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Assessment Of Lead, Copper And Zinc Contamination Of Soil From Cocoa Growing Farms In The Central Region Of Ghana

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***Abstract:** Concentrations of some heavy metals (Pb, Cu, Zn and Al) in the soil originating from the cocoa growing areas in the Abura/Asebu/Kwamankese district were assessed. Thirty soil samples were taken from five demarcated sites in six different cocoa growing farms. The range of the calculated mean concentrations (mean ± cv) and the range of the concentrations of the metals (mg/kg) in the soils from the farms analysed in the district were Cu,(2.068 ± 0.24 – 5.30 ± 0.60),(0.90-8.90) Pb, (4.16 ± 0.19- 9.54± 0.24), (2.63-12.86); Zn, (235.05 ± 0.33 – 550.84 ±0.13), (150.30-785.45) and Al, (238.36±0.41- 452.80), (130.30-574.14). The results indicated that the metal concentrations from the farms studied increased in the order; Cu<Pb< Zn. The variation trend in the distribution of the metals in the soils was found to be in the order Cu>Pb>Zn. The geoaccumulation index and the mean enrichment quotient indicated that the soils were polluted with Zn metal. The enrichment factor showed that the soil was enriched with the metals, and the degree of enrichment was in the order Cu<Pb<Zn. This indicates that zinc had the highest chance of being accumulated in the soil.*

***Keywords:** Ghana, Cocoa, Pollution, Copper, Zinc, Lead, Heavy metals, Soil.*

I. INTRODUCTION

Cocoa (*Theobroma cacao* L.) is cultivated mainly in West Africa, Asia, Central and South America [1]. In Ghana, agriculture is one of the major industrial activities and cocoa is the major cash crop grown. Ghana is the world's second largest producer of cocoa beans and cocoa has, for many years been the backbone of the country's economy. Studies on cocoa chemical composition and properties have shown that, a moderate consumption of cocoa may be beneficial for human health, because cocoa contains high polyphenolic compounds, particular flavonoids as antioxidants [2], which are responsible for the overall health of humans [3]. Other beneficial effects of cocoa, range from its free radical scavenging capacity [4], prevention of autoimmune diseases and hepatopathy [4, 5, 6], reduction of the risk of cardiovascular diseases, stroke and death [4, 7, 8] reduction of anxiety, depressive symptoms and supporting brain health [9, 12], to anti-cancer effect [4, 10], anti-inflammatory [11], stabilization of blood pressure [12], maintaining cholesterol level [12, 16]. Phenolics from cocoa also decrease the tendency of blood to clot [17]. Further, extract prepared from cocoa beans or cocoa powder exhibit antibacterial effect against streptococcus mutants formulated in mouth washes [13] and syrtocotozin induced diabetes mellitus [14] and reducing obesity [15].Various researchers over the years emphasized the importance of cocoa to the socio-economic development of Ghana in diverse ways, one school of thought described Ghana's cocoa as the backbone of Ghana's economy [18] whiles another summarized it in simple terms as "Cocoa is Ghana, Ghana is Cocoa" [19]. In West Africa chemical application control for the control of capsid is the most effective [20]. A wide variety of agrochemicals such as pesticides, herbicides fungicides and fertilizers are massively patronized by cocoa farmers [21] in recent times in Ghana with the resultant high output of cocoa beans.

Heavy metal accumulation in cocoa farm soils and farm crops raise concerns because they contribute toxic elements into the human food chain. Agriculture is one of the anthropogenic sources where heavy metal contamination of soil can occur [22, 23, 24]. These anthropogenic sources result in heavy metal accumulation in surface horizons of the soil making farmlands susceptible to heavy metal contamination [25]. The pollution of soil by heavy metals enhance plants uptake causing accumulation of the metals in the plant tissues and eventually phytotoxicity and change of plant community [26, 27].

These heavy metals often occur as cations which strongly interact with the soil matrix and may consequently become mobile as a result of changing environmental conditions [28]. The accumulated heavy metals such as Cu, Pb and Zn in the soil do not only circulate in the soil ecosystem but also enter crops grown in contaminated soils thereby gradually ending up in the food chain [29]. Though some can be beneficial, the non-degradable heavy metals are the most dangerous pollutant of the environment and human beings especially when their levels exceed specific limit [30; 31]. Zinc accumulation in the soil can lead to zinc uptake by the plants which eventually is transferred to consumer of cocoa products. Zinc toxicity may lead to anaemia and lethargy [32]; and cancers typically involving the skin, lung and bladder may result due to lead toxicity [33, 34].

About 7% of the lead in soil is taken and can be translocated into the cocoa beans which eventually end in the human system. Lead exposure is strongly associated with learning disorders and behavioural problems of children and the problems persist into adulthood [45, 46] High level of Pb poisoning can result in IQ deficits, violent crimes and unwed pregnancies, all of which have implications to an array of social and psychological outcomes [47]. Lead also causes long-term harm in adults, including increased risk of high blood pressure and kidney damage [48].

Copper is essential for good health and plays an important role in organisms as one of the so-called “essential” metals. However, exposure to higher doses can be harmful. Long-term exposure to copper dust can irritate ones nose, mouth, and eyes, and cause headaches, dizziness, nausea, and diarrhea. Further, high intakes of copper can cause liver and kidney damage and even death. In younger children, one of the major syndromes associated with copper excess is Attention Deficit Disorder (ADD). Pregnant copper toxic women give birth to copper toxic babies who may have birth defects, learning disabilities, and hyperactivity [49]. Koka *et al* observed that farmers are aggressively incorporating fertilizer use and application of copper fungicides to battle the attacks of various cocoa diseases [50].

II. MATERIALS AND METHOD

Six farm sites located in the Abura/Asebu/Kwamankese district in the central region of Ghana where agrochemicals were applied were sampled. Soil samples were collected from pre- selected sites in Abakrampa (AB), Batanyaa (BA), Edumifa (ED), Asuansi (AS), New Odonase (NO) and Obohen (OB). Each pre-selected sample site was divided into five areas before sampling. Five sets of soils samples were collected at random at a depth of 0-20cm, from each of the demarcated areas using a garden trowel into a plastic polyethylene bags for laboratory analysis.

III. SAMPLE TREATMENT

The 30 soil samples collected were digested using the method described by MAFF (1981). The soils were air-dried and then disaggregated using porcelain pestle and mortar and sieved with a 2-mm nylon mesh to give the fine earth fraction. The fine earth fraction (<2mm) was then used for the various analytical determinations. 1g of each of the homogenized samples of soils was put into a 100ml beaker and 10ml of concentrated HNO_3 was added. The mixture was heated until it was almost dried. Another 10ml of HNO_3 and 3ml of $HClO_4$ were added and the solution was heated and allowed to evaporate to about 1-2ml. 4ml of hot concentrated HCl placed in a labelled plastic polyethylene bag for laboratory analysis was added and then reflux for about 10 minutes. The wall of the beaker was wash down repeatedly with distilled water, filtered into a 50ml volumetric flask, and diluted to the 50ml mark of the flask. The entire blank and the digests solutions were analyzed for Pb, Cu, Zn and Al with an atomic absorption spectrometer (Spectral AA 220Fs, Varian). All experiments were repeated. In order to prove the precision of the analysis, reproducibility and recovery studies were done by analyzing repeatedly distilled water containing 1.0 ppm of Pb, Zn, Cu and Al and samples were spiked with 5.0 ppm standards respectively. Microsoft Excel 2016 and SPSS software (version 16.0 for windows) were used for the statistical analysis of the data. Spearman Rho method of regression and correlation was used to identify the relationship among the metal. The data was explored at 0.05 significant level using Shapiro-wilk test of normality.

IV. RESULT AND DISCUSSION

Variable	Pb	Cu	Zn	Al
Mean	0.986	0.996	0.986	0.997
Sd	0.018	0.040	0.012	0.016
CV	1.806	2.043	1.220	1.606
Std. Error	0.005	0.006	0.004	0.005

Table 1: Recovery of metals from 1.0 ppm standard

Table 1 reveals the results of precision and accuracy analysis of the metals. The percentage recovery of the metals Pb, Cu, Zn and Al, from the spiked samples was 98.60%, 99.60%, 98.60 % and 99.70% respectively.

AB

	Pb	Cu	Zn	Al
AB$_1$	8.20	3.50	250.06	280.10
AB$_2$	7.60	2.80	270.35	320.60
AB$_3$	10.90	8.90	416.50	601.67
AB$_4$	12.86	8.65	451.75	470.18
AB$_5$	8.16	2.67	415.95	540.30

BA

	Pb	Cu	Zn	Al
BA$_1$	10.77	2.20	150.30	178.30
BA$_2$	2.63	2.15	158.6	130.30
BA$_3$	5.30	2.17	320.60	320.80
BA$_4$	3.40	1.81	245.80	201.60
B BA$_5$	3 3.60	3.40	299.95	360.80

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	AS					ED			
	Pb	Cu	Zn	Al		Pb	Cu	Zn	Al
AS$_1$	4.90	2.85	560.20	280.15	**ED$_1$**	4.85	1.94	420.70	450.40
AS$_2$	3.70	2.90	452.70	175.60	**ED$_2$**	10.95	4.68	424.28	320.60
AS$_3$	6.45	4.79	570.30	259.25	**ED$_3$**	8.90	0.90	510.60	340.30
AS$_4$	6.75	2.35	650.50	280.90	**ED$_4$**	5.40	2.00	430.20	222.10
AS$_5$	3.95	3.04	520.50	260.60	**ED$_5$**	4.15	1.20	490.85	264.55
	NO					**OB**			
	Pb	Cu	Zn	Al		Pb	Cu	Zn	Al
NO$_1$	5.40	1.8	420.40	420.80	**OB$_1$**	4.60	2.30	462.10	345.35
NO$_2$	4.26	1.60	495.25	520.60	**OB$_2$**	4.60	2.14	482.65	424.51
NO$_3$	3.52	2.23	485.85	375.40	**OB$_3$**	4.55	2.00	405.15	365.85
NO$_4$	3.50	1.86	620.25	425.70	**OB$_4$**	4.75	3.55	572.75	554.16
NO$_5$	4.10	2.85	535.50	430.40	**OB$_5$**	4.15	2.94	785.45	574.14

Table 2: Concentration of Pb, Cu, Zn and Al in Soil Samples

Table 2 reveals the values of the total samples collected from the six farms analysed. The results indicate the metal concentrations (mg/kg) range between; Pb (2.63-12.86), Cu (0.09 – 8.65), Zn (150.30-785.45) and Al (175.60 – 574.14). The trend of general distribution of the metals in the soils is Cu< Pb<Al<Zn.

AB				
	Pb	*Cu*	*Zn*	*Al*
Mean	9.544	5.304	360.922	442.57
S.D	2.255	3.185	93.355	138.654
CV	0.23625	0.60058	0.25866	0.31329
S. Error	0.902	1.274	37.342	55.462
BA				
	Pb	*Cu*	*Zn*	*Al*
Mean	5.140	2.346	235.050	238.360
SD	3.295	0.610	78.539	98.009
CV	0.6410	0.2601	0.3341	0.4112
S. Error	1.318	0.2440	31.416	39.204
ED				
	Pb	*Cu*	*Zn*	*Al*
Mean	6.850	2.144	455.326	319.590
SD	2.933	1.494	42.164	86.711
CV	0.4281	0.6970	0.0926	0.2713
S.Error	1.173	0.598	16.866	34.684
AS				
	Pb	*Cu*	*Zn*	*Al*
Mean	5.150	3.186	550.840	251.300
SD	1.401	0.934	72.371	43.556
CV	0.2721	0.2931	0.1314	0.1733
S.Error	0.561	0.374	28.949	17.423
NO				
	Pb	*Cu*	*Zn*	*Al*
Mean	4.156	2.068	511.450	434.580
SD	0.774	0.493	73.525	52.887
CV	0.1862	0.2384	0.1438	0.1217
S.Error	0.310	0.197	29.410	21.155
OB				
	Pb	*Cu*	*Zn*	*Al*
Mean	4.530	2.586	541.62	452.802
SD	0.225	0.648	149.036	105.952
CV	0.0497	0.2505	0.2751	0.2340
S.Error	0.090	0.259	59.614	42.381

Table 3: The mean of the metals for the individual farms

Table3 shows the analysis of mean heavy metal concentrations in the soils from the individual cocoa farms sampled in district. The result reveals that the general trend for the metal distribution at all the six farms follows that, Zn>Pb>Cu.

There were variation trends in the levels of the metals at all the individual sites. The coefficient of variation (Table 3) indicate that, the variation in the distribution of the metals in the soil from AB farmland was in the order Cu>Zn>Pb. The mean concentrations (mean ± cv) and ranges of the metals in mg/kg for the site AB were Cu, 5.30 ± 0.60 (2.67- 8.90); Pb, 9.54 ± 0.24 (7.60-12.86); Zn, 360.92 ± 0.26 (250.06 - 451.75); Al, 442.57 ± 0.31 (601.67-280.10). The results from farm BA revealed that the mean concentrations (mean ± cv) and ranges of the metals in mg/kg were Cu, 2.35 ± 0.26 (1.81-3.40); Pb, 5.14 ± 0.64 (2.63-10.77); Zn, 235.05 ± 0.33 (150.30-320.60); Al, 238.36±0.41 (130.30-360.80).

Analysis from farm ED revealed that the mean concentrations (mean ± cv) and ranges of the metals in mg/kg were as follows Cu, 2.14 ± 0.70 (0.90-4.68); Pb, 6.85 ± 0.43 (4.15-10.95); Zn, 455.33 ± 0.09 (420.70-510.60); Al, 319.59±0.27 (222.10-450.40). The results from farm AS revealed that the mean concentrations (mean ± cv) and ranges of the metals in mg/kg were as follows Cu, 3.19 ± 0.29 (2.35-4.79); Pb, 5.15 ± 0.27 (3.70-6.75); Zn, 550.84 ± 0.13 (452.70 - 650.50); Al, 251.30±0.17 (175.60-280.90). Results from farm NO revealed that the mean concentrations (mean ± cv) and ranges of the metals in mg/kg were as follows Cu, 2.07 ± 0.24 (1.60-2.86); Pb, 4.16 ± 0.19 (3.50-5.40); Zn, 511.45 ± 0.14 (420.40 - 620.25); Al, 434.58±0.12 (375.40 - 520.60).

Analysis from farm OB revealed that the mean concentrations (mean ± cv) and ranges of the metals in mg/kg were as follows Cu, 2.59 ± 0.25 (2.00-3.55); Pb, 4.53 ± 0.05 (4.15-4.75); Zn, 541.62 ± 0.28 (462.10-785.45); Al, 452.80 ± 0.23 (345.35-574.14).The sites AS, NO, and OB close to the road had the highest amounts of Zn, with mean and ranges in mg/kg, being 550.84 ± 0.13 (452.70-650.50), 511.45 ± 0.14 (420.40-620.25); and 541.62 ± 0.28 (462.10-785.45) respectively but had relatively lowest amounts of both Pb and Cu.

The mean concentrations of Pb in all the six farms (range 9.54 ± 0.24 – 4.12 ± 0.19) lied within the acceptable limits of Pb= 1-500 mg/kg (average=50 mg/kg) recommended by the Interdepartmental Committee on Reclamation of Contaminated Land metals in soil used for agriculture**,** but much lower than the maximum tolerable levels proposed for agricultural soil (90-300 mg/kg DW) by Kabata-Pendias and Pendias [41]. All the Pb concentration in the soils analysed were lower than the WHO/FAO (36) permissible limit of 50.00 mg/kg for soils.

The mean concentrations of copper recorded in all the farms (range 5.30 ± 0.60 – 2.07 ± 0.24) were below the WHO/FAO (42) permissible limit of 100 mg/kg for soils. The levels of copper were within the normal range of 2-250 mg/kg recommended by Kabata-Pendias [41] and also below 300 mg/kg recommended by EC [43] and MAFF [44]. In general, the zinc level was found to be above the normal range of 10-30 mg/kg recommended by Logan [45] and the 100 mg/kg observed by EC [43] and MAFF [44].

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The mean concentrations of zinc (Zn) in the six farms ranged from 235.05 ± 0.26 – 550.84 ± 0.13 mg/kg mg/kg. 83.33% of the farms studied had mean concentrations above the WHO/FAO (42) permissible limit of 300.00 mg/kg for soils however; the mean concentration of Zn from the farm BA was below the WHO/FAO (42) permissible limit. However, considering the sample site 76.67% had levels above the recommended limit, and 23.33% had levels within the limits recommended by Alloway [46]. On the other hand 80% of the total samples were above the WHO/FAO (42) permissible limit while 20% were below.

Alloway, recommended that soil concentrations ranging from 70-400 mg/kg total Zn is classified as critical, above which toxicity is considered likely [46]. 83.33% of the mean concentrations had levels above the recommended limit, and 16.67% had levels within the limits recommended by Alloway [46].

AB

	Pb	Cu	Zn	Al
Pb	1			
Cu	0.9366	1		
	0.019			
Zn	0.7429	0.6604	1	
	0.1503	0.225		
Al	0.5018	0.5692	0.8843	1
	0.389	0.3166	0.0464	

BA

	Pb	Cu	Zn	Al
Pb	1			
Cu	-0.1304	1		
	0.8344			
Zn	-0.377	0.391	1	
	0.5316	0.5152		
Al	-0.138	0.6865	0.9079	1
	0.8248	0.2005	0.0331	

AS

	Pb	Cu	Zn	Al
Pb	1			
Cu	0.2716	1		
	0.6585			
Zn	0.8902	-0.0842	1	
	0.0429	0.893		
Al	0.6106	-0.0086	0.8345	1
	0.274	0.9891	0.0788	

ED

	Pb	Cu	Zn	Al
Pb	1			
Cu	0.6282	1		
	0.2564			
Zn	-0.0085	-0.6759	1	
	0.9892	0.2104		
Al	0.0737	0.0311	-0.1998	1
	0.9063	0.9604	0.7473	

NO

	Pb	Cu	Zn	Al
Pb	1			
Cu	-0.2572	1		
	0.6762			
Zn	-0.7529	0.1656	1	
	0.1418	0.7901		
Al	0.2168	-0.4562	0.0199	1
	0.7261	0.4399	0.9747	

OB

	Pb	Cu	Zn	Al
Pb	1			
Cu	0.025	1		
	0.9682			
Zn	-0.7314	0.6353	1	
	0.1602	0.2494		
Al	-0.3671	0.8558	0.8679	1
	0.5433	0.0643	0.0565	

Table 4: Correlation matrix for elements in the soils of study area

Regression and correlation analysis (Table 4) indicated that, there were no significant relationships among the three metals at 0.05 and 0.01 confidence levels.

The extent of contamination was evaluated by calculating the enrichment factor using the relation, $EF = \frac{[Cn/Cref]}{[Bn/Bref]}$ where Cn is the content of the examined element in the examined environment, C_{ref} is the content of the examined element in the reference environment, Bn is the content of the reference element in the examined environment and B_{ref} is the content of reference element in the reference environment. Al was used as the reference element for normalization. There are five contamination categories recognized on the basis of the enrichment factor; EF<2 states deficiency to minimal enrichment, EF=2-5 moderate enrichment, EF=5-20 severe enrichment, EF=20-40 very high enrichment and EF>40 extremely high enrichment [47]. Increase in anthropogenic activities causes increase in the enrichment factor values [48].

Site	Pb	Cu	Zn
AB	1.98	1.93	32.19
BA	1.97	1.57	38.73
ED	1.97	1.08	56.27
AS	1.89	2.04	86.64
NO	0.88	0.76	46.33
OB	0.92	0.91	47.09

Table 5: Summary of Enrichment factor values

The calculated enrichment factor values (Table 5) show that all soils ranged from deficient to minimal enrichment in Pb and Cu in exception of the soil from AS which is moderately enriched in Cu. However, enrichment factor values revealed that 33% of the farms analysed were very contaminated while 67% were extremely contaminated with Zn metal. are very high enriched while soils from the farms ED, AS, NO and OB are extremely enriched with Zn. However all the soils had minimal enrichment of Pb and Cu. The extent of enrichment was in the order Cu<Pb<Zn. A mean enrichment quotient (MEQ) for the three metals, which is determined by summing EFs for Cu, Pb, and Zn and dividing by three, was used to estimate the magnitude of human-induced change in the soil on the farmland. The MEQ value proves that, the soils were contaminated. This observation may be due to the prolong application of fertilizers and other agricultural chemicals. This observation is not unexpected as the applications of agricultural chemicals on farms eventually enrich the soils with heavy metals.

Sites	Pb	Cu	Zn
AB	0.08	0.07	1.25
BA	0.04	0.03	0.82
ED	0.06	0.03	1.58
AS	0.04	0.04	1.91
NO	0.03	0.03	1.78
OB	0.04	0.04	1.88

Table 6: Geo-Accumulation index values

Geo accumulation index (Igeo) was calculated in Table 6 using the formula; $Igeo = \log_2 (C_n/1.5B_n)$ where, C_n is the measured total concentration of the element, B_n is the average concentration of element n in shale (background) and 1.5 is the factor compensating the background data (correction factor). The following interpretations for the geo-accumulation index were given by Loska *et al* [49]: Igeo< 0 = Practically unpolluted, 0<Igeo<1 = Unpolluted to moderated polluted, 1<Igeo<2 = Moderately polluted, 2<Igeo<3 = Moderately to strongly polluted, 3<Igeo<4 = Strongly polluted, 4<Igeo<5=Strongly to extremely polluted and Igeo>5=extremely polluted. The values indicated that the soils were unpolluted with Pb and Cu but moderately polluted with Zn.

SITES	Pb	Cu	Zn
AB	0.38	0.37	6.24
BA	0.21	0.16	4.07
ED	0.27	0.15	7.88
AS	0.21	0.22	9.53
NO	0.17	0.15	8.85
OB	0.18	0.18	9.37

Table 7: Contamination factor values

Pollution load index (PLI) for the entire sampling site was determined as the nth root of the product of the n contamination factors (CF). $PLI = (CF_1\times CF_2\times CF_3\ldots\ldots)^{1/n}$. This empirical index provides a simple, comparative means for assessing the level of heavy metal pollution. Soils which has a value of PLI >>1 are considered to polluted [50]. CF<1 = low contamination CF=1-3 = moderate contamination CF=3-6 = considerable contamination CF>6 = very high contamination. All the farms analysed were uncontaminated in Pb and Cu however, very highly contaminated with zinc since their PLI >>1.

V. CONCLUSION

The Zn levels in the soil of cocoa farms analysed in the Abura/Asebu/Kwamankese district in the central region of Ghana were remarkably high with PLI >>1 a value considered to be very highly contaminated. However, the Zn levels varied within the individual farms. The results suggest that special attention must be given to the need to control the use of agricultural chemicals, because a large portion of metals in the soil sediments are likely to be translocated into cocoa crops grown on the soil. The high levels of zinc would inhibit the uptake of iron resulting in induced severe iron due to zinc toxicity. The resultant effect is that a pale yellow to white interveinal chlorosis on the younger leaves may be observed, which smay finally lead to necrosis of the leaf blades and growing point.

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