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ASSESSMENT OF COPPER AND ZINC IN COCOA GROWING AREAS IN EAST AKYEM MUNICIPALITY OF THE EASTERN REGION OF GHANA

BY:

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DECLARATION

It is hereby declared that this thesis is the outcome of research work undertaken by the author, any assistance obtained has been duly acknowledged. It is neither in part nor whole been presented for another degree elsewhere.

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DEDICATION

I wholehearted dedicate this work to my Lord and God, my Parents, Siblings, Friends, my Sweetheart, the very good people of Akyem Abuakwa Kingdom and all well-meaning Citizens who are working tirelessly to uplift the life of the ordinary citizens of the municipality.

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LIST OF ABBREVIATION

CCME	Canadian Council of Ministers of the Environment
COCOBOD	Ghana Cocoa Board
CODAPEC	Cocoa Diseases and Pest Control Program
CRIG-Tafo	Cocoa Research Institute of Ghana-Tafo
CSIR	Council for Scientific and Industrial Research
EAMA	East Akyem Municipal Assembly
GOG	Government of Ghana
ICCO	International Cocoa Organization
WCF	World Cocoa Foundation

ABSTRACT

There is an increasing awareness that trace elements and heavy metals present in soil at concentrations above threshold values have negative effects on human health and on the environment. The accumulation of trace elements in the soil is known to restrict the soil's function, cause toxicity to plants, and contaminate the food chain. This paper reports the concentration of copper and zinc in soils and cocoa beans in the East Akyem Municipality of the Eastern Region of Ghana. Sampling was done in 100 selected cocoa farms. Soil pH, percentage organic matter, copper and zinc were determined at different depth of 0-15 cm and 15-30 cm. The results of the study revealed that the pH of the soil was more acidic at depth 15-30 cm than at depth 0-15 cm and percentage organic matter was also higher at depth 0-15 cm than at depth 15-30 cm. The mean concentration of copper expressed in mg/kg at soil depth 0-15 cm ranged between 0.283±0.179 and 0.526±0.254 and at soil depth 15-30 cm ranged between 0.210±0.093 and 0.415±0.228. The mean concentration of zinc expressed in mg/kg at soil depth 0-15 cm ranged between 4.46±2.18 to 12.61±5.74 and at soil depth 15-30 cm ranged between 2.18±0.86 and 8.44±5.30. Although, the concentration of copper and zinc at depth 0-15 cm was generally higher than at depth 15-30 cm their mean difference was not significantly different (p-value > 0.05). The concentration of copper in the cocoa beans recorded values ranging between 0.879 mg/kg and 0.005 mg/kg whilst the concentration of zinc in the cocoa beans also recorded values in the range of 0.15 mg/kg to 0.01 mg/kg. Concentration of copper in the cocoa beans was always higher than that of zinc across all the sampling sites and their mean difference was statistically significant (p-value < 0.05). The concentration of Cu and Zn in the cocoa beans obtained in this study were below the

maximum recommended limits set by WHO/FAO and hence pose less or no risk upon consumption, thus, the cocoa beans were not polluted by the Cu nor Zn. The concentration of copper and zinc were higher in the cocoa farm soils than that of the control and their mean difference was significant (p-value < 0.05). Soil acidity was found to increase with decreasing organic matter. The mean pH at soil depth 0-15 cm and 15-30 cm differ significantly from percentage organic matter at depth 0-15 cm and at depth 15-30 cm respectively (p-value < 0.05). Pollution Index analysis suggests copper and zinc to have serious impacts on the farm soils. There was a strong positive association between the concentrations of Cu and Zn in the cocoa beans and the farm soil. It is expected that the results from this study would be relevant for all trace elements studies in cocoa farms.

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CHAPTER ONE

1.0 INTRODUCTION

1.1 Background

Over the years, researchers and individuals have emphasized in diverse ways the importance of cocoa to the socio-economic development of Ghana. Osei (2007), for example, described Ghana's cocoa as the backbone of Ghana's economy. Helena and Pärssinen (2009) put it in simple terms that "Cocoa is Ghana, Ghana is Cocoa".

Regrettably, the production of cocoa globally is constrained by several factors. Among these factors is the incidence of cocoa diseases and pests. Jonny *et al*. (2003) indicated that the yield of Cocoa (*Theobroma cacao)* is limited by pests and diseases and that they are important destabilizing factors in many producing countries. Asare (2011) reported that 30% of the cocoa produced in Ghana annually is lost to pests and diseases.

Over the decade, the Government of Ghana (GOG) has been implementing several programs to control and prevent cocoa pests and diseases, especially capsid attack and Black pod disease in the country. The GOG in 2005 spent an amount of 302,667 US dollars on the control of the Capsid bug and Black pod disease in the country (Asare, 2011). Specifically, the Government of Ghana introduced the Cocoa Diseases and Pests Control (CODAPEC)

Project, which involved mass spraying of cocoa farms using synthetic insecticides and fungicides against capsid and Black pod, respectively.

Many chemicals including fungicides and pesticides (for example, Ridomil, Nordox, Kocide, Akate master, Confidor, Funguran and Champion), which are usually used on cocoa farms in the East Akyem Municipality to control Cocoa Swollen Shoot Virus disease, Black pod, Cocoa mirids, Capsid bugs (Akate) and other insect pests on cocoa contain high amounts of copper (greater than or equal to 50% metallic Copper). Data from the Agric Extension office of the EAMA and confirmed by most farmers in the area reveals Sidalco Liquid NPK fertilizer with formulation of 10:10:10+Trace Elements) as the common and most widely used fertilizer in addition to Sulphate of Ammonia.

Background concentrations of trace elements in soils are important to environmental scientist due to recent interest in contamination potential and toxic effects of these elements on humans and the environment (Slagle *et al.*, 2004). Trace elements are defined as elements that are present at low concentrations in most soils, plants, and living organisms (Alloway, 1996). Some trace elements (e.g. Cu, Zn, Fe, Mn, Mo, and B) are essential to the normal growth of plants. Others such as Cu, Zn, Fe, Mn, Mo, Co and Se are essential to the growth and health of animals. However, some of these trace elements (e.g., Cu, Zn, Pb and Cd) are of environmental concern because of their tendency to cause contamination in soil, water, and food chains (Henry *et al*., 2004).

There is an increasing awareness that trace elements and heavy metals present in soil may have negative effects on human health and on the environment (He *et* *al*., 2005). However, there may also be significant influence from anthropogenic factors (i.e. urban, agricultural and industrial activities) on the levels of trace metals in soil.

Further work has shown that accumulation of trace elements, especially heavy metals, 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).

1.2 Problem Statement

Generally, yields of cocoa are lower in Ghana than in other major producing countries. Reasons for the low productivity include poor farm maintenance practices, planting low-yielding varieties and the incidence of pests and diseases (Abekoe *et al*., 2002). In an attempt to increase production, the government has been implementing policies aimed at reforming the cocoa sector since the early 1990s like the Cocoa Hi-Tech Program aimed at providing inorganic fertilizers and pesticides and the mass spraying program which involved the spraying of cocoa farms with cu-based fungicides.

Chemical control is the most effective in West Africa and for that matter Ghana, for the control of Capsid as reported by Asare (2011). For instance, the government initiated mass spraying campaign to control capsids between 1959 and 1962 using Lindane pesticides (Ebenezer, 2011). In 2001, the Government of Ghana again introduced mass cocoa spraying programs to combat black pod disease and control capsids. In 2010, Ghana's Cocoa production hit an all-time high of 735,000 tons and the annual production can go beyond the target one million tons, if cocoa trees infected by swollen shoot disease are treated and those above 30 years are cut and replanted ("Ghana's Cocoa production," 2011). Essel (2012), reports of a new inorganic fertilizer for cocoa production in the region. This comes to substantiate the fact that, Ghana's agroeconomy is highly reliant on use of agrochemicals (e.g. inorganic fertilizers, insecticides and pesticides) for the growing of cocoa. Continuous applications of fertilizers to soils are known to increase heavy metal concentrations to levels that may eventually exceed natural levels in soils (Vincent *et al*., 2012).

Food chain contamination by heavy metals (of which Cu and Zn are examples as trace elements) has become a burning issue in recent years because of their potential accumulation in biosystems through contaminated soil, water and air. The main sources of heavy metals to crops are their growth media (soil, air, nutrient solutions) from which these elements are taken up by the roots or foliage (Lokoshwad and Chandrappa, 2006). Recently, concerns have been raised over the levels of certain elements in the environment (soil, water, etc.). Thus the urgent need to carry out an assessment of copper and zinc in the soils and cocoa beans from the cocoa growing areas in the East Akyem Municipality.

1.3 Objectives

Main Objective

The main objective was to assess the levels of Cu and Zn in soils and cocoa beans in cocoa growing areas within the East Akyem Municipality of the Eastern Region of Ghana.

Specific objective are;

1. To determine the concentrations of Cu and Zn in the soils in selected cocoa farms in East Akyem Municipality of the Eastern Region of Ghana.
2. To determine the concentrations of Cu and Zn in cocoa beans from selected cocoa farms in East Akyem Municipality of the Eastern Region of Ghana.
3. To determine some physicochemical characteristics of the soil samples from the selected cocoa farms.

1.4 Justification

As already mentioned, cocoa production and its marketing undoubtedly play an important role in the socio-economic development of this country. However, black pod disease, cocoa swollen shoot disease and cocoa capsid have been and will continue to be a devastating disease and insect pest to the crop respectively. Currently, chemical control is the most effective means of controlling this important disease and insect of cocoa, which is done at the recommended rate of 4 times a year. Inorganic fertilizers are the main type of fertilizers approved by CRIG for use in the cocoa farms to increase production of cocoa. To be able to effectively sustain the growth of cocoa and ensure the soil's sustainability and the integrity of the cocoa beans, it is imperative that the effects of using Cu-based fungicide and inorganic fertilizers on the levels of Cu and Zn in soil and cocoa beans in the municipality. This study, therefore, seeks to provide baseline information on levels of Cu and Zn in the soils and cocoa beans in selected cocoa farms in East Akyem municipality of Ghana.

1.5 Organization of the Study

The present study comprises of six chapters. Chapter 1 includes the introduction and background statement, the problem statement, the objectives, and the relevance of the study. In chapter 2, a review of articles, scientific papers, documents and research reports relating to the theme of the study is presented. Chapter 3 includes the methodology employed in achieving the objectives of the study. The study area as well as all relevant concepts, variables and data used in the present study are described. Chapter 4 presents the empirical results of the study as chapter 5 also presents a scientific discussion of the results. Finally, Chapter 6 closes with conclusions and policy recommendations as other supporting data sheets are attached as appendix.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 Global Production of Cocoa

Cocoa is essential to the livelihoods of 40-50 million people worldwide, including over 5 million smallholder cocoa farmers who grow this valuable crop. It has been an important ingredient in global cultures and history, evolving over the years, and continues to be enjoyed today in thousands of different forms (WCF, 2012).

About 3,000,000 tons of cocoa are produced each year. The global production was 3,607,052 tons (3,550,084 long tons; 3,976,094 short tons) in 2004 which was a record breaking achievement. The production increased by 131.7 % in 30 years, representing a compound annual growth rate of 2.8 %. There were about 3.54 million tons of cocoa beans produced in the 2008-2009 growing year (ICCO, 2011) which runs from October to September. Of this total, African nations produced 2.45 million tons (69 %), Asia and Oceania produced 0.61 million tons (17 %) and the Americans produced 0.48 million tons (14 %) (WCF, 2010). West Africa has been the centre of cocoa cultivation for many decades, as two-thirds of the world's cocoa is produced in West Africa (Duguma *et al*., 2001). Two African nations, Côte d'Ivoire and Ghana, produce more than half of the world's cocoa, with 1.23 and 0.73 million tons (35 % and 21 %) respectively (WCF, 2010). Compared to other agricultural activities, cocoa has been a leading subsector in the economic growth and development of several West African countries (Duguma *et al.,* 2001). The largest cocoa bean-producing countries in the world are showed in Table 2-1.

Table 2-1: Global production of Cocoa

Country	Amount Produced (Tons)	Percentage of World production (%)
Cote d'Ivoire	1.23 Million	34.7
Ghana	730 Thousand	20.6
Indonesia	490 Thousand	13.8
Cameroon	210 Thousand	5.9
Nigeria	210 Thousand	5.9
Brazil	165 Thousand	4.7
Ecuador	130 Thousand	3.7
Malaysia	32 Thousand	0.9

Source: (World Cocoa Foundation, 2012)

2.2 Production of Cocoa in Ghana

Cocoa originated from the lower Amazon of Brazil and was brought to Ghana from Fernando Po in 1879 and from Sao Tome in the 1880's. The first recorded export of beans from Ghana was in 1891 and since then, cocoa has been the main export crop and a major source of foreign exchange and domestic income earner (Obeng *et al.*, 2005).

There are six cocoa growing regions in Ghana namely: Ashanti, Brong-Ahafo, Central, Eastern, Western, and Volta regions. Western Region currently accounts for more than half of the total annual production of cocoa in Ghana. Estimated productivity per hectare annually is 250 kg (COCOBOD, 1998). According to ICCO (2003) this yield rate is low compared to countries like Cote d'Ivoire and

Indonesia, which have annual yield rates estimated at 600 kg and 1000 kg per hectare, respectively. About 25 % of current cocoa-tree stocks are over 30 years old. In addition, over 60 % of cocoa farmers are currently over 50 years old and unwilling to take extra risk in investing in yield improvement strategies due to perceived high cost of input relative to producer price (Ministry of Finance, 1999). Hence, cocoa cultivation is a low input venture undertaken on small farms using rudimentary technology with very little purchased input (Anim-Kwapong and Frimpong, 2010).

2.3 Importance of Cocoa

2.3.1 Economic

Cocoa, the source of raw material for the chocolate industry, is the economic engine for West and Central African sub-regions (mainly Côte d'Ivoire, Ghana, and Cameroon). In the year 2005 and 2006, the sub-region produced 2,626 metric tons representing about 71.4 % of the world output of 3,674 metric tons (ICCO, 2007). Ghana is the world's second largest producer after La Côte d'Ivoire and the crop occupies a key position in the country's economy in terms of foreign exchange generation, domestic income, and source of revenue for the provision of socio-economic infrastructure. Gyimah (2012) described cocoa as the "cash crop whose foot print is seen in every aspect of life in Ghana". Appiah (2004) suggested that, cocoa has been the backbone of the Ghanaian economy for more than sixty years and it employs about 60 % of the national agricultural labour force.

On education, the Ghana Cocoa Board scholarship scheme is notable in all the cocoa growing areas in Ghana. From 1951 when the scholarship scheme was put in place, a number of prominent Ghanaians have benefited from the scheme (Gyimah, 2012). On foreign earnings, the cocoa crop generates about US$1 billion annually and is a major contributor to Government Revenue and GDP. In the 1964 and 1965 cocoa season, a total of 580,000 tons of cocoa was produced. This was about 33 % of global market share then, which made Ghana the biggest producer of cocoa in that year. The industry went into decline for almost twenty years. Production figures dropped to an all-time low of 158,956 tons in 1983 and 1984 growing season. This was just about 9 % of global cocoa production (Gyimah, 2012).

2.3.2 Health benefits of cocoa consumption

Chocolate and cocoa contain a high level of flavonoids, specifically epicatechin, which may have beneficial cardiovascular effects on health. Prolonged intake of flavanol-rich cocoa has been linked to cardiovascular health benefits, though it should be noted that this refers to raw cocoa and to a lesser extent, dark chocolate, since flavonoids degrade during cooking and alkalizing processes (Sudarsan and Sumana, 2001). Humphrey (2001) reports that the Kuna Indians living on the islands, who are heavy consumers of cocoa, had significantly lower rates of heart disease and cancer compared to those on the mainland who do not drink cocoa as on the islands. It is believed that the improved blood flow after consumption of flavanol-rich cocoa may help to achieve health benefits in hearts and other organs. In particular, the benefits may extend to the brain and have important implications for learning and memory. Foods rich in cocoa appear to reduce blood pressure (Humphrey, 2001).

2.4 Challenges of Cocoa Production in Ghana

Lack of reliable statistical data on cocoa farmers and their farm sizes is a major constraint in cocoa production in Ghana. Knowledge of farm size is important factor in determining the quantity of agrochemicals to be applied.

Pilfering and diversion of inputs remain one of the biggest challenges of cocoa production in the country as the Ghana police have made several arrest of people smuggling cocoa input outside Ghana and at places where the Cocoa Diseases and Pest Control Project (CODAPEC) operates, inadequate spraying gangs remains a set back to the success of the program as consequently full coverage of farms has not been possible throughout the country (George and Augustine, 2011).

In addition, lack of adequate cooperation from farmers on the basics of additional spraying against the black pod and the mirid menace. To realize optimum benefits from the spraying programme, farmers are advised to do additional spraying but most farmers ignore this advice and rely solely on what CODAPEC provides.

Application of unapproved chemicals and fertilizers on their farms is also a big challenge to the production of cocoa in Ghana. Using such unapproved chemicals does not help the trees to produce quality beans and slowly destroy the farms (Ofori, 2012).

2.5 Trace Elements Pollution

Heavy metals are the common trace component in the earth crust that has densities above 5 g/cm^3. Alloway (1995) reported that cadmium, chromium, lead, zinc and copper are the trace elements with potential hazards in soils. Rehman and Syed (2012) found that the majority of essential trace metals are beneficial when present below the limit of tolerance, but can be toxic if taken in excess. This transition between essentiality and toxicity varies from element to element. Substantial evidence supports the importance of trace elements in human nutrition. These trace elements play a crucial role in various biochemical functions of the body as some of these forms are integral enzyme cofactors. Some form of them, are commonly found naturally in foodstuffs, in fruits and vegetables, and in commercially available multivitamin products. Notable trace metals include cadmium, chromium, cobalt, copper, zinc, lead, iron, zinc and mercury.

2.6 Copper

Copper (Cu) occurs naturally in most soils, fruits and vegetables. Although, it belongs to elements whose natural content in the soil is mostly exceeded, it is indispensable for normal development of living organisms. Both its excess and deficiency are harmful (Jankiewicz *et al*., 1998). Both humans and animals need some copper in their diet. In humans, it helps in the production of blood haemoglobin (Bonham *et al*., 2002). Copper is a pliable, malleable metal, having a bright reddish metallic lustre and is an excellent conductor of both electricity and heat. Copper occurs naturally in a wide range of mineral deposits. It is used in making textiles, marine paints, electrical conductors and wires, plumbing fixtures and pipes, as well as coins and cooking utensils (Gyimah, 2012).

2.6.1 Sources of copper

Copper is a common trace constituent in the earth crust. Its concentration in the ambient environment has increased dramatically since the industrial revolution. However, the major source of copper in agricultural soils is through the continuous application of copper-based fungicides to control diseases of crops. This situation is gradually taking cocoa soils to a condition of deterioration because of the contamination load and the adverse effect on soil biodiversity (Aikpokpodion, 2010)[a].

2.6.2 Copper as fungicides

Aikpokpodion (2010)[b] suggests that the worldwide use of copper based fungicides has resulted in copper accumulations in some agricultural soils far in excess of trace amounts that are required for healthy plant growth, and numerous studies have indicated that prolonged use of copper-based chemicals often results in soil contamination.

According to Gyimah (2012) although copper is required as a micronutrient, it is a broad-spectrum biocide at higher concentrations. Copper fungicides can be described as insoluble compounds, yet their action as fungicides and bactericides is due to the release of small quantities of copper (Cu^{2+}) ions when in contact with water (Mehtar *et al*., 2008).

Formulations of inorganic Cu, most commonly as copper hydroxide and copper sulphate, are used as agricultural pesticides to control fungi, bacteria, and in some instances, invertebrates and algae. As a result, water insoluble copper compounds are used as fungicides (Martinez *et al*., 2006). Copper hydroxide is more water soluble at low pH (high acidity) and it is applied in spray solution such as water at a pH above 6 to avoid phytotoxicity (Gant *et al*., 2007). Concentrations that are reported as toxic vary; critical factors include the organism, whether acute or chronic toxicity was determined, the extraction method, and soil characteristics such as pH and organic matter and clay content. Phytotoxic effect of copper has been known since the 19th century from spraying of Bordeaux mixture in French vineyards (Gyimah, 2012).

Following absorption into the fungus or bacterium, the copper ions link to various chemical groups (imidazoles, phosphates, sulfhydryls, and hydroxyls) present in many proteins and disrupt the function of these proteins. Thus, the mode of action of copper hydroxide (or any other copper fungicide) is the nonspecific denaturation of cellular proteins. The toxic copper ion is absorbed by the germinating fungal spore and thus for best results Agrio (2005) recommended that copper must be reapplied as plants grow to maintain coverage and prevent disease establishment.

2.6.3 Copper fungicides for the control of black pod

Adu-Acheampong *et al*. (2007) wrote that the recommended fungicides for the control of black pod disease in Ghana were all copper-based. 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).

2.6.4 The fate of copper in copper-based fungicides

After foliar application of copper fungicides, a gradual redistribution of copper deposits by the weathering effect (rainfall and dew) may occur. Gyimah (2012) indicated that some of the copper are taken up by plant cells, while most redistribution occurs in downward direction and ultimately end up in litter and soils. This in turn redistributes itself within the soil profiles. However, there is no evidence of copper accumulation at depth below about 25 cm of the soil profile, which might be due to copper's strong affinity for organic matter, thus tending to dominate its interaction with surface soils, litter and vegetation. Some of the difference in exchangeable Cu between cocoa and forest can be attributed to pH differences, as Cu is more available at higher pH (Gyimah, 2012).

Keller *et al*. (2002) suggested that available copper in soils is held mainly as a cation (Cu^{2+}) on surfaces of clay minerals or in association with organic matter. They further indicated that organic matter and soil pH are the predominant factors influencing copper availability.

Copper availability decreases as organic matter in the soil increases. Organic matter binds to copper more tightly than any other micronutrient. This does not only reduce fixation by soil mineral and leaching, but also reduce availability to crops. Keller *et al*. (2002) found that total Cu content was more dependent on the organic matter status, as soil organic matter forms complex with copper to prevent it from leaching. The proportion of copper present in soil solution as Cu^{2+} increased as pH decreased. In soil, Cu is restricted mainly to the top layer because of its ability to tightly bind with carbonates, clay minerals, hydrous oxides of Al, Fe, Mn and organic matter (Gyimah, 2012).

Chaignon *et al*. (2003) writes that copper mobility along the soil profile, bioavailability for root uptake and consequently phytotoxicity threshold for crops depend on soil pH, cation exchange capacity (CEC), quality of organic matter and soil texture as also indicated by Brun *et al*. (2001). Copper is always present at a background level, but can be of concern in situations of heavy agronomic use of copper compounds (Parat *et al.*, 2002). Agricultural soils are reported to have average background levels of 20-30 ppm (Gyimah, 2012) with average overall US level found to be 15.5 ppm. Some vineyard soils in Europe, which have seen intensive use of copper sulphate containing Bordeaux mixtures for 100 years, have soil Cu concentrations ranging from 100-1500 ppm (Gyimah, 2012).

2.6.5 Effect of copper on nutrient availability

Nutrients are needed by plants to produce at maximum capability and to perform specific functions within the plant. When copper gets into the soil, it binds strongly to organic matter, clay minerals and hydrated oxides of iron (Fe), aluminium (Al) and manganese (Mn) (Gyimah, 2012) and either reduces the concentration of these nutrients in the soil or makes them unavailable to plants. Savithri *et al*. (2003) reported that as the copper content in the soils of grape farms increased because of continuous application of Bordeaux mixture, the amount of micronutrient such as zinc, manganese and iron decreased. Similarly, the available phosphorus contents of the soils decreased with fungicide application at both surface and subsurface layers. Gyimah (2012) found that increasing copper content of soils in cocoa results in nutrient imbalance.

2.6.6 Effect of copper on soil fauna

The build-up of copper is more in the surface soil (0-15 cm) (Savithri *et al*., 2003). Detrimental effects of elevated copper concentration on mycorrhizal associations, microbial population and functions have been well documented by Gyimah (2012). It is suggested that to circumvent toxic effects, earth worms may avoid surface litter and soil layers contaminated by certain pesticides. Earthworm aids decomposition and incorporation of organic matter, increase water soluble aggregates, improve water infiltration, aeration, drainage, root penetration, and increase microbial activity in soil. Earthworm casts and burrow walls exhibit higher concentrations of total and plant-available nutrients than surrounding soil and it has been recognized that surface feeding species horizontally and vertically transport microorganisms, spores, pollen and seeds and can reduce plant pathogens through digestion of fungal spores (Gyimah, 2012).

Copper is a relatively non-specific bactericide and fungicide and can kill naturally occurring microorganisms on leaves as well as those that have been applied as bio-controls including *Bacillus spp*., *Trichoderma spp*. and others. Gyimah (2012) suggested that copper suppressed the rates of nitrogen fixation by the bacteria rhizobium under some situations, at relatively high copper levels of 235 ppm.

2.6.7 Effect of copper on human health

Research in the 1990s found that the levels of cadmium, lead, copper and arsenic in foodstuff are of interest as these metals are generally considered as toxic to human beings. Information on the analysis of these metals in raw cocoa and finished chocolate products is, however, rather scarce (Koka *et al*., 2012).

Long-term exposure to copper can cause irritation of the nose, mouth and eyes. It causes headaches, stomach aches, dizziness, vomiting and diarrhoea. Dampare *et al*. (2006) found out that copper accumulates in liver and the brain. Its toxicity is known as a fundamental cause of Wilson's disease and high uptake of copper may cause liver and kidney damage and even death.

Research carried out by some environmental scientists has revealed that the occurrence and geographical distribution of certain diseases could be correlated with the presence of toxic elements in the geologic environment (Dampare *et al*., 2006).

2.6.8 Effects of soil pH on the availability of Copper

Ebenezer (2011) reports that copper is strongly adsorbed to soil particles and therefore has very little mobility relative to other trace metals. Because of this limited mobility, applied copper tends to accumulate in soil. The capacity of soil to adsorb copper increased with increasing pH, with a maximum holding capacity at neutral to slightly alkaline conditions (pH 6.7–7.8). Furthermore, soils with alkaline conditions tend to favour precipitation of copper; thus, copper is more mobile under acidic than alkaline conditions (CCME, 1999).

2.6.9 Effects of soil Organic matter on the availability of Copper

Copper has a very high affinity for organic matter and is more strongly bound than other trace elements (Ebenezer, 2011). This high adsorption ability of organic matter is likely due to its high CEC and chelating ability. Copper found in soil solution is often bound to dissolve organic matter and will only be released in an ionic form under strongly oxidizing conditions or through microbial degradation of the organic matter. Even though organic matter generally contributes to copper's immobility through binding, it can also increase copper's solubility by forming soluble complexes (CCME, 1999).

2.7 Zinc

According to Alvarez-Benedi and Munoz-Carpena (2005), although zinc is a heavy metal, at very high concentration, it may cause some toxic effects, it is an essential micronutrient. As a micronutrient, it has been indicated by Alloway (1995) to be beneficial to both plants and animals and has particular physiological functions in all living systems, such as the maintenance of structural and functional integrity of biological membranes and facilitation of protein synthesis and gene expression.

Brennen (2005) indicated that in about 1870, the beneficial effect of zinc on the growth of *Aspergillus niger* was known and that in the year 1926, the essentiality of zinc for higher plants came into light and showed in their research that higher plants generally absorb Zn as a divalent cation (Zn^{2+}) which acts either as a metal components of enzymes or as a functional, structural, or a regulatory cofactor of a large number of enzymes.

Globally, low zinc (Zn) soils are widespread, but one of the largest expanses of such soils is in southwest Australia. Early Zn research in the region determined how much fertilizer Zn was required for profitable production of spring wheat and subterranean clover, the major crop and pasture species at the time (Alloway, 2004).

2.7.1 The chemistry of zinc

Zinc appears to have a special role in regulating the uptake of nutrients as Zn treatments produced an increase of P and Mn concentrations in plants. Zinc has been found in the regulation of photosynthesis, involvement in the photosynthesis reaction of the plant involvement in stomatal opening (Brennen, 2005). Cakmak (2000) suggested the role of zinc in protecting cells by controlling both generation as well as detoxification of reactive oxygen species. Brennen (2005) proposed five chemical pools for Zn in soils as; (1) in soil solution, (2) on exchange sites of reactive soil components, (3) in complexes with organic matter, (4) occluded by co-precipitated with oxides and hydroxides of Al, Fe and Mn and (5) held in primary and secondary minerals. Pool 3 is generally considered the most important source of Zn for plants as most soil Zn often occurs in this pool. It has however been observed that if Zn exceeds certain limits in soils it becomes toxic to biota (Brennen, 2005).

Zinc deficiency in plants is widespread throughout the world and in Africa. Zn deficiencies have been reported in Nigeria, Guinea, the Ivory Coast, Sierra Leone, Sudan, and Zimbabwe. Zinc deficiency in plants is associated with calcareous high pH soils because of low Zn availability or with coarse textured (sandy), highly leached, acid soils because of their low total zinc content. Negative relationship between Zn and several other essential elements (e.g. P, N and Cu) can also lead to Zn deficiencies in plants (Loneragan and Webb, 1993).

2.7.2 Factors affecting plant uptake of zinc

2.7.2.1 Effects of Nitrogen

Addition of nitrogen can influence the response of plants to Zn. Nitrogen application has increased plant growth but decreased Zn concentrations of plants. It may affect the response of plants to Zn by decreasing the root to shoot ratio (Brennen, 2005). Any factor, which increases plant growth without concomitantly increasing the rate of absorption or the size of the root system, will result in a decrease in concentration of Zn in the plant (Brennen, 2005).

2.7.2.2 Alkaline earth cations

Cations such as the alkaline earth cations (Ca^{2+}, Mg^{2+}, Sr^{2+}, Ba^{2+}), K^{+} and NH_4^{+} inhibit Zn absorption by plants at levels which are not in themselves toxic (Loneragan and Webb, 1993). Loneragan and Webb (1993) showed that all cations of macronutrients inhibited the rate of Zn absorption strongly in solutions of low Ca concentrations.

2.7.2.3 Micronutrients

Micronutrients cations, particularly Cu^{2+}, have been reported to have toxic and inhibitory effects that may influence the uptake of Zn by plants (Loneragan and Webb, 1993). At high concentration of micronutrients, the effects are mainly toxic whereas at low concentrations the effect is an inhibition of Zn uptake. The inhibitory effects has been found to be due to the competition between Cu^{2+} and Zn^{2+} for absorption sites in the plasma membrane of roots (Brennen, 2005). The interaction between Fe and Zn is complex and there appears to be many conflicting results. The conflicting evidence is probably due to differences in experimental conditions, plants species, solution composition and or complexation of the Fe, and release of root exudates mobilizing iron (Brennan, 2001).

2.7.2.4 Anion effects

Anions, for example, phosphate (PO_4^-), nitrates (NO_3^-) and organic ligands affect Zn uptake by plants by a variety of mechanisms. The ratio of P/Zn has been suggested as a method of diagnosing Zn deficiency in crops. Nitrate may affect Zn uptake by influencing the soil pH. Decreasing pH increases Zn concentration in plants while increasing pH decreases Zn absorption (Loneragan and Webb, 1993). However, Brennen (2005) established that the effect of NO_3^- on the uptake of Zn varies with plant species and demonstrated that organic ligands and chelating reagents (anions) are able to increase Zn concentration in soils solution.

Possible factors that may control the effect of organic ligands on Zn uptake by plants include but not limited to the residual charge on the complexed molecule, the specificity of the ligands for Zn complexation and the nutrient status of the plant.

2.7.2.5 Total ion in solution

The effect of single ions on Zn absorption has often been studied in simple solutions. However, in a more complexed soil solution where a range of ions is present, the effects of the ions on the uptake of Zn by plants may be difficult to interpret. This is because Zn absorption increased when pH increased from 3 to 7 for a solution of Ca $(NO_3)_2$ whereas in a complete nutrient solution, Zn uptake was reduced when pH increased from 5.2 to 7.5 (Brennen, 2005).

2.7.2.6 Effects of soil pH on the availability of zinc

The soil pH has been described as the master variable controlling partitioning of metals between the soil solid and solution-phase (Bolan *et al*., 2003). The pH of soil is an important factor affecting the availability of Zn. Brennen (2005) noted that at high soil pH, Zn is more strongly absorbed on to the surface of soils and hence the availability of Zn to plants is diminished. That is, an increased in soil pH decreases Zn availability for plants uptake. On the other hand, lowering of soils pH (acidification) increased the concentration of Zn available to plants. Over the soil pH range of 5.5 to 7.0, the Zn concentration in plants may decrease by 3 to 4 times for each one unit increase in soil pH. High pH also causes metal to hydrolyse to the hydroxyl species (MOH^+), which are absorbed more strongly by the soil. Ammonium based fertilizers may increase Zn uptake by decreasing soil pH (Brennen, 2005).

2.7.2.7 Effects of soil organic matter on zinc availability

High soil organic matter can lead to zinc deficiency of crops as Zinc may bind to organic compounds that are unavailable for plant uptake resulting in Zn being less available for uptake by roots of plants (Gyimah, 2012).

Organic carbon can bind appreciable quantities of metals, particularly Cu which has a high affinity for the types of functional groups associated with organic compounds. Organic carbon is more soluble at higher pH than lower pH values (Gyimah, 2012).

2.8 Zinc deficiency

As Zn is essential for a range of enzymes activities and is associated with a range of other enzyme systems, deficiency of Zn disrupts many biochemical processes in the plant, which can manifest in distinctive symptoms. According to Marschner (1986) such symptoms include shortened internodes, interveinal chlorosis of leaves, death of the growing points and production of small distorted leaves. Blaylock (1995) indicated that zinc deficiency delayed the pod maturity in navy beans. According to Brennan *et al.*, (1993) the appearance of symptoms vary with environmental conditions, plant age, severity and stage of the deficiency, as well as the supply of other nutrients.

Mossu *et al.*, (1992) suggested that the main symptoms of zinc deficiency in cocoa are narrow and malformed leaves that are elongated and often furled in a sickle shape and very marked aberrant veining.

In order to prevent this deficiency, four strategies are normally used. These include: (i) soil applications; (ii) foliar applications; (iii) coating Zn fertilizer on seeds (seed dressings) and (iv) dipping seedlings in Zn solutions or suspensions at transplanting (Slaton *et al*., 2001). Srivastava and Sethi (1981) suggested that applications of manure to soils can also alleviate Zn deficiency of plants. Several other fertilizer practices also influences soil and plant Zn status. Depending on the rate and frequency of fertilizer use, the impurity of Zn in fertilizers can supply significant amounts of Zn for plants grown on soils of low Zn status (Riley *et al*., 1992).

Brennan (2005) suggested that fertilizer Zn applied to soil not only provides Zn for the plant uptake in the year of application but in the years after application. Knowledge of the residual value of Zn (amount of zinc supplied to plants after the year of application of fertilizer Zn) is important because it determines how long an application of fertilizer Zn provides adequate Zn for plant production and when a further application of fertilizer Zn is required to prevent Zn deficiency reducing plant yields and production as well as preventing zinc toxicity.

2.9 Health effects of zinc

Shankar and Prasad (1998) reported that severe zinc deficiency reduce the level of activity in the immune system and even can impair macrophage and neutrophil functions (Wintergerst, Maggini and Hornig, 2007). IMFNB (2001) indicated that the body requires zinc to develop and activate T-lymphocytes and that individuals with low zinc levels have shown reduced lymphocyte proliferation response to mitogens and other adverse alterations in immunity that can be corrected by zinc supplementation (Prasad, 2000). According to Wintergerst, Maggini and Hornig (2007), zinc helps maintain the integrity of skin and mucosal membranes that is responsible for wound healing. Patients with chronic leg ulcers have abnormal zinc metabolism and low serum zinc levels and clinicians frequently treat skin ulcers with zinc supplements (Anderson, 1995). Acute diarrhoea is associated with high rates of mortality among children in developing countries. Zinc deficiency causes alterations in immune response that probably contribute to increased susceptibility to infections, such as those that cause diarrhoea, especially in children (Wintergerst, Maggini and Hornig, 2007). Zinc in the form of lozenges or syrup is beneficial in reducing the duration and severity of the common cold in healthy people, when taken within 24 hours of onset of symptoms (Singh and Das, 2011). Willis *et al*., (2005) indicated that high zinc intake could inhibit copper absorption and sometimes producing copper deficiency and associated anaemia. For this reason, dietary supplement formulations containing high levels of zinc sometimes contain copper (AREDS, 2001).

2.10 Agrochemicals used in Cocoa Production in the Study Area

Eight fungicide types, Ridomil Gold 66 Plus WP (Cuprous oxide + mefenoxam), Metalm 72 Plus WP (Cuprous oxide + metalaxyl), Nordox 75 WG (Cuprous oxide), Funguran-0H WP (Cupric Hydroxide), Champion WP (Cupric hydroxide) and Kocide 2000 WP (Cupric Hydroxide), Fungikill WP (Cupric hydroxide + metalaxyl) and Agro-Comet WP (Cuprous oxide + metalaxyl) are recommended for spraying against the black pod disease.

Similarly, three insecticide types, Confidor (Imidacloprid), Akate Master (Bifenthrin) and Actara (Thiamethoxam) are mostly used in the country (Obeng *et al.*, 2005). Cocoafed, Sidalco liquid fertilizers, Atara and Confidor are some of the approved fertilizers by the Cocoa Research Institute of Ghana (CRIG-Tafo).

2.11 Impact of Agrochemicals on Cocoa Production through the CODAPEC Program

The use of agrochemicals especially in cocoa production in Ghana through the CODAPEC programme has been very productive. The programme is a source of employment for the youth. CODAPEC alone has engaged over 60,000 people as sprayers, supervisors and mechanics in the rural communities (Danso-Abbeam, 2010).

Because of the CODAPEC programme, the black pod disease incidence and mirid infestation have reduced significantly as shown by field evidence and by farmers' testimonies. Hitherto, loses due to black pod were about 60 to 100 %

whilst losses due to mirid were between 25 % and 35 %. Production figures show that yield per ha has increased substantially because of the supply of inorganic in virtually all the districts across the country (George and Augustine, 2011). Consequently, cocoa production in Ghana has gone up from 380,000 MT at the inception of the programme to almost 500,000 MT in 2002/2003 and reached an all-time high of 740,458 MT in the 2005/2006. It is worthy to mention that the introduction of a "mass spraying" exercise between 1959 and 1962 is believed to have resulted in the high production of over 580,000 MT recorded in the 1964/65 season. Farmers own testimonies strongly suggest that their financial positions have generally improved. CODAPEC has helped to generate more foreign exchange for the country through cocoa sales (George and Augustine, 2011).

The renewed enthusiasm of farmers following the introduction of CODAPEC has rekindled cocoa cultivation; new farms have been established and old ones rehabilitated. According to the Seed Production Unit of COCOBOD, the demand for planting materials has gone up substantially since the programme begun some nine years ago. The programme has demonstrated beyond doubt that Cocoa farming can be profitable (Danso-Abbeam, 2010).

2.12 Soil

Soil is the aggregate of decaying organic matter (OM); living organisms and weathered mineral materials. The high levels of heavy metals and other pollutants in the soils have been attributed to metal rich source rocks, atmospheric pollution from motor vehicles, combustion of fossil fuels, agricultural fertilizers, pesticides, organic manures, disposal of urban and industrial wastes, as well as mining and smelting processes (Bellamy, 2007).

Soil plays an important role in biogeochemical balance of the biosphere. Degradation of soil leads to a reduction or complete loss of its ecological and productive values. It is caused primarily by chemical pollution, especially with excessive, unnatural amounts of trace elements such as cadmium, lead, zinc and copper, which may disturb the function of the complex system of processes occurring in the soil, and cause negative changes in biological activity and physical properties of the soil (Jankiewicz *et al*., 1998).

Findings from many studies on soil samples have reported high concentrations of heavy metals which are released into the environment. Many soils in industrialized countries are affected by acid deposition, mine waste (containing toxic materials including heavy metals) and organic refuses, such as sewage sludge (Ebenezer, 2011).

2.13 Soil Quality Standards

In pollution studies, measured concentrations of various pollutants in the atmosphere, water and soil are normally compared with established set of standards or guidelines of notable agencies. This comparison enables researchers to evaluate the pollution status of any environment of interest. The standards and guidelines establish the threshold concentrations of the pollutants. The national bodies and international agencies may include the Environmental Protection Agency (EPA) of the various countries, World Bank, International Atomic Energy Agency (IAEA), World Health Organization (WHO) and other environmentally conscious bodies. Table 2-2 contains tentative soil quality criteria for some metals.

Table 2-2: Tentative Soil criteria

	Concentration [mg/kg dry weight]		
Element	**A [1]**	**B [2]**	**C [3]**
Arsenic	20	30	50
Cadmium	1	5	20
Chromium	100	250	800
Cobalt	20	50	300
Copper	50	100	500
Mercury	0.5	2	10
Nickel	50	100	500
Tin	20	50	300

[1] Reference value for 'good' soil quality

[2] Limiting value for soil quality having potential effects on human health or the environment and requiring investigation

[3] Limiting value for heavily polluted soil requiring remedial investigations and clean up

Source: VROM (1983)

2.14 Environmental Impact of Current Cocoa Farming Practices

Every anthropogenic activity is known to affect the environment in one way or the other. Gockowski (2007) reported that since the introduction of cocoa in West Africa, cocoa has been the major cause of land use change in the high forest zone of the region, where it has replaced agriculture that included fallowing to maintain fertility.

The progressive adoption of new varieties decoupled from recommended farming practices has come at a considerable cost in terms of deforestation and biodiversity loss. While clearing land for cocoa production inevitably implies some loss of forest cover, degradation has accelerated in recent years through the introduction and progressive replacement of the traditional shade-dependent and tolerant 'Tetteh Quarshie' variety with the new open-field hybrid cocoa, which unlike traditional trees that still need on average about 30 to 40 percent crown cover, grows in full sun conditions. In nearly three quarters of the area in Ghana shade is light (Table 2-3).

Table 2-3: Shade levels in the Cocoa belt of Ghana

SHADE LEVELS IN THE COCOA BELT OF GHANA		
Region	**None to Light**	**Medium to Heavy**
Western	0.7	0.21
Brong Ahafo	0.52	0.47
Ashanti	0.52	0.47
Eastern	0.5	0.49
Ghana	**0.72**	**0.29**

Source: Gockowski *et al.* , (2004)

Farmers have a strong preference for full sun systems because of the higher short-term profitability that is linked to their much shorter growing cycle (Obiri *et al*., 2007). However, in full sun systems, the damage from capsid attacks tends to be higher than in shaded systems and half contrary to the higher carbon sequestration potential of the traditional shaded cocoa systems (Norris, 2008) reduce carbon stores.

The best possible environmental alternative to the current one would be a mixed agroforestry system where the forest is selectively thinned and fruit tree species with economic value such as oil palm, avocado and citrus are left to grow next to cocoa trees, providing shade in addition to food and cash for the farming household (Gockowski *et al*., 2004). Obiri *et al*., (2007) reported that this practice, which is found in forest abundant southern Cameroon, could offer farmers up to 23 percent of total cash revenues from fruits and timber product species but is rarely practiced in Ghana. The remaining biodiversity hotspots in the country are located in remote areas of the Western region where the profitable marketing of agro-forestry products would not be easy. Moreover, past logging practices in which concessionaires harvested in a way that destroyed cocoa farms with no compensation for producers have discouraged the retention of these valuable trees on cocoa fields (Obiri *et al*., 2007).

2.15 Quantification of Soil Pollution

Among the commonly used methods in analyzing pollution intensity in the environments are the Contamination Factor (CF), Pollution Load Index (PLI) and Geoaccumulation Index (Igeo).

According to Boamponsem (2011), indices enable quality of the environment to be easily understood by non-specialist and they are also used to compare the pollution status of different areas of the environment.

2.16 Contamination Factor (CF)

The CF is the ratio obtained by dividing the concentration of each element in the soil sample by the baseline or background value (concentration in unpolluted soil):

$$CF = \frac{\text{Concentration of metal in sample}}{\text{Concentration of metal in background}}$$

According to Boamponsem *et al*. (2010), the contamination levels may be classified based on their intensities on a scale ranging from 1 to 6 (0= none, 1= none to medium, 2= moderate, 3= moderately to strong, 4= strongly polluted, 5=strong to very strong, 6=very strong).

2.17 Pollution Load Index (PLI)

Pollution Load Index (PLI) is used to find out the mutual pollution effect at different stations by the different elements in soils and sediments (Ebenezer, 2011). The PLI of a sampling point, community or an area is obtained by deriving Contamination Factors (CFs), using background concentrations or baseline or concentration of the element of interest in an unpolluted area (Adomako *et al*., 2008).

A number of contamination factors would be derived for different metals at each sampling site, and a site's pollution load index may then be calculated by multiplying the contamination factors and deriving the Nth root of the N factors as shown below;

$$PLI = \sqrt[n]{CF1 \times CF2 \times \ldots\ldots \times CFn}.$$

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

2.18 Contamination Degree (C_d) of Soil samples

To assess the excessive values of monitored elements in the soil samples, Boamponsem (2011) approach was followed using the equation:

$$C_d = \sum Cf_i$$

where C_d is the contamination degree, and Cfi is the contamination factor for the i-th element,

$$Cf_i = (Cn/Cb) - 1,$$

where, Cn is the analytical value of the i-th element, and Cb is the upper permissible limit of element in soil. In this study, the CRIG guideline values for soil quality were selected for the calculation of contamination degrees of the monitored elements.

CHAPTER THREE

3.0 MATERIALS AND METHODS

3.1 The Study Site

The East Akim Municipal is located in the central portion of Eastern Region with a total land area of approximately 725km^2. The Municipality is bounded by six districts namely Atiwa District to the north, West Akim District to north west, Fanteakwa District to the East, New Juaben to the south, Yilo Krobo District to the south east and Suhum-Kraboa-Coaltar District to the west. The district capital, Kyebi, is 55km from Koforidua, 105km from Accra and 179 km from Kumasi. Figure 3-1 shows the map of East Akim Municipality (EAMA, 2011). The Municipality has a total projected population, from the 2010 population and housing census of 181,153 people with 48% male and 52% female. The occupational structure of the municipality involves all the major economic activities of the country. These include agriculture, service, commerce, and industry (Table 3-1). More than half of the inhabitants (58%) are into agriculture whiles 21.5% are into Service, 11% are into commerce and 9.5% are into industry.

Table 3-1: Occupational Structure of the East Akyem Municipality

Category	Percentage of Population
Agriculture	58
Service	21.5
Commerce	11
Industry	9.5
Total	100

Source: EAMA (2011)

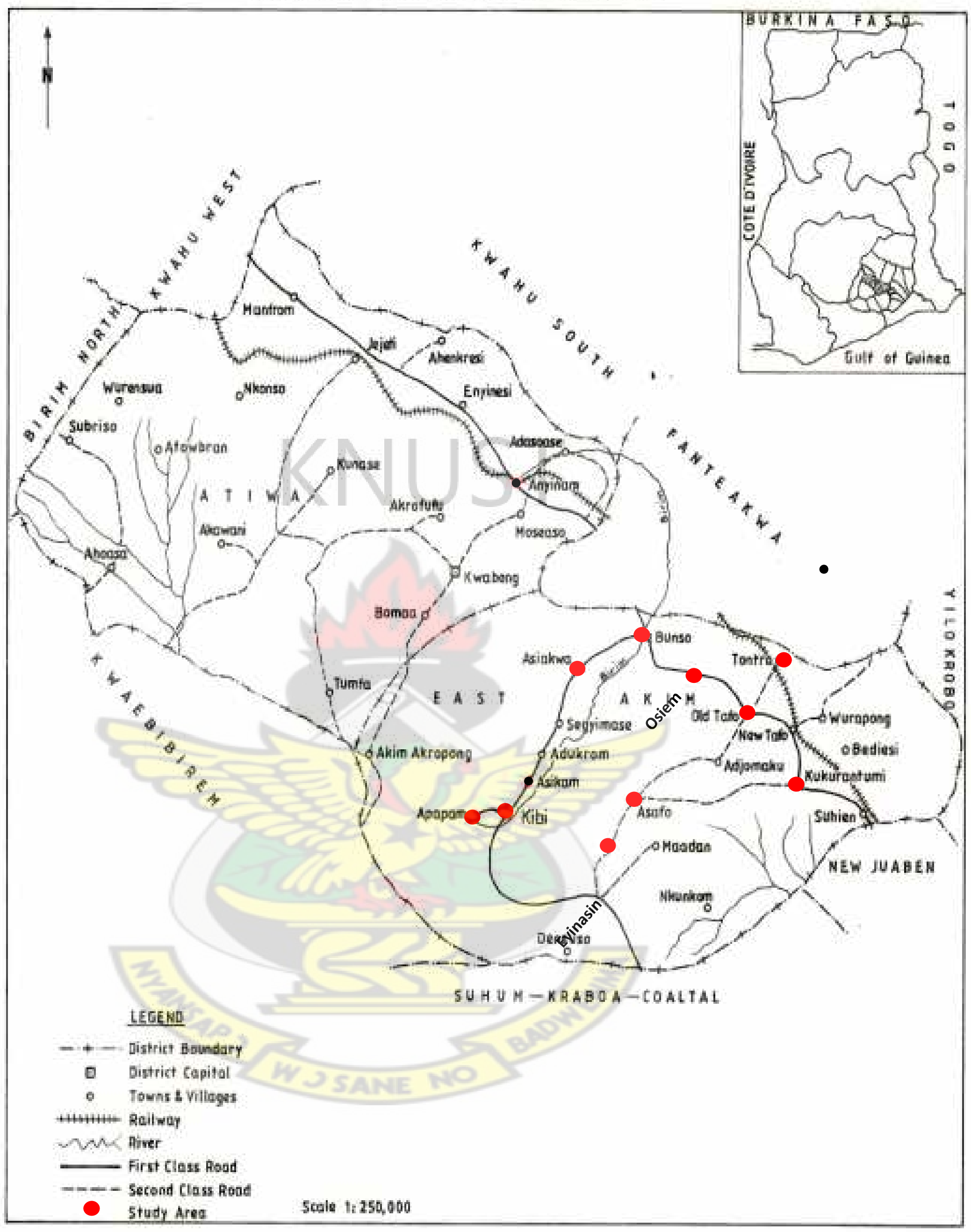

Figure 3-1 Map of East Akyem Municipal Assembly showing the study area (EAMA, 2011)

3.2 Soil and Cocoa Beans Sampling

Sampling was done in 100 selected cocoa farms in 10 towns along the length and breadth of the study area. Data from Produce Buying Company LTD was used for the selection of the ten (10) sampling towns. Towns that had previously recorded high cocoa returns were selected. Ten cocoa farms were selected from each town making a total of 100 cocoa farms. The selected farms were farms that had being under cocoa cultivation for not less than 5 years and not more than 30 years and also applies inorganic fertilizers (such as; Sidalco Liquid fertilizers, Cocoa fed, Atara, confidor and Sulphate of Ammonia) and cu-based fungicide (such as; Ridomil Gold, Metalm, Nordox, Funguran, Champion and Kocide) to their farms.

Figure 3-2 Author sampling soil from a cocoa farm


Figure 3-3 Soil samples being packed into soil bags

Figure 3-4 Soil samples kept at the CRIG-Tafo Soil Laboratory with their Labels


Figure 3-5 Soil samples being dried at the CRIG-Tafo soil drying house

3.3 Soil Sampling Preparation

Composite soil samples were collected from the 100 cocoa farms. The factors considered during sample collection were slope, drainage and erosion. The composite soil samples were collected at a depth of about 0-15 cm and 15 to 30 cm. The soil samples were kept in soil bags as their identification codes were tired to them and transported to the laboratory. The samples were disaggregated, air-dried, placed at room temperature for 3 days after which they were grinded. The samples were sieved using 2 mm sieve, packed in polyethylene bags, and stored in the laboratory until analysis. Samples from a reference forest at CRIG-Tafo were used as a control.

3.4 Cocoa Beans Sampling Preparation

Ten ripe cocoa pods were harvested from the cocoa tress in each of the selected farms, kept in labelled bags, and transported to the laboratory. The pods were separated into husk and beans. The beans were fermented for six (6) days, air dried to constant weight in the open air and milled to fine powder and kept in clean, dry glass bottles for further treatment.

3.5 Chemical Analysis of Soil and Cocoa Beans

The soil samples were analyzed for pH, percentage organic matter, copper and zinc using pH meter, Walkley-black method (Walkey and Black, 1934) and atomic absorption Spectrophotometer (AAS) respectively. Cocoa beans were also analysed for copper and zinc using AAS.

3.6 Quality Assurance

All chemicals used were of reagent grade and pure deionised water was used throughout the experimentation. All plastic were soaked in 10% HNO_3. Procedural blanks preparation of standard solutions under clean laboratory environment, calibration of the Spectra AA 220 FS model 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. 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.

3.7 Determination of soil pH using Glass Electrode

Soil pH was measured with a pH meter with a glass electrode using a 1:2.5 soil: water ratio (Snoeck *et al*., 2010). The pH meter was calibrated using standard buffer solutions (pH 4.0 and pH 7.0). Ten (10.0g) grams of each soil sample was weighed into a beaker. Twenty five (25) millilitres of distilled water was added and the solution stirred vigorously for 20 seconds and left to stand for 30 minutes (This was to make sure that the hydrogen ions have been extracted). The electrodes of the pH meter placed in the slurry, swirled carefully, and the pH read and recorded.

3.8 Determination of percentage Organic Carbon by Walkley-black method

Organic carbon was determined by the wet combustion method (Walkey and Black, 1934). Exactly 1.0 g of air-dried soil samples were weighed into 500 ml conical flasks, and were placed under fume chamber. About 10 ml of potassium dichromate ($K_2Cr_2O_7$) was added to the samples in the flasks, followed by 20 ml of concentrated sulphuric acid (H_2SO_4). (Potassium dichromate oxidizes carbon in the organic matter, itself being reduced in the process). The flasks were swirled vigorously for one minute and were allowed to stand for 30 minutes. 200

ml of distilled water was added, followed by 10ml of Orthophosphoric acid (H_3PO_4) (to sharpen the colour change at the end point of titration). Ten (10) drops of diphenylamine indicator was added to the contents in the flask and was swirled to mix well. The samples were then titrated with standard ferrous ammonium sulphate until the solutions were purple or blue. Small lots of the ferrous ammonium sulphate were added to the solutions until the colour flashed to green. Exactly 0.5 ml of standard potassium dichromate was added to give an excess and then titrated drop by drop with the ferrous ammonium sulphate until the blue colour just disappeared. Blank titrations were carried out in an identical way using the same reagents, but omitting the soil. The titrations were duplicated. The percentage organic carbon in the soil samples was then calculated using the formula below:

$$\%\ Organic\ C\ in\ soil = Vol\ of\ Dicromate\ used\ -\ F \times Titre\ value\ of\ sample \times SF$$

Where; **Dichromate used** = 10.5ml

$$F\ Factor = \frac{Dichromate\ used}{Mean\ Blank\ titre\ value}$$

(SF) Soil Factor = 0.39

$$\%\ Organic\ Matter = \%\ Organic\ Carbon \times 1.724$$

Where the factor of 1.724 = van Bennelen factor

3.9 Extraction of Copper and Zinc in soils using Mehlich-3 Extraction Method

The method described by Mehlisch (1984) was used in the extraction of the Cu and Zn for onward analysis with the AAS. Exactly two grams (2.0 g) of air-dried soil that had been grounded and sieved was weighed into shaker bottles. About 20 ml of Mehlich-3 Extractant was added and covered tightly with lid. The mixture was shook on a mechanical shaker for 10 minutes after which the mixture was filtered through Whatman No. 42 filter paper into 25ml volumetric flask. The concentrations of the elements were determined on an AAS (Spectra AA 220 FS model). The content of the element in the soil was calculated using the formula below:

$$\textbf{Element}\ \ \boldsymbol{mg/kg} = \frac{Concentration\ read\ on\ AAS \times Volume\ of\ Extractant}{Weight\ of\ sample}$$

3.10 Digestion and determination of Cu and Zn concentrations in Cocoa beans using AAS

This is a critical sample preparation step in quantitative analysis and steps were taken to ensure the reliability and reproducibility of the results by ensuring that samples were free from contamination and to avoid or minimize loss of analyte.

The aqua regia for the digestion was prepared by mixing 3:1 volumes of HCl and HNO_3 respectively in a hood. After storing the prepared aqua regia for 2 days to ensure a complete reaction and a uniform homogenous mixture between the acids, digestion of the samples commenced. One gram (1g) of the milled cocoa beans sample was weighed using a balance into 30 ml of the aqua regia in a pre-cleaned Teflon cup. The content of the sealed Teflon cup was heated on a hot plate at 200 ^{o}C in a hood and digestion continued for about 20 minutes. The digest after cooling, was transferred into a 50 ml volumetric flask by filtering through a whatman no. 40 filter paper. De-ionized water was added to make it up to the 50ml mark before being transferred and stored in pre-cleaned polypropylene tubes for analysis (Lokeshwari and Chandrappa, 2006). Spectra AA 220 FS model of AAS was used to determine the levels of copper and zinc.

All the samples were subjected to this procedure. Blank samples were digested and analyzed in the same way as described for the cocoa samples. Triplicate digestions were conducted for each sample.

3.11 Calculation of Pollution Indices

The Pollution Load Index (PLI) and Contamination Degree (C_d) were computed for the soil data using MS Excel and SPSS V16 software and the soil pollution status of the studied sites was quantified 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.

3.12 Statistical Analysis

Mean and standard deviation of soil and cocoa beans data were determined using SPSS version 16 software. The interrelationships among elemental concentrations in soil and cocoa beans samples were analyzed using Pearson's correlation. Graphical representation and charts (line and bar graphs) for soil and cocoa beans data were made using SPSS version 16 software (Boamponsem *et al*., 2010).

CHAPTER FOUR

4.0 RESULTS

In this chapter, the results of the study are presented as tables and graphs. First, a descriptive analysis of the data gathered is presented. This is followed by results of pollution index analysis of the data.

4.1 QUALITY ASSURANCE OF ANALYSIS

In an effort to obtain accurate and reproducible results in these analyses, a number of quality control measures were ensured; from the initial sampling process to the final analyses of the samples using atomic absorption spectrometer (Spectra AA 220 FS model).

Sampling of soil and cocoa beans from study sites was done in such a way that representative samples were taken. Precautions were taken to minimize possible contamination during the handling and preparation of the samples.

As mentioned earlier in this work, all reagents were of analytical grade and sample containers and apparatus were washed and rinsed thoroughly prior to their use. Since reagents could be reliable sources of contamination in analytical work, high purity reagents and deionized water were used in this work. Reagent blanks were analyzed in all tests. The concentrations reported in this work were thus actual concentrations of the samples relative to the reagent blanks. In addition, 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 Tables 4.1.

Table 4-1: Levels of Cu and Zn in IAEA-V-10 Standard reference materials (Hay Powder) and NIST standard reference material 1547 (Peach Leaves)

Trace Element	This work	Reported values	Absolute Error	% Error
	Levels of heavy metals in IAEA – V-10 Standard reference materials (Hay Powder)			
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)			
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

4.2 Concentration of Copper and Zinc in Soils

The results of soil analysis for copper and zinc for East Akyem municipality are presented in Table 4-2. Data on Cu and Zn content of cocoa beans are given in Figure 4-3. The highest mean value for zinc 10.52±5.59 mg/kg (Table 4-2) was recorded in the soil samples from Apapam and was closely followed by soil samples from Kyebi (8.67 mg/kg). The least mean concentration was recorded in the samples from Asiakwa (3.63±1.82 mg/kg). The highest mean Copper concentration of 0.47±0.24 mg/kg occurred at Apapam whereas the sampling points from Tafo recorded the least mean concentration of 0.25±0.16 mg/kg.

Table 4-2 Mean zinc and copper concentration in soil

Sampling Site	**Mean ± SD**	
	Zinc (mg/kg)	**Copper (mg/kg)**
Apapam	10.52 ± 5.79	0.47 ± 0.24
Kyebi	8.67 ± 4.28	0.34 ± 0.23
Asiakwa	3.63 ± 1.82	0.40 ± 0.19
Bunso	5.49 ± 2.74	0.29 ± 0.20
Tafo	5.91 ± 3.06	0.25 ± 0.16
Asafo	7.60 ± 2.58	0.35 ± 0.13
Osiem	8.05 ± 3.43	0.35 ± 0.13
Tontro	6.67 ± 2.94	0.27 ± 0.18
Kukurantumi	5.43 ± 2.47	0.25 ± 0.12
Eyinasin	5.98 ± 2.31	0.31 ± 0.17

4.3 Variation of copper and zinc concentration with soil depth

From Fig 4-1, it is seen that the concentration of copper was always higher at soil depth 0-15 cm than at soil depth 15-30 cm. Concentration of copper at depth 0-15 cm ranged between 0.283±0.179 mg/kg and 0.526±0.254 mg/kg. The highest mean concentration was recorded at Apapam whilst the least mean concentration was recorded at Tafo. The concentration of copper at soil depth 15-30 cm ranged between 0.210±0.093 mg/kg and 0.415±0.228 mg/kg. The highest mean concentration was recorded at Apapam whilst the least mean concentration was recorded at Osiem.

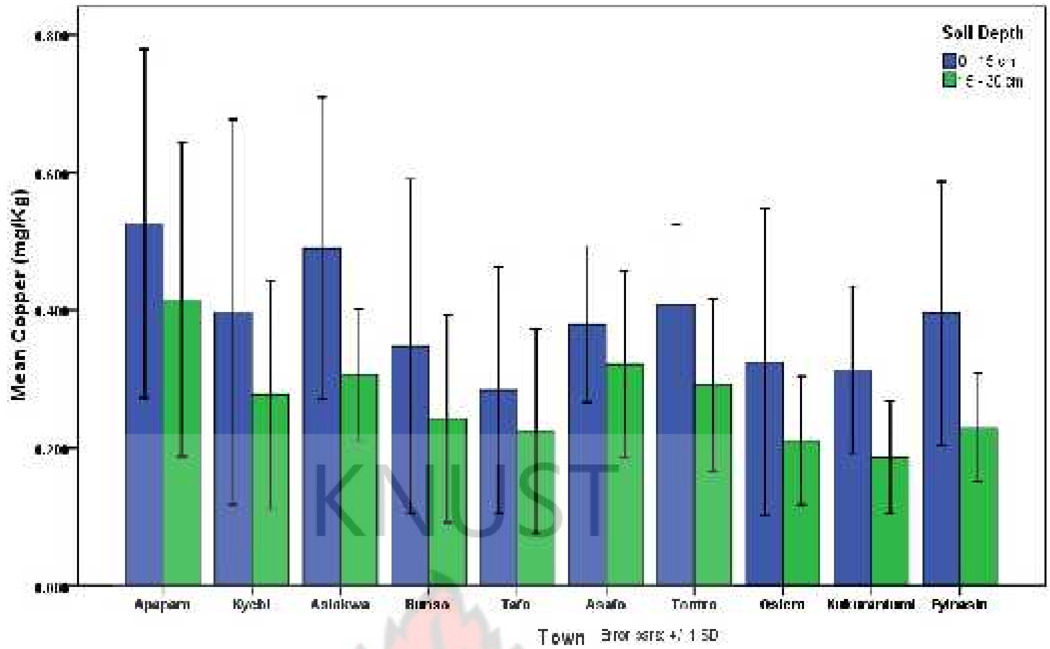

Figure 0-1 Differences in concentration of copper among the studied communities and at different depths

Similarly, from Fig 4-2, concentration of zinc was always higher at soil depth 0-15 cm than at soil depth 15-30 cm. Mean concentration of zinc at soil depth 0-15 cm ranged between 4.46±2.18 mg/kg to 12.61±5.74 mg/kg. At soil depth 0-15 cm, the highest mean concentration was recorded at Apapam whilst the least mean concentration was recorded at Asiakwa. Mean concentration of zinc at soil depth 15-30 cm ranged between 2.18±0.86 mg/kg and 8.44±5.30 mg/kg. The highest mean concentration was recorded at Apapam whiles the least mean concentration was recorded at Asiakwa.

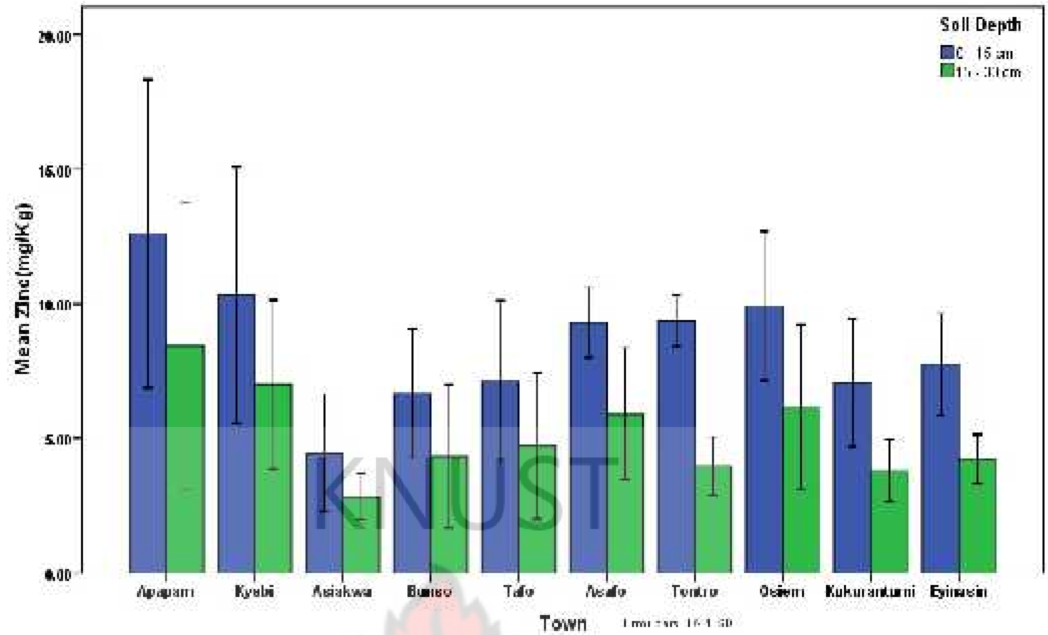

Figure 0-2 Differences in concentration of zinc among the studied communities and at different depths

4.4 Concentration of Copper and Zinc in Cocoa Beans

From Fig 4-3, the concentration of copper was always higher than the concentration of zinc in the cocoa beans and their mean difference was significant (p-value < 0.05) (Appendix 8). The least mean copper concentration of 0.087±0.082 mg/kg was registered by cocoa beans samples from Tafo whilst cocoa beans samples from Apapam recorded the highest mean copper concentration of 0.241±0.243 mg/kg. Samples from Apapam which recorded the highest value also had a minimum value of 0.079 mg/kg and a maximum value of 0.879 mg/kg. The highest concentration of zinc in the cocoa beans

(0.083±0.049 mg/kg) was recorded at Apapam whilst the least concentration of zinc in the cocoa beans (0.020±0.013 mg/kg) was recorded at Asiakwa.

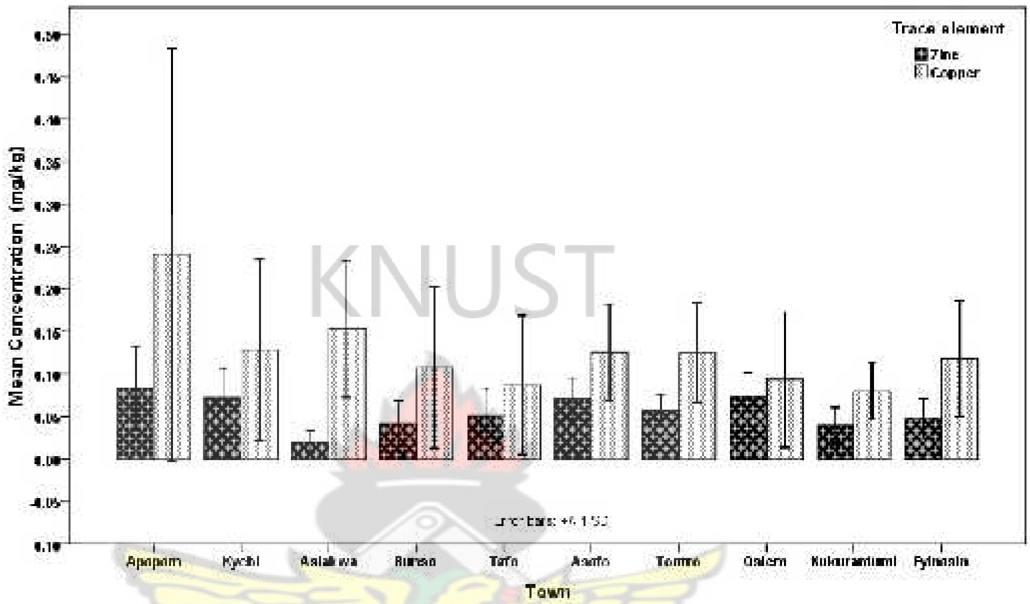

Figure 0-3 Concentration of copper and zinc in cocoa beans

4.5 Comparison of Cocoa farm soil with reference forest soil at different depth

The results for the cocoa farm soil and that of the reference soil are presented in Table 4-3. At soil depth 0-15 cm, copper concentrations were lower than that of the reference soil and at soil depth 15-30 cm, copper concentration in the cocoa farm soil was higher than that of the reference soil. Zinc concentration was higher in the cocoa farm soil at depth 0-15 cm as well as at depth 15-30 cm than that in the reference soil. The mean difference was significant (p-value < 0.05).

Table 4-3 Mean (±SD) values of reference and cocoa farm soils at different depths

	Copper		Zinc	
	0 - 15 cm	15 - 30 cm	0 - 15 cm	15 - 30 cm
Reference	0.50 (±0.34)a	0.01(±0.00)a	7.84(±0.02)a	3.46 (±0.02)a
Cocoa Farms	0.39 (±0.21)b	0.27 (±0.15)b	8.46 (±3.67)b	5.14 (±3.03)b
P-value	0.000	0.000	0.000	0.000

	pH		Organic Matter	
	0 - 15 cm	15 - 30 cm	0 - 15 cm	15 - 30 cm
Reference	6.50 (±0.13)a	6.00(±0.22)a	9.65(±0.32)a	6.58 (±0.12)a
Cocoa Farms	5.81 (±0.60)b	5.28 (±0.63)b	3.20 (±0.72)b	1.71 (±0.52)b
P-value	0.000	0.000	0.000	0.000

Within the same column numbers followed by the different letters are significant at LSD (0.05)

4.6 Soil pH

The variations of the measured pH values in the soil samples from the sampling points are shown in Table 4-4. Soil samples from Tafo had the highest pH of 6.03±0.54 and soil samples from Kyebi recorded the least value of 5.06±0.55.

Table 4-4 Mean physicochemical parameters of the soil samples

Town	Mean ± SD	
	pH	% Organic Matter
Apapam	5.42±0.52	2.66±1.04
Kyebi	5.06±0.55	2.58±1.16
Asiakwa	5.40±0.66	2.54±0.81
Bunso	5.57±0.63	1.90±0.81
Tafo	6.03±0.54	2.11±0.89
Asafo	5.49±0.73	2.68±1.03
Tontro	5.77±0.68	2.91±0.96
Osiem	5.57±0.60	2.06±0.94
Kukurantumi	5.61±0.73	2.38±0.87
Eyinasin	5.51±0.73	2.72±0.89

4.7 Percentage Organic Matter in Soil

From Table 4-4, the least average percentage organic matter value of 1.90±0.81 was recorded in soil samples from Bunso whilst the highest average value of 2.91±0.96 occurred in soil samples from Tontro.

4.8 Variation of pH and Organic Matter with Depth

The variation of the pH and percentage organic matter values with respect to soil depth are shown in Table 4-5. It was seen that generally samples at depth 0-15 cm recorded higher pH values than those recorded for depth 15-30 cm. The samples from Tafo at depth 0-15 cm recorded the highest pH value of 6.20±0.36 followed by samples from Tontro. At depth 15-30 cm, samples from Tafo recorded the highest value of 5.77±0.60 and that from Kyebi recorded 4.89±0.52 as the least pH value for depth 15-30 cm.

Table 4-5 Variation of pH and Organic matter with Soil depth

Sampling Site	pH		% Organic matter	
	0-15 cm	15-30 cm	0-15 cm	15-30 cm
APAPAM	5.65 ± 0.49	5.19 ± 0.47	3.59 ± 0.40	1.72 ± 0.41
KYEBI	5.23± 0.55	4.89 ± 0.52	3.52 ± 0.90	1.65 ± 0.32
ASIAKWA	5.61 ± 0.69	5.20 ± 0.60	3.21 ± 0.43	1.86 ± 0.41
BUNSO	5.78 ± 0.57	5.36 ± 0.64	2.50 ± 0.62	1.30 ± 0.47
TAFO	6.2 ± 0.36	5.77 ± 0.60	2.69 ± 0.72	1.53 ± 0.63
ASAFO	5.77± 0.64	5.22 ± 0.73	3.53 ± 0.68	1.83 ± 0.39
TONTORO	6.14 ± 0.61	5.39 ± 0.55	3.70 ± 0.32	2.12 ± 0.68
OSIEM	5.89 ± 0.48	5.24 ± 0.55	2.70 ± 0.84	1.43 ± 0.50
KUKURANTUMI	5.86 ± 0.66	5.36 ± 0.75	3.13 ± 0.52	1.64 ± 0.29
EYINASIN	5.86 ± 0.48	5.16 ± 0.78	3.41 ± .57	2.02 ± 0.53

The mean percentage organic matter as presented in Table 4-5 showed that at depth 0-15 cm samples from Tontro recorded the highest value of 3.70±0.32 followed by samples from Apapam with mean value of 3.59±0.40 whiles samples from Bunso recorded the least mean value of 2.50±0.62. At soil depth 15-30 cm, samples from Bunso recorded the least mean value of 1.30±0.47. The mean pH at soil depth 0-15 cm differs significantly from percentage organic matter at depth 0-15 cm (p-value < 0.05) (Appendix 4). The mean pH at soil depth 15-30 cm also differs significantly from percentage organic matter at depth 15-30 cm (p-value <0.05) (Appendix 5).

4.9 Relationships between Soil parameters in Cocoa farm foils

A scatter plot showing the associations between pH, percentage organic matter, copper and zinc at different depths of 0-15 cm and 15-30 cm are presented in Fig 4-4, to Fig 4-10. At soil depths 0-15 cm and 15-30 cm, pH showed a weak negative correlation with percentage organic matter (Fig 4-4, Fig 4-5). This reveals that as the pH was decreasing (becoming more acidic) the percentage organic matter was increasing.

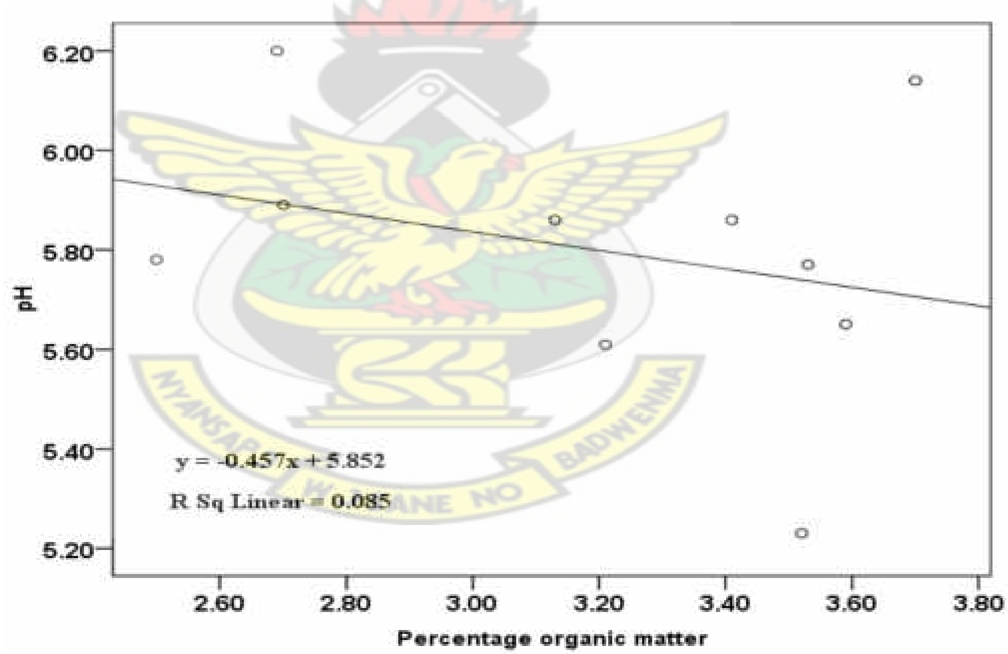

Figure 4-4 A graph of pH against percentage organic matter at soil depth 0-15 cm

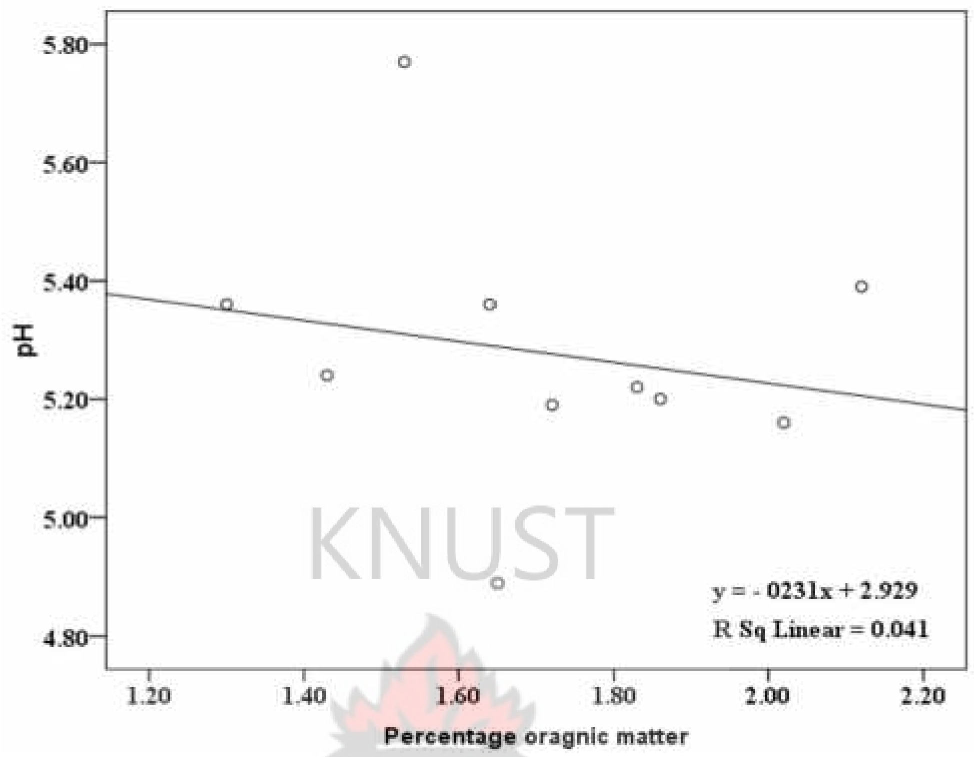

Figure 4-5 A graph of pH against percentage organic matter at soil depth 15-30 cm

From Fig 4-6 and Fig 4-7, pH showed a weak negative correlation with copper at both soil depth 0-15 cm and 15-30 cm. This indicated that as pH decreased (becoming more acidic), the concentration of copper also increased in the soil samples.

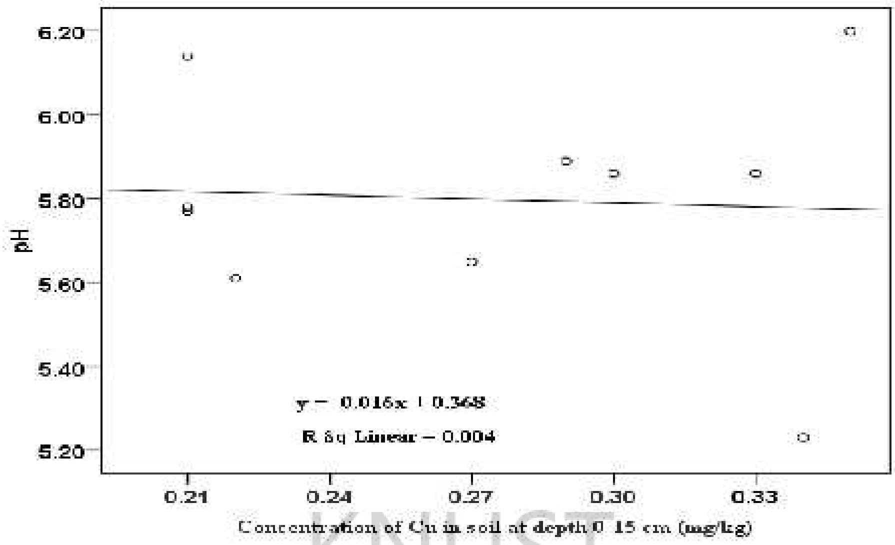

Figure 4-6 A graph of pH against copper at soil depth 0-15 cm

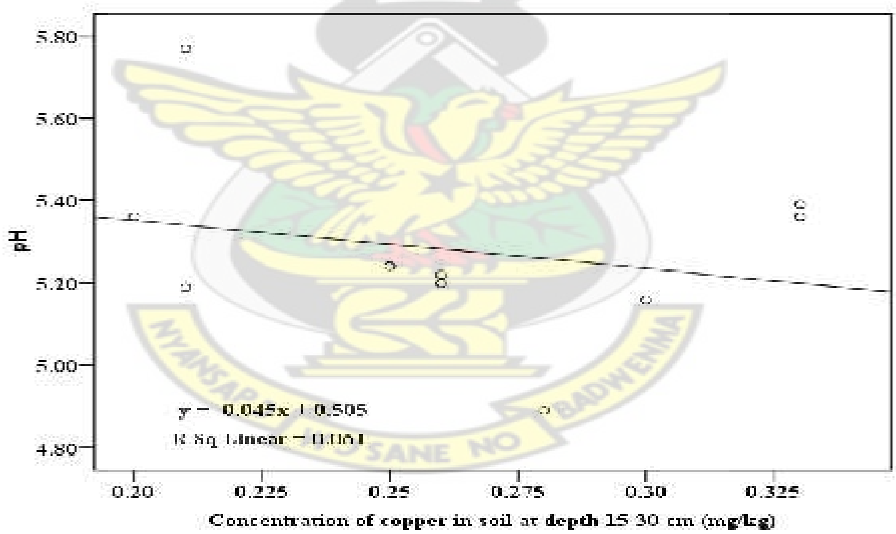

Figure 4-7 A graph of pH against copper at soil depth 15-30 cm

With reference to Fig 4-8 and Fig 4-9, pH showed a moderate negative correlation with zinc in the sol at depth 0-15 cm and 15-30 cm. This indicated that as pH decreased, the concentration of zinc also increased in the soil samples.

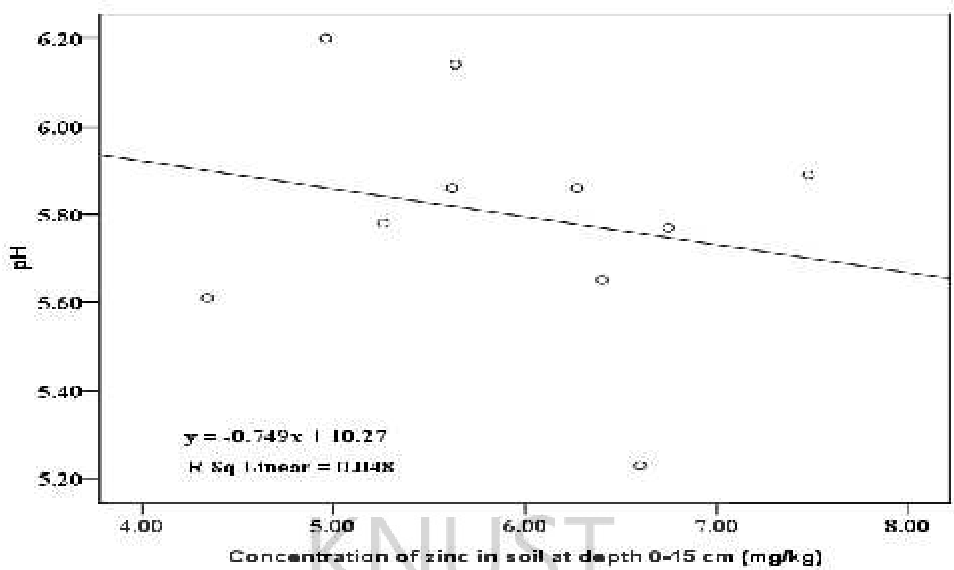

Figure 4-8 A graph of pH against zinc at soil depth 0-15 cm

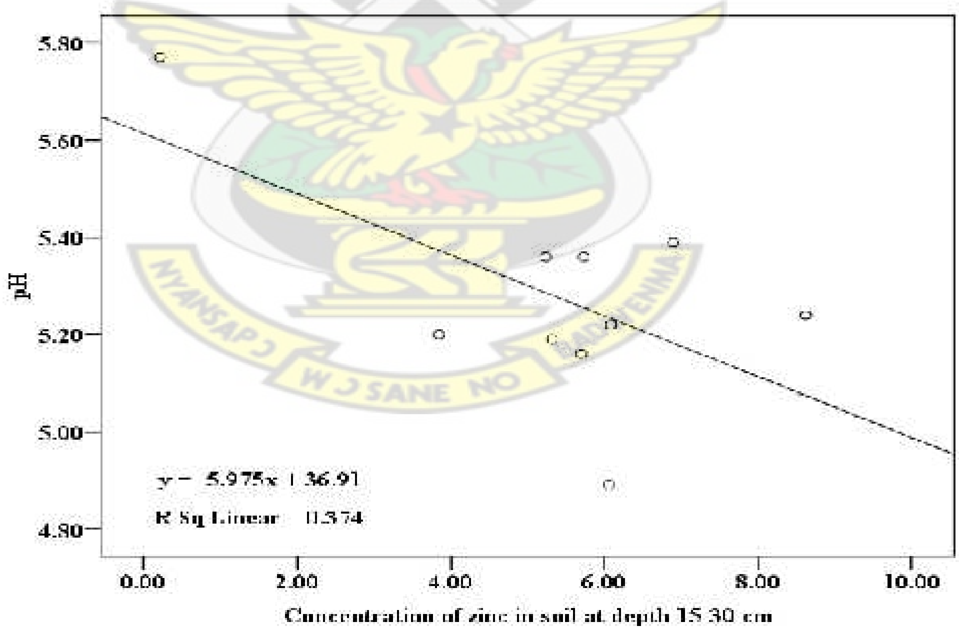

Figure 4-9 A graph of pH against zinc at soil depth 15-30 cm

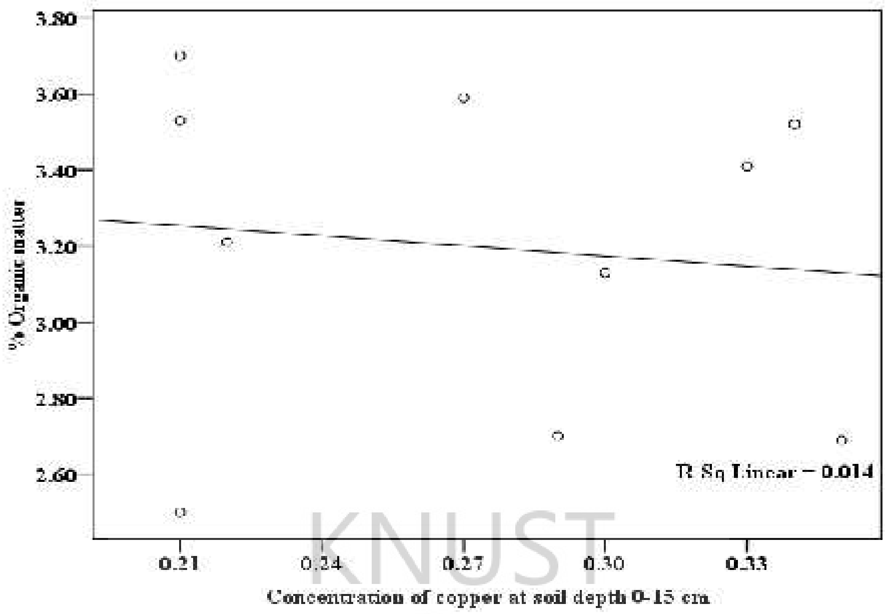

Figure 4-10 A graph of percentage organic matter against copper at soil depth 0-15 cm

At soil depths 0-15 cm percentage organic matter showed a weak negative correlation with copper (Fig 4-10). However, at soil depth 15-30 cm percentage organic matter showed a weak positive correlation with concentration copper (Fig 4-11).

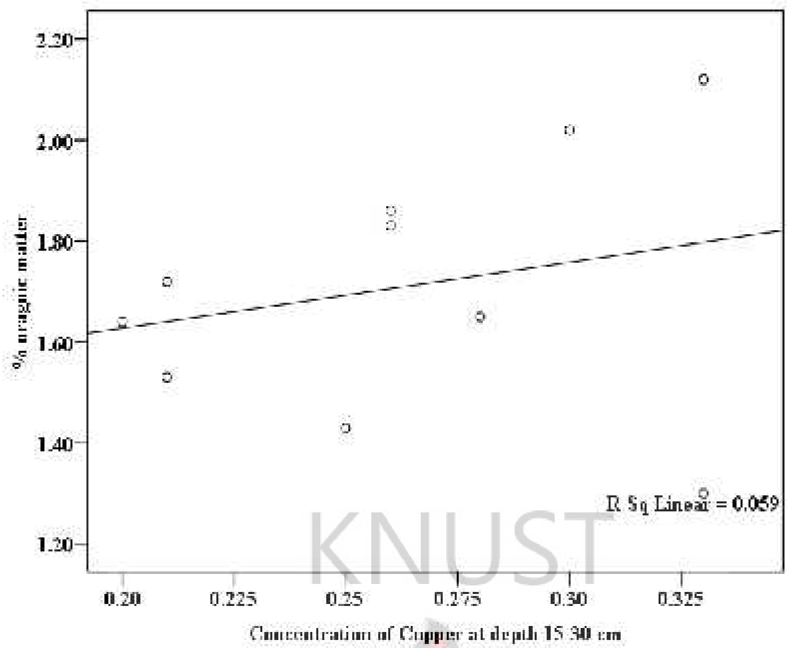

Figure 4-11 A graph of percentage organic matter against copper at soil depth 15-30 cm

From Fig 4-12 and Fig 4-13, at soil depths 0-15 cm and 15-30 percentage organic matter showed a weak positive correlation with zinc. This reveals that as the concentration of zinc increased with increasing percentage organic matter in the soil.

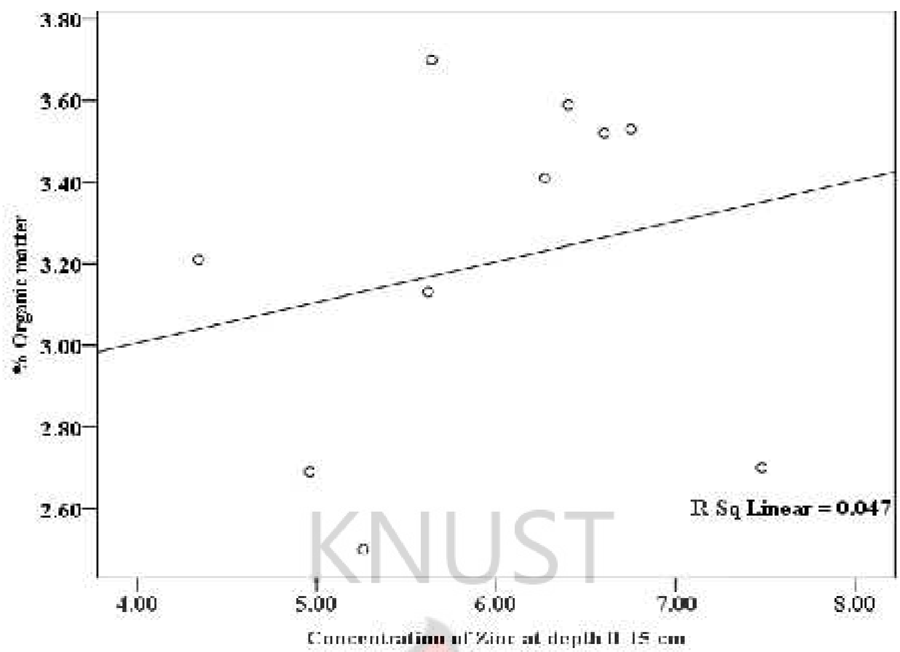

Figure 4-12 A graph of % organic matter against zinc at soil depth 0-15 cm

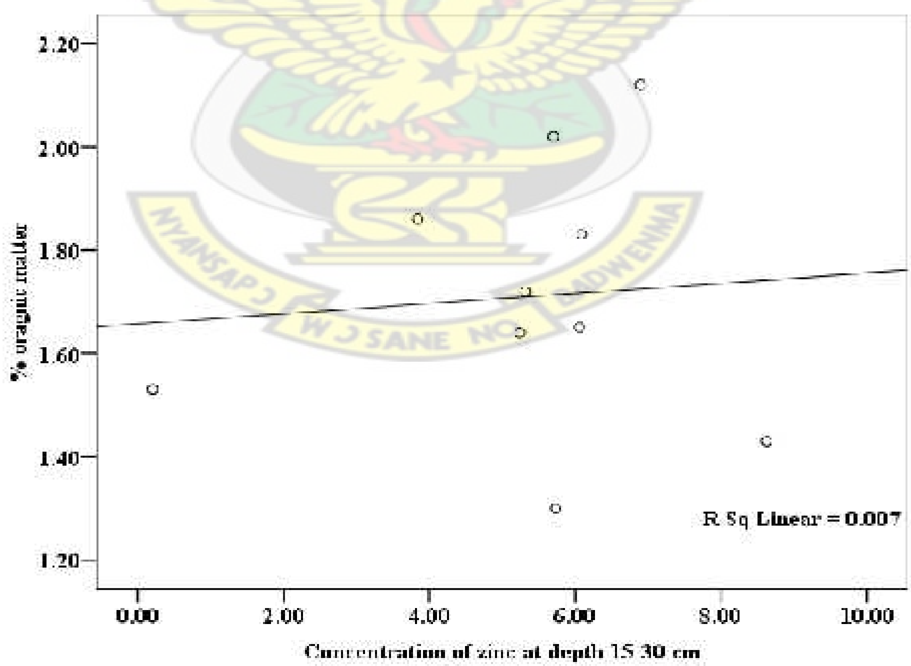

Figure 4- 13 A graph of % organic matter against zinc at soil depth 15-30 cm

4.10 Relationships of Copper and Zinc in Soils and Cocoa beans

The correlation matrix of the examined trace elements (Copper and Zinc) in the cocoa beans samples have been presented in Table 4-6 using Pearson's correlation method. The results showed that all the copper and zinc were strongly positively associated with each other since their correlation coefficients were statistically significant at 0.01 level.

Table 4-6 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).

4.11 Quantification of Pollution

The results of the quantification of the level of pollution at depth 0–15 cm and 15-30 cm in the soil samples using Pollution Load Index (PLI) and Contamination Degree (C_d) are presented in Table 4-7.

Table 4-7 Pollution Load Index (PLI) and Contamination Degree (C_d) of sampling sites

Sampling Site	(0 - 15 cm)				(15 - 30 cm)			
	CF_{Cu}	CF_{Zn}	PLI	C_d	CF_{Cu}	CF_{Zn}	PLI	C_d
Apapam	1.051	1.61	1.301	0.301	1.384	2.44	1.838	0.838
Kyebi	0.794	1.32	1.024	0.024	0.923	1.41	1.141	0.141
Asiakwa	0.98	0.568	0.746	-0.254	1.019	1.503	1.238	0.238
Bunso	0.695	0.85	0.768	-0.232	0.807	1.55	1.118	0.118
Tafo	0.567	0.91	0.718	-0.282	0.745	1.63	1.102	0.102
Asafo	0.759	1.19	0.95	-0.05	1.071	1.51	1.272	0.272
Tontro	0.817	1.195	0.988	-0.012	0.972	1.557	1.23	0.23
Osiem	0.649	1.27	0.908	-0.092	0.699	1.51	1.028	0.028
Kukurantumi	0.626	0.9	0.75	-0.25	0.621	1.55	0.981	-0.019
Eyinasin	0.791	0.99	0.885	-0.115	0.764	1.49	1.067	0.067

4.12 Contamination Factor (CF)

At depth 0–15cm, Apapam had the highest Cu contamination factor of 1.05 and Tafo registered the lowest CF value of 0.57. The sequence of Cu values of the sampling site is as follows; Apapam (1.05) > Asiakwa (0.98) Tontro (0.82) > Kyebi (0.79) > Eyinasin (0.79) > Asafo (0.76) > Bunso (0.69) > Osiem (0.65) > Kukurantumi (0.63) > Tafo (0.57). Samples from Apapam registered the highest CF value of 1.38 for Cu at depth 15–30cm whiles samples from Kukurantumi registered the least CF Cu value of 0.62. The order of the CF of Cu at depth 15-30cm is as shown below; Apapam (1.38) > Asafo (1.07) > Asiakwa (1.02) > Tontro (0.97) > Kyebi (0.92) > Bunso (0.81) > Eyinasin (0.76) > Tafo (0.75) > Osiem (0.72) > Kukurantumi (0.62).

The highest value of CF measured for Zn at depth 0-15cm was 1.61 and occurred at Apapam. Asiakwa had the lowest CF of 0.57. The sequence of CF of Zn values at depth 0-15cm of the sampling sites is as follows; Apapam (1.61) > Kyebi (1.32) > Osiem (1.27) > Tontro (1.20) > Asafo (1.19) > Eyinasin (0.99) > Tafo (0.91) > Kukurantumi (0.90) > Bunso (0.85) > Asiakwa (0.57). Samples from Apapam registered the highest CF value of 2.44 for Zn at depth 15–30cm whiles samples from Kyebi recorded the least CF Cu value of 1.41. The succession of the CF of Cu at depth 15-30cm is as follows; Apapam (2.44) > Tafo (1.63) > Tontro (1.56) > Kukurantumi (1.55) > Bunso (1.55) > Asafo (1.51) > Osiem (1.51) > Asiakwa (1.50) >Eyinasin (1.49) > Kyebi (1.41).

4.13 Contamination Degree (C_d)

Using Contamination Degree (C_d) method as used by Boamponsem *et al*. (2010), the pollution of the soil samples at depth 0-15 cm and 15-30 cm were quantified and the results presented in Table 4-7. Apapam registered the highest C_d value of 0.27 and the least value of -0.25 occurred at Asiakwa. All the sampling sites at depth 0-15 cm registered C_d values below unity (Fig 4-4). Kukurantumi recorded the least value of -0.02 as Apapam again registered the highest value of 0.84 for soil samples at depth 15-30 cm. All the sampling sites registered values below unity as depicted by the Fig 4-14. The mean difference between the Contamination degrees for soil depth 0-15 cm and 15-30 cm was significantly different (p-value < 0.05) (Appendix 10).

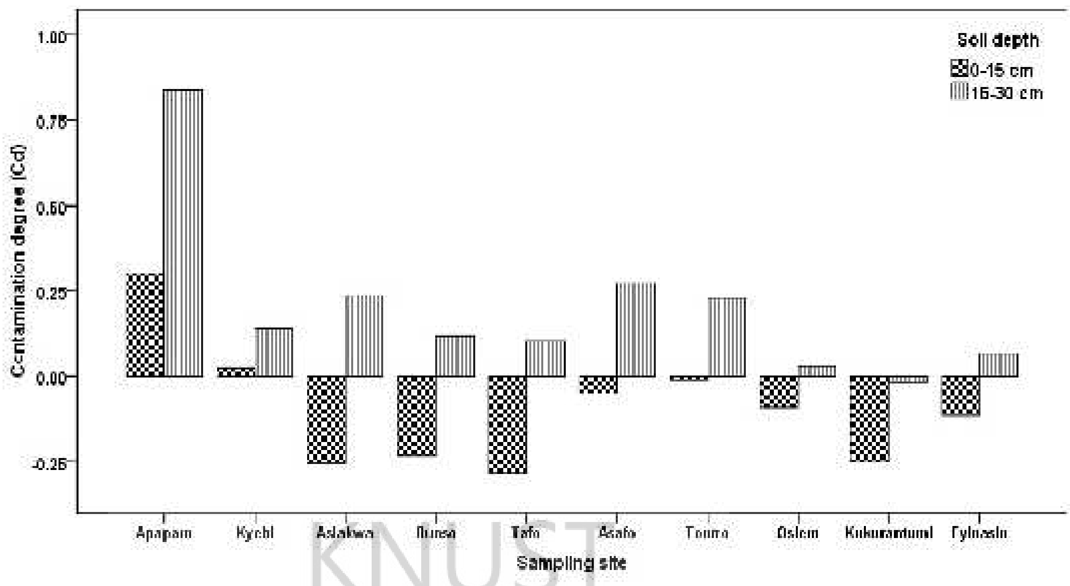

Figure 0-14 Comparison of the contamination degree of sampling sites

4.14 Pollution Load Index (PLI)

The ranking of the sampling sites in terms of pollution grading with respect to soil depths 0-15 cm and 15-30 cm are shown in Fig 4-15. The sequence of the PLI at depth 0-15 cm is as follows: Apapam (1.30) > Kyebi (1.02) > Tontro (0.9) > Asafo (0.95) >Osiem (0.91) > Eyinasin (0.89) > Bunso (0.77) > Kukurantumi (0.75) Asiakwa (0.75) > Tafo (0.72). At soil depth 0-15cm, about 10 % of the sampling sites registered values above the background threshold value of 1.0.

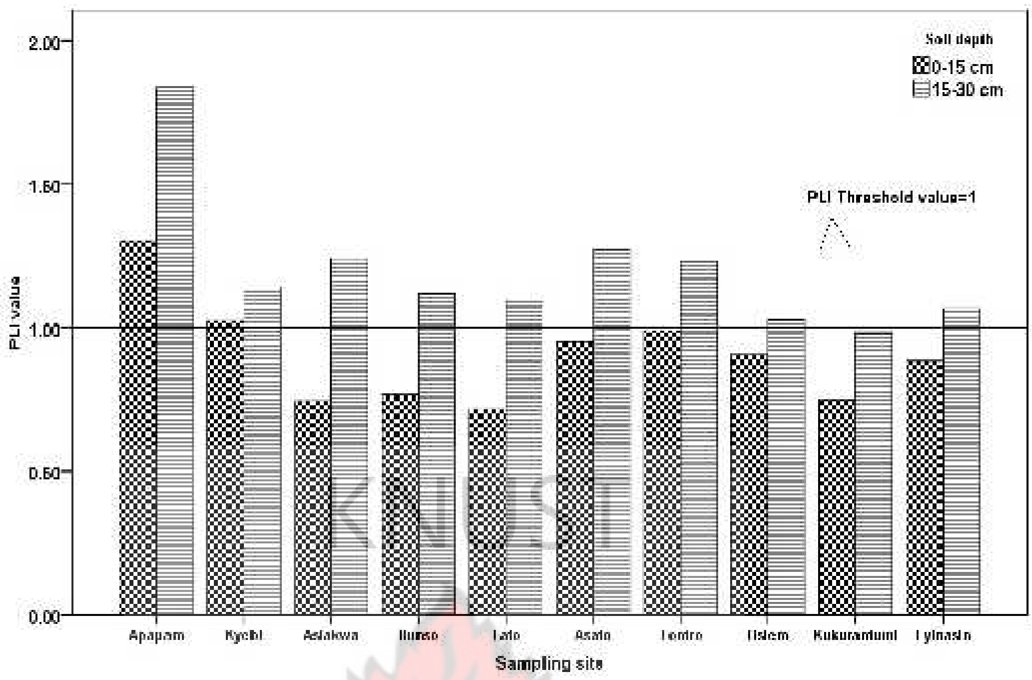

Figure 0-15 A comparative graph of the PLI values across the sampling sites

At soil depth 15-30 cm, Apapam registered the highest value of 1.84 and the least value of 0.98 occurred at Kukurantumi. With the exception of Kukurantumi, all the sampling sites recorded PLI values above the threshold value of 1 for the monitored trace elements. The sequence of the PLI at depth 15-30 cm is as follows; Apapam (1.84) > Asafo (1.27) > Asiakwa (1.24) > Tontro (1.23) > Kyebi (1.14) > Bunso (1.12) > Tafo (1.10) > Eyinasin (1.07) > Osiem (1.03) > Kukurantumi (0.98). At soil depth 15-30 cm, about 90% of the sampling sites registered value above the PLI threshold value of 1. The mean difference between the Pollution Load Index for soil at depth 0-15 cm and 15-30 cm was significantly different (p-value < 0.05) (Appendix 9).

CHAPTER FIVE

5.0 DISCUSSION

5.1 Concentrations of Copper and Zinc in Soil

All the trace elements: Copper (Cu) and Zinc (Zn) were within their respective levels as predicted by Turekian and Wedepohl (1961). Turekian and Wedepohl (1961) reported that the concentrations of Cu and Zn in the world average shale soils were 45 and 95 kg/mg respectively. Wild (1993) suggested that the maximum metal concentration of Cu and Zn permitted under EU regulation are 140 mg/kg and 300 mg/kg respectively. Comparing these reported values to that reported in this work, it suggests that, the concentrations of copper and zinc in the soils from the study area is far below the world average values. The concentration of copper in the soil samples was within the reference value for good soil quality suggested by VROM (1983) (Table 2-2). Owusu-Donkor (2011) reported soil concentrations of copper and zinc for four different districts as: Ejisu-Juaben (Cu; 4.43 mg/kg, Zn; 16.17 mg/kg), Asante Akim North (Cu; 4.8 mg/kg, Zn; 18.7 mg/kg), Obuasi (Cu; 4.5 mg/kg, Zn; 25.43 mg/kg), Sekyere West (Cu; 3.63 mg/kg, Zn; 15.1 mg/kg). Comparing the means of the copper and zinc concentrations in this work to these reported values, it is seen that the concentrations of copper and zinc reported in this work is lower than those values. In a similar study by Koka *et al.* (2011) [a] in the central region of Ghana, they reported an average concentration of copper to be 0.265 mg/kg which is lower than the overall average values reported in this work. The concentration of zinc reported in this work is higher than the values reported by Aikpokpodion (2010) [a] (zinc; 6.59 mg/kg). Aikpokpodion *et al*. (2010) suggested that only 15% of applied fungicides get to the target while the remaining 85% end up in the soil and therefore it is could be suggested that, the continual application of copper-based fungicide will result in the elevated levels of copper in the soil.

The table at Appendix 11 show the work done by Nartey *et al.* (2012) at the Department of Chemistry, Legon in which they determined the effects of various fertilizer types on the pH of soil, the levels of some heavy metals in soil samples and cocoa nibs from the Western Region of Ghana. In most of the determinations made, the levels of heavy metals in fertilizer amended soils (FS) were higher as compared to natural soils (NS).They suggested the observed increase in the FS as due to the fact that the soils could be retaining those heavy metals sourced from the applied fertilizers. From their work, the pH values of the FS were lower than those of the NS (Nartey *et al.*, 2012). However, metals easily enter soil solutions at low pH level and become mobile; as such their intake by plants may increase. This phenomenon Nartey *et al.* (2012) suggested contributed to the elevated levels of heavy metals in cocoa beans from fertilizer amended soils. This substantiates the fact that the application of inorganic fertilizers to soils contributes to the presence and subsequent uptake of heavy metals by plants. 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.

5.2 Concentrations of Copper and Zinc in Cocoa Beans

From Figure 4-3, the concentration of copper was always higher than the concentration of zinc in the cocoa beans and their mean difference was statistically significant (p-value < 0.05). This 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 farm. Koka *et al*. (2011)[a] suggested that cocoa pods is also a route through which copper gets into the cocoa beans. Aikpokpodion *et al.* (2013) 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 results in Table 4-6 showed a significant (p-value < 0.05) positive correlation existed between concentration of copper in soil and cocoa beans. The values recorded for Cu and Zn in the cocoa beans in this work (Cu; 0.03 mg/kg, Zn; 0.06) is lower than that reported by Ebenezer (2011) (Cu; 1.044 mg/kg, Zn; 0.08 mg/kg) and the concentration reported by Aikpokpodion (2010)[a] (Zn; 0.005 mg/kg). The concentration of Cu in the cocoa beans reported in this work compares well with values reported by Koka *et al* (2011) [a] (Cu; 0.13 mg/kg). Brennan (2005) reported that as soil pH increases, there is a corresponding decrease in Zn availability for plants uptake and on the other hand lowering of soils pH (acidification) increased the concentration of Zn available to plants.

5.3 Soil pH

Generally, the pH of the soil at depths 0-15 cm and 15-30 cm ranged from a pH grade of very acidic to slightly acidic (appendix 1). This is normal from this type of humid soils. For most plants, the optimum pH range is from 5.5 to 7.0. The soil's pH was within the range that will support normal growth of the cocoa trees. According to CSIR classification of soil pH (1994), samples from Apapam, Kyebi, Asiakwa, Asafo and Eyinasin were acidic and samples from Bunso, Tafo, Tontro, Osiem and Kukurantumi were moderately acidic. From Table 4-4, the pH of the soil was more acidic at depth 15-30 cm than at depth 0-15 cm. The mean difference between the recorded pH values at soil depth 0-15 cm differed significantly from the mean soil pH at depth 15-30 cm (p-value <0.05) (Appendix 13). This trend can be attributed to the application of inorganic fertilizers to the soil (Vincent *et al*., 2012).

5.4 Organic Matter

With reference to Table 4-4, it can be seen that only samples from Bunso recorded organic matter values that were low per the CSIR (1994) grading of percentage organic matter. All the sampling sites registered values that were moderate on the grading of soil organic matter as shown in Appendix 2. The mean difference between the percentage organic matter values at soil depth 0-15 cm differed significantly from the mean values recorded at depth 15-30 cm (p-value <0.05) (Appendix 12). The recorded values falls within the recommended level for organic matter by CRIG-Tafo and that gives an indication for a fertile soil to support cocoa production.

5.5 Variation of pH and Organic Matter with Depth

At soil depths 0-15 cm and 15-30 cm, pH showed a weak negative correlation with percentage organic matter. This reveals that as the pH was decreasing (becoming more acidic) the percentage organic matter was seen to be increasing. This trend is explained by the fact that at depth 0-15 cm, there is more organic matter decomposing on the surface of the soil and as such, it is expected to record high organic matter value. Soil acidity increased with depth of soil. The usual application of agrochemicals could also be a contributing factor to this trend. The mean pH at soil depth 0-15 cm differs significantly from percentage organic matter at depth 0-15 cm (p-value <0.05) (Appendix 4) and also the mean pH at soil depth 15-30 cm differs significantly from percentage organic matter at depth 15-30 cm (p-value <0.05) (Appendix 5).

5.6 Relationships between Copper and Zinc in Soils and Cocoa Beans

Table 4-10, indicates a strong positive correlation of 0.903 for concentration of copper in the soil and cocoa beans. This correlation was also significant (p-value

< 0.01). From Table 4-10, there was a strong positive correlation (0.940) between the concentrations of zinc in soil and that in the cocoa beans. This correlation was also significant (p-value < 0.01). With reference to these strong associations observed in the soil and cocoa beans, it could be suggested that the concentration in the cocoa beans could increase if that in the soil also increase.

5.7 Comparison of Cocoa Farm Soil with Reference Forest soil at Different Depths

From Table 4-3, there was a high significant difference between the cocoa farm soils and that of the reference soil at the depth of 0-15cm and 15-30cm in relation to Copper, Zinc, pH and Organic matter. The significant difference were very high at (p-value < 0.05).This is a clear indication that the application of cu-based fungicides and inorganic fertilizers may have a direct effect on the quality of the soil.

5.8 Quantification of Soil Pollution

The Pollution Load Indices of the ten communities reflected the generally low concentrations of the elements in the soil samples at depth 0-15 cm (Table 4-7). With the exception of Apapam and Kyebi sampling sites, which recorded values above Threshold value of one (1.0), all the other sampling sites registered values that were below the PLI Threshold value. This suggests that agrochemical application to the cocoa farms soils at soil depth 0-15 (top soil) have little impacts on the soil as far as copper and zinc are concerned. Table 4-8 reflects that the PLI for the study sites at soil depth 15-30 cm was mostly above the PLI Threshold value of unity except for Kukurantumi sampling sites, which registered a value of 0.981, which is below the PLI Threshold. Sampling sites that recorded PLI Threshold values below unity indicates that the sampling site were not polluted with the studied trace elements whilst those with PLI values greater than one (1) gives an indication of pollution and a grounds for environmental health concern.

CHAPTER SIX

6.0 CONCLUSION AND RECOMMENDATION

6.1 Conclusion

The mean concentration of copper expressed in mg/kg at soil depth 0-15 cm ranged between 0.283±0.179 and 0.526±0.254 and at soil depth 15-30 cm ranged between 0.210±0.093 and 0.415±0.228.

The mean concentration of zinc expressed in mg/kg at soil depth 0-15 cm ranged between 4.46±2.18 to 12.61±5.74 and at soil depth 15-30 cm ranged between 2.18±0.86 and 8.44±5.30.

The concentration of copper and zinc at depth 0-15 cm was generally higher than at depth 15-30 cm.

The concentration of copper in the cocoa beans recorded values ranging between 0.879 mg/kg and 0.005 mg/kg whilst the concentration of zinc in the cocoa beans also recorded values in the range of 0.15mg/kg to 0.01mg/kg.

The concentration copper in the cocoa beans was always higher than that of zinc across all the sampling sites and their mean difference was significant.

The concentration of Cu and Zn in the cocoa beans obtained in this study were below the maximum recommended limits set by WHO/FAO and hence pose less or no risk upon consumption, thus, the cocoa beans were not polluted by the Cu nor Zn.

The concentration of copper and zinc were higher in the cocoa farm soils than that of the control with a significant mean difference.

Soil acidity was found to increase with decreasing organic matter.

There was a strong positive association between the concentrations of Cu and Zn in the cocoa beans and the farm soil.

The high PLI and Cd values suggest that the cu-based fungicide and inorganic fertilizers used in East Akyem Municipality may have serious impacts on the farm soils as far as copper and cinc are concerned.

6.2 Recommendations

Based on the findings of this study, it is recommended that:

1. An alternative form of fungicide devoid of copper should be explored for the control of cocoa pest and diseases.
2. An alternative way of controlling cocoa pest and disease (such as biological control methods) should be explored.
3. Farmers should be educated to adhere to the manufacturers' and CRIG recommendation in the preparation and use of Cu based fungicides in their cocoa farms.
4. The maximum permissible limits for trace elements in agricultural soil in Ghana should be established to be used as a basic for regular monitoring.

5. Further research is required to determine the concentration of copper and zinc in soil and cocoa beans in other cocoa growing regions in the country.

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Appendix

Appendix 3 Soil nutrient (mineral) content

Soil pH	
pH	**Rank/Grade**
< 5.0	Very Acidic
5.0 – 5.5	Acidic
5.6 – 6.0	Moderately Acidic
6.1 – 6.5	Slightly Acidic
6.6 – 7.0	Neutral
7.1 – 7.5	Slightly Alkaline
7.6 – 8.5	Alkaline
>8.5	Very Alkaline

Source: CSIR(1994)

Appendix 4: Soil Organic Matter

Percentage Organic Matter	Rank/Grade
< 1.5	Low
1.6 – 3.0	Moderate
>3.0	High

Source: CSIR (1994)

Appendix 3: Maximum metal Concentration in soils permitted under EU regulation

Metal	Concentration (mg/kg)
Zinc	300
Copper	140
Nickel	75
Cadmium	3
Lead	300
Mercury	1.5

Source: Wild (1993)

Appendix 4: T-test results for pH and % organic matter at depth 0-15 cm

	pH 0-15 cm	**% Organic Matter 0-15 cm**
Mean	5.799	3.198
Variance	0.075076667	0.184728889
Observations	10	10
Hypothesized Mean Difference	0	
df	15	
t Stat	16.1367524	
P(T<=t) one-tail	3.44627E-11	
t Critical one-tail	1.753050325	
P(T<=t) two-tail	**6.89254E-11**	
t Critical two-tail	2.131449536	

α=0.05

Appendix 5: T-test results for pH and % organic matter at depth 15-30 cm

	pH at depth 15-30 cm	***% Organic matter at depth 15-30 cm***
Mean	5.278	1.71
Variance	0.050128889	0.0654
Observations	10	10
Hypothesized Mean Difference	0	
df	18	
t Stat	33.19552545	
P(T<=t) one-tail	6.68496E-18	
t Critical one-tail	1.734063592	
P(T<=t) two-tail	**1.33699E-17**	
t Critical two-tail	2.100922037	

α=0.05

Appendix 6: T-test results for Cu at soil depth 0-15 cm and 15-30 cm

	Cu at depth 0-15 cm	**Cu at depth 15-30 cm**
Mean	0.34522	0.31194
Variance	0.032236497	0.022181633
Observations	100	100
Hypothesized Mean Difference	0	
df	191	
t Stat	1.426630529	
P(T<=t) one-tail	0.077659498	
t Critical one-tail	1.652870548	
P(T<=t) two-tail	**0.155318995**	
t Critical two-tail	1.972461946	

α=0.05

Appendix 7: T-test results for Zn at soil depth 0-15 cm and 15-30 cm

	Zn at depth 0-15 cm	**Zn at depth 15-30 cm**
Mean	6.5614	7.0307
Variance	7.20350004	12.85152728
Observations	100	100
Hypothesized Mean Difference	0	
df	183	
t Stat	-1.04794605	
P(T<=t) one-tail	0.14802277	
t Critical one-tail	1.653222804	
P(T<=t) two-tail	**0.29604554**	
t Critical two-tail	1.973011873	

α=0.05

Appendix 8: T-test results for Cu and Zn in cocoa beans

	Cu in Cocoa beans (mg/kg)	**Zn Cocoa beans (mg/kg)**
Mean	0.12588	0.05552
Variance	0.01206041	0.001101949
Observations	100	100
Hypothesized Mean Difference	0	
df	117	
t Stat	6.13280235	
P(T<=t) one-tail	6.03135E-09	
t Critical one-tail	1.657981659	
P(T<=t) two-tail	**1.20627E-08**	
t Critical two-tail	1.980447532	

α=0.05

Appendix 9: T-test results for PLI at soil depth 0-15 cm and 15-30 cm

	PLI at 0-15 cm	**PLI at 15-30 cm**
Mean	0.9038	1.2015
Variance	0.031481067	0.058843611
Observations	10	10
Hypothesized Mean Difference	0	
df	16	
t Stat	-3.132388524	
P(T<=t) one-tail	0.003214177	
t Critical one-tail	1.745883669	
P(T<=t) two-tail	**0.006428353**	
t Critical two-tail	2.119905285	

α=0.05

Appendix 10: T-test results for Contamination degree at soil depth 0-15 cm and 15-30 cm

	Cd at depth 0-15 cm	**Cd at depth 15-30 cm**
Mean	-0.0962	0.2015
Variance	0.031481067	0.058843611
Observations	10	10
Hypothesized Mean Difference	0	
df	16	
t Stat	-3.132388524	
P(T<=t) one-tail	0.003214177	
t Critical one-tail	1.745883669	
P(T<=t) two-tail	**0.006428353**	
t Critical two-tail	2.119905285	

α=0.05

Appendix 11: Mean values for heavy metal levels (μg/g) in Natural soils (NS) and fertilizer amended soils (FS)

Sampling town	Cocoa type	Cu	Mn	Ni	Cd	Cr	Pb	Zn	Fe
Sefwi A/N	NS	8.14±0.01	233.40±9.20	20.60±1.30	ND	5.25±4.85	2.38±0.01	14.50±5.50	8600.00±1000
	FS	11.30±3.60	287.00±61.90	29.70±4.40	ND	8.00±7.00	2.60±0.30	14.40±0.60	7890.00±1880
Wassa Akr.	NS	2.01±0.47	28.80±2.03	5.71±0.06	ND	12.80±2.63	1.12±0.16	2.01±0.25	1659.80±440
	FS	2.82±0.22	14.10±2.90	7.03±1.62	ND	19.60±0.40	1.52±0.55	1.99±0.05	2500.00±230
Bogoso	NS	2.77±0.35	46.80±14.40	5.99±0.44	ND	13.60±0.57	1.32±0.41	2.43±0.83	2410.00±180
	FS	3.25±0.53	57.40±8.24	6.27±1.05	ND	13.00±1.20	1.76±0.36	2.76±0.17	2052.00±18

Asawinso/Nkatieso (A/N) Akropong (Akr.)

Source: (Nartey *et al*., 2012)

Appendix 12: T-test results for percentage organic matter at soil depth 0-15 cm and 15-30 cm

	% organic matter at soil depth 0-15 cm	**% organic matter at soil depth 15-30 cm**
Mean	3.198	1.71
Variance	0.184728889	0.0654
Observations	10	10
Hypothesized Mean Difference	0	
df	15	
t Stat	9.408513324	
P(T<=t) one-tail	5.53839E-08	
t Critical one-tail	1.753050325	
P(T<=t) two-tail	**1.10768E-07**	
t Critical two-tail	2.131449536	

α=0.05

Appendix 13: T-test results for pH at soil depth 0-15 cm and 15-30 cm

	pH at soil depth 0-15 cm	**pH at soil depth 15-30 cm**
Mean	5.799	5.278
Variance	0.075076667	0.050128889
Observations	10	10
Hypothesized Mean Difference	0	
df	17	
t Stat	4.656138857	
P(T<=t) one-tail	0.000113169	
t Critical one-tail	1.739606716	
P(T<=t) two-tail	**0.000226337**	
t Critical two-tail	2.109815559	

α=0.05