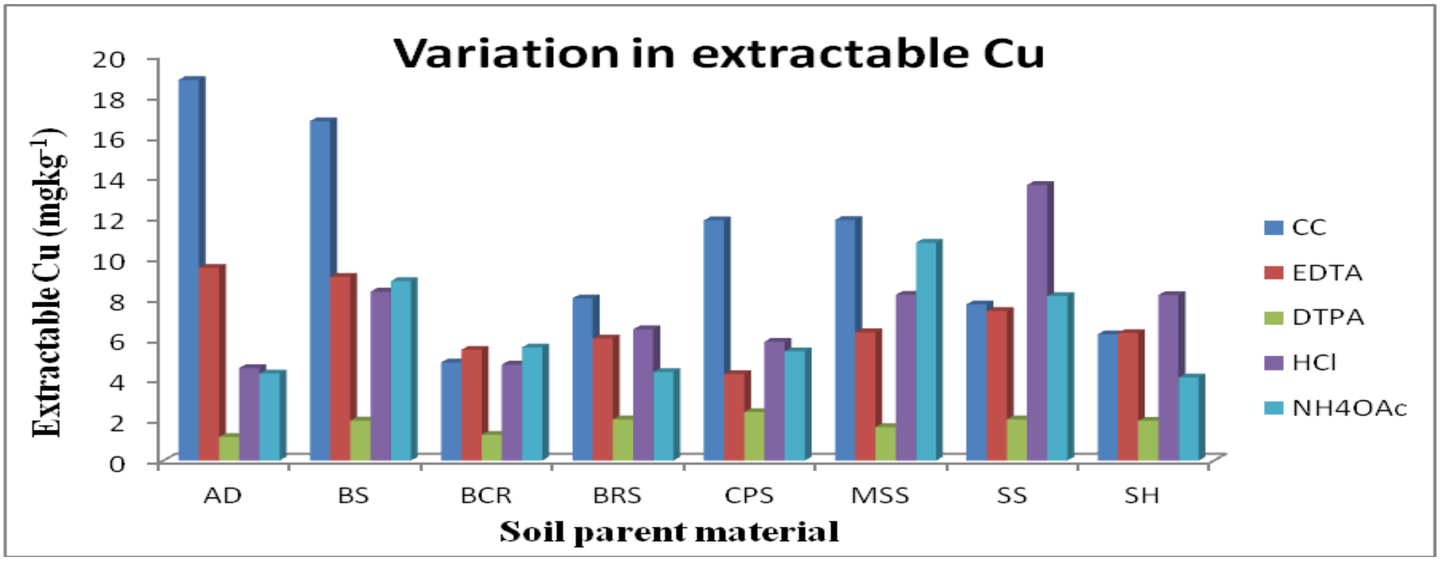

Figure 2: Effect of parent material on the variability of extractable Cu under long-term farming systems.

3.6 *Correlation study between the extractable copper and soil characteristics*

Reactions of Cu in soils are influenced by pH, organic matter, clay con-tent, and cation exchange capacity (Sims and Johnson 1991; Haddad and Evans 1993). The correlation coefficients (r) between extractable forms of copper in soils and some major soil properties under long-term farming are shown in Table 4. Thus, Coca-cola extractable Cu had positive significant correlation with silt (r = 511*) and SOM (r = 0.762**) but negative significant correlation with ECEC (r = -0.837**). EDTA extractable Cu had positive and significant correlation with clay (r = 0.684**), SOM (r = 0.711**) but, negative significant correlation with sand (-0.602*). DTPA extractable Cu had a negative significant correlation with SOM (-0.832**). HCl extractable Cu had positive significant correlation with sand (r = 469*) and pH (r = 0.642**) but, negative significant correlation with clay (-0.532*). Also, NH4OAc extractable Cu had negative significant correlation with clay (-0.313*) but, positively and significantly correlated with pH (r = 0.512*) and ECEC (r = 0.693**).

The form of extractable Cu that showed a significant positive correlation with clay fractions, soil OM, and ECEC, suggests that these extractants have strong associations with these soil properties. The clay fraction and soil OM in soils will provide more sites for adsorption of Cu, thereby providing more availability of soil Cu for plant use (Oyinlola and Chude, 2010). This may be due to Cu transformation and availability in soils, which depends on various forms of this nutrient element with which Cu have a significant correlation. Previous studies by Yadav (2008) showed that the relative availability of Cu was found to be much higher in organic than in mineral soils. Ibrahim et al. (2011) and Bassirani et al., (2011) Havlin et al., (2012) noted that available Cu is more strongly bound to OM than any other micronutrient hence increasing OM in soils decreases Cu availability. It was further explained that the organic binding of Cu in soils differs to some extent from that described for other divalent ions.

On the other hand, the significant negative correlation of the extractable Cu with these soil properties, suggests that less soil Cu will be made available for plant use. However, in the case of pH, significant positive correlation with extractable Cu suggests low availability while the negative correlation indicates that there will be an increase in the availability of soil Cu for plant use. The high available Cu by Coca-cola and HCl methods could be attributed to low pH of the soils which favoured solubility of copper. Similar studies by Sims (1986), Ibrahim et al., (2011), Mustapha et al. (2011) and Hassan et al., (2016) have indicated that soil pH influences micronutrients availability by favouring conditions which accelerates oxidation, precipitation, and immobilization.

Accordingly, Kparmwang et al. (2000), Yadav (2008) and Yeshaneh (2011) noticed that Cu is generally more readily available in acid than alkaline soils. These authors further emphasized that the availability of Cu depends mostly on soil

Soil properties	Available Cu by different extraction methods				
	Coca-Cola	EDTA	DTPA	HCl	NH$_4$OAc
Sand	-0.301	-0.602 *	-0.135^{ns}	0.469*	-0.113 ^{ns}
Silt	0.007 ^{ns}	-0.128 ^{ns}	0.084 ^{ns}	-0.317 ^{ns}	-0.208 ^{ns}
Clay	0.511*	0.684**	-0.368 ^{ns}	-0.532*	-0.713**
pH (KCl)	-0.164 ^{ns}	-0.077 ^{ns}	-0.151 ^{ns}	0.642**	0.512*
Org. matter	0.762**	0.711**	-0.832 **	-0.212 ^{ns}	-0.148 ^{ns}
ECEC	-0.837**	0.203 ^{ns}	0.309 ^{ns}	-0.665 **	0.693**

Ns = not significant at $P < 0.05$

* = significant at $P < 0.05$

** = significant at $P < 0.01$

3.7 *The dynamics within different extractable forms copper by different extraction methods under long-term farming*

Table 5 shows the dynamics within different extractable forms copper by different extractants. The best correlation was found between DTPA extractable Cu and NH$_4$OAc (r= 0.816**), EDTA extractable Cu and DTPA (r = 0.809**) and between Coca-cola extractable Cu and HCl (r = 0.717**). The high significant positive correlations among the content of extractable Cu with the extraction methods may be explained by the fact that the chemical extraction principle of the two procedures is the same. Other lower relationships includes, EDTA extractable Cu and NH$_4$OAc (r= 0.413*) and DTPA extractable Cu and HCl (r = 0.438*). The result is at par with the results published by Pradhan *et al*. (2015), which suggest that the extractants that have a good relationship between them may have removed Cu of similar forms from the soil. All forms of extractable Cu which is highly and significantly correlated with each other indicat-es that they could remove Cu of similar forms from about the same pools from the soil. However, Yeshaneh (2015) noted that the trends of Cu displacement from soils into solution tend to be similar irrespective of extraction methods. On the other hand, a lower and nonsignificant relationship between any pair of extractants suggests that the ability of Cu extrac-

Extractant	**Available Cu by different extraction methods**				
	Coca-Cola	EDTA	DTPA	HCl	NH$_4$OAc
Coca-Cola	1.000				
EDTA	0.000^{ns}	1.000			
DTPA	0.185^{ns}	0.809**	1.000		
HCl	0.717$_{**}$	0.008^{ns}	0.336*	1.000	
NH$_4$OAc	0.176	0.438*	0.816**	0.006^{ns}	1.000

Ns = not significant at $P < 0.05$

* = significant at $P < 0.05$

** = significant at $P < 0.01$

4. Conclusion

A soil test is an essential agronomic tool for determining crop nutrient needs, predicting the nutrient-deficient areas, and preventing the deficiency. In this study, substantial variations in the content of extractable forms of copper in soils of different land use and parent materials under long-term farming systems were establish.

The content of extractable Cu varied significantly from 1.72-10.76 mg kg^{-1} by DTPA and Coca-cola methods, and these were rated from low to moderate, respectively. The study further shows that, the comparative extraction capacity of these extractants followed the order: Coca-Cola > O.1N HCl > 0.05M EDTA > NH$_4$OAc > 0.005M DTPA. Correlation data also indicated that the fractions of Cu by different extractants were in a state of dynamic equilibrium and dependent were on pH, organic matter, ECEC, and clay content.

The wide variability of the extractable Cu in the wetland soils under long-term farming suggests that the availability of Cu in the soil are haply influenced by the agricultural locations, type of land use systems and soil parent materials, respectively. Further studies are expected to correlate the extractable forms of Cu with crop uptake in both greenhouse and field studies to inform the selection of extractants and to determine the critical limit and optimum levels of Cu for fertilizer recommendation, in wetland soils of Cross River State, Nigeria.

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