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Analysis of water soluble Copper residue in the top soils of some Cocoa growing areas of the central region of Ghana

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ABSTRACT

Water soluble copper concentrations in some topsoil samples collected between February and March 2000 from eleven cocoa growing towns in the central Region of Ghana were determined. In all a total of hundred and eighty soil samples were taken randomly at a depth of 0-20cm from preselected farms. copper fungicides were applied in ten of the farms and the eleventh farm which served as a control had no fungicide application. Some physical and chemical properties of the soils were determined. Analysis for copper was done using atomic absorption spectrometer after the extraction process. Water-soluble copper in the soils ranged from 0.05 to 0.40mg kg⁻¹ with a mean concentration of 0.265 mg kg⁻¹. The correlation was done to determine the factors responsible for the differences in the absorption levels of water-soluble copper. Water soluble copper correlated negatively and insignificantly ($P>0.5$) with cation exchange capacity, organic carbon, available phosphorus, nitrogen, moisture, and silt while an insignificant ($P>0.05$) positive correlation existed between copper level and pH of the soil. Also a significant ($P<0.05$) negative moderate correlation existed between water soluble copper concentration and soil clay content while a significant ($P<0.05$) positive correlation existed between copper concentration and sand content of the soil.

Key Words: Soil, Copper fungicides, soluble Copper, Central Region,

INTRODUCTION

Agriculture is the main driving force behind Ghana's economy, accounting for approximately 42 percent of the country's GDP and employing 54 per cent of its work force. In 2006 -2007 season Ghana produced 720,000 tons of cocoa equivalent to 20.7% of world's production making it the world's second largest producer after Cote d'Ivoire [1]. Insecticides, fungicides and herbicides are agrochemicals designed to combat the attacks of various pests on agricultural crops. However, in many cases hazardous residues are left, becoming a permanent danger to quality of food, environment and consumers health and for that purpose their determination is a priority goal [2]

Globally, blackpod disease, caused by Phytophthora fungi, predominantly *P. palmivora* Butl. and *P. megakarya* Bras. & Griff, is the major biotic yield constraint, resulting in estimated losses of 450 000 tonnes per year [3]. In Ghana two Phytophthora species, *P. palmivora* and *P. megakarya*, are the main causal agents of black pod disease of cocoa, and are differentially distributed in the cocoa-growing regions of the country. Phytophthora *palmivora* is found in all the six (Eastern, Ashanti, Brong Ahafo, Central, Volta and Western) cocoa-growing regions while *P. megakarya*, since its first report in the Ashanti region in 1986, has spread to other regions with the exception of the Eastern region [4,5]. Of the two species, *P. megakarya* is more aggressive, causing significantly greater losses [4, 5, 6] and has been threatening the livelihood of many cocoa farmers [7].

Copper fungicides are known to effectively control a whole host of fungus diseases of plants. In Ghana, copper fungicides such as Kocide 101 (cupric hydroxide 77%), Copper Nordox (cuprous oxide), Champion (Cupric Hydroxide 77%), Ridomil (Copper Oxide 60%) and Caocobre Sandoz (50% Copper Oxide) are used for controlling cacao diseases. Long term use of Cu fungicides might have negative impacts on soil fauna and other non-target organisms. In temperate zones, it has been demonstrated that earthworms are more susceptible to heavy metals (such as Cu) than most other groups of soil invertebrates [9, 10] exhibiting chronic toxic responses at Cu concentrations of less than 16 mg kg⁻¹ [11]. Cu was shown to be the primary factor influencing earthworms in fruit plantation soils in temperate Australia [12].

One of the limiting factors in the use of copper compounds is their serious potential for phytotoxicity, or poisonous activity in plants [13]. Copper can kill plants by disrupting photosynthesis. Since these fungicides are systemic and can be translocated from the soil through the roots to other parts of the plants and other food crops (such as cassava, cocoyam, maize and plantain grown on the cocoa farm), it is therefore necessary to investigate the levels of copper in these soils. In this present work, soluble copper in topsoil of eleven tropical cocoa farms in the Central Region of Ghana has been determined and it was investigated whether the copper residue correlated with the soil properties.

The toxicity of copper in soil depends more on the available concentration of copper than it does on the total concentration. Available means that the copper is in a form that can be taken up by plants, microbes, or animals [23]. The aim of the present work was to determine the relationship between soil properties and soluble copper due the application of copper fungicides in cocoa farms.

MATERIALS AND METHODS

Sampling technique

Random sampling techniques were adapted to select cocoa farming communities and farms where copper fungicides had been applied to farms in each community. Soils samples were collected from Jukwa (Ju), Twifo Manpong (TM), Edumfa (ED), Wawase (WW), Brase (BRA), Brema Ahumase(BA), Bisease (BI), Effutuakwa (EFF), Dominase (DO), Ajumako Kokoben (AK), and Abura Dunkwa(AD) in February and March 2000.

In all eleven cocoa farms in different villages/towns in Central Region were analysed. In Edumfa no copper fungicide was applied. The composite soil samples were obtained randomly at a depth between 0-20 cm with a soil auger. Each composite soil samples consisted of 10-20 cores depending on the farm size which ranged from 2.0- 5.0 hectares. They were thoroughly mixed, spread on clean brown sheet and sub sampled for composite. The location of the farm, name of

the farmer, depth of sampling, name of the sampler and the date sampled were used to identify each sample in the laboratory.

Digestion of Soil

Exactly 0.350g of soil samples were accurately weighed and each transferred into 250ml flask. 100ml of deionised water was added to each flask, stoppered tightly and shaken for one minute. The resultant suspension of each flask was warmed in 30°C water bath for one hour with shaking of suspension every 15minutes. 50ml suspension of the sample was centrifuged for 20minutes at 3000rpm taking care to avoid increase in temperature. The resultant solution was filtered and stored for analysis. 25.0ml of the sample was pipette into a 500ml volumetric flask and 1.0ml dil. HNO₃ was added and diluted with deionised water to the volume and mixed. Atomic Absorption spectrometer (Shimadzu model 6401F) was used to determine absorption at 324.7nm [14].

Laboratory Analysis

Soil samples were air-dried, ground and passed through 2-mm soil sieve. Soil pH (1:2.5water) was measured with a glass electrode method [16]. Total carbon and organic matter were determined by wet combustion [17]. Flame photometer was used to determine exchangeable potassium while atomic absorption spectrophotometer was used to determine calcium and magnesium after extraction with 1.0 M ammonium acetate [18]. Total N was determined by the Kjeldahl digestion [19]. Soil available P was extracted with a HCl: NH₃F mixture method [20]. Mechanical analysis was by the pipette method [21].

RESULTS AND DISCUSSION

Table 1 Soil characteristics

Soil Sample	% Sand	% Silt	% Clay	% Moisture	Texture
DO	65.82 ± 0.30	27.52 ± 0.20	6.66 ± 0.03	16.64 ± 0.12	Sandy Loam
TM	61.76 ± 0.30	17.40 ± 0.30	20.84 ± 0.20	25.20 ± 0.23	Sandy Clay Loam
BRA	57.76 ± 0.20	15.40 ± 0.20	26.84 ± 0.10	28.40 ± 0.20	Sandy Clay Loam
AD	65.70 ± 0.15	9.58 ± 0.30	24.72 ± 0.02	22.40 ± 0.20	Sandy Clay Loam
JU	65.71 ± 0.25	9.59 ± 0.20	27.72 ± 0.15	29.50 ± 0.10	Sandy Clay Loam
EFF	59.64 ± 0.20	19.52 ± 0.20	20.84 ± 0.20	18.40 ± 0.10	Sandy Clay Loam
WW	81.58 ± 0.30	7.52 ± 0.02	10.90 ± 0.10	6.42 ± 0.02	Sandy Loam
BI	53.52 ± 0.10	18.30 ± 0.20	28.18 ± 0.20	30.20 ± 0.20	Sandy Clay Loam
BA	59.58 ± 0.20	16.24 ± 0.10	24.18 ± 0.10	21.60 ± 0.20	Sandy Clay Loam
AK	43.46 ± 0.10	18.24 ± 0.10	38.30 ± 0.15	35.00 ± 0.20	Clay Loam
ED	37.70 ± 0.10	27.46 ± 0.20	34.84 ± 0.20	25.50 ± 0.10	Clay Loam

The particle size distribution analysis of soils revealed that the soils range in texture from clay loam to sandy clay loam. Predominantly the soils are characterized by sandy clay loam in texture constituting 64% of total while sandy loam and clay loam are of equal distribution of 18% each. The sand contents of the soils lie between 37.70% and 81.58% .The low clay contents ranging from 6.66% and 38.30% and silt contents ranging from 9.58% and 27.52% (Table 1). Soils from DO and WW, were sandy loamy because of their high sand content and very low clay. Soils from TM, BRA, AD, JU, EFF, BI and BA were sandy clay loam because of their high sand contents and moderately high clay contents. The soils from AK and ED are clay loam with moderately high clay content.

The high sand contents of the soils are an indication of very low organic carbon or organic matter and tendency of such soils to adsorb fungicides would be low (22). The soils contain low amounts of organic carbon ranging from 1.24 to 3.95 % (Table 2.0).The results indicated that

organic carbon content increases with increasing clay content of the soils. The adsorption of the copper fungicide would thus be expected to increase with increasing clay content and organic carbon content. The implication is that the fungicide will persist for longer periods in such soils containing high clay and organic carbon content.

Table 2 Chemical Properties of the Soil

Soil Sample	pH	%N	Available P(mgkg ⁻¹)	% OC
DO	5.85±0.07	0.15±0.01	14.2±0.28	1.50±0.14
TM	5.43±0.18	0.17±0.03	12.5±0.20	1.70±0.03
BRA	6.92±0.03	0.30±0.02	15.2±0.20	3.00±0.20
AD	5.48±0.02	0.19±0.01	12.6±0.26	1.84±0.03
JU	4.81±0.03	0.22±0.02	16.6±0.30	2.20±0.20
EFF	6.21±0.01	0.15±0.01	25.5±0.50	1.50±0.10
WW	6.17±0.03	0.13±0.02	16.3±0.30	1.24±0.20
BI	6.82±0.15	0.28±0.01	25.5±0.20	2.74±0.03
BA	7.12±0.04	0.27±0.27	22.1±0.20	2.70±0.10
AK	7.86±0.14	0.40±0.03	24.5±0.20	3.95±0.03
ED	5.15±0.05	0.23±0.02	22.3±0.21	2.40±0.20

A significant ($P < 0.05$) negative moderate correlation existed between water soluble copper and clay content in the soil (Table 4). The lack of significant ($P > 0.05$) relationship between copper absorbed and organic carbon could be due to low activity clay of the soils, which are generally encountered in semi deciduous rainfall zones in the tropics possibly due to instability of the complexes as a result of dissociation. Secondly, moderately high clay content has inhibitory effect on the degradation of some compounds. The inhibitory effect is attributed to adsorption of compounds by clay minerals, especially smectite, rendering them less vulnerable to microbial attack. Thirdly, fungicides may be bound so strongly to the clay that the extraction method may not be able to remove them. Also, there could be leaching of the copper to a depth beyond the level sampled. The distribution of active ingredient of a fungicide in the soil obviously depends on the mode of formulation. Application of fungicide to the soil at an average dose of 5 kg/ha may not saturate the surface area of the soil colloids in the top 3cm of soil.

The soil moisture contents ranged between 6.42% and 35%. The moderately high moisture content of the soils favours dissolution of the copper fungicides since they are all water soluble. A negative correlation existed between soluble copper and moisture content but this was not significant ($P > 0.05$).

The pH of the soils ranged from strongly acidic to slightly alkaline (Table 2). Soils from JU, are strongly acidic ($pH < 5$) and those from DO, TM, AD, EFF, ED and WW are slightly acidic ($5.00 < pH < 6.50$) soils from BRA and BI are neutral (pH approximately 7) soils from BA and BI are slightly alkaline ($pH > 7$). In general soils which have their effective cation exchange capacity (ECEC) less than 10 cmolc kg^{-1} are considered as low activity clays. Hence soils from DO, TM, JU, EFF and WW can be said to be low activity soils (Table 3.0). The high ECEC of the soils from BRA, AD, BI, BA, ED and AK could be attributed to their high exchangeable bases. The dried leaves on the farm are burnt occasionally; the ash produced contains K^+ , Na^+ , Ca^{+2} and Mg^{+2} , which cause an increase in the exchangeable bases, a decrease in acidity and an increase in pH, which agrees with observations made by Oladokum and Nwoboshi (8, 15). The exchangeable cation is dominated by Ca^{+2} , which occupied more than 50% of the ECEC followed, by Mg^{+2} then K^+ and Na^+ .

Table 3.0 Exchangeable Cations of the soil

Soil Sample	Exchangeable Cations (C mole kg ⁻¹)				Ea C mole Kg ⁻¹	ECEC CmoleKg ⁻¹
	K ⁺	Na ⁺	Mg ⁺	Ca ⁺²		
DO	0.24±0.01	0.32±0.02	1.20±0.01	4.81±0.01	1.26±0.04	7.83 ± 0.14
TM	0.18±0.01	0.32±0.01	2.33±0.01	3.55±0.02	2.21±0.15	8.59±0.10
BRA	0.76±0.02	0.67±0.02	4.81±0.02	16.91±0.01	0.03±0.01	23.18±0.04
AD	0.24±0.02	0.29±0.01	1.59±0.04	6.54±0.02	4.07±0.02	12.73±0.05
JU	0.51±0.01	0.53±0.03	2.35±0.01	5.79±0.04	4.20±0.03	9.60±0.02
EFF	0.45±0.02	0.47±0.02	2.63±0.03	4.40±0.03	1.41±0.01	9.36±0.10
WW	0.20±0.01	0.29±0.01	1.07±0.01	3.44±0.02	1.62±0.01	6.61±0.02
BI	0.40±0.02	0.44±0.02	2.21±0.02	16.76±0.03	0.22±0.01	20.03±0.21
BA	0.46±0.01	0.47±0.01	2.13±0.01	29.55±0.02	0.04±0.01	22.65±0.20
AK	0.85±0.03	0.73±0.02	5.71±0.14	29.69±0.15	0.06±0.01	27.04±0.22
ED	0.25±0.01	0.35±0.01	1.91±0.01	6.74±0.03	1.67±0.01	10.95±0.12

Table 3 revealed, a negative insignificant ($P>0.05$) correlation existed between soluble copper and ECEC. This is associated with increased Cation exchangeable Capacity (CEC) as the pH dependent charges increase. This will lead to precipitation of copper as $\text{Cu}(\text{OH})_2$ and thus decreasing the content of soluble copper in the soils. There was a positive significant ($P<0.05$) correlation between soil pH and water soluble copper. This was expected as the soluble copper under acidic conditions tends to precipitate when pH increases. It is well known fact that soil pH has the greatest influence on the solubility or retention of metals in soils with a greater retention and lower solubility of metal occurring at high soil pH.

It is evident from the result that silt and available phosphorus correlated negatively and Correlation coefficients revealed that the relationship was almost significant. Again N_2 correlated negatively with water soluble copper in the soil but the relationship is not significant ($P>0.05$) and less pronounced than that with phosphorus.

A significant ($P<0.05$) positive correlation existed between water soluble copper and percentage sand.

Table 4. Statistical analysis of soil properties with Copper Level in the soil

Soil properties	Coefficient Correlation	MEAN	STD	P
pH	0.124	6.167	0.9360	$P>0.05$
Sand	0.778	59.294	11.7493	$P<0.05$
Silt	-0.499	16.979	6.5787	$p>0.05$
Clay	-0.626	24.002	9.2422	$P<0.05$
Moisture	-0.478	23.569	7.8330	$P>0.05$
Acidity	0.158	1.526	1.5002	$P>0.05$
Organic C	-0.290	2.252	0.8084	$P>0.05$
ECEC	-0.112	14.416	7.3304	$P>0.05$
%N	-0.251	0.226	0.0812	$P>0.05$
A P(mg kg ⁻¹)	-0.479	18.846	5.1839	$P>0.05$

There was variation in soil characteristics (Table 4). The standard deviation of soil characteristic determined reveal that the extent of variation follows the deceasing order of sand>clay>moisture> ECEC> silt>Phosphorus> acidity>pH>organic Carbon> N_2 . The persistence of copper in these soils would vary, and would therefore depend on the combined effects of the characteristics on their degradation rate.

Table 5. Mean concentration of water soluble copper in soil

Sample Site	Cu mg kg ⁻¹	Sample Site	Cu mg kg ⁻¹
DO	0.39 ± 0.02	EFF	0.23 ± 0.01
TM	0.17 ± 0.01	WW	0.40 ± 0.02
BRA	0.30 ± 0.02	BI	0.20 ± 0.01
AD	0.36 ± 0.05	BA	0.26 ± 0.01
JU	0.29 ± 0.02	AK	0.26 ± 0.01
ED	0.05 ± 0.01		

CONCLUSION

It is possible that after several years copper could accumulate in soil to levels that become toxic to soil microbes and crops. This could slow organic matter decomposition and nutrient cycling in soil (especially conversion of organic nitrogen to plant available nitrogen) and crop production could be reduced because of direct toxic effects of copper on the plants as well as reduced soil fertility [23].

The potential for accumulation of toxic levels of copper in soil is a critical issue because there is no practical way to reverse the problem if it occurs. On the other hand it is a problem that will take many, many years to develop and can easily be avoided. Copper is an essential element for all living organisms so plants and microbes need a constant small supply. All soils naturally contain some copper and it is only when the availability of soil copper becomes too large that toxicity could result [23].

Water soluble copper was detected in all the tropical soils studied with the concentration in the surface soils ranging 0.05 to 0.40mg kg⁻¹ with a mean concentration of 0.265 mg kg⁻¹ (Table 5). Comparatively, copper residue values were higher for farms sprayed with copper fungicides than the farm where no fungicides were applied. Application of the fungicides thus increased the available copper by over three to eight times in the soil.

The result of this research will contribute significantly to the fungicides residue monitoring by the Ghana Environmental Protection Agency. The findings in this study will be a springboard for the study of copper level from cocoa farms in the other regions of Ghana. It also constitutes a significant contribution to the joint FAO/WHO pesticide residue programmes, which recommends strongly that individual countries should provide information on all relevant fungicide data to help the joint FAO/WHO meeting of experts on pesticide residues to make recommendations on the use of copper fungicides against cocoa diseases.

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