

Fungicide-Derived Copper Content in Soil and Vegetation Component, Owena Cocoa (*Theobroma Cacao* L.) Plantations in Nigeria

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Abstract

This work reported the results of copper content in the soil profiles of three different aged cocoa plantations subjected to copper- fungicide application and the various vegetational components (pod, beans, leaves, trunk bark, lateral root and twig). Soil copper at various depth considered ranged from 5.0 -42.0 μgg^{-1} . Copper contents in both fresh and dry leaves of cocoa and banana were consistently high in all the three plantations. The copper contents ranged from 56-300 μgg^{-1} (dry wt.) in cocoa trunk bark and 86-161 μgg^{-1} in banana trunk bark. There was evidence of age-dependent accumulation of copper in cocoa pod and beans; hence it can be used to assess the degree of copper contamination. Copper contents from roots ranged from 408-2, 203 μgg^{-1} (dry wt.). The soil did not appear contaminated by copper but alternative fungicide is recommended since copper accumulation in the cocoa beans was evident.

Introduction

Copper fungicides are successfully employed in the control of plant pathogens from each of the three classes of fungi (Phycomycetes, Ascomycetes and Basidiomycetes) and many of those which are classified as fungi imperfect.¹ In the tropics, farmers employ copper fungicide in their control of various tree crop diseases such as anthracnose of mango (*Colleterichium gloeosporioides*), black pod of cocoa (*Phytophthora palmivora*), sigatoka of banana (*Mycosphaerella musicola*), blister blight of tea (*Exobasidium vexans*), coffee

leaf rust (*Hemileia vastatrix*), brown pod of citrus (*Phytophthora sp.*) and guava rust (*Puccinia psidii*).²⁻⁴

Phytotoxic effect of copper has been known since the 19th century from spraying of Bordeaux mixture in French vineyards.⁵ The fungitoxic component of all copper fungicides is the copper ion (Cu^{2+}) which is also potentially phytotoxic at elevated concentrations in the soils. Its continual application is being questioned because of this detrimental

environmental effects.^{6,7} After foliar application of copper fungicides, a gradual redistribution of deposits by the weathering effect (rainfall and dew) may occur. Some are taken up by plant cells, while most redistribution occurs in downward direction and ultimately end up in litter and soils.¹ This in turn redistributes itself within the soil profiles. However, there is no evidence of copper accumulation at depth below about 25cm of the soil profile which might be due to copper's strong affinity for organic matter, thus tending to dominate its interaction with surface soils, litter and vegetation.⁸⁻¹³ Copper phytotoxicity may not be easily noticed in coffee and cocoa plants, since they can tolerate copper contamination of the soil to a greater extent than many other plants. It was reported for Costa Rican banana plantation under copper fungicide fumigation for two decades that chlorosis was prevalent in rice plants grown in replacement in the area after ten years of abandonment.⁵

The distribution levels and effects of fungicide-derived copper in soils, coffee (*Coffea arabica* L.) and grape (*Vitis vinifera*) plants have been reported in literature.^{8,10,14-18} In Nigeria, some workers have reported copper content of some selected soils.^{19,20} However, little attention has so far been paid to the extent to which copper has accumulated in Nigerian cocoa plantation soils, vegetation and beans.

This is of concern because of the waning interest in cocoa cultivation in many parts of Nigeria and the plausible effect of accumulated copper on the replacement crops in the light of its phytotoxicity. Also the elevated contents of copper in feed and food plants that reflect man-made pollution need evaluation from the environmental health point of view. Thus the objectives of the present study were to determine the copper accumulation pattern within the soil profile, various components in cocoa plantation and its effect on cocoa bean quality from an average of 24 years old cocoa plantation placed under regular copper fungicide fumigation programme.

Materials and Methods

The field surveys were carried out in Cocoa Research Institute of Nigeria (CRIN) located at Owena, one of the cocoa growing areas in the country in 2001. The plantation was established on an undulating land of about 52 hectares. Foliar application of copper fungicide begins in June and ends in August yearly (this is however subjected to variation in precipitation pattern). Currently the plantations considered are being placed on a programme of 6-7 sprays/annum at the rate of 50kg/hectare at about 21 days interval.

Samples were collected from three plantations established in 1973 (PL-A), 1974 (PL-B) and 1975 (PL-C). An additional sam-

ple was obtained from unfumigated adjacent banana plantation (PL-D) which serves as background reference for the other three studied plantations. Soil samples were collected from 0-3, 3-10, 10-20, 20-30 and 30-40 cm depth increments by manual coring before the yearly fumigation programme commenced. This sampling scheme was replicated in five places in each of the four locations. In each location, a composite sample of each depth increment was conveyed in polythene bags to the laboratory. Soil samples were air dried and ground to pass 850 μ m stainless steel sieve.

Plant materials (plant barks, leaves, roots, twig and cocoa pod) were collected (randomly) at five different points in each plantation, pooled and a composite of each was bagged. All leaves and root samples were washed in distilled water and over-dried prior to analyses.

2g of soil sample was placed in a beaker and the copper content was extracted by adding 15ml of 50 % HNO₃ and placed on a hot plate with a watch glass cover and heated at 95^o C for 15 min. This heating was later continued with partial covering without boiling till the solution got reduced to about 5ml and cooled. 2ml of distilled water and 3ml of 30 % H₂O₂ were then added and heated gently to start the peroxide reaction. This was followed by the addition of 5ml concentrated HCl, 10 ml distilled water and refluxed again for 15min

without boiling. After cooling, the solution was filtered and the filtrate quantitatively transferred into a 50ml volumetric flask and brought to volume with distilled water.²¹ A blank sample was also treated in the same way. Samples were analyzed for Cu using atomic absorption spectroscopy (Buck Scientific 200 AA model).

Plant materials were charred with concentrated H₂SO₄ and oxidations of plant tissues were accomplished by H₂O₂ addition.²² Samples were analysed for Cu after appropriate dilution by atomic absorption spectroscopy (Buck Scientific 200 AA model). All determinations were made on homogenized composite sub-samples.

Result and Discussion

The profiles of the three plantations (PL-A, PL-B and PL-C) showed similarity with respect to their copper distributions (Figs. I-III). The highest concentration occurred at the surface soil and diminished with depth except in plantation A, which showed a little accumulation at the sub-surface level (30-40 cm). The ranges of copper concentration within plantation PL-A, PL-B and PL-C are 5.0 -42.0; 6.0 - 15.0 and 9.0 - 20.0 μ gg⁻¹ respectively. The corresponding mean values were 16.5, 10.1 and 12.4 μ gg⁻¹ respectively. This was compared with the unfumigated control plot ranging from 11.5 - 17.0 μ gg⁻¹ with a mean value of 15.4 μ gg⁻¹ (Fig. IV).

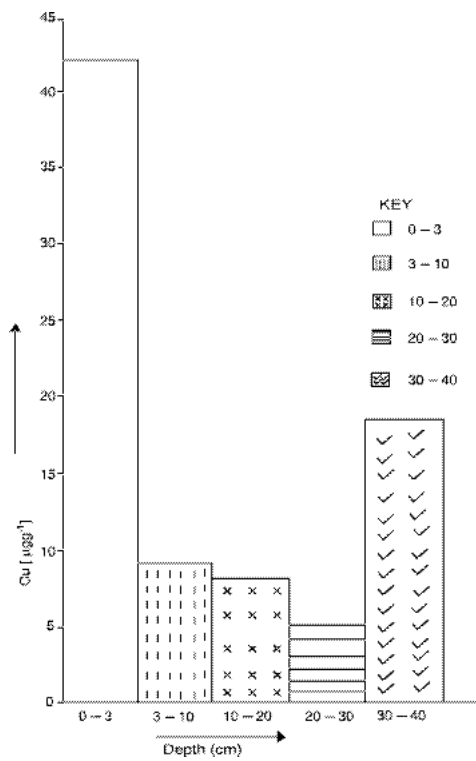


Fig. 1. Mean concentration of copper [μgg^{-1}] in the soil profiles of plantation. A (PL - A)

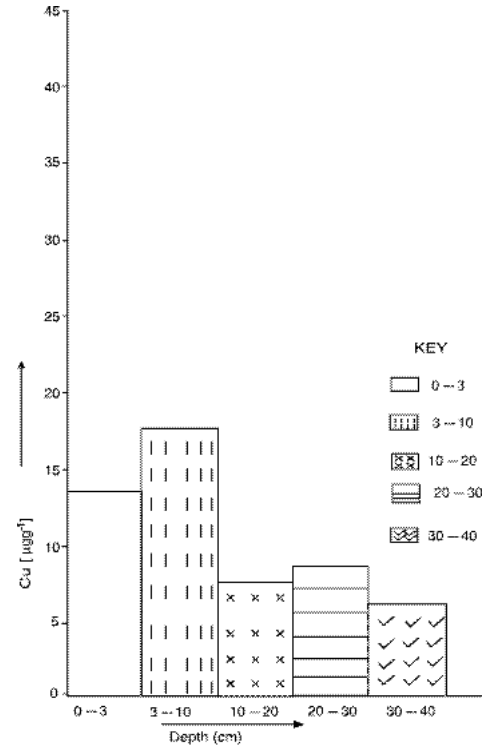


Fig. 2. Mean concentration of copper [μgg^{-1}] in the soil profiles of plantation. B (PL - B)

These values are also within the range reported in literature, Udo *et al.* reported a range of 7-12ppm for selected sandy soils and podzols and 21- 41ppm for loess and silty soils.²⁰ Osiname *et al.* obtained a range of 3-19mg/kg and a mean value of 11.1mg/kg for some Western Nigerian surface soil; and Eastern China Coastal Plain grape plantation (Table III) but lower than the range reported for Kenya Coffee Plantation; Australian orchard soil (Table III)

and West Germany soil with a range of 273- 522 mg/kg.^{19,23} Table I shows the soil Cu enrichment factor based on the background reference soil copper (PL-D) and the world soil copper average. The enrichment was generally lower than 1.0 from either standards. This suggests that no major contamination has occurred in the soil profile resulting from the use of Cu-based fungicide in PL-A, PL-B and PL-C, since a soil may not be considered contaminated if

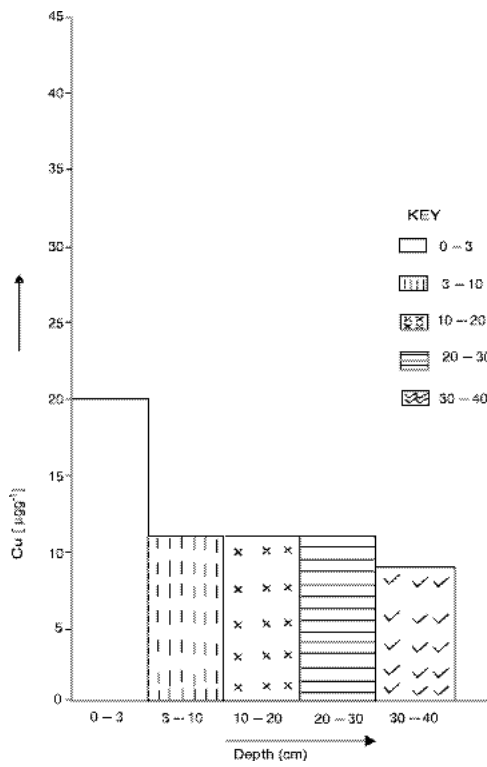


Fig. 3. Mean concentration of copper [$\mu\text{g g}^{-1}$] in the soil profiles of plantation. C (PL - C)

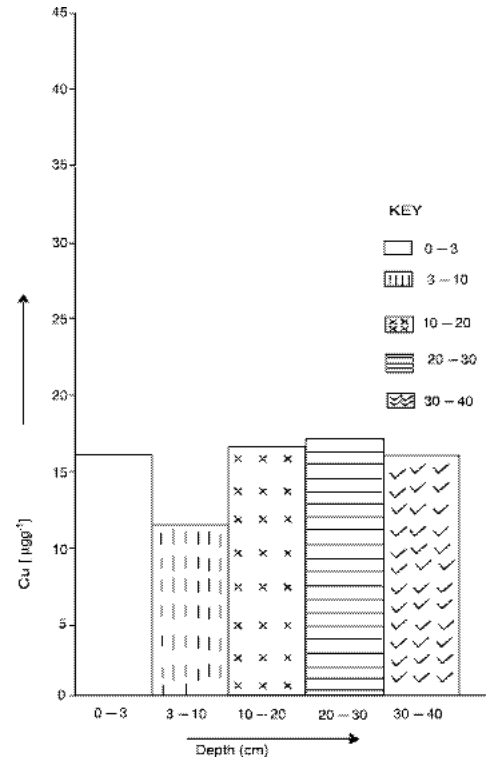


Fig. 4. Mean concentration of copper [$\mu\text{g g}^{-1}$] in the soil profiles of plantation. D (PL - D)

Table I. Soil copper enrichment factors

Depth in profile (cm)	PL-A ^a	PL-A ^b	PL-B ^a	PL-B ^b	PL-C ^a	PL-C ^b
0-3	2.6	2.1	0.8	0.7	1.2	1.0
3-10	0.8	0.4	1.3	0.8	1.0	0.6
10-20	0.5	0.4	0.4	0.4	0.7	0.6
20-30	0.3	0.2	0.5	0.4	0.6	0.6
30-40	1.2	0.9	0.4	0.3	0.6	0.4

a = Enrichment factor calculated, based on obtained at each depth increment in the porfile of unfumigated site (PL - D).

b = Enrichment factor calculated, based on the World Soil - Cu average.³³

concentrations of element in soil are not up to two or three fold greater than the mean of background levels.^{24,25} However, there is a slight accumulation of copper in the surface soils (0-10cm), particularly in PL-A. This is also in consistent with the study of Frank *et al.* who reported that the orchard and vineyard surface soils at Ontario were only slightly raised by the application of copper fungicide over a period of 80 years.²⁶ This may be due to the presence of more organic matter on surface soils which possess high complexing ability with copper, which makes it resistant to leaching and thus long residence time.²⁷

For the purpose of statistical analysis, the figures were treated as blocks while the depths were the treatments (trt.). However, both the blocks and treatment were not significantly different at a confidence level of $p < 0.05$. On

the other hand in Table I, the depth was the block while column was the treatment part; while the depth was significantly different, the plantation copper enrichment factors (blocks) were not significantly different from each other at $p < 0.05$.

The copper contents of the plantations' vegetational components are presented in Table II. The data are given for both cocoa (*Theobroma cacao* L.) and banana (*Musa sapientum* L.) plant parts found in the various plantations since both are commonly grown together in Africa.

Copper contents of both fresh and dry matured leaves of cocoa were consistently high in all the three plantations. Banana leaves found in the various plantations were correspondingly high too, though cocoa

Table II. Copper concentration ($\mu\text{g g}^{-1}$ dry weight) in the various vegetational components

Plant component	PL-A	PL-B	PL-C	PL-D	Mean ^c
Cocoa components					
Pod	240	224	119	NCA	194
Cocoa beans	642	257	104	NCA	334
Mature green leaves	360	1435	190	NCA	662
Mature dry (brown) leaves	281	129	225	NCA	211
Trunk bark	138	300	56	NCA	164
Lateral root	408	2203	2071	NCA	1561
Twig	60	180	227	NCA	156
Banana components					
Mature green leaves	148	286	50	46	161
Trunk bark	161	1554	86	46	600

c = Calculated mean for PL-A, PL-B and PL-C, NCA = Component not available

foliage had more copper than the corresponding banana in the same plantation (Table II). This may be expected since different plant species have different tendencies of accumulating copper in their tissues.²⁸ Also fungicide was not applied directly on banana plants but it receives only as aerosol. The copper present in the foliage of the three plantations (except banana components and cocoa trunk bark in PL-C) are more than 3 times higher than those found at the unfumigated site (PL-D). Copper in cocoa leaves is higher than the range reported for replacement pasture in Australian orchard and Kenyan coffee but lower than that of Chinese grape.²³ Copper contents in cocoa and banana trunk barks were also higher than the banana trunk bark at the unfumigated site. Copper concentration in cocoa and banana trunk bark ranged from 56-300 $\mu\text{g g}^{-1}$ (dry wt.) and 86-161 $\mu\text{g g}^{-1}$ (dry wt.) respectively at the fumigated sites. These values were within the range (97-415 $\mu\text{g g}^{-1}$) quoted by Lepp *et al.* for coffee (*Coffea arabica* L.) plant in Kenya. Twig copper mean content ranged from 60-227 $\mu\text{g g}^{-1}$ (dry wt.), this is also in a close range with the range for Kenya coffee twig. (Table III).¹⁰

Age dependent accumulation of copper in cocoa pod is evident, thus it can be used to assess the degree of contamination. Copper concentration in the lateral roots obtained

from various plantations were consistently high, it ranged from 408-2, 203 $\mu\text{g g}^{-1}$ (dry wt.), this is much higher than the range (46- 33 $\mu\text{g g}^{-1}$) (dry wt.) quoted for Kenya coffee roots.¹⁰ Out of all the cocoa plant components considered, the roots were observed to possess the highest sink for copper in all the various plantations. This might be due to the reported strong capability of root tissue to absorb and hold copper against transportation to shoot under conditions of both excessive and deficient copper.²⁸ The results showed that the average copper content in the trunk bark, foliage and root was 10, 23 and 104 times higher than the copper content in soil respectively. Thus the copper content in plant parts may not solely be a function of plant uptake. According to Hogan and Wotton, the amount of metals in foliage did not imply explicitly that foliar levels of metal were a direct result of concentrations present in the soil.²⁹ This was further buttressed by Hughes *et al.*, who reported that direct xylem transport following roots absorption was not the only route of metal transfer to the foliage.³⁰ There are two other possible routes : (a) absorption across the bark and translocation to the foliage by xylem or phloem and (b) deposition onto the foliage and subsequent incorporation into the body of the leaf. These last two possibilities may likely play a major role in the incorporation of fungicides. The differences in the

Table III. Ranger of copper (μgg^{-1}) in cocoa plantation soil and vegetation with comparison data of plantations from other sources under copper-fumigation

	Cocoa plantation (this study)		Comparison data		
	No. of samples	Range	Orchard ^d	Coffee plantation ^e	Grape plantation ^f
Soil					
Surface soil (0-20cm)	12	7.5 - 42.0	25 - 270	24.5-136.06	2.64-34.20
Sub-surface soil (20-40cm)	6	5.0-18.5	2 - 60	15.95-56.6	1.36-6.00
Selected vegetational components					
Foliage	6	122-1444	3.6-10.5g	103.92-129.08	753-9845
Twigs	3	58-236	DNA	100.82-220.44	DNA
Crops	3	84-646 ^h	DNA	17.6 ⁱ	0.33-1.71 ^j

d = Range of Cu concentration in Australia orchard soil and plant.

e = Range of Cu concentration in Kenya coffee. *Coffea arabica* L. plantation.¹⁰

f = Range of Cu concentration in Chinese grape, *Vitis vinifera* plantation.⁸

g = Range of Cu concentration in replacement pasture.

h = Range of Cu concentrations in *Theobroma cacao* L. beans.

i = Range of Cu concentrations in *C. arabica* L. bean.³⁴

j = Range of Cu concentration in *V. vinifera* pulp.

DNA = Date not available.

root, stem bark, pod and foliage copper were due to the fact that copper tends to be immobile within the plant.³¹

Age-dependent accumulation of copper was evident in the cocoa beans (Table II) thus the duration of routine copper fungicide applica-

tion may be a major determinant of their extent of contamination. It ranged from 104-642 μgg^{-1} (dry wt.). This is much higher than the grape pulp and coffee bean of 68 years old coffee bush (Table III). The high copper content in these beans may reduce its food quality since the Food Standard

Committee (FSC) recommendation is 2 ppm for most ready to drink beverages and the general limit of 20ppm for most other foods.³² It is noted here that while significant differences existed in copper concentration in the cocoa parts, no significance difference existed in the banana components at $p < 0.05$.

Conclusion

The copper concentration in the soil profiles fell within the proposed Maximum Acceptable Concentration (MAC) of the trace element in agricultural soils. Thus, plantations where the spraying rate is kept at this level, the envisaged problem of phytotoxicity by most subsistence farmers may not be encountered by their shallow rooted replacement crops.

However, copper content of the vegetation component were very high and may reduce yield. Continual use of copper fungicide appears to impair the food quality of cocoa beans, hence, this call for the use of alternative fungicide in the control of fungi in cocoa plantation. Also the use of cocoa leaves as food wrapper in the local areas may not be safe for human health, particularly if unwashed before use.

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