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Copper and Zinc Pollution in Cocoa Growing Areas in a Low-income Country

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Abstract
The application of copper-based fungicides and inorganic fertilizers affects the integrity of the soil which can result in bioaccumulation of copper and zinc in the cocoa beans to levels that are of public health concern. Cocoa farmers over the years have applied these agrochemicals in the control of pets and disease. The concentration of copper and zinc in soils and cocoa beans in the East Akyem municipality was then determined. Soil pH was measured with a pH meter with a glass electrode using a 1:2.5 soil: water ratio whiles Walkley-black method was used to determine Organic Carbon. Copper and Zinc in the soil were extracted using Mehlich-3 Extractant. The concentrations were determined using Atomic Absorption Spectrometer (Spectra AA 220 FS model). Cocoa beans samples were acid digested and Varian AA-240FS was used to determine the concentration of Copper and Zinc. Pollution Indices was used to quantify the pollution status of the soil. The mean concentration of Cu and Zn at depth 0-15cm was generally higher than at depth 15-30cm.The concentration of Cu and Zn were higher in the cocoa farm soils than that of the control farms. Soil acidity was found to increase with decreasing Organic matter. However, the Cocoa beans were not polluted with Cu nor Zn as their concentrations were found within the permissible limits. Pollution Index analysis suggest agrochemicals to have serious impacts on the farm soil. The soil-cocoa bean correlation matrix reveals that the concentration of Cu and Zn in the cocoa beans depends on the amount in the soil.

Keywords: Ghana, Cocoa, Pollution, Copper, Zinc, Agrochemicals

1. Introduction

The importance of cocoa to the socio-economic development of Ghana has been emphasized in diverse ways by researchers over the years. Osei (2007) in his research described Ghana's cocoa as the backbone of Ghana's economy whiles Helena and Pärssinen (2009) put it in simple terms that "Cocoa is Ghana, Ghana is Cocoa".

Regrettably, the production of cocoa is constrained by several factors, key among which is the incidence of cocoa pests and diseases. Jonny et al. (2003) indicated that pests and diseases are important destabilizing factors in many cocoa producing countries. Asare (2011) reported that 30 percent of the cocoa produced in Ghana annually is lost to pests and diseases, mostly; Phytophthora pod rot (black pod) and Mirids.

Chemical control is the most effective in West Africa for the control of Capsid (Asare 2011) and the commonest method of control has been the routine use of fungicide (Addo-Fordjour 2013). The recommended fungicides for the control of black pod disease in Ghana are all copper-based (Adu-Acheampong et al. 2006). These include Ridomil Plus 66 WP (12% Metalaxyl-M and 60 % Copper (I) oxide), Champion WP (77 % copper hydroxide and 23 % inert ingredient: 50 % metallic copper equivalent), Nordox 75WG (86 % Cuprous oxide and 14 % inert ingredients: 75 % metallic copper equivalent), Funguran OH WP (77 % copper hydroxide and 23 % inert ingredient: 50 % metallic copper equivalent), Kocide 101 WP (77 % copper hydroxide and 23% inert ingredient: 50 % metallic copper equivalent) and Metalm 72 WP (12 % Metalaxyl-M and 60 % Copper (I) oxide) (KoKa et al. 2012).

The continuous applications of fertilizers to soil increase heavy metal concentrations to levels that may eventually exceed natural levels in soils (Nartey et al. 2012). Food chain contamination by heavy metals has become a burning issue in recent years because of their potential accumulation in biosystems. The main sources of heavy metals to crops are their growth media (soil, air, and nutrient solutions) from which these elements are taken up by the roots (Lokeshwari and Chandrappa 2006).

The continuous application of these agrochemicals is being questioned because of the ability of the soil and plants to accumulate their residues. To be able to effectively sustain and increase the growth of cocoa and ensure the soil's sustainability and the integrity of cocoa beans, it is imperative to know the impact of these copper-based fungicides and the inorganic fertilizers used in the production of cocoa.

East Akyem Municipality is one of the leading producers of cocoa in the Eastern region of Ghana which is the third leading producer of cocoa in the country. This study, therefore, seeks to assess levels of Copper (Cu) and Zinc (Zn) pollution of the soil and cocoa beans in cocoa plantation in the East Akyem municipality.

2. Materials and Methods

2.1. *Soil sampling and preparation*

Ten towns that had reported high cocoa bean production for the past years were selected. Ten farms from each of the ten selected towns that had been in cocoa cultivation for not less than 10 years and not more than 30 years and apply copper-based pesticides and inorganic fertilizers were selected for this study. Soil samples from Cocoa Research Institute of Ghana (CRIG) control farm were used as control for this study. Composite soil samples were collected at a depth of about 0-15 cm and 15-30 cm. The soil samples were then kept in soil bags with their identification codes and transported to the soil science laboratory at CRIG-Tafo.

2.2. *Quality assurance*

All chemicals used were of reagent grade and pure deionised water was used throughout the experimentation. All plastics were soaked in 10% HNO_3. Procedural blanks preparation of standard solutions under clean laboratory environment, calibration of the Atomic Absorption Spectrophotometer (AAS) (Spectra AA 220 FS model) using certified standards. Calibration was repeated after 10 samples run to ensure that the instrument remained calibrated. Accuracy of the method was evaluated through the analysis of two reference materials: IAEAV-10 SRM certified Hay Powder and NIST 1547 SRM certified Peach Leaves.

2.3. *Cocoa beans sampling and preparation*

Ripe Cocoa pods were harvested from the cocoa trees and separated into husk and beans. The beans were fermented and air dried to constant weight and milled to fine powder.

2.4. *Chemical analysis of cocoa beans*

Cocoa beans samples from each sampling site were acid digested for the determination of copper and zinc following the methods described by Lokeshwari and Chandrappa (2006). Spectra AA 220 FS model AAS was used to determine the levels of copper and zinc. Replicate analyses were carried out for each determination to ascertain reproducibility and quality assurance.

2.5. *Chemical analysis of soil*

Percentage organic matter and pH were determined following methods described by Meersmans et al. (2009) and Snoeck et al., (2010). Copper and zinc were extracted using the methods described by Mehlich (1984) and elemental concentrations determined on an Atomic Absorption Spectrophotometer (Spectra AA 220 FS model).

3. Statistical Analyses

Means and standard deviations were determined using SPSS version 16 software and MS Excel. The interrelationships among elemental concentrations in soil and cocoa beans were analysed using Pearson‘s correlation and t-test. Graphical representation and charts were then generated.

4. Quantification of Soil Pollution

The Pollution Load Index (PLI) and Contamination Degree (C_d) were computed for the soil data using Contamination Factor (CF) approach as described by Boamponsem et al. (2010). PLI is an empirical index which provides a simple, comparative means for assessing the level of trace elements pollution. PLI was therefore used to find out the mutual pollution effect of Cu and Zn on each of the sampling sites using the equation below;

$$\mathrm{PLI} = \sqrt[n]{\mathrm{CF1} \times \mathrm{CF2} \times \ldots\ldots \times \mathrm{CFn}}. \qquad (1)$$

Pollution Load Index value of one (1) indicates heavy metal load close to the background level, and value above 1 indicates pollution (Boamponsem, 2011).

5. Results and Discussion

5.1. *Accuracy and reliability of instruments*

The accuracy and reliability of the measurements were ascertained with the analysis of two reference materials; NIST 1574 SRM certified Peach Leaves and IAEA-V-10 SRM certified Hay Powder. The measured concentrations for this work along with their corresponding certified or reported values for the reference materials are presented in (Table 1).

Table 1 Levels of Cu and Zn in two Standard reference materials

	Levels of heavy metals in IAEA – V-10 Standard reference materials (Hay Powder)			
Trace Element	This work	Reported values	Absolute Error	% Error
Cu	9.12 (7.98-10.25)	9.4 (8.8 - 9.7)	0.285	3.13
Zn	23.25 (23.25-24.47)	24 (23 - 25)	0.14	0.59
	Levels of heavy metals in NIST standard reference material 1547 (Peach Leaves)			
Trace Element	This work	Reported values	Absolute Error	% Error
Cu	11.61 (10.67-12.55)	12 (11-13)	0.39	3.36
Zn	24.64 (22.53-26.74)	25 (22-28)	0.365	1.48

5.2. *Variation of copper and zinc concentration with soil depth*

The mean Cu and Zn concentration in the soil samples are presented in (Fig. 1) and (Fig. 2) for both soil depth 0-15 cm and 15-30 cm. The general trend of Cu and Zn at soil depth 0-15 cm was higher than at soil depth 15-30 cm. This could be as a result of the method of application of the copper-based fungicides and the inorganic fertilizers to the soil since farmers were observed spraying these agrochemicals directly on the cocoa plant without taking keen interest in the amounts that gets to the soil. Apapam registered the highest mean concentrations for both Cu and Zn (Fig. 1 and Fig. 2).

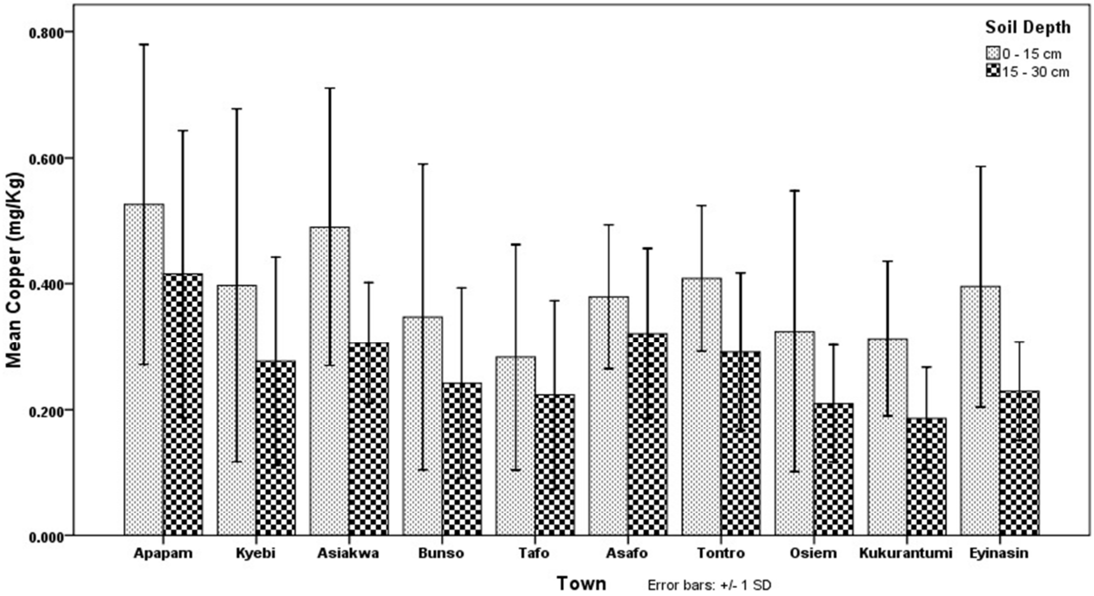

Fig. 1 Difference in concentration of copper among the studied communities and at different depths.

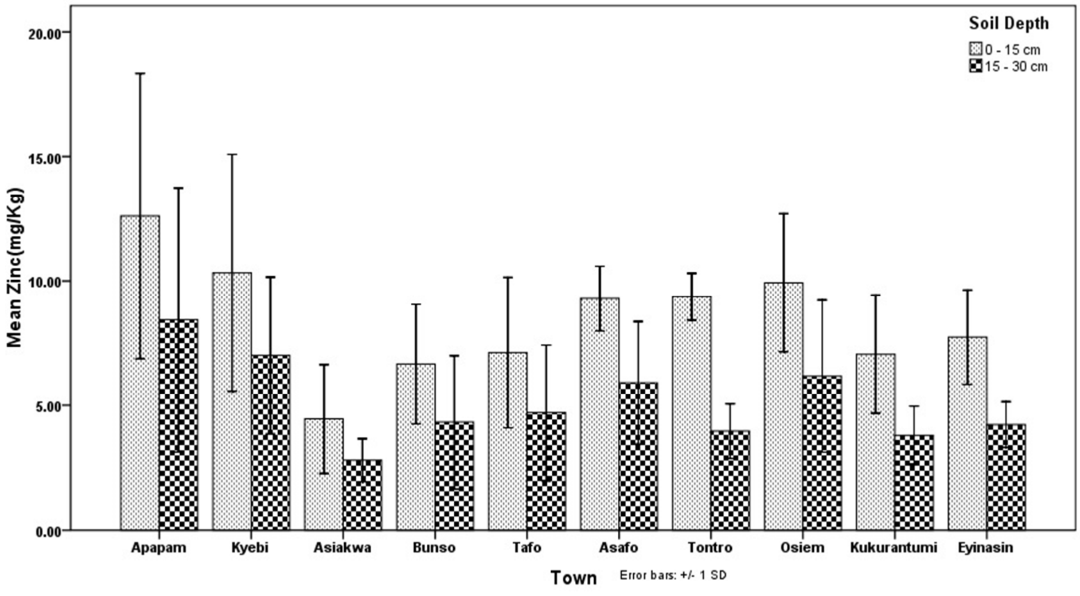

Fig. 2 Difference in concentration of zinc among the studied communities and at different depths.

The permissible limit of Cu and Zn are 135–270 and 300–600 mg/kg respectively per Indian Standard for Soil (ISS) (Awasthi 2000), and according to Wild (1993), the maximum metal concentration of Cu and Zn permitted under EU regulation are 140 mg/kg and 300 mg/kg respectively. Koka et al. (2011)a reported Cu concentration to be 0.265 mg/kg whiles Aikpokpodion (2010) also reported Zn concentration to be 6.59 mg/kg in a similar study to this current work. Aikpokpodion et al. (2010) suggests that only 15% of applied fungicides get to the target while the remaining 85% end up in the soil. Nartey et al. (2012) reported the levels of heavy metals in fertilizer amended soils (FS) as compared to natural soils (NS). They indicated that the FS recorded higher metal concentrations than the NS, and suggested the observed increase in the FS was because of the soil retaining those heavy metals sourced from the applied fertilizers. Zinc concentration may also be affected by the application of Ammonium based fertilizers as reported by Brennan (2005). Chude and Obatolu (1987) indicated that 7.90 mg/kg copper disturbed growth in cocoa seedlings while copper value of 3.80 mg/kg did not, suggesting that some level of tolerance of the cocoa plant.

6. Concentration of Copper and Zinc in Cocoa Beans

The highest concentration of Cu (0.241±0.243 mg/kg) and Zn (0.083±0.049 mg/kg) in the Cocoa beans were recorded at Apapam as in (Fig. 3).

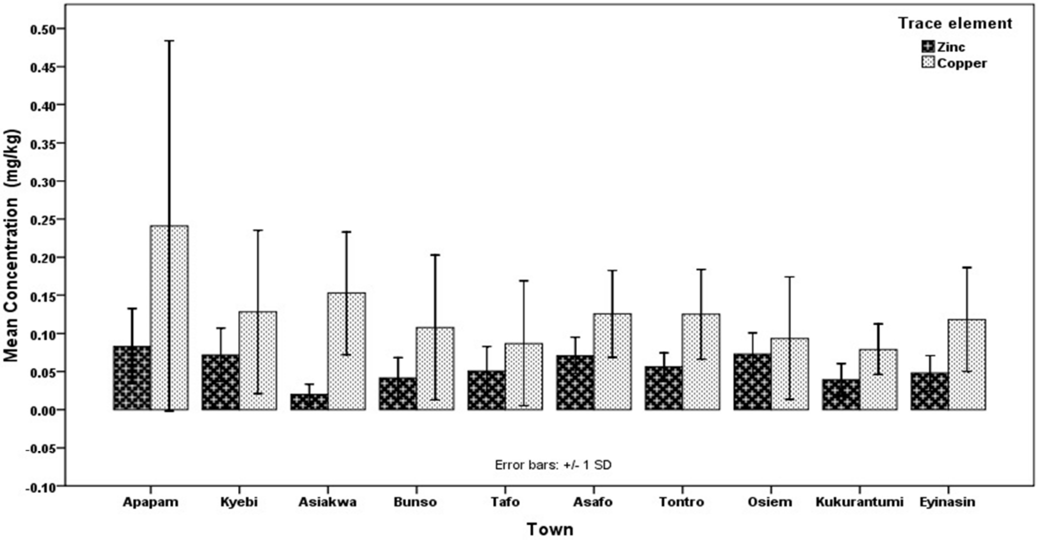

Fig. 3 Concentration of copper and zinc in cocoa beans

The elevated levels of Cu could be due to the regular application of copper-based fungicides to the cocoa tress and pods as a means of controlling black pod disease and Mirids on the cocoa farms. Koka et al. (2011)a indicated that cocoa pods is also a route through which Cu gets into the Cocoa beans and Aikpokpodion et al. (2013), also reported of the two possible pathways through which copper gets into cocoa beans on the field; uptake and translocation of Cu from soil and permeation of cocoa pod cuticle by copper after fungicide application. The values recorded for zinc in the cocoa beans in this work compares well with values reported by Koka et al. (2011)b (Cu; 0.13 mg/kg) but higher than the concentration reported by Aikpokpodion (2010) (Zn; 0.005 mg/kg).

Table 2 Correlation matrix of levels of copper and zinc in soils and cocoa beans

	Correlations			
	Zinc in Soil	Zinc in Cocoa beans	Copper in soil	Copper in Cocoa beans
Zinc in Soil	1			
	100			
Zinc in Cocoa beans	.940**	1		
	1.90E-47			
	100	100		
Copper in Soil	1.51E-01	1.21E-01	1	
	1.33E-01	2.30E-01		
	100	100	100	
Copper in Cocoa beans	9.02E-02	5.56E-02	.903**	1
	3.72E-01	5.83E-01	7.82E-38	
	100	100	100	100

** Correlation is significant at the 0.01 level (2-tailed).

The results as shown in Table 2 showed a significant (p-value < 0.05) positive correlation between both

Copper and Zinc concentration in soil and the cocoa beans. This indicates that as the concentration of copper and zinc increases in the soil, there is a direct increase in the cocoa beans.

7. Quantification of Pollution

7.1. *Contamination factor (CF)*

The Contamination Factor (CF) for copper at soil depth 0-15 cm as depicted in Table 3 revealed all the sampling sites were uncontaminated but at depth 15-30 cm, Apapam sampling sites was lightly polluted. The CF for Zinc at soil depth 0-15 cm indicates that five (Asiakwa, Bunso, Kukurantumi, Tafo, Eyinasin) of the sampling sites were unpolluted whiles the other five sampling sites; Apapam, Kyebi, Asafo, Tontro and Osiem were lightly polluted. The CF for Zinc at soil depth 15-30 cm, all the sampling sites were designated as lightly polluted except for Apapam which was medium polluted.

Table 3 Pollution Load Index (PLI) and Contamination Degree (C_d) of sampling sites

Sampling Site	CF_{Cu}	CF_{Zn}	PLI	C_d	CF_{Cu}	CF_{Zn}	PLI	C_d
	(0 - 15cm)				(15 - 30cm)			
Apapam	1.05	1.61	1.301	0.301	1.38	2.44	1.838	0.838
Kyebi	0.79	1.32	1.024	0.024	0.92	1.41	1.141	0.141
Asiakwa	0.98	0.57	0.746	-0.254	1.02	1.50	1.238	0.238
Bunso	0.70	0.85	0.768	-0.232	0.81	1.55	1.118	0.118
Tafo	0.57	0.91	0.718	-0.282	0.75	1.63	1.102	0.102
Asafo	0.76	1.19	0.950	-0.050	1.07	1.51	1.272	0.272
Tontro	0.82	1.20	0.988	-0.012	0.97	1.56	1.230	0.230
Osiem	0.65	1.27	0.908	-0.092	0.70	1.51	1.028	0.028
Kukurantumi	0.63	0.90	0.750	-0.250	0.62	1.55	0.981	-0.019
Eyinasin	0.79	0.99	0.885	-0.115	0.76	1.49	1.067	0.067

7.2. *Contamination degree (C_d)*

The contamination degrees of the monitored soils are shown in Figure 4. All the sampling sites registered values below the Threshold Value of 1.

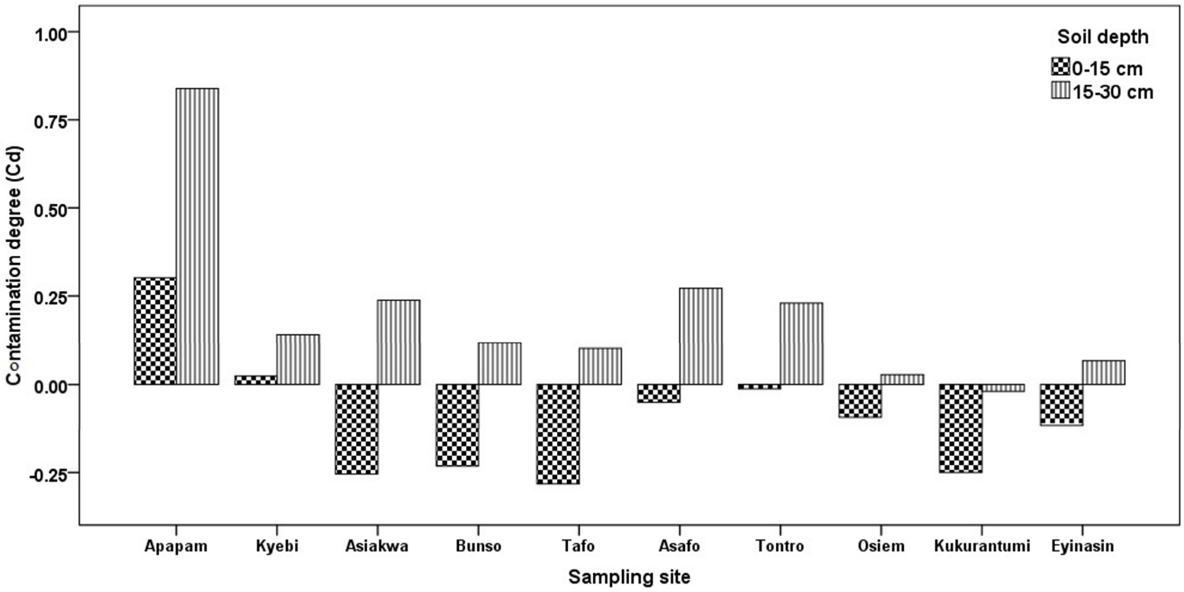

Fig. 4 A comparison of the contamination degree of sampling sites

8. Pollution Load Index (PLI)

The ranking of the sampling sites in terms of pollution grading with respect to depth is shown in Figure. 5. The sequence of the PLI at depth 0-15 cm is as follows; Apapam (1.27) > Kyebi (1.15) > Osiem (1.13) > Tontro (1.09) > Asafo (1.09) Eyinasin (0.99) > Tafo (0.95) > Kukurantumi (0.95) > Bunso (0.92) > Asiakwa (0.75). At soil depth 0-15 cm, about 50% of the sampling sites registered values above the background Threshold value of 1. The PLI for soil depth 15-30 cm was mostly above the Threshold value of 1 except for Kukurantumi sampling sites which registered a value below the PLI Threshold. The PLI analysis reveals the sub-soils (15-30 cm) to be polluted giving room for environmental health concern.

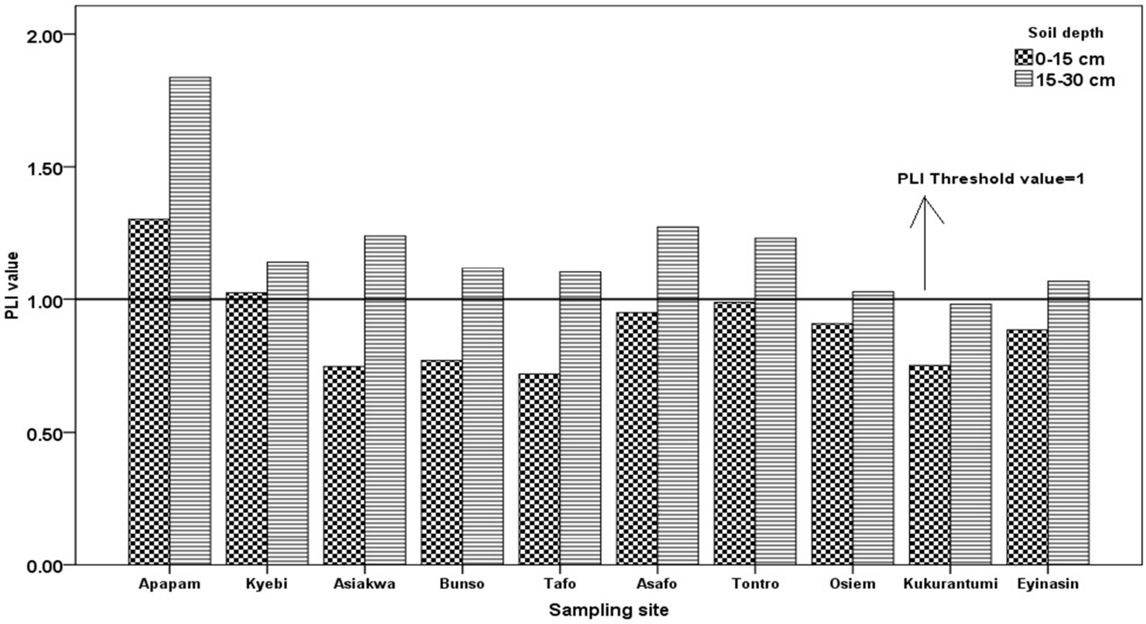

Fig. 5 A comparative diagram of the PLI values across the sampling sites

9. Ecological Implication

Elevated Copper and Zinc concentrations above threshold hold values can kill naturally occurring microorganisms and suppress the rates of nitrogen fixation by the bacteria Rhizobium (Manivasagaperumal et al. 2011). This can also cause earth worms to avoid surface litter as well as leads to nutrient imbalance. Accumulation of trace elements in the soil has the potential to restrict the soil's function, cause toxicity to plants, and contaminate the food chain (He et al. 2005). Thus, continuous accumulation of Copper-based fungicide and inorganic fertilizers can affect the soils fertility and therefore its ability to support plant life. Furthermore, run off from these soils could introduce Copper and Zinc into nearby water bodies, thereby contaminating them (Addo-Fordjour 2013).

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10. Conclusions

The study showed that Copper concentration was always higher than Zinc concentration in the soil. Concentration of Copper and Zinc at soil depth 0-15 cm was generally higher than at soil depth 15-30 cm. Although copper concentration was generally higher than that of zinc in the cocoa beans, these concentrations were within acceptable limits hence the cocoa beans were not polluted by the studied elements. Soil acidity was found to increase with decreasing organic matter. The Pollution Load Index and Contamination Degree values suggest that the agrochemicals have serious impacts on the integrity of the soil. As the concentration of the copper and zinc increases in the soil, there is a direct increase in the cocoa beans. The study also showed that soil from Apapam was polluted with both Copper and Zinc. Further investigation of the soil environment of Apapam would help explain its pollution status. An alternative form of fungicide devoid of Copper should be explored for the control of cocoa pest and diseases or an alternative way of controlling cocoa pest and disease (such as biological control methods) should be explored.

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