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Assessment of heavy metals pollution in fungicide treated Cocoa plantations in Ondo state, Nigeria

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ABSTRACT

Objective: To assess the impacts of copper-based cocoa fungicides on the environmental quality of cocoa plantations in Ondo State, Nigeria.

Methodology and results: The contents of five elements (Cu, Zn, Pb, Cd and Fe) were assayed in Cocoa plantations across Idanre, Owena and Bamikemo in Ondo 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 test revealed that all the studied cocoa plantations are highly contaminated with copper while the rest of the heavy metals are most likely to be from natural sources.

Conclusion and application of findings: The pollution load index values confirmed that the quality of the cocoa soils studied is deteriorating and this may have severe impact on soil biodiversity and ground water. Result suggests that alternative means of crop protection using biodegradable fungicides should be identified.

Key words: Cocoa, Nigeria, pollution load index, enrichment factor

INTRODUCTION

Agriculture has contributed immensely to Nigerian rural development, industrial growth, food security and non- oil foreign exchange earnings. Nigeria is currently the fourth largest producer of Cocoa (*Theobroma cacao*) with 200 metric tonnes in 2008. Cocoa is a crop of economic importance with more than 650,000 ha being cultivated in Nigeria (Sanusi & Oluyole, 2005). It ranked first amongst agricultural export crops in its contribution to foreign earnings (Tijani et al., 2001).

General and localized studies have identified the greatest factor responsible for the dwindling of cocoa production in Nigeria to be the 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 use copper based fungicides which are believed to be the fastest and most reliable means of managing the disease. Black pod disease outbreaks occur annually and the degree of prevalence depends on the rate of precipitation and humidity. This necessitates annual application of copper based fungicides if the farmers are to harvest any cocoa pods at the end of the year. On average Nigerian cocoa farmers apply Cu-based fungicides at least eight times in a year, which implies considerable 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 (Dalman et al., 2006). 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 (Loska & Wiechula, 2003).

There is increased awareness that heavy metals present in soil may have negative consequences on human health and on the environment (Abraham, 2002; Selinus et al., 2005). 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 potential hazards in soils are Cadmium, Chromium, Lead, zinc and copper (Alloway, 1995). The concentration of these toxic elements in soils may increase from various sources including anthropogenic pollution, weathering of natural high background rocks and metal deposits (Senesi et al., 1999). At present, relatively little data is available on the extent of environmental pollution as a consequence of using heavy metal- based fungicides on Cocoa.

Ondo State is the highest cocoa producing area in Nigeria and most of the farmers use copper based fungicide for the control of black pod disease. It is therefore necessary to assess heavy metals contamination levels in soils under cocoa plantations due to their potentially harmful effect on human health.

MATERIALS AND METHODS

Soil samples were collected from five major cocoa farms in Idanre (7^{0}06'N, 5^{0}6'E), two from Owena (0708'N, 5.06'E) and three major cocoa farms from Bamikemo (07^{0}18'N, 4^{0}45'E) in April, 2009. Farm selection was done on the basis of major cocoa producing areas within the state. Most of the cocoa farms were over 40 years old except for few farms that were between 8 and 10 years. 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.

A portion of each sample was leached with 1N ammonium acetate. The leachate was analyzed for exchangeable cations (Ca^{2+}, Mg^{2+}, K^+ and Na^+) (Sharman et al., 1942; Schollenberger & Simon, 1945) 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 (1934); total Nitrogen was determined by the Macro Kjedahl method (Jackson et al.,1986); available Phosphorus was determined using Bray and Kurtz (1945). Another portion (1g) of the soil sample was extracted with 10ml of 0.1N HCl for heavy metal analysis. 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 parameters quantify 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 value from a geologically pristine/uncontaminated area.

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

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

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 (Hakanson, 1980), with values of < 8 to > 32 whereby C deg < 8 implies low degree of contamination (table 1).

Table 1: 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 expressions 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:

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

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

Where, i, C_m and B_m are as defined above. According to Meybeck et al.(2004), MCI was designed to describe general trace elements contamination on a scale from 0 to 100, with MCI of < 5 implying very low contamination; 25 – 50 high contamination; 50 – 10 very high contamination and > 100 implying extremely high contamination.

Enrichment factor: The use of the enrichment factor (EF) for the assessment of soil contamination with metals has been suggested by Beat – Merond (1979). For assessing the contamination of various environmental media it is expressed as follows:

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

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 as 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 environment 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 (Loska et al, 1997). Five contamination categories are recognized on the basis of the enrichment factor (table 2). In this work, Fe was used as the reference element.

Table 2: Metal contamination categories

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 (Reinmann and Caritat, 2000) 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 Mueller (1979) has also been widely used to evaluate the degree of metal contamination in terrestrial, aquatic as well as marine environments (Sahu and Bhosale, 1991; Singh et al, 1997; Sutherland, 2000;) It is expressed as

$$I_{geo} = \log_2 \frac{Cn}{1.5\ Bn}$$

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 (table 3).

Table 3: Classes of the geoaccumulation index as distinguished by Muller (1981).

$I_{geo} \leq 0$	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 metal with respect to the background value (Mueller, 1979).

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

Enrichment factor: Results of the enrichment factor (EF) of Cu, Pb, Zn and Cd in the studied coca plantations is presented in table 4. Result showed that the EF of Cu ranged from 4.76 -36.79 with a mean value of 17.20. According to the contamination categories established by Loska et al. 1997, the studied cocoa plantations have moderate copper enrichment to very high contamination. The enrichment factor values were higher than the values reported by Aikpokpodion et al.,(2010) in a similar work carried out on cocoa plantation soils in Cross River, Nigeria with Cu EF range of 2.55-5.77 with a mean value of 4.03. The higher values from Ondo soils could be attributed to the age difference between cocoa farms in Ondo and those of Cross River. History of the studied cocoa plantations revealed that, cocoa farms in Ondo were much older than the farms in Cross River. The youngest of all the cocoa farms studied had the lowest Cu enrichment factor of 4.76. This suggests that the accumulation of copper in cocoa plantation could be a consequence of continuous, long term use of copper based fungicides.

Results (Table 4) showed that the enrichment factor of Pb ranged from 0.61 – 1.2 with an average value of 0.932. It showed that the enrichment of Pb in the studied cocoa plantations was between depletion to minimal. It then infers that the soils are not contaminated with Pb but rather, the content of lead in the soil is from parent materials and not as a result of anthropogenic activity. Similar work carried out in Cross River state, Nigeria, by Aikpokpodion et al., (2010) showed that, EF of Pb ranged from 0.77-3.07 with a mean value of 1.35. The difference in the mean values of Pb enrichment factors from Cross River State and Ondo State suggests that, the native Pb content of cocoa soils in Cross River is higher than that of ondo.

The EF of Zn in the studied area ranged from 0.39 – 2.08 with a mean value of 1.28, which according to Loska et al.(1997) ranged from depletion to moderate enrichment, while the Cd EF ranged from 0.74 – 1.38 with an average value of 1.05, classified as being between depletion to minimal.

Geoaccumulation index: Result of the geoaccumulation index (I_{geo}) (Table 5) showed that Cu ranged from 0.95 – 4.26 with a mean value of 3.28. Based on the categorization of Loska et al. (1997), these values were from moderate to heavy contamination level. Geoaccumulation index of Cu in studied Cross River cocoa plantation soils ranged from 0.77 to 2 with a mean value of 1.46 (Aikpokpodion et al., 2010).The higher values I_{geo} of Cu in Ondo state compared with Cross River state further revealed the positive relationship between the period of fungide application and metal accumulation in the soil. The uptake of Cu by plants is proportional to the content of its soluble forms in soil which increases at low pH (Kabata-Pendias & Pendias, 1999). Moreover, Copper compounds from anthropogenic sources are more available to plants than the ones from natural sources.

Table 4: Enrichment factor of heavy metals in cocoa plantation soils in Ondo state, Nigeria.

FARM	Cu	Pb	Zn	Cd
Idanre 1	12.05	0.74	0.63	0.74
Idanre 2	7.45	1.08	2.08	1.38
Idanre 3	28.31	0.95	1.27	1.07
Idanre 4	24.08	1.17	1.12	0.82
Idanre 5	4.76	1.2	1.03	1.12
Owena 1	13.62	0.87	1.71	0.92
Owena 2	36.79	0.87	2.07	1.01
Bankemo1	15.38	0.61	0.39	1.24
Bankemo2	11.68	0.96	1.09	1.08
Bankemo3	17.83	0.87	1.42	1.07
Mean	**17.20**	**0.932**	**1.281**	**1.045**
Min	**4.76**	**0.61**	**0.39**	**0.74**
Max	**36.79**	**1.2**	**2.08**	**1.38**
Std dev	**9.4**	**0.17**	**0.53**	**0.18**

Table 5: Geoaccumulation index of heavy metals in cocoa plantation soils in Ondo state, Nigeria.

Cocoa farm	Cu	Pb	Zn	Cd
Idanre 1	3.37	-0.58	-0.88	-0.67
Idanre 2	0.95	-1.32	0.36	-0.03
Idanre 3	4.3	0.97	-0.17	-0.42
Idanre 4	4.03	-0.32	-0.38	-0.84
Idanre 5	1.79	-0.32	-0.6	-0.4
Owena 1	3.4	-0.56	0.42	-0.47
Owena 2	4.26	-0.67	0.58	-0.45
Bankemo1	3.74	-0.92	-1.6	0.11
Bankemo2	3.11	-0.49	-0.3	-0.34
Bankemo3	3.83	-0.54	0.18	-0.2
Mean	**3.278**	**-0.475**	**-0.239**	**-0.371**
Min	**3.278**	**-1.32**	**-1.6**	**-0.84**
Max	**0.95**	**0.97**	**0.58**	**0.11**
Std dev.	**1.04**	**0.56**	**0.64**	**0.27**

Geoaccumulation index (I_{geo}) for Pb in the studied soils ranged from – 1.32 to 0.97 with a mean value of – 0.475. The I_{geo} for Pb being negative showed that the cocoa soils studied are practically uncontaminated with this metal. This implies that the Pb content of the soils is not from anthropogenic sources rather it is from natural source. The geoaccumulation index of Zinc ranged from -1.6 to 0.58 with a mean value of – 0.239 . I_{geo} result classifies the soils studied as uncontaminated with Zn according to Muller (1981) classification. The lack of contamination with Zn was also confirmed by the average enrichment factor. I_{geo} for Cd ranged from – 0.84 to 0.11 with an average value of – 0.371. 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 was solely from natural source.

Contamination Factor: Result of contamination factor (table 6) showed that for copper it ranged between 4.17 and 29.74 with a mean factor of 17.81. CF of Pb ranged from 0.59 to 1.2 with a mean factor of 0.98 while the CF of Zn ranged from 0.5 to 2.25 with an average value of 1.35 and the CF of Cd ranged from 0.84 to 1.62 with a mean of 1.173. According to the contamination factor classification of Hakanson (1980), the soils studies were minimally to moderately contaminated with Pb, Zn and Cd.

Metal Contamination Index (MCI) : Result of Metal Contamination Index (figure 1) showed a range between 4.53 and 29.19 . According to Meybeck et al; (2004) classification, the studied soils ranged from very low to high contamination. Result of contamination factor (Table 6) showed that Cu contamination level in the studied soils is responsible for the high contamination level of the entire studied area since MCI is a combination of all the examined metals.The contribution of Pb, Zn and Cd is minimal to the overall contamination of the soils.

Table 6: Contamination factor of heavy metals in cocoa plantation soils in Ondo state Nigeria.

FARM	Cu	Pb	Zn	Cd
Idanre 1	15.55	0.96	0.81	0.95
Idanre 2	4.17	0.59	1.53	1.41
Idanre 3	29.74	1	1.33	1.13
Idanre 4	24.57	1.2	1.15	0.84
Idanre 5	5.19	1.2	1.03	1.12
Owena 1	15.93	1.02	2	1.08
Owena 2	28.7	0.95	2.25	1.1
Bankemo 1	20	0.79	0.5	1.62
Bankemo 2	12.96	1.07	1.21	1.2
Bankemo 3	21.31	1.04	1.69	1.28
Mean	**17.812**	**0.982**	**1.35**	**1.173**
Min	**4.17**	**0.59**	**0.5**	**0.84**
Max	**29.74**	**1.2**	**2.25**	**1.62**
Std dev	**8.37**	**0.17**	**0.51**	**0.21**

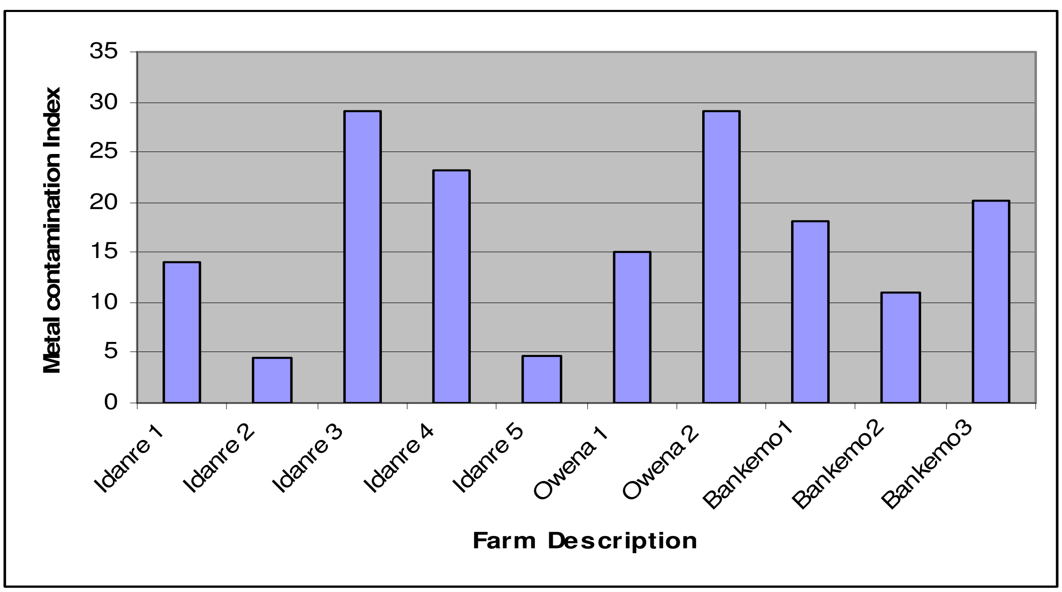

Figure 1: Metal contamination index in fungicide treated cocoa soils in Ondio state, Nigeria.

Pollution load index: Results of Pollution load index (PLI) which is the n^{th} root of the multiplication of all the contamination factors for all the examined heavy metals are presented in figure 2.

According to Tomlinson et al. (1980), (0.0) indicates perfection, a value of one (1.0) indicates only baseline levels of pollutants present and values above one (> 1.00) would indicate progressive deterioration of the site. PLI values of the studied cocoa plantation soil ranged from 1.52 to 2.87 with a mean value of 2.15 which confirmed that the studied cocoa farms are polluted. The PLI can provide some vital information to the cocoa farmers in Ondo State and other parts of country who use copper based fungicide in combating the menace of black pod disease on the aftermath effects of copper application on agricultural soil quality. Pollution load index also provides valuable information and advice for the policy and decision makers on the metal -pollution level of cocoa soils in Ondo State.

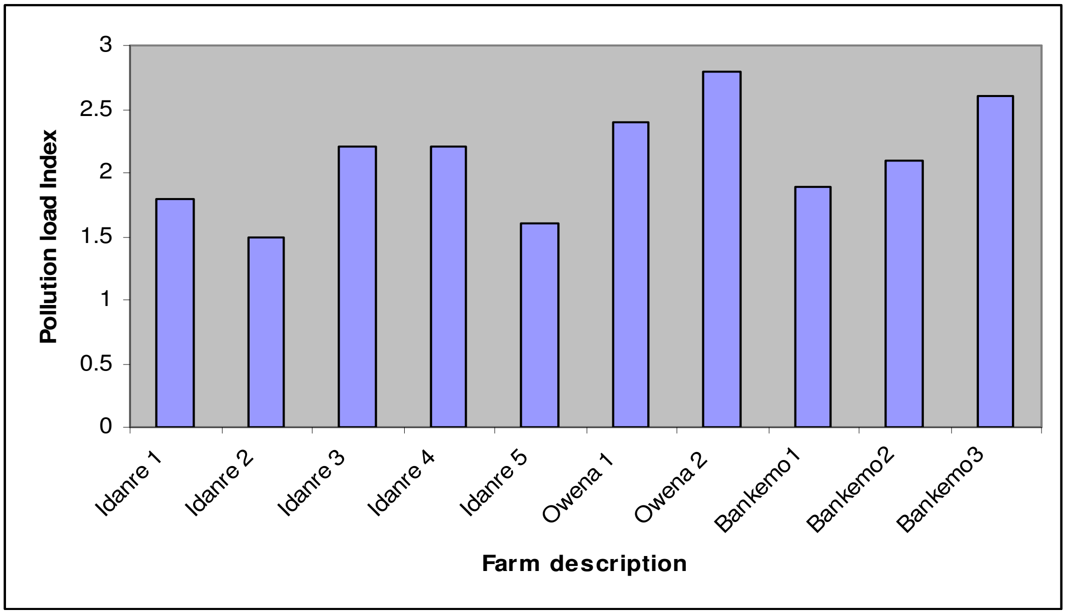

Figure 2: Pollution load index of heavy metals in fungicide treated cocoa soils in Ondo state, Nigeria.

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 (1985) 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 (Alva and Graham, 1991). 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.The work carried by Aikpokpodion (2010) showed that, Cu significantly reduced K in soil, reduced extractable Ca, Mg, Na, Zn, Fe, N and available P in the studied soils and also had negative correlation with Ca, K, Fe, Zn, N and P in the foliage. Hence, interaction of copper with soil chemicals can lead to reduced availability of vital nutrients and minerals in plants' environment if not properly managed.

Geochemical carriers: Pearson correlation matrix for analyzed soil parameters was calculated to determine if some of the parameters were interrelated (Table 7). Examination of the matrix also provides clues about the carrier substances and the chemical association of trace elements in the studied areas (Forstner, 1981: Jaquet et al., 1982).

Results showed that Zn had significant negative correlation with organic carbon and nitrogen (Table 4). Zn showed negative correlation with most of the physicochemical properties except sand which implies that the presence of these properties influences the accumulation of zinc in the studied soils. Most of the physicochemical parameters of the soils showed significant correlation with one another. Cu, Pb and Zn showed negative correlation with pH, which indicates that the lower the pH, the higher the concentration of heavy metal in the soil solution. Organic carbon had negative correlation with most of the metals.

Table 7: Correlation coefficient matrix between physicochemical properties and heavy metal concentration in soil in cocoa plantations in Ondo state, Nigeria.

	N	C	Sand	Clay	Silt	P	pH	EC	Cu	Pb	Zn	Cd	Fe
N	1.00												
C	0.84**	1.00											
Sand	-0.76*	-0.78**	1.00										
Clay	0.65*	0.49	-0.78**	1.00									
Silt	0.56	0.72*	-0.91**	0.54	1.00								
P	0.39	0.39	-0.35	0.13	0.38	1.00							
pH	0.01	0.32	0.16	-0.39	-0.14	-0.06	1.00						
EC	0.70*	0.80**	-0.79**	0.43	0.80**	0.33	0.21	1.00					
Cu	0.21	-0.01	-0.01	0.04	-0.05	0.39	-0.20	0.31	1.00				
Pb	0.17	-0.01	0.09	0.27	-0.19	0.14	-0.08	0.08	0.53	1.00			
Zn	-0.75*	-0.70*	0.45	-0.20	-0.40	-0.47	-0.43	-0.59	-0.02	-0.07	1.00		
Cd	-0.58	-0.27	0.09	-0.05	0.02	0.01	0.12	-0.13	-0.20	-0.13	0.38	1.00	
Fe	-0.09	-0.15	0.07	0.01	-0.13	0.22	0.14	-0.27	-0.40	-0.26	-0.31	0.39	1.00

** Correlation significant at 0.01 level.

This implies that the higher the amount of heavy metals in soil solution, the lesser the amount of organic carbon that will be present. Except for Zn, available phosphorus had positive correlation with most of the heavy metals though not at a significant level. The positive correlation between phosphorus and Cu, Pb, Cd and Fe indicates the association between phosphate and trace metals. Majority of the heavy metals showed negative correlation with one another except Zn – Cd and Fe –Cd. This result is at variance with the report of Mohiuddin et al. (2010) on trace metals in water and sediments of the Tsurumi river.

CONCLUSION

This work has revealed the present status of heavy metal contamination in cocoa soils of ondo state. The various environmental parameters used to qualify the status showed that, copper is the major heavy metal contaminant which came as a result of continuous application of copper-based fungicides by cocoa farmers when controlling the attack of black pod disease. This situation is gradually taking cocoa soils in the studied area to a condition of deterioration because of the contamination load and the adverse effect on soil biodiversity. It is therefore expedient to start seeking for other alternatives (fungicides) which are biodegradable and environmentally friendly so as to protect the soil environment from untimely degradation. Farmers should also be educated on good agricultural practices (GAP) which will reduce the frequency of pesticide application. Due to the fact that, land is a limited resource coupled with the fact that, industrialization and population growth are competing with agriculture for land use, it is expedient to develop remediation techniques which will be used to clean up the copper contaminated cocoa soils.

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