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Heavy Metals Contamination in Fungicide Treated Cocoa Plantations in Cross River State, Nigeria

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Abstract: *Phytophtora* pod rot is currently the most important limiting factor in the Nigeria Cocoa Industry with a total annual loses estimated at up to 30% - 90% of the total global crop loss. In order to combat the ravages caused by *Phytophtora megakarya* and *P. palmivora*, application of copper- based fungicide is generally the most reliable and popular with Nigerian farmers. Unfortunately, it has been established that only 15% of applied fungicides gets to the target while the remaining 85% end up in the soil. The contents of five elements (Cu, Zn, Pb, Cd and Fe) were assayed in Cocoa plantations across Boki-biakwan, Yahunde,Okundi, Bendege, Efraya, Grassfield Efraya 3--corner and Efraya strabag all in Cross River State. The contamination of the soils was assessed on the basis of geoaccumulation index, enrichment factor, contamination factor, metal contamination index and pollution load index. The obtained results revealed that all the studied cocoa plantations are contaminated with copper while the rest heavy metals are most likely to be from natural sources. However, the PLI values confirmed that the quality of the cocoa soils studied is deteriorating and this may have severe impact on soil biodiversity and ground water.

Key words: Cocoa · Nigeria · Heavy metal contamination · Enrichment factor

INTRODUCTION

Agriculture in Nigeria economy has contributed immensely to rural development, Industrial material, food security and non- oil foreign exchange earnings. Nigeria is currently the fourth largest producer of Cocoa (*Theobroma cacao*) with 190 metric tones in 2008. Cocoa is a crop of economic importance with more than 650,000 ha being cultivated in Nigeria [1]. It ranked first amongst agricultural export crops in its contribution to foreign earnings [2]. General and localized study have identified that the greatest factor responsible for the dwindling of cocoa production level in Nigeria is the ravages caused by black pod disease caused by *Phytophthora palmivora* and *P. mergakaya*. The major economic loss is from the infection of the pods which in turn affect the quality of the beans within the pods. Nigerian cocoa farmers make use of copper based fungicide which is believed to be the fastest and most reliable means of arresting the situation. The incidence of black pod disease is an annual occurrence and the degree of prevalence depends on the rate of precipitation and humidity. This naturally calls for annual application of copper based fungicide if the farmers must make harvest of cocoa pods at the end of the year. In other words, an average Nigerian cocoa farmers apply cu-based fungicide at least eight times in a year. The implication of this act is the accumulation of copper which is a heavy metal in the soil. Pollution of the natural environment by heavy metals is a worldwide problem because these metals are indestructible and most of them have toxic effects on living organisms [3]. Heavy metals are of high ecological significance since they are not removed from soil as a result of self purification, but accumulate in reservoirs and enter the food chain [4].

There is increase awareness that heavy metals, present in soil may have negative consequences on human health and on the environment [5, 6]. From the environmental point of view, all heavy metals are largely immobile in the soil system, so they tend to accumulate and persist in agricultural soils for a long time. The most frequently reported heavy metals with regards to potential hazards and the occurrence in contaminated soils are Cd, Cr, Pb, Zn and Cu [7]. The concentration of these toxic

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elements in soils may be derived from various sources including anthropogenic pollution, weathering of natural high background rocks and metal deposits [8]. At present, relatively little data are available on the extent of environmental pollution as a consequence of heavy metal- based fungicides used on Cocoa.

The study area covered the major cocoa producing areas of Ondo State which is the highest cocoa producing state in Nigeria. Most of cocoa farmers within this state use copper based fungicide for the control of black pod disease. Therefore, high levels of heavy metals might have been released into the soil environment as a result of the long term application of fungicides. It is therefore necessary to carry out an assessment of heavy metals contamination levels in soils under cocoa plantations in these major cocoa producing areas, because heavy metals, which are potentially harmful to human health, persists for a long time. In addition, the study will provide baseline information on the anthropogenic impact of environmental pollution from heavy metals on cocoa plantation more so, that these metals can be hazardous when they enter into food chain in a high concentration that can be toxic to man and animals.

MATERIALS AND METHODS

The soil samples were collected from Boki-biakwan, Yahunde, Okundi, Bendege, Efraya, Grassfield Efraya 3-corner and Efraya strabag The sampling sites were selected in order to cover the major cocoa producing areas in Cross river State. Most of the cocoa farms in the state were less than thirty years in age. Soils samples were taken with soil auger at a depth of 0-30cm. Twenty-five samples were collected in a hectare and composite samples were made from the individual soil samples. Control (background) soil samples were collected from uncultivated adjacent forests to the cocoa farms. The soil samples were air dried and sieved with a 2mm sieve.

Portion of samples were leached with 1N ammonium acetate. The leachate was analyzed for exchangeable cations (Ca^{2+}, Mg^{2+}, K^+ and Na^+) determination [9, 10]. Soils were analyzed for particle size by the Boyocous hydrometer method soil pH was measured with glass electrodes in 1:2.5 soil-water suspensions. The organic carbon was determined using Walkley and Black method [11]. Total Nitrogen was determined by the Macro Kjedahl method [12] Available Phosphorus was determined according to [13]. Another portion (1g) of the soil sample for heavy metal analysis was extracted with 10ml of 0.1N HCl. The extracts were analyzed for Cu, Pb, Zn, Cd and Fe using air/acetylene atomic absorption spectrophotometer (Unican 929 Model).

Anthropogenic Contamination Factor (CF) and degree of Contamination (Cdeg): These are quantification of the degree of contamination as single-metal index (CF) and as overall degree of contamination (C deg). The measure is relative to either average crustal composition of the respective metal or to a measured background values from a geologically pristine/uncontaminated area.

$$CF = \frac{Cm}{Bm}$$

$$C\ deg = \Sigma\left(\frac{Cm}{Bm}\right)i$$

Where:

i. represents the respective metals (i.e. Cu, Pb, Zn, Cd), Cm is the measured concentration in soil while Bm is the background (adjacent forest) concentration value of metal (m) within the area of study. For the C deg, Hakanson recognized four descriptive classes [14], with values of < 8 to > 32 whereby C deg < 8 implies low degree of contamination.

$C_{deg} < 8$	Low degree of contamination
$8 \leq C_{deg} < 16$	Moderate degree of contamination
$16 \leq C_{deg} < 32$	Considerable degree of contamination
$32 \leq C_{deg}$	Very high degree of contamination

Element contamination index (ECI) and overall metal contamination index (MCI) are expression of single metal contamination within a sample or combined metal contamination for a sample relative to the background values of the respective metal and are expressed as:

$$ECI = \left(\frac{Cm - Bm}{Bm}\right)$$

$$MCI = \Sigma\left(\frac{Cm - Bm}{Bm}\right)i$$

Where:

i, C_m and B_m are as earlier defined above. According to [15], MCI was designed to describe general trace elements contamination on a scale from 0 to 100, with MCI of < 5 implies very low contamination; 25-50 high contamination; 50-10 means very high contamination and > 100 implies extremely high contamination.

Enrichment Factor: The use of the enrichment factor (EF) for the assessment of soil contamination with metals has been suggested by [16]. Its version adapted to assess the contamination of various environmental media is as follows:

$$EF = \frac{Cn/Cref}{Bn/Bref}$$

Where:

Cn-Content of the examined element in the examined environment,

C_{ref}-Content of the examined element in the reference environment.

B_n –Content of the reference element in the examined environment

B_{ref}-Content of the reference element in the reference environment.

An element is regarded a reference element if it is of low occurrence and is present in the environment in trace amounts. It is also possible to apply an element of geochemical nature whose substantial amounts occur in the environmental but has no characteristic effects. i.e. synergism or antagonism towards an examined element. The most common reference elements are Sc, Mn, Al and Fe [17]. Five contamination categories are recognized on the basis of the enrichment factor. In this work, Fe was used as the reference element.

EF < 2	Deficiency to minimal enrichment
EF = 2-5	Moderate enrichment
EF = 5-20	Significant enrichment
EF = 20-40	Very high enrichment
EF > 40	Extremely high enrichment

Despite certain shortcomings [18] the enrichment factor, due to its universal formula, is a relatively simple and easy tool for assessing enrichment degree and comparing the contamination of different environmental media.

Index of geoaccumulation (I_{geo}) as proposed by [19] has also been widely used to evaluate the degree of metal contamination in terrestrial, aquatic as well as marine environments [20-22]. It is expressed as

$$I_{geo} = \log_2 \frac{Cn}{2.5Bn}$$

Where:

C_n is the measured concentration of the element n in the soil and B_n is the geochemical background value of element n in the background or control within the study area. The constant 1.5 is a factor which allow us to analyze natural fluctuations in the content of a given substance in the environment and very small anthropogenic influences.

Mueller [23] has distinguished six classes of the geoaccumulation index:

$I_{geo} = 0$	Practically uncontaminated
$0 < I_{geo} < 1$	Uncontaminated to moderately contaminated
$1 < I_{geo} < 2$	Moderately contaminated
$2 < I_{geo} < 3$	Moderately to heavily contaminated
$3 < I_{geo} < 4$	Heavily contaminated
$4 < I_{geo} < 5$	Heavily to extremely contaminated

However, an Igeo of 6 is said to be indicative of 100-fold enrichment of a mental with respect to the background value [16].

Pollution Load Index (PLI): Pollution load index for a particular site, has been evaluated following the method proposed by Tomilson *et al*. (1980). This parameter is expressed as

$$PLI = (CF_1 \times CF_2 \times CF_3 \ldots\ldots\ldots\ldots CF_n)^{1/n}$$

Where:

n is the number of metals and CF is the contamination factor. The contamination factor can be calculated from the following relation

$$CF = \frac{\text{Metal concentration in soil}}{\text{Background value of the metal}}$$

RESULTS AND DISCUSSION

Result of the enrichment factor of Cu, Pb, Zn and Cd in the studied coca plantations is presented in Table 1. Result showed that, the EF of Cu ranged from 2.55- 5.77 with a mean value of 4.03. According to the contamination categories established by [17]. The studied cocoa plantations have moderate enrichment to significant enrichment. This is higher than [23]. The youngest of all the cocoa farms studied had the lowest Cu enrichment factor.This suggests that, the age of cocoa plantation could be a factor contributing to copper contamination of cocoa plantation soils.

Table 1 showed that the enrichment factor of Pb, which ranged from 0.77 - 3.07 with an average value of 1.35. It showed that the enrichment of Pb in the studied cocoa is depletion to moderately enriched. It then infers that the soils are not contaminated with Pb rather, the content of lead in the soil is from parent materials and not as a result of anthropogenic activity.

Result of enrichment factor (Table 1) showed that the EF of Zn in the studied area ranged from 1.15-3.99 with a mean value of 2.49. The enrichment factor category according to [17] showed that Zn enrichment in

Table 1: enrichment factor of heavy metals in cocoa soils

Farm	Cu	Zn	Pb	Cd
Grassfield1	4.3	3.17	1.09	0.98
Grassfield2	4.29	2.05	0.96	0.89
Efraya 1	4.38	3.68	1.02	0.87
yahunde	3.27	2.53	1.06	0.94
Efraya2	3.96	2.16	0.77	0.93
Boki bia 1	5.77	2.36	1.48	1.01
Boki biak2	3.3	1.15	1.21	0.87
Okundi 1	4.78	2.11	2.12	0.76
Boki biak3	3.34	2.7	1.2	0.95
Bendege	4.97	3.99	3.07	0.94
Efraya strab	3.41	2.55	1	1.03
Okundi 2	2.55	1.45	1.23	0.97
Min	2.55	1.15	0.77	0.76
Max	5.77	3.99	3.07	1.03
Mean	4.03	2.49	1.35	0.93

Table 2: Geoaccumulation index of heavy metals in cocoa soils

Farm	Cu	Zn	Pb	Cd
Grassfield1	1.48	1.04	-0.49	-0.66
Grassfield2	1.53	0.47	-0.62	-0.73
Efraya 1	1.57	1.32	-0.53	-0.58
yahunde	1.11	0.74	-0.51	-0.51
Efraya2	1.37	0.5	-1	-0.48
Boki bia 1	2	0.71	0.03	-0.52
Boki biak2	1.94	-0.06	-0.32	-0.61
Okundi 1	1.67	0.51	-0.49	-0.65
Boki biak3	1.11	0.8	-0.29	-0.49
Bendege	1.74	2.17	-0.59	-0.62
Efraya strab	1.23	0.8	-0.49	-0.64
Okundi 2	0.77	-0.06	-0.3	-0.47
Min	0.77	-0.06	-1	-0.73
Max	2	2.17	0.03	-0.47
Mean	1.46	0.75	-0.47	-0.58

Table 3: Contamination factor of heavy metals in cocoa soils

Farm	Cu	Zn	Pb	Cd
Grassfield1	4.21	3.11	1.07	0.99
Grassfield2	4.34	2.07	0.97	1.01
Efraya 1	4.47	3.75	1.04	0.98
yahunde	3.24	2.5	1.05	1.02
Efraya2	3.88	2.12	0.76	1.01
Boki bia 1	6	2.45	1.54	0.87
Boki biak2	3.27	1.14	1.2	0.76
Okundi 1	4.78	2.11	2.12	0.97
Boki biak3	3.24	2.62	1.16	1.03
Bendege	5.02	4.03	3.1	0.97
Efraya strab	3.51	2.63	1.03	0.87
Okundi 2	2.55	1.45	1.23	1.02
Min	2.55	1.14	0.76	0.76
Max	6	4.03	3.1	1.03
Mean	4.04	2.5	1.36	0.96

the studied areas ranged from depletion to moderate enrichment, while the Cd enrichment factor ranged from 0.76-1.03 with an average value of 0.93 (Table 1). Hence, Cd enrichment ranged from depletion to minimal.

Geoaccumulation Index: Result of the geoaccumulation index (I_{geo}) is presented in Table 2. Geoaccumulation index of Cu ranged from 0.77-2 with a mean value of 1.46. Based on the categorization of [17], the studied soils ranged from moderately contamination to heavily contamination level. This I_{geo} mean value is higher than the value reported by [24] which was negative in farming soil. The intake of Cu by plants is proportional to the content of its soluble forms in soil which increases at low pH [25]. Moreover, Copper compounds from anthropogenic sources are more available to plants than the ones from natural sources.

I_{geo} for Pb in the studied soils ranged from-1 to 0.03 with a mean value of-0.47. The I_{geo} being negative showed that the cocoa soils studied are practically uncontaminated with Pb. This implies that, the Pb content of the soils is not from anthropogenic sources rather it is from natural source. I_{geo} result showed that the range of Zn contamination is from uncontaminated to moderately contaminated according to Muller, 1981 classification. By the classification of Muller, 1981 and Loska *et al*., 1997, the soils studied were practically uncontaminated with cadmium. The Cd content of the soils ranged from -0.73- 0.47. It then infers that the Cd in cocoa plantations examined in this work is solely from natural source.

Contamination Factor: Result of contamination factor of the studied soils is presented in Table 3. Contamination factor of copper ranged between 2.55 and 6 with a mean factor of 4.04. contamination factor of Pb ranged from 0.76 to 3.1 with a mean factor of 1.36 while the contamination factor of Zn ranged from 1.14 to 4.03 with an average value of 2.5 and the contamination factor of Cd ranged from 0.76 to 1.03 with a mean of 0.96. According to the contamination factor classification of Hakanson [14], the soils studies were minimally to moderately contaminated with Pb, Zn and Cd. The I_{geo} mean values of these three heavy metals are lower than the I_{geo} mean value (2.8) reported by Loska [24].

MCI (Metal Contamination Index): Result of Metal Contamination Index is presented in Fig. 1. It ranged from 2 to 9.6. According to [15] classification of MCI, the studied soils ranged from very low contamination to high contamination. Result of contamination factor (Table 3)

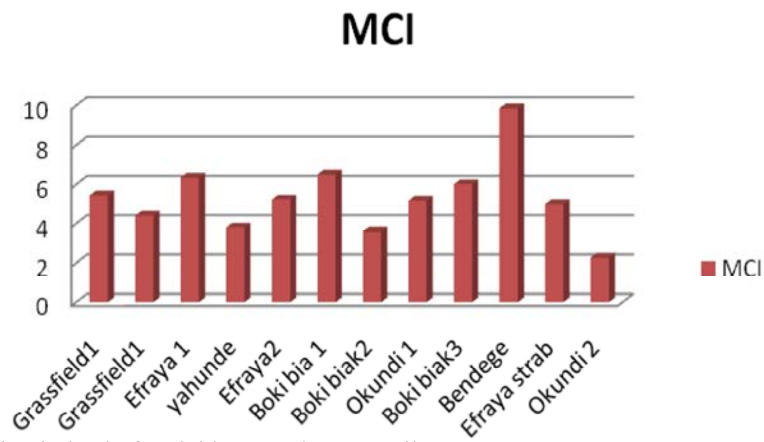

Fig. 1: Metal contamination index in fungicide treated cocoa soils

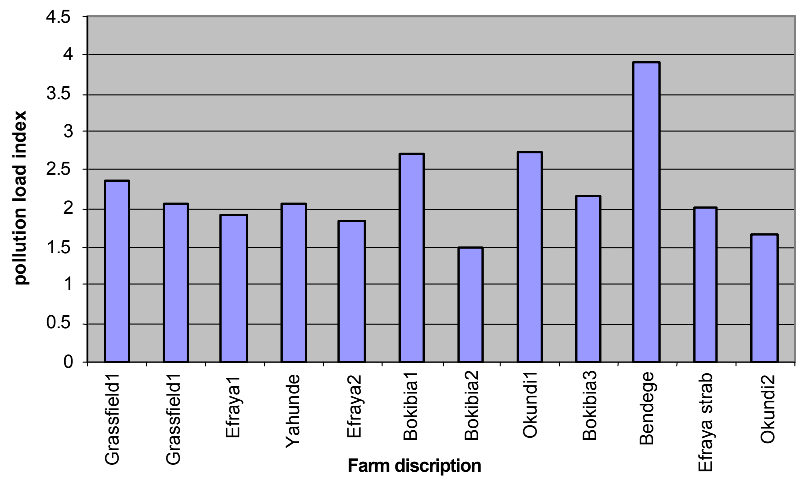

Fig. 2: Pollution load index of heavy metals in fungicide treated cocoa soils

Table 4: Correlation copper in soil with soil macro and micro nutrients

	Ca	Mg	K	Na	Fe	Mn	P	C	pH	Cu	Zn	Pb
Ca	1.00											
Mg	0.47	1.00										
K 0.53	0.76**	1.00										
Na	0.31	-0.18	-0.26	1.00								
Fe	-0.5	-0.44	-0.71**	0.22	1.00							
Mn	-0.34	-0.26	-0.38	0.56	0.57	1.00						
P 0.53	0.22	0.54	0.38	-0.44	-0.06	1.00						
C 0.44	0.34	0.40	0.34	-0.16	-0.09	0.5	1.00					
pH	0.50	0.36	-0.04	0.41	0.09	-0.04	0.02	-0.04	1.00			
Cu	0.15	-0.07	-0.21	0.53	0.04	0.02	0.33	0.05	0.52	1.00		
Zn	0.13	-0.15	-0.53	0.52	0.18	0.02	-0.01	-0.13	0.65*	0.68*	1.00	
Pb	-0.21	0.11	0.11	-0.16	-0.33	-0.35	0.13	-0.47	0.37	0.54	0.27	1.00

** Correlation significant at 0.01 level

showed that, Cu contamination is responsible for the high contamination of the entire studied area. The contribution of Pb, Zn and Cd is minimal to the overall contamination of the soils.

Pollution Load Index: Result of Pollution load index (PLI) which is the nth root of the multiplication of all the contamination factors for all the examined heavy metals is presented in Fig. 2.

According to [26], (0.0) indicates perfection, a value of one (1.0) indicates only baseline levels of pollutant present and values above one (> 1.00) would indicate progressive deterioration of the site. PLI values of the studied cocoa plantation soil ranged from 1.5 to 3.9. Result confirmed that the studied cocoa farms are polluted. The PLI can provide some understanding to the cocoa farmers in Ondo State and all the cocoa growing states in Nigeria at large who use copper based fungicide in combating the menace of black pod disease about the quality of agricultural soils which is component of their environment.

In addition, it also provide valuable information and advice for the policy and decision makers on the pollution level of cocoa soil in Ondo State and the entire nation at large.

It is usual for Nigerian cocoa farmers to raise cocoa seedlings using soils collected under their cocoa farms whenever they are ready to increase the size of their plantation or replace missing cocoa stands. When these highly copper- contaminated soils are collected for raising seedlings, there may be incidence of heavy metal toxicity which could lead to inhibition of root development of the seedlings and may eventually cause death to the seedlings. Chude [27] indicated that 7.90mg/kg copper disturbed growth in cocoa seedlings while copper value of 3.80mg/kg did not. Excess of copper in soil was reported to have caused iron chlorosis in plant [28]. Copper has been found to suppress rates of nitrogen fixation by Rhizobium under some solutions at copper levels of 235ppm. Results of numerous tests have proved that metals have diversified influence on micro-organisms. Their effects depend on the kind of micro-organisms, metal concentration and time of exposure. A change in biological activity may be connected with a possible decrease in microflora enzymatic activity due to heavy metals and lowering the level of biochemical reactions.

Geochemical Carriers: Correlation matrix for analyzed soil samples parameters was calculated to see if some of the parameters were interrelated with one another (Table 4) Examination of the matrix also provides clues about the carrier substances and the chemical association of trace elements in the studied areas [29, 30].

Matrix correlation showed that magnesium had positive significant correlation with potassium at 0.01 level, K had significant negative correlation with Fe. This infers that as k was increasing in the soil, Fe was reducing.there was significant positive correlation at 0.05 level between soil pH and Zn while there was also positive significant correlation between Cu and Zn. There was positive correlation between P and the soil macronutrients though not at significant level. It was also observed from the matrix correlation that Cu had positive correlation with all the soil chemical parameters considered in this work except Mg and K which had negative correlation with Cu. It could then be drawn from this result that, Na, P and pH are most likely to be geochemical carriers in the areas investigated.

CONCLUSION

The result of the various environmental factors used (enrichment factor, geoaccumulation index, contamination factor,metal contamination index and pollution index) showed that all the cocoa plantations studied were polluted with heavy metals. Result also showed that the overall pollution is mainly due to the presence of copper in the soil as a consequence of cu-based fungicide application by farmers during black pod disease control. However, the PLI values confirmed that the quality of the cocoa soils studied is deteriorating and this may have severe impact on soil biodiversity and ground water.

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