CONTENTS AND PROFILE DISTRIBUTION OF TOTAL AND EXTRACTABLE ZINC AND COPPER MICRO NUTRIENTS IN PLEO-PLEISTOCENE SOILS OF DELTA STATE, NIGERIA

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Date submitted: 29 January, 2014; Date accepted: 30 August, 2014

Abstract

The study was conducted in three Pleo-pleistocene soil formations in Delta State, Nigeria in order to assess the contents and profile distribution of Copper (Cu) and Zinc (Zn) micro nutrients. Aerial photo interpretation and field work were carried out and three profile pits dug to represent the soil units. Soil samples were collected from each of the pedogenetic horizons for the estimation of particle size distribution, soil pH and organic matter content. Total and extractable Zn and Cu micro nutrients were extracted with 0.005 M DTPA; 0.1.M $CaCl_2$ and 0.1M TEA (pH 7.3) and determined with Atomic Absorption Spectrophotometer. Data collected were subjected to descriptive statistics and correlation analysis was performed to show statistical relationship between some soil physical properties, total and extractable Zn and Cu micro nutrients. Results of the study showed remarkable physical variability between locations and within soil horizons as the textures ranged from loamy sand, sandy clay, loam and dominantly clay in the inland valley and mangrove swamp soils. The soil units were generally acid with a mean pH range of 4.53 to 5.70. Organic matter content was low (< 20 gkg^{-1}) in the coastal plain sand and inland valley, and moderate (>20 gkg^{-1}) in the mangrove swamp soil. Simple correlation analysis showed that total clay significantly correlated with Zn (0.735***) and Cu (0.654***) at 5% level of probability. There was also positive and significant correlation between soil organic matter and Zn (0.765***) and soil organic matter and Cu (0.845***) at 5% level of probability. The results of the study clearly indicated that soil pH, total sand and organic matter has significant influences on the content and profile distribution of the micro nutrients investigated.

Keywords: Copper (Cu) and Zinc (Zn), micronutrients, pleo-pleistocene, profile distribution.

Introduction

Micronutrients are involved in the entire metabolic enzyme system of plants. They are very important for gene expression, biosynthesis of proteins, nucleic acids, metabolism of carbohydrates and lipids as well as stress tolerance in plants (Rengel, 2007; Gao *et al,* 2008 and Tsado *et al*, 2010). The effects of micronutrient deficiencies can be very severe in terms of stunted growth of plants; low yields, dieback and even total plant death (Brady and Weil, 2007). In most developing countries of the World, the demand for micronutrients in crop production is relatively low due to under-utilization of land resources for intensive crop production (Umar *et al.*, 2001). Despite their importance in plant nutrition, only very little attention has been given to its studies in pleo-pleistocene (Egbuchua, 2011).

Soils of Pleo-pleistocene formation are essentially wetland soils with recent pedogenetic processes. They are usually characterized by electrochemical and biochemical events such as reduction reactions, changes in pH and partial pressure of CO_2. Production of fermentation products, humic substances, and ionic interaction are known to control, in one way or the other, the micronutrient regime in the soil (Neue and Mamaril, 1985).

Like the macronutrients, the availability of micronutrients in the soil is controlled by the relationship between the amount in the solid phase, the equilibrium concentration in the solution phase and the rate of equilibrium between the solid and aqueous solution phase (Agbenin, 1995). Generally, the pool of micronutrients in soils could be in various forms such as water soluble, exchangeable, absorbed, and chelated or complexed. These pools determine, to a larger extent, the micronutrients supplying capacity of the soils.

In recent years, increasing attention is being directed towards micronutrient deficiencies for the following reasons as outlined by Brady and Weil, (2007).

i. Intensive plant production practices have increased crop yields resulting in greater removal of micronutrients from the soil.
ii. The trend towards high analysis fertilizers has reduced the use of impure salts and organic manures which formally supplied significant amounts of micronutrients.
iii. Increased knowledge of plant nutrition and improved methods of analysis in the laboratory are helping in the diagnosis of micronutrients deficiencies that might have formally gone un-noticed and;
iv. Increasing evidence indicates that food grown on soils with low levels of trace-elements may provide insufficient human dietary levels of certain elements, even though the crop plants show no signs of deficiency themselves

Investigations reported by Havlin *et al.*, (2005) have shown that deficiencies of Zn and Cu micronutrients are well pronounced in sandy soils and other soils high in acidity. Their availability is also determined by several interacting factors such as soil pH, organic matter content, clay accumulation, redox potentials and partial pressure of CO_2.

Many diagnostic techniques have been developed for micronutrient investigation in respect of Zn and Cu. Amongst these are the Sodium Carbonate Fusion, Dilute Acid Extraction Agbenin, (1995), and DTPA Extraction by International Institute of Tropical Agriculture (IITA), (1979). Because of the importance of pleo-plestocene soil formation in rice cultivation and their increasing use for other intensive cultivation, it is therefore the objective of this study to assess the Zn and Cu status of these soils which are involved in the entire metabolic enzymes system of plants.

Materials and Methods

Description of the study area

The study was conducted in Delta State, Nigeria. The state is located within latitude 5º 43^1 and 5º 30^1 N and Longitudes 6º 14^1 and 6º 49^1 E. The state is characterized by district seasons: Wet (April to October) and dry (November to March). The rainfall pattern is bimodal with peak periods in July and September. The mean annual rainfall varies from 1,250 – 1,750 mm. The mean average temperature (2000 – 2012) was 27.8ºC while the mean relative humidity was 72% (NIMET, 2013). The general topography is undulating with about 2 – 4% slope gradient. Geologically, the entire state is underlain by varying degrees of quartzites, granites, gneiss, schists and isolated deposition of amphibolites (Perekeme, 2010). The vegetation is typically of rainforest type but has been reduced to secondary type due to continuous cultivation and lumbering activities. Some aquatic grasses, sedges, broad leaf weeds and numerous stands of trees are found all over the area. Land use in the area is based on rain-fed agriculture and typical crops cultivated include roots and tuber crops, cereals, pulses, vegetables and grains. Pockets of economic trees such as rubber, oil palm and kola nuts are found in most areas of the state.

Aerial photo-interpretation/Soil Sampling

The field work was preceded by aerial photo-interpretation at a scale of 1:10,000. The rigid grid method was used for sample collection. Each landform was transversed by four grid lines spaced at 50mm apart, and two distinct pedons dug to varied depths. For each location, four (4) replicates were collected and bulked for each soil depth to form a composite sample for each of the three (3) land forms. A total of sixty-four (64) replicate samples were collected.

Sample preparation and Laboratory analysis

The collected soil samples from each pedon were air-dried in an ambient room temperature of 25 - 27ºC for 3 days, crushed and sieved through 2 mm sieve mesh. Sub samples were crushed and further sieved through 100 mm sieve mesh for the determination of Zn and Cu micro nutrients.

Analytical procedure

Physico-chemical properties

The particle size distribution was determined by Bouyoucous hydrometer method using Sodium-hexametaphosphate as the dispersing agent (IITA, 1979). Organic matter was determined by the Dichromate wet-oxidation method and soil pH, determined calorimetrically using pH meter.

Determination of Total Zn and Cu micronutrients

This was done by weighing 10g of 2mm sieved soil samples into 50ml of centrifuge tube and followed by extraction procedure which involved the addition of 0.005 M Diethyl enetriaminepentaacetic acid (DTPA); 0.1M $CaCl_2$ and 0.1M triethanolamine (TEA) at a pH of 7.3. The content was shaken vigorously for 30 minutes after which the suspension was filtered through a Whatman No 40 filter paper. The contents of Zn and Cu in the filtrate were finally determined using Atomic Absorption Spectrophotometer (AAS) Model SOLAAR 969 Unican Series.

Statistical analysis/coefficient of variation

Descriptive statistics such as mean, standard deviation and coefficient of variation was employed. Correlation analysis was also performed to show statistical relationship between measured parameters. Statistically difference means were separated using the procedure of Fisher's least significant difference (F-LSD) at 5% level of probability. The coefficient of variation values were obtained by the methods of Wildling and Dress (1983). Where;

CV (%)	< 15%	=	least variable
	15 – 35%	=	moderately, variable
	> 35%	=	highly variable

Results and Discussion

Soil physical properties

The results of the soil physical properties are shown in Table 1. The individual soil fractions (sand, silt and clay) tend to fluctuate with depth and showed remarkable variability between locations and across soil horizons (Table 3.) Wilding and Rehage (1998) and Egbuchua (2007) attributed this phenomenon to the illuviation of clay into finer textural sub-soils and other mechanisms such as sedimentary discontinuities, ferrolysis, in-situ weathering of primary minerals and differential transport of eroded sediments. There was observed increase in clay with depth at some instances. This trend could be adduced to clay migration by lessivage to produce the process of illuviation. The irregular distribution and stratification of clay in the lower horizons of the pedons suggests different periods of sediments. Observers of this clay sequence and the dominance of total sand especially in the coastal plain sand and inland valley soils affirmed that the soils of the study areas would have been formed from a variety of origins. This statement was strongly supported by Zonn (1986).

The values of silt/clay ratio (Table 1) varied from 1.30 – 2.50 for coastal plain sand; 0.25 – 1.35 for inland valley and 0.25 – 0.54 for mangrove swamp soils. Generally, low value of silt/clay ratios (<0.75) indicates old age of the surface deposit; values between 0.75 and 1.5 indicate moderate pedogenetic weathering processes; while higher value (> 1.5) indicate recent pedogenetic processes. According to Andriesse (1986) and Brinkman and Blockhus (1986) respectively, soil of pleo-pleistocene formation are essentially wetland soil and of recent pedogenetic processes. The texture of the soil varied from one mapping unit to another and within horizons. It ranged from loam sand at the surface horizon of coastal plain sand fine loam sand at the mid-horizons through dominantly sand at the lower horizons.

The inland valley soil was sandy clay loam at the surface and dominantly clay down the profile, while the mangrove swamp soil were clay loam at the surface horizon and clayey down the profiles indicating strong variability within soil horizons.

Chemical properties

Some chemical properties of the soils evaluated is shown in Table 1. The soil pH slightly varied in values but generally acidic in nature. The values ranged from 5.4 – 6.1 (strong acid to slight acid) in the coastal plain sand; 4.6 and 6.1 (very strongly acid to slight acid) in the inland valley; and 4.30 – 4.70 (extremely to very strong acid) as in the mangrove swamp soils. The extremely to very strong acid associated with the mangrove swamp soils was an indication that the soil is under reduced condition. It could also be associated with respiration and exudation of mangrove rootlets and microbial metabolism which result in organic matter oxidation and generation of organic acids (Havlin *et al*, 2005). Organic matter content was generally low in the coastal plain sand and inland valley (<20 gkg^{-1}) (FMANR, (1996) and higher in the mangrove swamps (>20 gkg^{-1}). The low organic matter content associated with coastal plain sand and inland valley soils could be associated with erosion effects, seasonal bush burning of the soil units and continuous cultivation without returning harvested crop residues back to the soil. On the other hand, the high organic matter content of the mangrove swamps could be due to the vegetational attributes of the mangrove ecosystem, slow decomposition rate of litters, fibrous mangrove rootlets and reduced microbial activities on organic residues (Egbuchua, 2007).

Profile distribution of Zn and Cu

The results of profile distribution of total and extractable Zn and Cu micronutrients are shown in Table 2.

Table 2: Profile distribution of Zn and Cu (mgkg^{-1}) in the mapping units of the study area

Sample location	Horiz. Depth (cm)	Zn	Cu
		→ Mgkg^{-1} ←	
Coastal Plain Sand	0-15	3.54	4.25
	15-30	3.45	3.30
	30-65	3.40	3.45
	65-80	2.35	1.75
Inland valley	0-8	3.46	6.50
	8-24	3.42	4.35
	24-56	3.37	3.54
	56-80	3.20	2.15
Mangrove swamp soil	0-10	3.25	6.35
	10-25	3.75	6.51
	25-45	4.25	7.20
	45-60	4.75	8.54

Concentration of Zn and Cu cations were found at the surface horizons in all the mapping units and decreased with depth except in Mangrove swamp soil. The mean values were 3.85mgkg^{-1} for Zn and 2.94mgkg^{-1} for Cu in the coastal plain sand; 3.36mgkg^{-1} and 3.19mgkg^{-1} in the inland valley soils and 4.00mgkg^{-1} and 7.15mgkg^{-1} respectively in the mangrove swamp soils. These values according to FMANR (1996) for the ecological zone are rated moderate and suitable for crop production.

Table 3: Mean, Standard deviation and coefficient of variation (*CV* %) of the soil properties in the study areas

Soil properties	$\bar{x}$	Sd	*CV*%
	Coastal Plain Sand		
Sand (%)	77.5	2.65	3.40
Silt (%)	14.5	2.65	18.25
Clay (%)	8.0	1.63	20.44
Soil pH (H_2O)	5.70	0.32	5.55
Organic matter (gkg^{-1})	9.98	3.09	30.97
Zn (mgkg^{-1})	3.85	0.56	17.57
Cu (mgkg^{-1})	2.94	1.08	36.78
	Inland Valley		
Sand (%)	48.25	0.50	17.62
Silt (%)	15.75	4.99	31.69
Clay (%)	44.0	3.75	8.50
Soil pH (H_2O)	5.25	0.64	11.79
Organic matter (gkg^{-1})	10.45	2.07	19.82
Zn (mgkg^{-1})	3.36	0.11	3.40
Cu (mgkg^{-1})	3.19	1.05	32.79
	Mangrove Swamp Soil		
Sand (%)	40.0	4.08	10.21
Silt (%)	16.0	4.16	26.02
Clay (%)	44.0	3.74	8.50
Soil pH (H_2O)	4.53	0.17	3.77
Organic matter (gkg^{-1})	21.45	1.64	7.64
Zn (mgkg^{-1})	4.00	0.65	16.14
Cu (mgkg^{-1})	7.15	0.10	13.95

Legend: $\bar{x}$ = Mean, Sd = Standard deviation, CV (%) Coefficient of variation

Table 4: Simple correlation coefficients relating soil properties, Zn and Cu micronutrients

Soil properties	Zn	Cu
Sand	-0.215	-0.257
Clay	0.735***	0.654**
Soil pH	-0.654**	-0.575**
Soil Organic Matter	0.765***	0.845***

Legend: ** and *** = significant at 5% level of probability

In any landform, the vertical distribution and top soil accumulation of micronutrients are due to plant cycling, human induced activities on the soil, leaching and erosion effects. Its distribution on the other hand, is a factor of soil pH, organic matter content and cation exchange capacity (Jiang *et al.*, 2009).

In related reports, Aghimien, (1989), and Fagbami, *et al*, (1989) adduced that, Zn and Cu distribution in a soil are determined by several interacting factors associated with soil pH, redox potentials organic matter accumulation, clay content, partial pressure of CO_2 and soil salinity. In another development, White and Sasoski (1999); Rengel (2007), and Brady and Weil (2007) have reported that cationic micronutrients like Zn^{++} and Cu^{++} have the tendency to react with certain organic molecules in the soil to form chelates (Organometallic complexes) which can increase the availability of micronutrients and prevent it from precipitation reactions.

The variability of soil properties was measured by estimating their coefficient of variation:

$$CV(\%) = \frac{Sd}{\overline{x}} \times 100;$$

Where: Sd = Standard deviation

$\overline{x}$ = Sample mean

The results of the study showed that in the Coastal plain soil, total sand and soil pH were least variable. In the inland valley soils, clay and Zn were least variable; while in the Mangrove Swamp soils, clay and organic matter were also least variable. The moderately variable soil properties include silt, clay, organic matter and Zn in the coastal plain sand. While in the inland valley soil, sand, silt, organic matter and Cu were moderately variable. The highly variable soil property (Cv > 35%) was associated with Cu in the coastal plain sand. In the Mangrove swamp soil, the moderate soil properties were Zn and silt. The moderate to high variability of these nutrient elements could be attributed to differences in pedogenetic processes, agronomic management and cultural practices often used in the mapping units studied.

Correlation Analysis

Simple Correlation coefficient relating Zn and Cu micronutrients to sand, clay, soil pH and soil organic matter is shown in (Table 4). The result showed that sand was negatively correlated with Zn (-0.215) and Cu (-0.257). Clay showed significant positive correlation with Zn (0.735***) and Cu (0.654***) at 5% level of probability. According to Tsado *et al*, (2010) deficiencies of Zn and Cu micronutrients occur in sandy soils that are high in acidity. Soil pH had negative correlation with Zn and Cu in all the profiles examined (Table 4). According to Brady and Weil (2007), under acid condition, Zn and Cu are very soluble and their ionic forms are bound to change to insoluble hydroxides. Thus, for every unit increase in soil pH, solubility of cationic micronutrients may decrease from 100 - fold for divalent cations to 10 - fold for trivalent cations (Rengel, 2007). Soil organic matter was positively and significantly correlated with Zn and Cu in all the profile indicating the role of soil organic matter in enhancing the availability of Zn and Cu in the soil. According to Stalk (1994) and Jiang *et al*. (2009) soil organic matter immobilizes and mobilizes micronutrients. At higher content of soil organic matter, micronutrients are higher than under deficiency condition. This is attributed to the formation of humate-complexes and the dissolution in the soils under high organic matter level (Di Palma *et al.*, 2007).

Conclusion

The results of the study clearly showed that contents and profile distribution of micronutrients of Zn and Cu were independently affected by profile depth, organic matter content, soil pH and particle size distribution of the soil. There was a significant and positive correlation between organic matter, clay and total Zn and Cu micronutrients as, their availability were influenced by their contents. Sand and soil pH negatively influenced micronutrient availability and as a result, sandy soils should be improved by the addition of organic manures, while soil acidity, could be controlled by application of calcium based fertilizers and strict liming programme.

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