Global Journal of Environmental Research 6 (1): 30-35, 2012
ISSN 1990-925X

DOI: 10.5829/idosi.gjer.2012.6.1.385

Assessment of Heavy Metals Mobility in Selected Contaminated Cocoa Soils in Ondo 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 losses of 30-90% crop loss. To overcome this problem, Nigerian cocoa farmers solely use copper-based fungicides to control the disease. Copper being a metal is not biodegradable. Hence, it accumulates in the soil as a result of continual use. Heavy metals are potentially toxic to soil microbes and soil environment in general. Toxicity depends on chemical association in soil. For this reason, determining the chemical form of a metal in soils is important to evaluate its mobility and bioavailability. Sequential extraction was used to fractionate four heavy metals (Cu, Zn, Cd and Pb) in soils from ten contaminated cocoa plantations across Ondo State, Nigeria into six operationally defined pools: water soluble, extractable, carbonate, Fe-Mn oxide, organic and residual. The organic fraction was the most abundant pool for copper and zinc, extractable fraction for Lead and residual for cadmium. Mobility and bioavailability of these four metals in the studied soils were in the order : Pb>Zn>Cd>Cu. This indicates that lead had the highest chance of being accumulated in cocoa beans.

Key words: Cocoa % Contamination % Heavy metals % Black pod % Ondo

INTRODUCTION

Nigeria is currently the fourth largest producer of cocoa in the world. Cocoa is a crop of economic importance with more than 650,000 ha of land being cultivated in Nigeria [1]. It ranked first amongst agricultural export crops in its contribution to foreign earnings [2]. Incidence of black pod disease caused by *Phytophtora sp*. has being implicated in the dwindling production of cocoa in Nigeria. The main economic loss is from the infection of the pods which in turn affect the quality of the beans in the pods. In order to check the menace of *Phytophtora* sp. on Cocoa, Nigerian cocoa farmers solely use copper based fungicide which is known to be the most effective means of controlling black pod disease. For farmers to get optimum yield of cocoa beans during harvest, they use fungicides on regular basis. Leonila [3] reported that, when pesticides are applied to protect crops from the attack of pests and diseases, only 15% of it hits the target while the remaining 85% is distributed between soil and air. The soil is the main matrix for pesticide disposition and the bulk of pesticides are generally confined to the upper 5cm of the top soil. Pollution of the natural environment by heavy metals is a global problem because of their indestructible nature and most of them have toxic effects on living organisms [4]. Many studies have been conducted on heavy metal contamination in soils from various anthropogenic sources such as industrial waste [5], automobile emissions [6] and agriculture practice [7]. Soils samples collected from cocoa plantations which had received application of copper-based fungicides over the years in Ondo and Cross River States (both in Nigeria) were reported contaminated with copper [8]. Based on primary accumulation mechanisms in soil, heavy metal can be classified into six categories: (i) water soluble (ii) Extractable (iii) bound to carbonate phases (iv) bound to reducible phases (Fe and Mn oxides) (v) bound to organic matter (vi) detrital or lattice metals (Residual) [9]. Heavy metals present in these categories have different remobilization behaviors under changing environmental conditions [10]. Geochemical forms of heavy metals in soil affect their solubility, which directly influence their bioavailability [11]. Therefore, determining total heavy metals is insufficient to assess their environmental impact on soil and sediments. It therefore implies that, it is the

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chemical form that determines metal behavior and remobilization potential. There is little or no information on the chemical partitioning of heavy metals in Nigerian cocoa soils. Since the bioavailability of heavy metals for plant uptake is determined by chemical speciation of heavy metals in soil, it is therefore necessary to provide information on heavy metal speciation in selected cocoa plantations in Ondo State which is the major cocoa producing State in Nigeria with a view to generate information on the mobility and bioavailability of the studied metals.

MATERIALS AND METHODS

Soil samples were collected at the depth of 0-15cm with soil auger under cocoa plantations in Iloro-ldanre (7°N and 5° E), Bamikemo (7°18N and 4°54E) and Owena (7°10N and 4°59N) all in Ondo State of Nigeria. All the selected cocoa plantations had received Cu-based fungicides for more than twenty five years. Collected soil samples were air-dried and (sieved with 2mm sieve prior to analysis).

The procedure of Tessier *et al.* [12], selected for this study was designed to separate heavy metals into six operationally defined fractions: water soluble, exchangeable, carbonate bound, Fe-Mn oxides bound, organic bound and residual fractions. A summary of the procedure is as follows:

One gram of each soil was weighed into 30ml polypropylene sample bottle and the following fractions obtained.

- (F1) water soluble. Soil sample extracted with 15ml of deionized water for 2 hours.
- (F2) Exchangeable. The residue from water soluble fraction was extracted with 8ml of 1ml $MgCl_2$ (pH 7.0) for I hour.
- (F3) Carbonate -Bound. The residue from exchangeable fraction was extracted with 8ml of IM Ammonium acetate (adjusted to pH 5.0 with Acetic acid) for 5 hours.
- (F4) Fe-Mn oxides-bound. The residue from carbonate fraction was extracted with 0.04M NH_2 OH. HCl in 25% (v/v) Acetic acid at 96°C with occasional agitation for 6 hours
- (F5) Organic- Bound. The residue from Fe-Mn oxides bound fraction was extracted with 3ml of 0.02M Nitric acid and 5ml of 30% H_2O_2 (adjusted to pH 2 with HNO_3) was added and the mixture heated to 85°C for 3 hours, with occasional agitation. A second 3ml aliquot of 30% H_20_2 (pH 2 with HNO_3) was added and the mixture heated again to 85°C for 3hours with intermittent agitation. After cooling, 5ml of 3.2m NH_4OAc in 20% (v/v) HNO_3 was added and the samples was made up to 20ml with deionized water and agitated continuously for 30min.
- (F6) Residual. The residue from organic fraction after drying was digested in a conical flask with 10ml of 7M HNO_3 on a hot plate for 6 hours. After evaporation, 1ml of 2M HNO_3 was added and the residue after dissolution was diluted to 10ml. the residue was washed with 10ml of deionized water.

After each successive extraction separation was done by centrifuging (Beckman Model J2-21) at 4000 rpm for 30min. The supernatants were filtered and analyzed for heavy metals. The residue was washed with 8ml of demonized water followed by rigorous hand shaking and then followed by 30min of centrifugation before the next extraction.

Quality Assurance: All chemicals used were of reagent grade and pure deionized water was used throughout the experimentation. All plastic materials used were soaked in 10% Nitric acid Procedural blanks preparation of standard solutions under clean laboratory environment, calibration of the Buck 200A Atomic Absorption spectrophotometer (AAS) using certified standards and the analysis of calibrated standards after 10 samples to ensure that the instrument remained calibrated were some of the measures taken during the experimentation.

RESULTS AND DISCUSSION

Result in Table 1 shows that copper was mostly concentrated in the organic fraction in most of the selected cocoa soils. Copper ranged from (5- 43.65) mg/kg with a mean of value of 26.45mg/kg soil. Among the ten studied soils, Idanre 4 had the least value while Idanre 1 had the highest value of copper in the organic fraction. Water extracted fraction had the least mean copper content among the six heavy metal fractions. Copper ranged from 0.15-1.88 with a mean value of 0.85mg/kg (Table 1). It was observed that, Idanre1 and Idanre 3 soil samples had their water soluble copper below detection limit while Idanre while Idanre 2 had the least value of 0.15mg/kg. Extractable fraction of the copper in the studied soils ranged from 0.53 to 2.33 mg/kg with a mean value of 1.41mg.kg. Among the various soils Idanre 3 had the least value for extractable copper while Owena 2 had the highest copper value of 2.33mg/kg (Table 1).

Table 1: Copper speciation in Ondo State Cocoa soils

	Water	Extra	Carbona	Fe-Mn	Organic	Res	Sum	Res.(%)	Nonres (%)
Idanre 1	BDL	1.13	10.65	8.12	43.63	1.67	65.2	11.33	88.67
Bamkem1	0.38	1.05	10.1	4.5	18.63	5.96	40.62	5.63	94.37
Afun 2	0.82	1.88	21.83	9.75	33.61	3.37	71.26	32.93	67.07
Afun 1	1.88	1.5	0.15	4.95	38.25	10.47	57.2	23.96	76.04
Idanre 2	0.15	0.9	2.48	5.7	20.88	4.87	34.98	3.81	96.19
Bamkemo2	0.67	1.3	16.13	10.35	7.38	13.13	48.96	27.83	72.17
Idanre 3	BDL	0.53	14.66	8.85	26.25	1.88	52.17	23.53	74.47
Idanre 4	0.45	1.95	5.2	1.52	5	23.91	38.03	44.63	55.37
Owena 1	1.62	1.53	0.26	5	36.2	11	55.61	22.1	77.9
Owena 2	0.9	2.33	1.15	8.61	34.7	10	57.69	50.02	49.98
Mean	0.85	1.41	8.26	6.73	26.45	8.62	52.34	24.57	75.22
STD	0.60	0.54	7.59	2.81	13.18	6.72	31.47	15.28	15.28

Res: Residual; Non res: Non residual

Table 2: Lead speciation in Ondo State cocoa soils

	Water	Extra	Carbona	Fe-Mn	Organic	Res	Sum	Res. (%)	Nonres (%)
Idanre 1	BDL	17.1	2.63	2.5	12.13	6.2	40.56	15.29	84.71
Bamkemo1	BDL	20.55	BDL	7.58	7.5	2.17	37.8	5.74	94.26
Afun 2	BDL	18.06	0.3	0.3	3.5	3.22	25.38	12.42	87.58
Afun 1	BDL	23.45	2.63	2.33	4.5	1.72	34.63	4.97	95.03
Idanre 2	BDL	1.8	BDL	0.6	3.13	24.77	30.3	81.75	18.25
Bamkem2	BDL	17.33	1.35	5.18	4	4.84	32.7	14.94	85.06
Idanre 3	5	13.65	1.8	3	4	21.75	49.2	23.88	76.12
Idanre 4	BDL	1.5	2.52	8.02	BDL	26.06	38.1	68.4	31.6
Owena 1	BDL	20.71	0.21	8.63	3.2	5.14	37.89	13.55	86.45
Owena 2	BDL	18.5	1.07	6.12	2.78	9	37.47	24.02	75.98
Mean	5	15.26	1.56	4.42	4.97	10.47	36.40	26.49	73.50
STD		7.62	0.99	3.08	3.02	9.73	24.47	26.54	26.54

Table 3: Zinc speciation in Ondo state cocoa soils

	Water	Extra	Carbona	Fe-Mn	Organic	Res	Sum	Res. (%)	Non res (%)
Idanre 1	0.83	6.38	8.48	7	12	1.41	36.1	3.91	96.09
Bamkemo1	0.6	8.25	10.45	9.08	10.39	1.43	40.2	3.56	96.45
Afun 2	0.83	4.95	4.58	5.03	12.5	1.51	29.4	5.14	94.87
Afun 1	7.58	8.32	4.05	6.24	12.75	0.46	39.4	1.17	98.92
Idanre 2	0.15	1.5	3.98	14.18	11	6.26	37.07	16.87	83.04
Bamkemo2	0.6	4.88	2.78	2.25	28.38	2.77	41.66	6.65	93.51
Idanre 3	0.53	7.13	3.9	4.13	15.5	2.51	33.7	7.48	92.55
Idanre 4	0.68	2.55	5.2	7.15	10.75	0.17	26.5	0.64	99.36
Owena 1	1.1	4.16	9.25	10.05	11.22	1.2	36.98	3.24	96.76
Owena 2	0.87	3.62	10.07	7	10.35	1.12	33.03	3.39	96.61
Mean	1.37	5.17	6.27	7.21	13.48	1.88	35.40	5.20	94.81
STD	2.19	2.32	2.93	3.33	5.45	1.72	4.80	4.61	4.64

Table 4: Cadmium speciation in Ondo state cocoa soils

	Water	Extra	Carbona	Fe-Mn	Organic	Res	Sum	Res. (%)	Non res (%)
Idanre 1	0.47	0.43	0.37	0.68	1	6.17	9.12	67.65	31.8
Bamkemo1	0.53	0.77	0.47	0.87	1.11	0.25	4	6.25	93.75
Afun 2	0.61	1	0.25	0.77	1.2	1.87	5.7	32.81	67.19
Afun 1	0.53	1.58	0.17	0.57	1.21	1.64	5.7	29.3	71.23
Idanre 2	0.74	0.48	0.22	1.58	1.1	0.68	4.8	14.17	85.84
Bamkemo2	0.83	0.21	0.3	0.99	0.86	5.51	8.7	63.3	36.67
Idanre 3	0.8	0.51	0.38	0.69	0.95	5.67	9	62.99	37.01
Idanre 4	0.7	0.56	0.36	0.62	1.34	4.82	8.4	57.38	42.62
Owena 1	0.7	0.95	0.3	0.85	1.15	2.15	6.1	35.25	64.74
Owena 2	0.81	1.03	0.26	0.76	0.99	2.05	5.9	34.94	65.26
Mean	0.67	0.75	0.30	0.83	1.09	3.08	6.74	40.40	59.61
STD	0.12	0.39	0.08	0.28	0.14	2.22	1.88	21.49	21.61

Table 5: Heavy metals mobility factor (%) in studied soils

Sample	Cu	Pb	Zn	Cd
Idanre 1	18.07	48.64	43.46	13.92
Bamkemo1	15.71	54.37	48	44.25
Afun 2	34.42	72.92	35.24	32.63
Afun 1	6.17	75.31	50.63	40
Idanre 2	10	5.94	15.18	30
Bamkemo2	36.97	57.65	19.83	15.4
Idanre 3	29.12	67.98	34.3	18.78
Idanre 4	19.98	10.55	31.81	19.29
Owena 1	6.13	55.65	39.24	31.97
Owena 2	7.59	52.22	43.87	35.59
Mean	18.41	50.12	36.15	28.18
STD	11.61	23.81	11.55	10.66

Carbonate fraction of copper in the soils ranged from 0.15 to 21.83mg/kg with a mean value of 8.26mg Cu/kg soil (Table 1). Copper fraction bound to Fe-Mn oxides in the studied soil ranged from 1.52- 10.35mg/kg with a mean value of 6.73mg/kg. The residual fraction of copper in the soils ranged from 1.67 to 23.91 with a mean value of 8.62mg/kg. On the average, copper resident in the organic fraction (Table 1) is consistent with the report of Harrison [13] who found significant amount of Cu in roadside soils associated with the organic fraction. The metal speciation pattern in the studied soils is also consistent with the report of Ma and Rao [14] who found significant amount of copper in nine contaminated soils associated with the organic fraction. The strong association of Cu with the organic fraction in most of these soils suggests high formation constant of organic-Cu complexes in most of these soils [15]. Copper distribution in various chemical fractions seemed to dependent on the total Cu content in most of the structured soils (Fig. 1).

As the total Cu concentration in the soils increased, the percent of total Cu in the water soluble, carbonate, Fe-Mn oxide and organic fractions increased and Cu in the residual fraction decreased. Report of Ma and Rao is in agreement with this work. Result then suggests that, as Cu contamination in soils increases, more Cu tends to be associated with the non residual fractions, which may consequently increase potential Cu mobility and bioavailability in theses soils.

Lead was largely associated with extractable fraction. It ranged from 1.5 to 23.45 mg/kg with an average value of 15.26mg/kg Idanre 4 had the least value (1.5mg/kg) while Afun 1 had the highest value (23.45mg/kg) among the studied soils (Table 2) Idanre 2, Idanre 3 and Idanre 4 soils had lead ions largely associated with the residual fraction (24.77, 21.75 and 26.06) mg/kg respectively (Table 2).

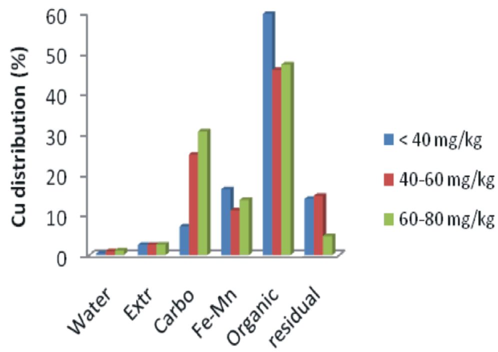

Fig. 1: Distribution of Cu in various fractions as a function of total metal content in soils

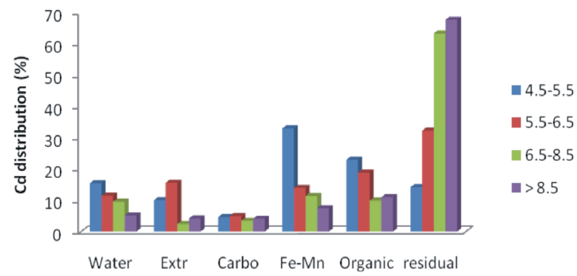

Fig. 2: Distribution of Pb as a function of total metal content in soils

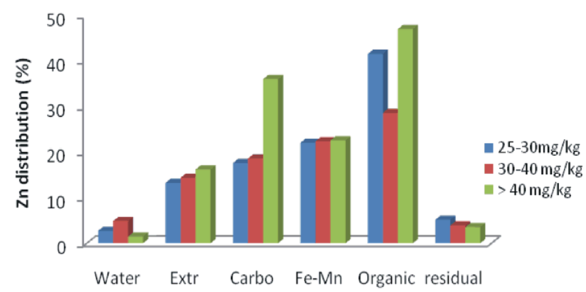

Fig. 3: Distribution of zinc as a function of total metal content in soil

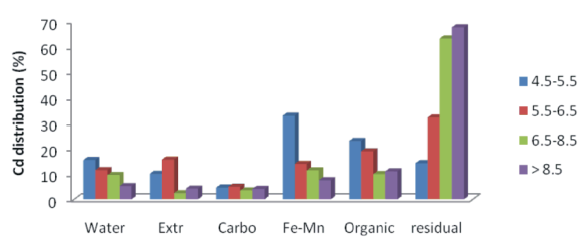

Fig. 4: Distribution of cadmium as a function of total metal content in soil

Result shows that, all the soils from Idanre axis of Ondo State except Idanre 1 had lead (Pb) contents in the residual fraction. Out of all the studies soils only Idanre 3 had lead associated with water extractable fraction with a value of 5mg/kg soil. The bulk of lead present in the extractable fraction suggests that, lead in the studied soils can easily be taken up by cocoa and this may be responsible for the moderately high lead values found in cocoa beans collected from Ondo State. It is therefore necessary to remediate these lead contaminated soils so as to reduce the risk of lead translocation to the various parts of the plants. Only three out of the ten soil samples (30%) examined had lead concentrated in the residual fraction. The residual fraction had lead values ranged from 1.72 to 26.06 with a mean value of 10.48mg/kg soil. Result also suggests that, the lower the total lead content of the soil, the higher the Pb associated with the extractable (mobile) fraction (Figure 2). Result then suggest that, Pb may be loosely held by electrostatic force to the soil surface which makes it potentially bioavailable for Cacao uptake. Result of this work is in contrast with the pattern of lead association reported by Kabata-pendias and Pendias [16], Ramos *et al.* [17] and Yusuf [18] who reported Pb being largely associated with Fe-Mn oxide and organic fractions.

Result in Table 3 shows that, zinc was largely associated with the organic fraction. It ranged from 10.35 to 28.38 with a mean value of 13.48mg/kg. Soil samples obtained from Bamikemo 1 had the least value of Cu in organic fraction (10.35mg/kg) while samples from Bankemo 2 had the highest value of 28.38mg/kg water exactable fraction had Zn ranged from 0.15 to 7.58 with a mean value of 1.37mg/kg. Zinc in carbonate fraction ranged from 3.9 to 10.35 with a mean value of 6.27mg/kg while zinc in Fe-Mn oxide fraction ranged from 2.25 to 14.18 mg/kg with a mean value of 7.21mg/kg.

Zinc in the residual fraction ranged from 0.17 to 6.26 mg/kg with a mean value of 1.88mg/kg soil. Of all the examined cocoa soils, none of them was contaminated with zinc. Result shows that, the higher the total concentration of zinc in the soil, the higher the value of zinc associated with organic fraction and the lower the value of Zn associated with carbonate and water soluble fraction (Fig. 3) this suggest that, zinc toxicity potential will be low in these studied soils. The high association of zinc with the organic fraction in the studied soils also suggested that, Zn may have high formation constants of organic-Zn complexes.

Cadmium was largely associated with the residual fraction in all the studied soils with the exemption of samples obtained from Bankemo 1 and Idanre 2 which had cadmium predominantly in organic fraction and Fe-Mn oxide fraction respectively(Table 4). Cd in residual fraction ranged from 0.25 to 6.17 mg/kg with a mean value of 3.08mg/kg. However soils obtained from Bankemo 1, Afun 2, Afun1, Idanre 2 and Owena 2 were associated with water soluble and extractable fractions which suggest that Cd in these five soils is potentially bioavailable for plant uptake [19].

The strong association of Cd with the residual fraction is in agreement with the observation of Kuo *et al.* [20]. Distribution pattern of Cd in the studied soils suggests that, the higher the total soil Cd, the higher its tendency to be associated with the residual fraction (Fig. 4).

The mobility of metals in soil samples may be assessed on the basis of absolute and relative contents of fraction weakly bound to soil components. The relative index of metal mobility was calculated as a mobility factor (MF) on the basis of the following equation [21-23].

$$MF = \frac{(F1 + F2 + F3)}{(F1 + F2 + F3 + F4 + F5 + F6)} \times 100$$

Result of mobility factor of heavy metals in the studied soils is presented in Table 5. Mobility factor of copper ranged from 6.17 to 36.97%. The range was higher than the values reported by Yusuf who reported MF for copper not more than 10% in landfill site at Ajota, Lagos, Nigeria. The indices of mobility were comparatively highest for Pb with a mean value of 50.12% Zn (30.15%), Cd (28.18%), while Cu had the lowest factor of 18.41%. High mobility factor values have been interpreted as symptoms of relatively high lability and biological availability of heavy metals in soils [24].

On the overall, the results of the present study suggested that the mobility and bioavailability of the four heavy metals examined, reduced in the following order:

$$Pb >> Zn > Cd > Cu$$

CONCLUSION

The use of total metal content of a soil in contamination characterization is a useful parameter. However, the speciation of heavy metals with selective extractants gives additional information on the fundamental reactions controlling the behavior of metals in soils. Fractionation of heavy metals also gives information on which of the various fractions is bioavailable for plant uptake..Copper and Zinc were predominantly associated with the organic fraction while lead was largely associated with the extractable and Cd was mostly associated with the residual fraction. This study revealed that, the lower the total Copper in the studied soils, the higher its bioavailability. Lead (Pb) was the most potentially bioavailable metal among the four examined heavy metals while Cu was the least potentially mobile.

ACKNOWLEDGEMENT

Authors are grateful to Mr. Omotoso of Rotas soilab for his assistance during the instrumental analysis of heavy metals. The effort of Mr A. Adewoye, Mr Azowata F and Mr Adeduntan during the sequential extractions is equally acknowledged.

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