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Copper Fractions and Selected Soil Characteristics of A Tropical Toposequence

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Abstract

*For plants to grow and develop as well as to finish their life cycle, copper is a necessary element. This study aims to investigate copper fractions and how they relate to specific soil characteristics. The study location is in the Tumu-Sarari region of Nigeria, which is on the outskirts of the Jos Plateau. Purposive sampling was used in the fieldwork process. Topographic features were used to stratify the research area. To reflect the average soil conditions in each topographic unit, one soil profile pit was excavated. Sequential extraction processes were used to analyze the water soluble, exchangeable, particularly sorbed/carbonate bound, Fe-Mn oxide bound, organic matter bound, and residual bound Cu fractions for laboratory analysis. Copper fractions associated with water soluble, organic and carbonate did not have significant relationship with selected soil properties. However, there was a significantly and positively correlation (r = 0.70**, 0.78** respectively) between exchangeable copper fractions, clay content and soil textural class. In addition, there was a significant negative correlation (r = -0.74, -0.86 respectively) between Fe and Mn associated copper fractions, clay content and soil textural class. Moreover, sand content and copper fractions linked to Fe and Mn oxides have a highly substantial positive association. This can be because sand content affects soil aeration. In the same vein, residual copper percentages and sand concentration exhibit a strong positive correlation (r = 0.76*). The outcome showed that the copper fractions' magnitudes occur in the following order: residual > carbonate bound > organic matter bound > Fe and Mn bound > exchangeable fraction > water soluble. The water soluble and exchangeable fractions which constitute the available forms of copper are at optimum levels and range from 0.70 to 1.69 mg/kg. Therefore, careful management of soil organic matter through the use of conservation tillage, green manure, crop rotation, and the application of biochar and other organic amendments is essential to maintaining the copper content and enhancing the fertility of these soils.*

Keywords: micronutrients; copper; toposequence; topography; Jos Plateau

Introduction: The parent material from which soils are formed, as conditioned by topography throughout time, is a major determinant of soil properties. These factors affect the distribution and quantity of total and extractable Cu in the soil profile. However, the profile distribution of Cu can be altered by several pedological factors, such as chemical, biological, and physical ones (Adriano, 2001). According to Purves (2003), soil contamination by substances like copper, lead, and zinc seems to be mostly irreversible. Because of their cumulative nature and lack of biodegradability, metallic pollutants are hazardous even in very small concentrations (Tembo, 2006). Although the soil serves as a sink or filter, heavy metals in soil have lengthy residence durations, in contrast to other environmental compartments including the atmosphere and water (Lombi, Gerzabek, and Horak, 1998).

The availability of copper (Cu) to plants varies widely and occurs in several forms. Okoli, Uzoho, Ihem, and Okon (2019) have reported the presence of Cu in several chemical pools, including those that are water soluble, readily exchangeable, adsorbed, precipitated with secondary minerals, and bonded to primary minerals. The change in soil texture, pH, calcium carbonate ($CaCO_3$), organic matter, and other soil factors determines the kind and quantity of different forms of Cu (Kabala and Singh, 2001). Chelation is the process by which copper is bonded to organic matter in soil (Jassal, Sandhu, and Dhaliwal, 2016). Complexation with clay-humus particles and/or the development of insoluble humic complexes typically reduce the solubility of Cu in soil (Sharma, Brar, Kaur, Sharma, and Singh, 2015). Until now, not much has been done with respect to investigating the relationship of the various chemical fractions of copper with respect to hill slope soil development in the Tumu Sarari locality of the Jos Plateau, Nigeria. Consequently, the objective of this study is to examine copper fractions and their relationships with selected soil properties.

Materials and Methods: **Field work:** The study site is in Tumu-Sarari area, on the fringes of the Jos Plateau, Nigeria. The climate is tropical continental, and the geology of the area consists of basement complex and younger granites (Directorate of Overseas Surveys, 1977). The elevation characteristics of the study site are presented in Figure 1 and topographic characteristics of the area is presented in Figure 2. Field work involved a purposive sampling approach. The study site was stratified based on topographic characteristics; one soil profile pit was dug to represent average soil conditions in each topographic unit. Morphological properties were described using guidelines in the soil survey manual (Soil Survey Division Staff, 1993). Soil samples were obtained from each genetic horizon and the geographic coordinate of each profile pit is latitude is 10.070100° and longitude 8.914970°; latitude 10.070010°

and longitude 8.915360°, latitude 10.070580° and longitude 8.916260°; latitude 10.070790° and longitude 8.924550° for summit, backslope, foot slope and toe slope positions respectively.

Laboratory Analysis: Salbu *et al*.'s (1998) sequential extraction method was used to estimate the Cu fractions. Copper fractions examined were water soluble, exchangeable, and carbonate-bound, organic matter-bound, Fe-Mn oxide-bound, and residual fractions. Following Kissel and Sonon's (2014) procedures, the pH of the soil was measured in 0.01M $CaCl_2$ solution at a ratio of 1:2.5 for the soil to water or solution. The hydrometer approach, as described by Hossain, Islam, Badhon, and Imtiaz, (2021), was used to determine the particle size distribution. Organic matter was determined using the dry combustion method. In the dry combustion method, which is based on loss on ignition, soil samples that have been oven dried are put in a crucible and burned for at least three hours at 550 +/- 25°C in a muffled oven. After 30 minutes of cooling in the desiccator, the sample-filled crucible is weighed and the weight loss is then used to compute the organic matter (Ivezić et al., 2016).

Statistical Analysis: Soil data were analyzed using descriptive statistics. The relationship between soil characteristics and copper levels was evaluated using correlation analysis.

Results and Discussion: Soil Morphological Characteristics: Soil morphological characteristics of the study area is presented in Table 1. The soil is very shallow at the summit and back slope positions but moderately deep at foot and toes slope positions. Furthermore, horizonal development is rudimentary at the summit and back slope positions. Only the A horizon is observed at the back slope position, and erosional process could have limited further horizonal development. Consequently, the soil in the summit and back slope positions is classified as Entisols. Similarly, Norton *et al*. (2003) after a study of hill-slope soils concluded that dynamic erosion and deposition are significant factors affecting soil development on the landscape. According to Owonubi (2017), topography also affects how much precipitation is absorbed and held in the soil, how quickly soil is lost to erosion, and how soil develops as a result of the deposition of eroded materials. The soil structure type in the study area is sub-angular blocky. The grade and size of the structure indicates that the structure is well developed. This could be due to the fact that agricultural activities on these soils began only in the recent past (about 3 years), hence the influence of anthropogenic activities on soil structural development has been low. Soil colour in the study area is generally yellowish red with hues ranging from 2.5 to 7.5. Munsell colour values are usually lower in the A horizon, most likely as a result of higher levels of organic matter content. The observe colour characteristics are typical of soil of the northern guinea savanna area as noted by Owonubi (2017).

Soil consistencies for the air-dry moisture states in the A horizons are generally hard to very hard. For the summit and backslope positions, soil consistencies for moist and wet moisture states are friable and non-sticky slightly plastic. This implies that the soil would be suitable for tillage activities at these moisture states. However, A horizons of the foot and toe slope positions have very friable, slightly sticky, and slightly plastic soil consistencies most likely as a result higher clay content at these slope positions. Consequently, tillage activities would best take place at the moist moisture states

Physical and Chemical Soil properties: Results on soil physical characteristics is presented in Table 2. Clay content tends to increase from summit to toe slope positions and from A to B or BC horizons. Erosional processes are likely to influence movement of clay materials in suspension through runoff downslope. On the other hand, illuviation processes and in-situ soil weathering due to higher rate of absorption and retention of precipitation at the foot and toe slope positions are probably responsible for higher clay content in the B horizons. As a result, the toe slope location has sandy clay loam soil texture, while the summit has sandy loam soil texture. The research area's soils have a mean bulk density of 1.69 g/cm3 with a range of 1.34 to 2.09. Density values generally tend to increase with increase in soil depth. Taking into consideration bulk density values and soil texture characteristics, soil of the foot and toes slope positions have higher degree of compaction that would affect root growth. The distribution of soil pH and pH-buffer capacities is presented in Table 3. Mean soil pH in the study area is 5.65 with minimum and maximum values of 4.98 and 6.36 respectively. Consequently, soil reaction ranges from slightly to moderately acidic of A horizons at the summit to upper slope positions. However, at the foot to toe slope positions the soils are moderately to strongly acidic. This could be due to leaching of basic cations out of the soil profile as a result of absorption and retention of greater amounts of water from precipitation and overland flow from summit positions. The pH values are however within the range observed by Owonubi (2017) for basement complex soils in the northern guinea savanna. Though Olowolafe (2003) and Fasina and Adeyanju (2006) had noted that the low pH values in these soil types could in addition be attributed to acidic nature of the basement complex rocks from which the soils were derived. Organic matter content in soil of the study area is high (> 3.0) and range from 3.69 to 5.75 mg/kg. The content of organic matter in these soils could have been higher in the surface soils if the soils of the summit to foot slope position had not been brought under cultivation for the first time 3 years ago. Brady and Weil (1999) had noted that soil cultivation hastens the rate of oxidation of soil organic matter thereby leading to its depletion.

Copper Distribution in Soils: Table 3 displays the distribution of copper fractions in the soils of the study area. The magnitude of the copper fractions occurs in the order: Residual > Fe and Mn bound > Carbonate bound > Organic matter bound > Exchangeable fraction > water soluble. In contrast, Okoli *et al* (2019) in a study noted reported that Fe and Mn bound copper fractions were the most dominant. Furthermore, studies by Kabala and Singh (2001) indicate that the order of magnitude of the various copper fractions is dependent on soil type and land use. The readily available fraction according to Okoli *et al* (2019) constitute the water soluble and the exchangeable fractions. Together using the rating provided by Buchholz (2004), the content of readily available copper in these soils is high. Closely following the readily available fraction is the copper fraction that is associated with organic matter. This fraction is moderately available as the copper in the organic matter is released into the soil after mineralization. Organic matter has been reported to significantly influence soil nutrient dynamics especially in tropical Nigerian soils (Chude *et al*., 2012). Consequently, copper fractions in the residual, and Fe and Mn bound are categorized as unavailable and weathering processes would have to release copper in these fractions to the soil. Studies of some urban soils by D¥Bkowska-Naskrêt *et al*., (2016) showed that copper occurred mostly low bioavailable fractions. Furthermore, Jassal *et al*., (2016) noted that organically bound copper ranged from 0.06 to 1.60 $mgkg^{-1}$ and accounted for 3.66% of total soil copper in some salt affected soils.

Relationships between copper fractions and some selected soil properties are presented in Table 4. Copper fractions associated with water soluble, organic and carbonate did not have significant relationship with selected soil properties. However, there was a significant ($P < 0.05$) positive high degree of correlation between exchangeable copper fractions and clay content and soil textural class. This is not unlikely as Weil and Brady (2017) noted that clays are significant soil constituent influencing cation exchange capacity. Also, there was a significant ($P < 0.05$) negative correlation between Fe and Mn associated copper fractions and clay content and soil textural class. This could be due to the fact that these soils are relatively young, and soil development would tend to favour the production of silicate clays rather than Fe and Mn oxide which are more dominant in highly weathered soils (Weil and Brady, 2017). Furthermore, there is a highly significant positive correlation between copper fractions associated with Fe and Mn oxides, and sand content. This could be due to the influence of sand content on soil aeration. The influence of sand content on soil aeration has been underscored by Weil and Brady (2017). Similarly, there is a significant ($P < 0.05$) positive correlation between residual copper fractions and sand content. This could be connected to significant amounts of copper bearing minerals in the sand fractions. Primary minerals make up the majority of the sand and silt fractions in most soils, according to Huang and Wang (2005).

Conclusion: The study shows the relationship between copper and selected soil properties of the study area. The readily available fraction which constitutes the water soluble, and the exchangeable fractions were rated as optimum in these soils. However, of major concern is the organic bound fraction which serves as a reserve should the readily available fractions but might be depleted over time through continuous cropping as it is being practiced in the area. Consequently, to sustain the copper content and improve the fertility of these soils; prudent soil organic matter management through the uses of conservation tillage, green manure, crop rotation and application of biochar and other organic amendments is imperative.

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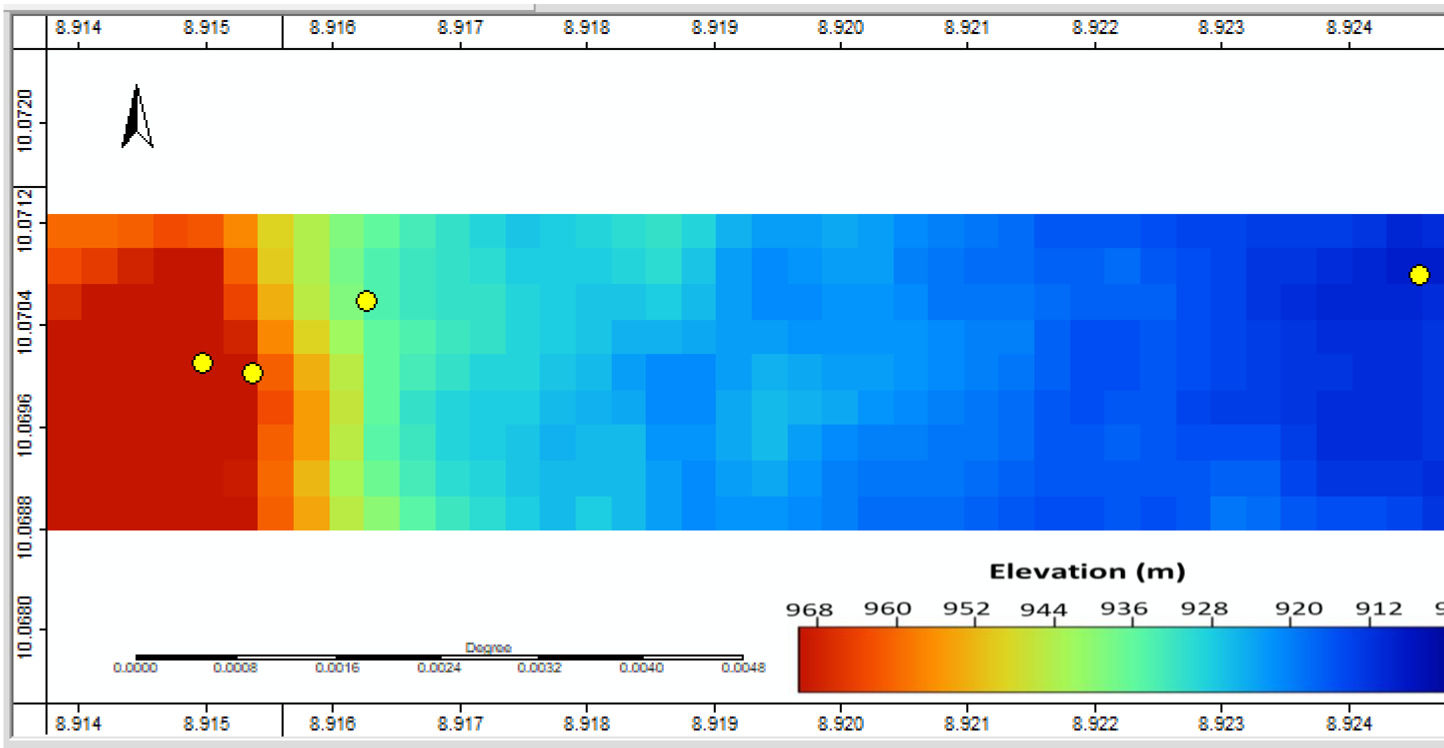

Figure 1: Map of study area showing elevation and location of profile pits

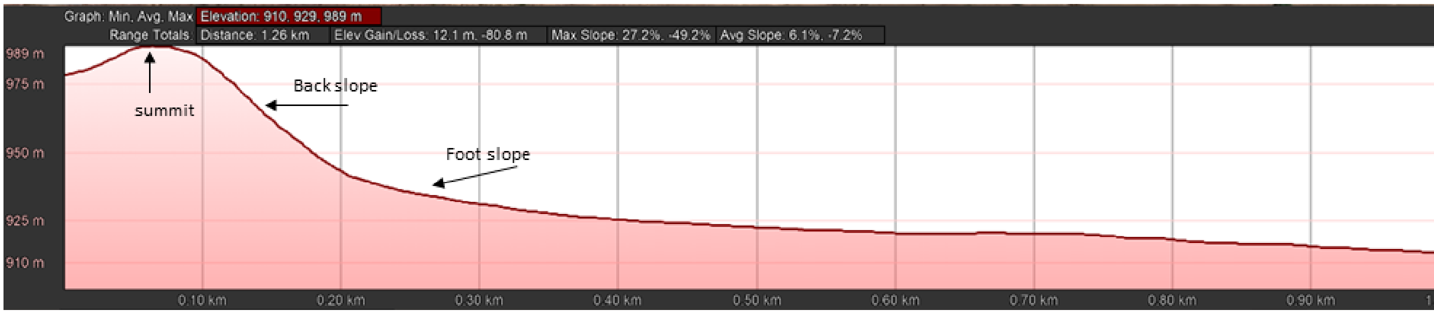

Figure 2: Topographic characteristic of the study area

Table 1: morphological characteristics in various slope positions

Profile	Horizon	Depth (cm)	Structure	colour	air-dry	moist	wet
						Soil Consistence	
				SUMMIT			
1	Ap	0-10	strong platy breaking to sub-angular blocky	7.5YR 3/2	slightly hard	friable	non- sticky, slightly plastic
	AC	10 -25	strong sub-angular blocky	7.5YR 3/3	very hard	friable	sticky, slightly plastic
	C	> 25					
				BACK SLOPE			
2	A	0-26	strong sub-angular blocky	7.5YR 3/2	hard	friable	non-sticky, slightly plastic
	R	>26					
				FOOT SLOPE			
3	A	0 -12	strong sub-angular blocky	2.5YR 2/4	hard	very friable	slightly sticky, slightly plastic
	B	12 -60	strong sub-angular blocky	7.5YR 4/6	very hard	very friable	slightly sticky, plastic
	BC	60 – 90	strong sub-angular blocky	7.5YR 4/6	very hard	very friable	slightly sticky, slightly plastic
	C	> 90					
				TOE SLOPE			
4	A	0 – 15	strong sub-angular blocky	2.5YR 2/4	very hard	very friable	slightly sticky, slightly plastic
	B	15 – 65	strong sub-angular blocky	5YR 5/3	Extremely hard	very friable	slightly sticky, plastic
	BC	65 – 90	strong sub-angular blocky	2.5YR 4/2	very hard	very friable	non-sticky, non-plastic

Table 2: Physical soil characteristics and organic matter distribution in soils of various slope positions

Slope Position	Profile	Horizon	Depth	Bulk Density	Clay	Silt	Sand	Gravel	Textural Class	Organic matter
Summit	1	Ap	0-10	1.32	18	16	66	39	Very gravelly sandy loam	4.74
		AC	10 -25	2.09	22	10	68	37	Very gravelly sandy clay loam	3.98
		C	> 25	nd	nd	nd	nd	nd	nd	

Back slope	2	A	0-26	1.39	16	12	72	48	Very gravelly sandy loam	5.44
		R	> 26	nd	nd	nd	nd	nd	nd	
Foot slope	3	A	0 -12	1.34	14	22	64	11	Sandy loam	5.45
		B	12 -60	1.73	26	12	62	7	Sandy clay loam	3.84
		BC	60 - 90	1.79	30	14	56	10	Sandy clay loam	3.69
		C	> 90	nd	nd	nd	nd	nd	nd	
Toe slope	4	A	0 - 15	1.86	26	26	48	10	Sandy clay loam	4.65
		B	15 - 65	1.97	44	14	42	38	Very gravelly clay	5.24
		BC	65 - 90	1.69	26	12	62	48	Very gravelly sandy clay loam	5.75

Note: nd = not determined, Units of depth = cm, bulk density = g/cm^3, clay silt, sand, gravel, organic matter = %

Table 3: Copper fractions (mg/kg) in soils of various slope positions

Slope Position	Profile	Horizon	Depth	W	E	O	C	Fe and Mn	R
Summit	1	Ap	0-10	0.138	0.563	6.225	3.013	7.563	63.700
		AC	10 -25	0.188	0.938	8.025	4.550	3.800	59.400
		C	> 25	Nd	nd	nd	nd	nd	nd
Back slope	2	A	0-26	0.013	0.763	6.350	2.850	6.538	52.500
		R	>26	Nd	nd	nd	nd	nd	nd
Foot slope	3	A	0 -12	0.138	0.775	4.875	1.713	5.588	38.500
		B	12 -60	0.063	0.900	4.450	2.713	5.075	42.400
		BC	60 - 90	0.038	1.050	6.200	2.825	4.500	48.700
		C	> 90	Nd	nd	nd	nd	nd	nd
Toe slope	4	A	0 - 15	0.450	0.888	4.375	2.238	2.200	38.400
		B	15 - 65	0.100	1.175	4.613	2.713	2.050	29.400
		BC	65 - 90	0.363	1.325	5.963	2.138	4.525	49.400

Note: W = water soluble Cu, E = exchangeable Cu, O = organic matter bound Cu, C = carbonate bound Cu, Fe & Mn = iron and manganese oxide bound Cu, R = residual Cu.

Table 4: Correlation between copper fractions and selected soil properties

	Clay	Silt	Sand	Textural class	Organic Matter	pH
Water soluble	0.029	0.502	-0.301	0.206	0.245	0.226
	0.941	0.169	0.432	0.594	0.526	0.559
Exchangeable	0.687	-0.301	-0.474	0.775	0.136	-0.100
	0.041	0.431	0.198	0.014	0.727	0.798
Organic	-0.323	-0.584	0.618	-0.216	-0.196	-0.114
	0.397	0.099	0.076	0.577	0.614	0.771
Carbonate	0.031	-0.596	0.297	0.161	-0.545	-0.570
	0.937	0.090	0.438	0.679	0.129	0.109
Fe and Mn oxide	-0.742	-0.221	0.809	-0.860	0.107	0.502
	0.022	0.569	0.008	0.003	0.784	0.169
Residual	-0.570	-0.419	0.758	-0.520	-0.221	0.154
	0.109	0.262	0.018	0.152	0.568	0.693

Cell Contents
Pearson correlation
P-Value