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A STUDY OF COPPER SORPTION IN SOILS AS INFLUENCED BY SOIL CHARACTERISTICS USING A LABORATORY COLUMN LEACHING TECHNIQUE

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ABSTRACT

Decisions on containment of potential Cu toxicity require an understanding of its behaviour in the soil. Two experiments arranged in a Randomized Complete Block Design (RCBD), with four replications, were carried out separately, to assess the distribution of Cu. The treatments were 0.00, 12.33, 18.50 and 24.70 g/m². Two different soils, Gleyic Arenosol (Nta series) and Eutric/Dystric Gleysol (Temang series) were used for the studies. The study showed Cu sorption increased with increasing soil organic matter (SOM) content. Whilst the correlation between Cation Exchange Capacity (CEC) and Cu sorption was positive in the Gleyic Arenosol, it was negative in the Eutric/Dystric Gleysol. The clay content did not show any regular pattern with Cu sorption. Copper sorption increased with increasing pH in both soil types. Gleyic Arenosol adsorbed more Cu than the Eutric/Dystric Gleysol at all levels of Cu application. The results showed the annual Cu movement in the soil to be 4.17 and 4.58 cm y⁻¹ for the Gleyic Arenosol and Eutric/Dystric Gleysol respectively. Continuous application of Cu may have serious groundwater implications especially under low pH and SOM. Industries processing heavy metals are encouraged to set up large column leaching apparatus to clean industrial effluents before disposing them.

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INTRODUCTION

Copper is extensively used in agriculture as a fungicide to protect coffee, cocoa, tea, banana, citrus, and other plants from major fungal leaf and fruit diseases such as blight, downy mildew, and rust (HSDB, 2008). Copper oxide is used as an active ingredient in various pesticides formulations and comes with various trade names such as Kocide 2000, Champion 80 WP, Nordox 75, Nordox Super 75 WG, Ridomyl Gold plus 65 and 66 WP. Copper may reach the soil directly via deliberate application (agrochemicals) or via indirect routes (i.e. waste water, sewage sludge, soil or air, and wet or dry deposition) (OECD, 2004). It is reported that less than 0.1% of the applied materials reach the target pest (Pimentel and Levitan, 1986), and the majority of the remaining fraction is dispersed in the environment. High levels of heavy metals are reported in the environment as a result of these activities and are therefore of great concern (Cooper et al., 1999). Although copper has known functions and are needed by plants as parts of coenzymes and enzymatic prosthetic groups (Antosiewicz, 1992), it is toxic to plants at high levels (Antosiewicz, 1999; Nedelkoska and Doran 2002).

The observed levels of copper found in plants, most often than not, correlates with the levels present in the environment (Vesk and Allaway, 1997). Salim et al. (1993) found that concentrations of copper increased in radish plants when treated with an increasing concentration of this metal. The uptake of copper from the soil by plants is influenced by a variety of factors, including soil pH, temperature, ions, cation exchange capacity, organic matter content, the concentration of copper in the soil, and the plant species (Antosiewicz, 1992; Salim et al. 1993). Despite constraining legislations with respect to the kind and amount of copper to apply, copper use still causes environmental contamination. The fate of copper in soils, has, therefore, attracted urgent agricultural and environment concerns. Considering the inherent toxicity and the possible deleterious effect of copper, an understanding of the distribution and partitioning of copper and its leaching potential would contribute significantly to the proper use and management of copper-based formulations in agriculture. This study will also be useful in the design and management of effluent disposal of industries processing heavy metals and land disposal systems for sewage sludge and city refuse containing heavy metals. The objective of the study, therefore, was to assess the impact of selected soil chemical and physical properties on Cu distribution and sorption and to establish the

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relative susceptibility of selected soils to copper toxicity towards selecting disposal sites for copper laden sludge or refuse.

MATERIALS AND METHODS

Study Area

The study was carried out at the Soil Science Laboratory of the Department of Crop and Soil Sciences at the Kwame Nkrumah University of Science and Technology (KNUST), Kumasi. The soils used belong to the Nta and Temang series, classified as Gleyic Arenosol and Eutric-Dystric Gleysol, respectively. The Temang series was sampled from a Forest reserve whereas Nta was under a Forb regrowth mainly *Panicum maximum*. The former was at the Bobiri Forest Sanctuary at Kubease and the latter at KNUST, both in the moist semi-deciduous forest zone of Ghana. The rainfall regime is bimodal averaging 1450 mm per annum. The soils are the most extensively cultivated soil to vegetables.

Soil Sampling

The laboratory column leaching method was used for the experiment. The non-sectionable columns consisted of polyvinyl chloride (PVC) pipes with an inner diameter of 10.16 cm and a height of 60 cm. The 20 PVC pipes used in sampling each of the two soil types were bevelled at the lower end to provide a cutting edge to minimize penetration resistance during field core sampling. The sampling depth was 30 cm leaving an extra height of 30 cm to the brim. This extra 30 cm height served to receive the 'spike' solution. Smaller core samplers, 10x10 cm were also used to take soil samples for initial physico-chemical analyses.

Preparation of Soil Columns

The soils were saturated in 0.01M CaCl₂ "artificial rain", equilibrated and allowed to drain freely under gravity for a period of 48 h to attain field capacity before the treatments were imposed.

Experimental Treatments

The source of Cu was Nordox 75 % WG of high purity (99.4 %). It contained 86 % cuprous oxide with an equivalent amount of 75 % metallic copper. The treatments were 0.00 mg, 100 mg, 150 mg and 200 mg Nordox powder per column with an area of 81.04 cm², which is equivalent to 0.00 g/m², 12.33 g/m², 18.50 g/m² and 24.70 g/m² respectively. The Nordox powder was mixed with 10 mL of distilled water and applied at the surface of the soil columns and allowed to stay overnight. The next day the surface of the soil columns were covered with a filter paper (Whatman No. 42) in preparation for the application of the artificial rain to minimize disturbance of the surfaces of the soil column. Based on the inner diameter of the soil column (10.16 cm) and the average annual rainfall of the agroecological zones (1450 mm) of the study areas, 924.433 mL "of artificial rain" (simulated from a dropping funnel) was used to leach each soil column at a flow rate of 10mL per minute. The leachates were collected at 30 minutes intervals. After the leaching process, the soil was extruded from the PVC pipes following a day of free drainage and was sectioned into segments of 0-10 cm, 10-20 cm and 20-30 cm.

Each soil segment was then analyzed for the test substance, Cu.

Depth to Groundwater

The assessment of the depth to groundwater was necessary to facilitate the determination of the rate of movement of copper and the time to reach the groundwater. A survey using a 10 m long line level was used to determine the depth to groundwater at the sampling point. The depth to the groundwater was the vertical distance between the sampling point and the surface of the stream at the valley bottom.

Laboratory Analysis

Particle size analysis was determined by the hydrometer method. A pH meter (JENWAY 3510 pH), was used to determine soil pH in 0.01M CaCl₂ at a 1:1 soil: solution ratio. Percentage organic carbon was estimated using Walkley and Black Wet oxidation method, digesting soil with excess dichromate solution and titrating against a standard ferrous sulphate solution to determine the amount of unreduced dichromate solution. The CEC and Cu were determined by the ammonium acetate method and Diethylenetriamine pentaacetic acid (DTPA), respectively (FAO, 2008). The falling head permeameter method was used in determining saturated hydraulic conductivity (K_s) Bonsu and Laryea (1989). The Available Water Capacity (AWC) was determined as the difference between the Field Capacity water (FC) and Permanent Wilting Point. (PWP) using a pressure plate apparatus. The dry bulk density was determined from soil cores collected at the field (two days after rains) with core samplers (Klute, 1986).

Preparation of standard curve

Five standard solutions were read within range before and after each group of 12 test solutions and oA (absorbance) was re-established each time. A calibration curve was prepared from average of each standard before and after test group. Unknown concentrations were then read from a plot of (oA) against C (mg/L)

Calculation

The amount of copper metal in the sample (mg/kg) = $C \mu\text{g/mL} \times 2$ (dilution factor) (3.2)

Where:

2=Dilution factor(soil sample taken=10.0 g and DTPA used=20 mL);

C=Concentration of metal copper as read from the standard curve for the given absorbance (g/mL).

Determination of Copper Ions in Soil Segments

After the leaching study was over, the soil columns were extruded and sectioned into three segments of 0-10 cm, 10-20 cm and 20-30 cm. These segments were analyzed by weighing 10 g of the soil sample into a 100-mL narrow-mouthed polypropylene bottle. Twenty millilitres (20 mL) of extraction solution (DTPA) was added and the bottle stoppered. It was then shaken for 2 hours at room temperature (25°C). This was followed by filtering the content into polypropylene bottle. A blank solution without soil as control was prepared. Copper

content was then determined by atomic absorption spectrophotometer (Model 210 VGP). A 200 mg Nordox application was considered for the sorption studies.

Prediction of the annual movement of copper

Equation (4.0) was used to predict the center of mass of the copper metal

$$X = \frac{Q/W}{1 + \rho_b K_d / \theta_v} \dots \dots \dots (4.0)$$

Where;

- X = Chemical displacement [L]
- Q = Annual precipitation [L]
- W = Available water content [L³]
- ρ_b = Bulk density [ML³]
- K_d = Partition coefficient, K_d value for copper from literature is 2.7 g/L. (Allison *et al.*, 2005) [ML³]
- θ_v = Volumetric moisture content at field capacity [L³]

Statistical analysis

The data collected on the various parameters were subjected to analysis of variance using GenStat statistical package (12th Edition). The design used for both sites was Randomized Complete Block Design (RCBD). Means were separated using least significant difference (Lsd) at 5 % probability level. Regression among the parameters were also established. Standard Error of difference was used to compare the difference between the two sites.

RESULTS

Physical properties of the soils

The mean values of the physical and hydraulic properties of the experimental soils are presented in Table 1. The texture of both Nta and Temang series were all sandy loam at all depths except at the 0-10 cm depth of Temang series, which was loamy sand. The saturated hydraulic conductivity and available water content were higher in Nta series than the Temang series.

Table 1. Physical and hydraulic properties of the experimental sites

Parameters	Nta series			Temang series		
	Depth (cm)					
	0-10	10-20	20-30	0-10	10-20	20-30
% Sand	74.48	71.38	75.28	75.28	69.78	72.28
% Silt	21.8	19.4	11.50	20.75	20.00	19.25
% Clay	3.72	9.22	13.22	3.97	10.22	8.47
Texture	S L	S L	S L	L S	S L	S L
K_s (cm/h)*	3.78			3.24		
ρ_b (g/cm ³)*	1.570			1.560		
θ_v FC (cm ³ /cm ³)*	0.308			0.307		
θ_v PWP (cm ³ /cm ³)*	0.123			0.138		
AWC (cm ³ /cm ³)*	0.185			0.169		

*Parameters were measured within 0-30 cm depth of soil; S L = Sandy Loam; L S = Loamy Sand.

Table 2. Chemical properties of the experimental soils

Depth (cm)	Nta series				Temang series			
	CEC cmol (+)/kg	pH (1:1)	O.C. (%)	Cu mg/kg	CEC cmol (+)/kg	pH (1:1)	O.C. (%)	Cu mg/kg
0-10	1.96	6.72	0.90	0.19	1.35	5.03	0.41	0.17
10-20	1.90	6.56	0.38	0.15	2.25	4.65	0.13	0.05
20-30	1.42	6.23	0.29	0.13	2.42	4.67	0.06	0.06
Lsd (5 %)	0.72	0.53	0.27	0.08	0.72	0.19	0.09	0.06

The permanent wilting point was higher at Temang series than Nta series. The soil bulk density and water content at field capacity of both soil series were similar.

The chemical properties of the experimental soils

The selected chemical properties of the experimental soils are presented in Table 2. The mean values of organic carbon were higher in Nta than Temang series at all depths, although the values were low. As expected, the soil organic carbon content at the 0-10 cm depth in both soil series was significantly higher than those of the other depths. The values recorded for the Nta series ranged from 0.290 to 0.898 % for the 20-30 cm and 0-10 cm depths respectively with a mean of 0.523 %. The corresponding values for the Temang soil were in the range of 0.060 to 0.411 % with a mean value of 0.199 %. The pH values of the Temang series, ranging from 4.67 to 5.03 were in the strongly acidic range. On the other hand, the pH of the Nta series was neutral, slightly acid and moderately acid for the 0-10cm, 10-20 and 20-30 cm depths. The CEC of both Nta and Temang series were low with values of Nta ranging from 1.42 to 1.96 cmol (+)/kg at the 20-30 cm and 0-10 cm depths respectively whereas it ranged from 1.350-2.420 cmol (+)/kg for 0-10 cm and 20-30 cm respectively with a mean value of 1.885 cmol (+)/kg. However, there was no significant difference ($p < 0.05$) among them at each site. The CEC at 0-10 cm was 3.06 % and 27.6 % higher than 10-20 and 20-30 cm depths respectively. Between the latter two depths, the former was 25.3 % higher in CEC. While the CEC decreased with depth in the Nta series, it increased in the Temang series with the values of the latter ranging between 1.35 and 2.42 mg/kg at the 0-10 cm and 20-30 cm respectively. The CEC of the 20-30 cm depth was 44.2 % and 7.0 % greater than that of the 0-10 cm and 10-20 cm depths respectively. There was no significant difference observed in the initial Cu content recorded in Nta soil series at the various soil depths whereas in the Temang soil series significant differences were observed. The amount of Cu recorded at the 0-10 cm depth was significantly higher than that of the 10-20 cm and 20-30 cm depths in both soil series. The available copper content recorded under the Nta series was generally higher than that under the Temang series.

The impact of Copper load on sorption

The different application rates significantly ($p < 0.05$) affected copper sorption in the Nta and Temang series. At all the rates of copper applied, considerable differences in copper sorption were recorded in the Nta series but not in the Temang series. The different rates of copper applied significantly increased copper sorption in relation to the control in the Temang series but among the different application rates, no significant difference was recorded. A particular trend was observed in Temang soil series where the amount of copper ion sorbed to the soil at 100 mg was higher than both the 150 and 200 mg application rates but the differences observed between 100 and 200 mg application rates were not significant. Conversely, application of Cu at 200 mg in the Nta series recorded higher Cu sorption in comparison to the 100 and 150 mg application rates. Also, a significant difference in Cu sorption was observed between the 100 and 150 mg application rates. The increasing order of copper sorption was $0 < 150 < 100 < 200$ and $0 < 150 < 200 < 100$ for Nta and Temang soil series respectively. Also across the sites at the various copper load significant difference was observed in only the 0.00 mg application rate.

Table 3. Effect of copper load on Cu sorption

Rates (mg)	Nta series	Temang series	SED
	mg/kg		
0	0.153	0.085	0.020
100	0.962	0.914	0.458
150	0.582	0.656	0.281
200	1.113	0.739	0.414
Lsd (5 %)	0.190	0.262	-

SED= Standard Error of Difference

Cu distribution with soil depth

The vertical distribution of copper along the soil columns differed significantly ($p < 0.05$) as soil depth increased (Table 4). Generally, the amount of copper sorbed decreased with increasing soil depth in both soil series. Significantly higher Cu sorption was recorded at the 0-10 cm soil depth than at the 10-20 and 20-30 cm depths in soils under both series. The Cu sorbed at the 20-30 cm soil depth in Nta series was significantly higher than that of Temang series. In relation to the Cu sorbed at the 0-10 and 10-20 cm soil depths, no statistical differences were recorded between the two sites.

Table 4. Impact of soil depth on Cu sorption

Depth (cm)	Nta series	Temang series	SED
	mg/kg		
10	1.639	1.458	0.363
20	0.275	0.246	0.072
30	0.193	0.091	0.019
Lsd (5 %)	0.164	0.23	-

Prediction of the annual movement of copper at both sites

The chemical displacement of copper in both soil series varied, with Temang soil series recording the higher chemical displacement as compared to Nta soil series. Annual movement of copper at both sites were 4.17 cm and 4.58 cm for Nta and Temang soil series, respectively. The average time required for Cu centre of mass to reach the groundwater

aquifer in the Nta and Temang soil series was 40.72 and 75.55 years, respectively.

Relationship of Soil Organic Carbon, Soil pH, Clay and CEC with sorbed Copper

Copper sorption was correlated with organic carbon, soil pH, clay and CEC for both soil series and the results are presented in Figures 1a, 4.1b, 4.1c and 4.1d. From the results, The R^2 values for Nta soil series were 0.999, 0.6682, 0.8988 and 0.4487 whereas that for Temang soil series were 0.9964, 0.9714, 0.85156 and 0.9992 for Organic carbon, Soil pH, Clay and CEC respectively in both sites. There was negative correlation between Clay and copper sorption in both soil series. Also, CEC had a negative relationship with copper sorption at Temang series whereas that for Nta series was positive.

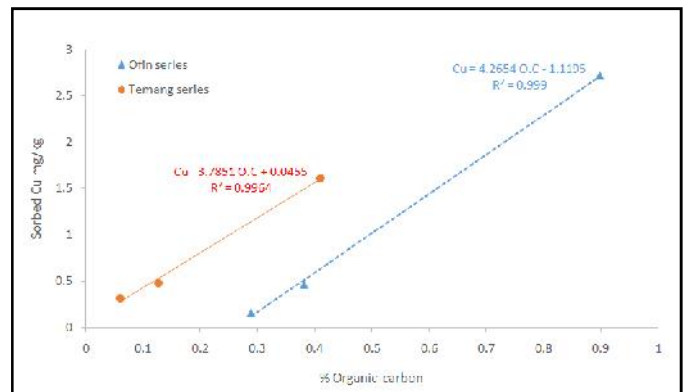


Figure 1a. Relationship between copper sorption and Organic carbon

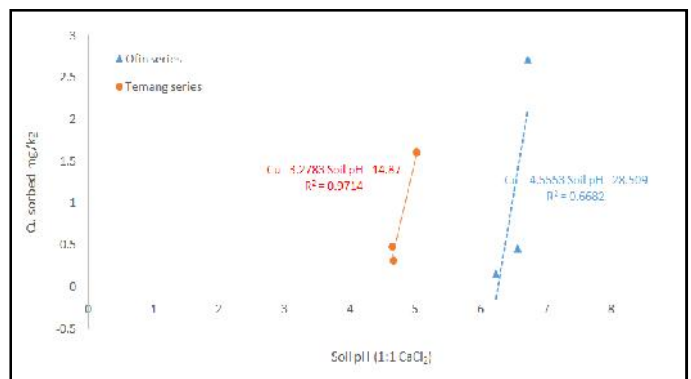


Figure 1b. Relationship between copper sorption and Soil Ph

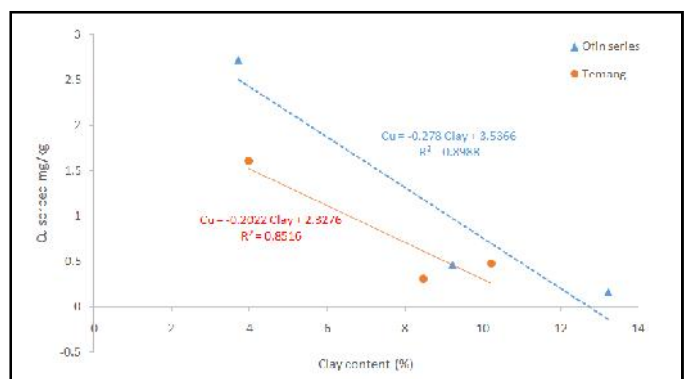


Figure 1c. Relationship between copper sorption and Clay

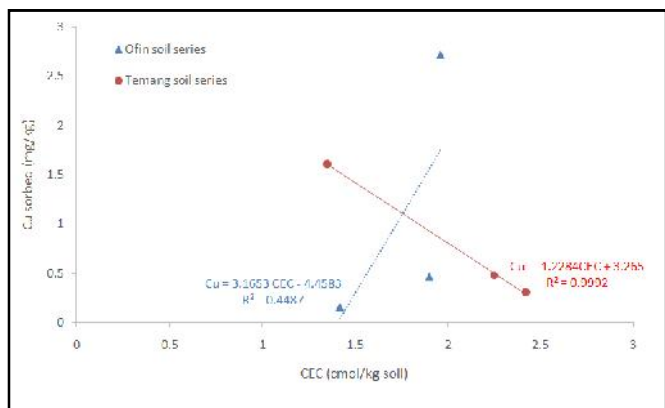


Figure 1d. Relationship between copper sorption and CEC

Relationship between copper application rate with copper sorption

The copper sorption correlated positively with copper application rate (Figure 2) in both soil series, with R² of 0.67 and 0.55 for Nta and Temang series, respectively.

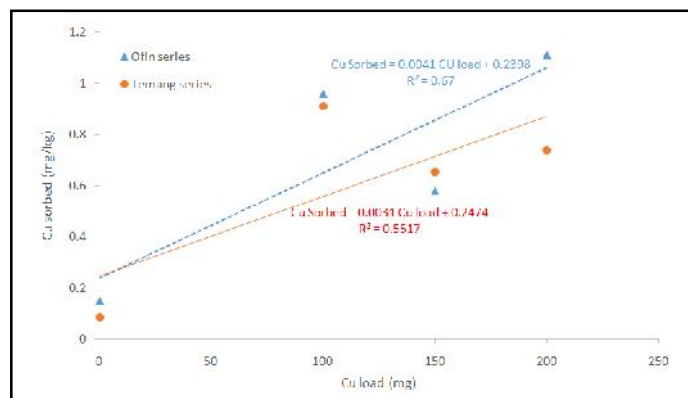


Figure 2. Relationship between copper application rates with copper sorption

Relationship between soil depth and copper sorption

The relationship between soil depth and copper sorption in both soils is presented in Figure 3. The regression equations for the selected soil characteristics and Cu sorption are presented in Tables 6. It is clear from these presentations that, soil depth was negatively correlated with the amount of Cu sorbed.

DISCUSSION

Physico-chemical properties of the soils

Using the Bruce and Rayment (1982) guidelines, the soil pH of both sites differed considerably, with Nta soil series being neutral, slightly acid and moderately acid at soil depths of 0-10 cm, 10-20 cm and 20-30 cm, respectively whereas Temang soil series was generally in the range of very strong acid. According to Boermer, *et al.*, 1995 ratings, the bulk density of both sites were high and the Organic carbon was low at 0-10 and 10-20 cm and very low at 20-30 cm for Nta soil series whereas it was low at 0-10 cm and very low at both 10-20 and 20-30 cm for Temang soil series. Also according to Landon, 1996, ratings the CEC at both site and depth fell within low. The saturated hydraulic conductivity was moderate at both sites based on FAO, 1963 ratings.

Impact of soil characteristics on copper sorption

Several soil characteristics may affect the kind of interaction Cu may have with a soil matrix. The impact of some soil properties on copper sorption are discussed below.

The impact of soil organic carbon on copper sorption

Organic carbon is a major component of the soil which accounts for the magnitude of copper sorption in the soil (del Castillo *et al.*, 1993; Sauve *et al.*, 1997).

Table 6. Relationship table between Cu sorption and the selected soil characteristics

Explanatory variable	Nta series		Temang series	
	Equations	R ²	Equations	R ²
O.C	Cu = 4.265O.C. - 1.120	0.999	Cu = 3.785O.C. + 0.05	0.996
pH	Cu = 4.555pH - 28.509	0.668	Cu = 3.278pH - 14.87	0.971
Clay	Cu = -0.278C + 3.537	0.899	Cu = -0.202C + 2.328	0.852
CEC	Cu = 3.165CEC - 4.458	0.449	Cu = -1.228CEC + 3.265	0.999
Cu app. Rate	Cu = 0.004CuL + 0.240	0.67	Cu = 0.003CuL + 0.247	0.552
Soil depth	Cu = -0.723D + 2.148	0.792	Cu = -0.684D + 1.965	0.834

O.C. = Organic Carbon; D = Soil depth; C = Clay content; CuL = Cu load;

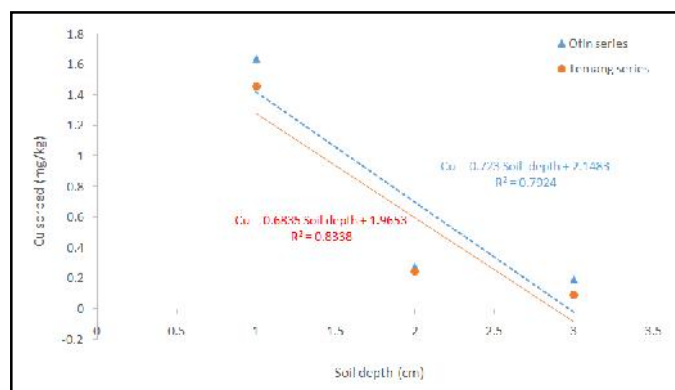


Figure 3. Relationship between soil pH with copper sorption

By its characteristics negative charges, soil organic carbon (SOC) is capable of bonding and forming stable complexes with copper and thereby increase its sorption. Increasing amount of SOC is, therefore, expected to increase the sorption of copper, the total of which ranges from 2 to 100 mg kg⁻¹ in soil (Landon, 1991). This is amply demonstrated by the results of this study Tables 2 and 5. The highest SOC within the 30 cm soil depth, which was at the 0-10 cm depth, recorded the highest sorbed Cu in both the Nta and Temang soil series. As the SOC decreased with depth, so also did Cu sorption, this is further supported by the positive correlation of Cu with SOC, the regression equations of which recorded R² of 0.999 and 0.996 under the Nta and Temang soil series respectively (Figure 1a). The regression equations showed that a unit

increase in the amount of SOC increased Cu sorption by 4.27 and 3.79 mg kg⁻¹ in the Nta and Temang soil series respectively. The former soil, therefore, sorbed more Cu than the latter, being 11.24 % per unit increase in SOC. The implication of these observations are that, increased Cu sorption has the potential to influence the concentration of Cu in the soil solution as indicated by Landon (1991). This, in turn, can affect the bioavailability of Cu to plants (del Castilho, 1993) since Cu availability is governed mainly by its total amount in the soil. On the other hand, increased SOC through organic matter addition can reduce Cu toxicity (>100 mg kg⁻¹), especially in areas where agricultural soils are subject to continuous application of copper-based fungicides or at mining areas. Intuitively, by sorbing Cu, increasing the SOC of agricultural soils, particularly at the surface 10 cm layer, can reduce the transport of Cu through overland flow into surface water bodies and leaching into groundwater. This is a desirable effect in managing Cu pollution of rivers, streams and aquifers. The practical way of achieving SOC increases in agricultural landscapes is through retaining as much vegetative residues on the soil as possible, application of manure, non-burning of crop residues, prevention of bush fires and controlling water and wind erosion.

The impact of soil pH on copper sorption

All micronutrients, including Cu, become more available with increasing acidity. According to Landon (1991), the availability of Cu decreases slowly with increasing pH, but the nature of the interaction is not completely understood. A plausible mechanism could be sought from the impact of pH on Cu sorption. The results of the study showed Cu sorption to increase with increasing pH (Figure 1b). This could potentially constrain Cu availability as generally observed. As reported by Garbisu and Alkorta (2001) and Gisbert *et al.* (2003), increasing soil pH to 6.5 or higher can result in copper immobilization in the soil making it less available to plants. This is because Cu is more soluble at lower pH levels. In this study (Table 2), a pH change from 6.23 to 6.72 (a 7 % increase), increased Cu sorption from 0.193 to 1.639 cmol/kg soil (an increase of 88 %) in the Nta series. For the Temang series, an increase of pH from 4.67 to 5.03 (an increase of 7.2 %), increased Cu sorption from 0.091 to 1.458 cmol/kg (an increase of 94 %). Small increases in soil pH can, therefore, cause tremendous increases in Cu sorption and thereby potentially restrict the availability of Cu to plants.

The relationship of soil pH and Cu sorption revealed a positive correlation with *r* being 0.985 and 0.817 for the Nta and Temang soil series respectively. The regression equations showed a unit increase in soil pH to increase Cu sorption by 3.28 and 4.56 mg kg⁻¹ in the Temang and Nta soil series. It is noteworthy to point out these impacts of the dependent variables have been presented in the context of their magnitude in the different soil depths (0-10 cm, 10-20 cm and 20-30 cm) which did not have the same contact time of the spiked Cu solution due to the lag in the transport rate of the solution with depth. Thus, the contact time of the surface layers was more than the sub-layers with a potential for increased sorption. This is a characteristic of the column leaching method used in this study which is a closer simulation of fungicide transport under field conditions. It will be instructive to study what the relationship of Cu sorption would be if a given soil with different levels of the dependent variables (e.g SOC, Clay, pH, CEC) was spiked with Cu solutions under similar contact time.

It is envisaged that the relationship of the variables with Cu sorption could be different.

The effect of clay on copper retention

Apart from SOC, clay minerals also adsorbed Cu. Although there are reported cases of a positive correlation existing between copper sorption and clay (silicate minerals), oxides and hydroxides (Pampura *et al.*, 1993), the results obtained from this study showed a negative correlation (Figure 4.1c). For instance, in Nta soil series, at 0-10 cm soil depth, the clay content of 3.72 % sorbed 2.718 mg/kg of Cu. By the positive correlation (as reported in literature), Cu sorption, which was expected to increase in the layers below because of higher clay contents of 9.22 and 13.22 % at depth of 10-20 cm and 20-30 cm, respectively rather decreased. This behaviour was similar to those observed in the Temang soil series where copper sorption was greatest in the upper layer (0-10 cm) containing the least amount of clay. This deviation may be due partly to the method employed in this study. In most cases, the sorption of pesticides is measured with soil suspensions through the batch method (Chaplain *et al.*, 2011). The intensive shaking of the soil-pesticide solution using the method can lead to the pulverization and dispersion of soil structure, which increase the sorption sites for Cu sorption. This is in contrast to the leaching method used in this study which involves transport of Cu through undisturbed soil columns and therefore simulates what happens in the field. Therefore, the batch method can lead to an overestimation of sorption. The decreased sorption of Cu with increasing clay content with respect to soil depth could be due to the longer contact time of the leaching solute with the top 0-10 cm depth with lower clay than the 10-20 and 20-30 cm depths which had higher clay content.

The effect of CEC on copper sorption

The mean Cu sorption for the 30 cm depth was 0.702 and 0.598 mg kg⁻¹ in the Nta and Temang series, respectively, being 15 % higher in the former soil. The assessment of the impact of CEC on Cu sorption was done through a regression analysis, which gave two contrasting results, whilst the correlation between CEC and Cu sorption was positive in the Nta series, it was negative in the Temang series. The implication is that Cu sorption increased with increasing CEC in the Nta series and decreased with increasing CEC in the Temang series. According to Landon (1991), measured CEC values often depend critically on soil pH, as well as SOC and the amount and type of clay minerals. The complex interaction of these influential factors and their interrelationships in different soils may account for the observed results. Nevertheless, an attempt was made to explain the underlying causes of these observations by examining the relationship between CEC and the influential factors of SOC, clay and pH. It is presumed that the relative dominance of these factors on the magnitude of CEC and their impact on cationic adsorption may effect similar trends in the relationship of CEC with Cu sorption. In the Nta series, CEC correlated positively with SOC ($r = 0.69$; $R^2 = 0.48$) and pH ($r = 0.97$; $R^2 = 0.95$); and negatively with clay ($r = -0.87$; $R^2 = 0.76$). The CEC was positively correlated with Cu sorption ($r = 0.67$; $R^2 = 0.45$) as did SOC ($r = 0.99$; $R^2 = 0.99$), (Graphs are shown in the appendix). It was therefore presumed that, the dominant determinant of CEC in the Nta series was SOC. In the case of the Temang series, the correlation of CEC was positive with clay ($r = 0.91$; $R^2 = 0.83$); and negative with SOC ($r = -0.999$;

$R^2 = 0.999$) and pH ($r = -0.98$; $R^2 = 0.96$). In this circumstance, clay was presumed to be the major determinant of the magnitude of CEC, since both correlated negatively with Cu sorption with r and R^2 being -0.999 and 0.999 for CEC; and -0.92 and 0.85 for clay. These observations amply indicate that undisturbed field soil columns could cause variable and complex responses to Cu sorption in different soils and under variable influential factors, the underlying reasons of which defy simple one factor explanations.

The relative Cu sorption capacity of Nta and Temang series

The capacity of a soil to adsorb Cu is an important factor in managing high levels of Cu and toxicity in the soil. A soil with a low content of inherent Cu is expected to have a high potential to take more of applied Cu because of free cation adsorption sites. Such a potential was implicit in the two experimental soils due to their low inherent Cu content compared with the common total Cu of 2 to 100 mg kg⁻¹ found in soils. In this context, the Nta series adsorbed more Cu than the Temang series at all levels of Cu application. The increased sorption could be due to the relatively higher SOC content and pH of the Nta than Temang series which, for the 30 cm depth, averaged 0.52 % and 6.5 respectively for the Nta and 0.21 % and 4.78 for the Temang. The SOC of the former soil series was 60.23 % higher than the latter series with their corresponding slightly acidic and strongly acidic conditions. As indicated earlier, Cu sorption is positively correlated with SOC and pH, implying that a soil with relatively higher SOC content and pH, as in the Nta than the Temang series, will adsorb more copper as shown by the result of the study.

Apart from the chemical properties of the soil such as SOC, pH and CEC, the physical properties, such as texture, water content, bulk density and hydraulic conductivity, play a major role in the movement of Cu within the soil to the groundwater. The results showed the annual Cu movement in the soil to be 4.17 and 4.58 cm y⁻¹ for the Nta and Temang series respectively. If the depth to groundwater was the same, Cu movement into groundwater would be faster in the Temang series (Loamy sand at the 0-10 cm and Sandy loam at both 10-20 and 20-30 cm) than the Nta series (Sandy loam for the 0-30 cm depth). However, because of the variable topo-site of the two soils, the distance to the groundwater will differ being 1.70 m and 3.46 m for the Nta and Temang series respectively (appendix 2). Accordingly, the travel time to the groundwater will also differ. The calculated average time to reach the groundwater aquifer was 40.72 and 75.55 years under the Nta and Temang series respectively. Such information is relevant in decisions concerning the disposal and management of municipal liquid waste or industrial effluents containing Cu.

The impact of copper application rates on copper sorption

Areas subjected to continuous application of Cu-based agrochemicals (fungicides, pesticides) such as Nordox in cocoa farms may accumulate high levels of Cu in the soil. Such a situation can arise with increasing rates of copper application. This, in turn, can provide more Cu in the soil to be available for various depletion and immobilization processes, such as, plant uptake, leaching, erosion and adsorption by SOC and Clay minerals. Because these processes occur simultaneously and interactively at any given time, it is difficult to isolate and establish consistent trends in the sole

impact of increasing Cu application rates on any of the processes, particularly, sorption which is the subject matter of this study. Thus, the results of the main effect of the different rates of Cu application did not show any consistent decreasing or increasing Cu sorption trends. However, in both soils, Cu was significantly less ($p < 0.05$) under the control than any of the increased rates. In the Nta series, the 100 and 200 application rates did not effect significant differences in the magnitude of Cu sorption, but recorded significantly ($p < 0.05$) higher sorption than the 150. Sorption under the 200 application rate was, however, 13.6 % higher than that of the 100. Copper sorption in the Temang series did not differ significantly under the application rates of 100, 150 and 200. However, sorption under 100 was 28 % and 19 % higher than 150 and 200 respectively. In order to establish the relationship between Cu sorption and increasing rates of Cu application, the data was subjected to regression analysis. In both soils, the correlation was positive, being 0.82 and 0.74 for the Nta and Temang series. The respective coefficients of determination were 0.67 and 0.55. The regression equations showed that a unit increase in copper application rate, increases Cu sorption by 0.003 and 0.004 mg kg⁻¹ in the Temang and Nta series respectively.

Variation of copper sorption with soil depth

The amount of Cu sorbed was also influenced by soil depth. For a 30 cm soil depth at 10 cm increments from the surface, Cu sorption decreased with depth, being highest and lowest at the 0-10 cm and 20-30 cm depths respectively. The pH, SOC, CEC and clay at the different depths and their relationship with Cu adsorption are implicated in this observation. In both the Nta and Temang series, pH and SOC decreased with depth, whilst clay increased. The relationship of these three parameters with Cu sorption showed pH and SOC to be positively correlated with Cu sorption whilst that with clay is negative. The implication is that decreasing pH and SOC and reducing clay result in reduced Cu sorption. It is therefore not surprising that Cu sorption decreased with soil depth.

Relationship of Organic Carbon, Soil pH, Clay and CEC with Sorbed Copper

From the various relationships established, known quantities of soil organic carbon/ soil pH/ clay or CEC could be used to predict the amount of Cu that will be sorbed. For an instance, in the case of Nta soil series with regression equation for organic carbon and Cu; $Cu = 4.265 \text{ O.C.} - 1.120$ meant that an increased in soil organic carbon value by one unit will cause sorption to increase by 4.256, and an R^2 of 0.999 meant that 99 % of the variations in copper sorption could be explained by changes in soil organic carbon with the remainder being residuals. These relationships established could also be a useful predictive tool in terms of estimating the amount of copper that would be sorbed within the magnitude of the measured parameters. It must therefore be pointed out that since the equations are empirical, they are, in the main, valid for the conditions and methodology (column leaching) under which this study was conducted.

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