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Determination of Levels of Water Soluble Copper Residue in the Topsoils of Some Tiger Nut Growing areas of the Central Region of Ghana

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ABSTRACT

Copper fungicides are extensively used to control leaf necrosis and tuber rot produced by fungi in tiger nut farms. However, information on the levels of copper due to application of copper fungicides are scarce. The levels of water soluble copper of the top soils from eleven preselected tiger nut growing towns from three different districts in the Central Region of Ghana were analysed using atomic absorption spectrometer after the extraction processes. A total of two hundred and twenty top soil samples were taken randomly at a depth of approximately 20cm. Copper fungicides were applied in ten of the farms and the eleventh farm which served as a control had no copper fungicide application. Some physical and chemical properties of the soils were determined. Levels of water-soluble copper in the soils ranged from 0.07 to 0.36 mg kg^{-1} with a mean concentration of 0.229 mg kg^{-1}. Application of copper fungicides increased water soluble copper levels in the top soils between 257 to 514% in the tiger nut farms analysed. 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 but significantly ($P<0.5$) with sand, while negative correlation but insignificantly ($P>0.5$) with silt, organic carbon, cation exchange capacity nitrogen and available phosphorus. An insignificant ($P>0.05$) but positive correlation existed between water soluble copper level and moisture, acidity, pH and soil clay.

Introduction

Tiger nut (Cyperus esculentus L.) belongs to the family cyperaceae and is made up of over 4000 species [1]. It is a monocotyledonous plant with a root tuber and grows up to 90 cm tall. It is an annual plant that grows in wet areas and often occurs as a weed especially on farmlands used for cultivation of vegetables [2].

In Ghana, it is called,"atadwe" by the Fantis and Akwapims 'atadweɛ' by the Akans, "atangme" by the Gas "nansaxa" by the Dagombas and 'fio' by the Ewes. The black and brown varieties are the two main types cultivated in Ghana. The nuts are chewed like sweets, or made into a highly cherished milk like beverage referred to by the Ewes in Ghana as "fio milk". Tiger nuts are crazily consumed by Ghanaian men since they believe the two varieties of the nuts can "recharge their batteries" a term use to describe the aphrodisiac effect of the tiger nut when consumed by men. Nutritionally, the tiger nut tubers contain pretty high fiber content than oats, cabbage, carrot, plums and Chia seeds which help in the prevention of constipation in organisms [2] and also help in the control of body weight, as well act as an appetite suppressant. Because tiger nut has similar lipid profile to olive oil which is considered one of the healthiest oils, cardiologists recommend eating tiger nut to reduce heart related disease. Due to their high amount of amino acids, tiger nuts are quite helpful in controlling the blood pressure of the body. Again many important amino acids and some B-complex vitamins in tiger nuts are quite good for diabetics to regulate blood sugar levels.

Tiger nuts are also used to deal with stomach cramps, irritable bowels and other stomach issues while traditionally, they are used for curing diarrhea, flatulence, dysentery and indigestion [2].

However**,** diseases such as leaf necrosis and tuber rot produced by fungi have been detrimental for tiger nut crop (4, 5, 6). A new syndrome producing black spots in the tuber skin has emerged affecting tubers with severe symptoms (almost or completely black) making them unmarketable and inconsumable and must be discarded with the consequent economical losses for the farmers [7]. To combat the attacks of these fungi diseases on tiger nuts, 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 applied.

Copper is essential for plant nutrition and actively participates in the bio-ecological cycle. However, when its concentration in the soil is high, it may become toxic to plants, animals and humans [16]. Determination of Copper fungicides should be given high attention because any hazardous residues left can cause lasting danger to quality of tiger nuts and its products, the environment and consumers' health. A critical issue is that because there is no practical way to reverse the problem of accumulation of toxic levels of copper in the soil if it occurs, hence the tendency for its accumulation should be avoided [3]. On the other hand it is problem that will take many, many years to develop and can easily be avoided.

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Materials and Methods

Sampling Technique

The areas of study were randomly sampled to select the tiger nut farming communities and farms where copper fungicides were applied. Soils samples were collected from Assassin (A), Besease (B) and Kokoben (C) all in the Ajumako/Enyan/Essiam District, Ampenyi (D), Brenue Ayinim (E), Eguafo (F) and Abrem Agona (G) all in the Komenda/Edina/Eguafo/Abirem Municipal District, New Edu (H), Old Edu (I), New Odonase(J), and Nyamedom (K) all in the Abura/Asebu/Kwamankese District,

In all eleven tiger nut farms in different villages/towns from three different districts in Central Region were analysed. In Nyamedom (K) the eleventh sample site and the fourth in the Abura/Asebu/Kwamankese District, no copper fungicide was applied in the tiger nut farm. The composite soil samples were obtained randomly at a depth between 0-20 cm with a soil auger [3]. The composite soil sampled consisted of 5-10 cores each depending on the farm size which ranged from 05-2.0 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

The soils were digested using the method described by MAFF (1981). Soil samples were air-dried and passed through 2 mm mesh.1g of each of the homogenized samples of soils were put into a 100 ml beaker and 10 ml of concentrated HNO_3 added. The mixture was heated until it almost dried. Further 10 ml of HNO_3 and 3 ml of $HClO_4$ were added and the solution heated and then allowed to evaporate to about 1-2 ml. 4ml of hot concentrated HCl was placed into a labeled plastic polyethylene bags for laboratory analysis was added and then reflux for 10 minutes. Finally, the wall of the beaker was wash down with double distilled water, filtered into a 50 ml volumetric flask, and diluted to the 50 ml mark. All the digests and the blank solutions were analyzed for Copper with an atomic absorption spectrometer (Spectra AA 220Fs, Varian). All experiments were carried out in duplicate [8].

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 [9]. Total carbon and organic matter were determined by wet combustion [10]. Flame photometer was used to determine exchangeable potassium while atomic absorption spectrophotometer was used to determine calcium and magnesium after extraction with 1.0M ammonium acetate [11].Total N was determined by the Kjeldahl digestion [12]. Soil available P was extracted with HCl: NH_3F mixture method [13]. Mechanical analysis was by the pipette method [14].

Results and Discussion

From Table1, the analysis of the particle size distribution of the soils disclosed that the soils texture range from clay loam to sandy clay loam similar to what was observed from the cocoa farms analysed by Koka et al [3]. Approximately 55% of total number of soils analysed are sandy clay loan in texture while 27% represent clay loam and sandy loam constitutes 18%.The sand contents of the soils from the farms analysed lie between 36.32 % and 71.78% while silt contents ranged from 8.64% and 28.38%; with the clay contents ranging from 9.90% and 48.54%. Soils from A, B, D, F, H and I were sandy clay loam because of their high sand contents and moderately high clay contents while soils from J and K, were sandy loamy because of their high sand content and very low clay. The soils from C, E, and G are clay loam with moderately high clay content [3]. The soil moisture content is moderately high ranging between 10.62% and 43.20% this implies that the dissolution of the copper fungicides would be favoured since all the applied fungicides were water soluble.

Table 2.0 revealed that the soils contain low amounts of organic carbon ranging from 1.10 to 3.22 %. There is a direct relationship between the organic carbon content and the clay contents in soils. With increasing clay and organic carbon contents of the soil the prediction is that copper fungicide adsorption would increase, consequently copper fungicide will persevere for longer duration of time [3]. However, the low organic carbon/organic matter contents and the high sand contents of the soils are indications that the tendency of such soils to adsorb fungicides would be low **[**15].

Table 1. Soil characteristics.

Soil Sample	Sand %	Silt %	Clay %	Moisture %	Texture
A	58.38 ± 0.10	16.34 ± 0.20	25.28 ± 0.20	20.40 ± 0.10	Sandy Clay Loam
B	51.52 ± 0.10	17.32 ± 0.20	31.16 ± 0.20	29.20 ± 0.20	Sandy Clay Loam
C	42.82 ± 0.25	8.64 ± 0.20	48.54± 0.15	28.30 ± 0.1 0	Clay Loam
D	64.70 ± 0.15	9.68 ± 0.30	25.62 ± 0.02	20.40 ± 0.20	Sandy Clay Loam
E	36.32 ± 0.20	28.38 ± 0.10	35.30 ± 0.30	24.40 ± 0.20	Clay Loam
F	61.20 ± 0.30	17.56 ± 0.10	21.24 ± 0.20	17.60 ± 0.10	Sandy Clay Loam
G	44.30 ± 0.10	20.30 ± 0.10	35.40 ± 0.20	43.20 ± 0.20	Clay Loam
H	59.16 ± 0.30	18.40 ± 0.50	22.44 ± 0.30	24.20 ± 0.23	Sandy Clay Loam
I	57.76 ± 0.20	15.40 ± 0.20	26.84 ± 0.10	28.40 ± 0.20	Sandy Clay Loam
J	71.78 ± 0.10	18.32 ± 0.10	9.90 ± 0.10	10.62 ± 0.20	Sandy Loam
K	60.62 ± 0.30	28.32 ± 0.20	11.06 ± 0.03	15.84 ± 0.12	Sandy Loam

Table 2. Chemical Properties of the Soil.

Soil Sample	pH	%N	Available P(mgkg-1)	% OC
A	5.40±0.10	0.25±0.01	15.30±0.20	1.60±0.10
B	5.73±0.18	0.20±0.02	10.40±0.30	1.65±0.20
C	6.72±0.04	0.30±0.03	16.21±0.20	2.90±0.30
D	6.49±0.03	0.20±0.02	14.60±0.26	2.84±0.10
E	5.80±0.02	0.22±0.03	15.45±0.30	1.10±0.20
F	6.28±0.05	0.18±0.02	24.50±0.50	2.40±0.20
G	6.40±0.02	0.15±0.03	17.30±0.30	1.56±0.12
H	7.42±0.10	0.29±0.01	26.40±0.20	2.76±0.10
I	7.15±0.06	0.26±0.20	21.10±0.20	2.50±0.10
J	7.76±0.12	0.42±0.04	25.47±0.20	2.82±0.10
K	5.65±0.06	0.25±0.01	23.30±0.21	3.22±0.10

The pH of the soils ranged from slightly acidic to slightly alkaline Soils from A, B, D, E, F, G and K are slightly acidic (5.00<pH<6.50) whiles soils from C and I could be considered neutral (pH approximately7). Soils from H and J are slightly alkaline (pH>7). The available phosphorus concentration in the soils analysed ranged between10.40 to 26.40 mg kg^{-1} while nitrogen analysed ranged between 0.15 to 0.42%.

Generally effective cation exchange capacity (ECEC) values predict the activity of the soil clays. ECEC values greater soil 10 Cmolc kg^{-1} are considered as high activity clays while soils with ECEC values less than 10Cmolc kg^{-1} are considered as low activity clay [3]. Table 3 therefore revealed that soils from A, B, E and G could be said to be low activity soils while soils C, D, F, H, I, J and K with high ECEC values are said to be high activity clays.

The high ECEC of the soils studied could be attributed to their high exchangeable bases. The ash produced from the periodic burning of dried leaves from these farms contained K^+, Na^+, Ca^{+2} and Mg^{+2}, which cause a decrease in acidity due to increase in the exchangeable bases. The exchangeable cation is dominated by Ca^{+2}, which occupied approximately 76.5 % of the ECEC followed, by Mg^{+2} contributing about 18% of the total ECEC while K^+ and Na^+ contributed 3% and 2.5% respectively.

Table 4 revealed an insignificant (P>0.05) negative correlation between soluble copper and ECEC this could be attributed to increase in Cation exchangeable Capacity (CEC) as the pH dependent charges increase. The implication is that copper will precipitate in the form of $Cu(OH)_2$ hindering the dissolution of the copper fungicide in the soil hence decreasing the available soluble copper content in the soils. Therefore fungicide will persist for a long time in the soil with long term accumulation side effects. The solubility or retention of copper in soils is pH dependent the higher the pH the greater retention and lower the solubility of the copper fungicide. An insignificant (P>0.05) but positive correlation between soil pH and water soluble copper was observed and this was not unexpected since acidic conditions tend to enhance dissolution of the copper while increasing pH tends to precipitate the metal [3].

The results demonstrated that a significant (P<0.05) but negative correlation existed between water soluble copper and sand. However, an insignificant (P>0.05) but negative correlation existed between water soluble copper and silt, nitrogen and available phosphorus. The order of downhill linear relationship increasing strength follows sand<available phosphorus <nitrogen<silt.

An insignificant (P>0.05) but positive correlation relationship was observed between water soluble copper and soil clay content while an insignificant (P>0.05) but negative correlation relationship was observed between water soluble copper and organic carbon in the soil. These trends of lack of significant could be attributed to several factors namely, the distribution of active ingredient of a fungicide in the soil obviously depends on the mode of formulation. Application of copper fungicide to the soil at an average dose of 3kg/ha may not saturate the surface area of the soil colloids in the top 20 cm of soil sampled. Secondly, the low activity clay of the soils, which are commonly encountered in semi deciduous rainfall zones in the tropics possibly due to instability of the complexes as a result of dissociation could be a factor. Thirdly, the moderately high clay content has inhibitory effect on the degradation of some compounds [3]. The inhibitory effect is attributed to adsorption of compounds by clay minerals, especially smectite, rendering them less vulnerable to microbial attack. Moreover, the extraction method applied may not be effective enough to remove the copper fungicides which may be bound so strongly to the clay. Furthermore, the possibility of copper fungicides leaching to a depth beyond the level sampled could result in the trend of observations encountered [3]. Finally, due to financial constrain some farmers dilute the copper fungicide beyond the recommended concentration leading to the low availability of soluble copper fungicide in the soils.

Table 4 revealed that there was variation in soil characteristics. However, the standard deviation of soil determined revealed the persistence of copper in these soils would vary and the degradation rate of the soils analysed would therefore depend on the combined effects of the soil characteristics studied [3].

Table 3. Exchangeable Cations Levels of the S oil.

Soil Sample	Exchangeable Cations (C mole kg-1)				Ea C mole Kg^{-1}	ECEC $CmoleKg^{-1}$
	K^+	Na^+	Mg^{+2}	Ca^{+2}		
A	0.20±0.01	0.42±0.01	2.40±0.10	3.80±0.01	2.24±0.10	9.80 ±0.10
B	0.16±0.02	0.35±0.02	1.35±0.10	4.55±0.02	1.26±0.20	7.60±0.10
C	0.60±0.02	0.53±0.02	3.75±0.20	14.60±0.01	0.40±0 .02	24.20±0.20
D	0.24±0.01	0.69±0.01	2.40±0.10	7.60±0.02	5.80±0.01	14.80±0.40
E	0.41±0.03	0.55±0.02	2.30±0.10	6.60±0.04	6.20±0.02	8.60±0.20
F	0.55±0.02	0.49±0.02	3.43±0.20	4.50±0.03	4.46±0.02	10.30±0.20
G	0.30±0.01	0.25±0.03	1.27±0.10	5.40±0.02	2.64±0.20	6.74±0.02
H	0.50±0.02	0.43±0.01	2.61±0.20	18.80±0.03	0.42±0.02	21.40±0.20
I	0.36±0.01	0.45±0.02	2.73±0.10	25.40±0.02	0.10±0.01	20.70±0.22
J	0.65±0.01	0.74±0.02	4.80±0.20	30.54±0.15	0.08±0.01	28.40±0.24
K	0.35±0.02	0.36±0.02	2.91±0.10	8.70±0.03	2.60±0.02	12.90±0.10

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

Soil properties	Coefficient Correlation	MEAN	STD	P
pH	0.1425	6.436364	0.770341	P>0.05
Sand	-0.0192	55.32364	10.51082	P<0.05
Silt	-0.4313	18.06000	6.219029	p>0.05
Clay	0.2606	26.61636	11.06554	P<0.05
Moisture	0.2367	22.68727	7.297563	P>0.05
Acidity	0.2600	2.62000	1.642000	P>0.05
Organic C	-0.2700	2.304545	0.702131	P>0.05
ECEC	-0.1644	15.04000	7.450906	P>0.05
%N	-0.2616	0.247273	0.073361	P>0.05
A P(mg kg -1)	-0.2258	19.09364	5.291135	P>0.05

The increasing order of the standard deviation of soil characteristic follows as N_2<organic Carbon<pH<acidity <Phosphorus<silt<ECEC<moisture <clay<sand.

Table 5. Mean Concentration of Water Soluble Copper in Soil.

Sample Site	Cu mg kg^{-1}	Sample Site	Cu mg kg-1
A	0.30 ± 0.02	E	0.24 ± 0.01
B	0.18 ± 0.01	F	0.36 ± 0.02
C	0.20 ± 0.02	G	0.21 ± 0.01
D	0.30 ± 0.05	H	0.22 ± 0.01
E	0.20 ± 0.02	I	0.24 ± 0.01
K	0.07 ± 0.01		

Conclusion

Table 5 revealed that water soluble copper was detected in all the tropical soils studied with the concentration in the surface soils ranging 0.07 to 0.36 mg kg^{-1} with a mean concentration of 0.225 mg kg^{-1}. Copper levels in the soils of tiger nut farms where copper fungicides applied ranged between 0.18 and 0.36 mg kg^{-1} while the level of copper in the farm where no copper was applied was 0.07mg kg^{-1}. Application of copper fungicides increased water soluble copper levels in the top soils between 257 to 514% of the farms analysed. Copper accumulation in soil to levels that become toxic to soil microbes and crops is possible in the long term. The implication is that organic matter decomposition and nutrient cycling in soil (especially conversion of organic nitrogen to plant available nitrogen) could slow down. Hence crop production could be reduced because of direct toxic effects of copper on the plants as well as reduced soil fertility [17].

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