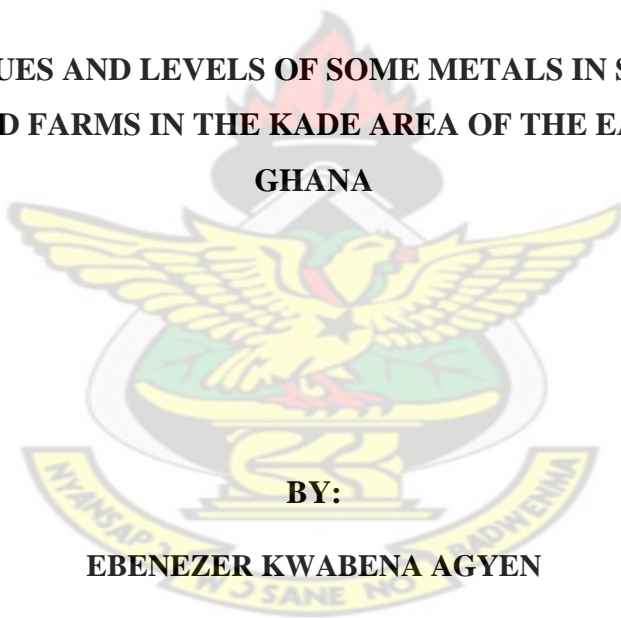**KWAME NKRUMAH UNIVERSITY OF SCIENCE AND TECHNOLOGY, KUMASI**

COLLEGE OF SCIENCE

DEPARTMENT OF ENVIRONMENTAL SCIENCE

PESTICIDE RESIDUES AND LEVELS OF SOME METALS IN SOILS AND COCOA BEANS IN SELECTED FARMS IN THE KADE AREA OF THE EASTERN REGION OF GHANA

BY:

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JUNE, 2011

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GHANA

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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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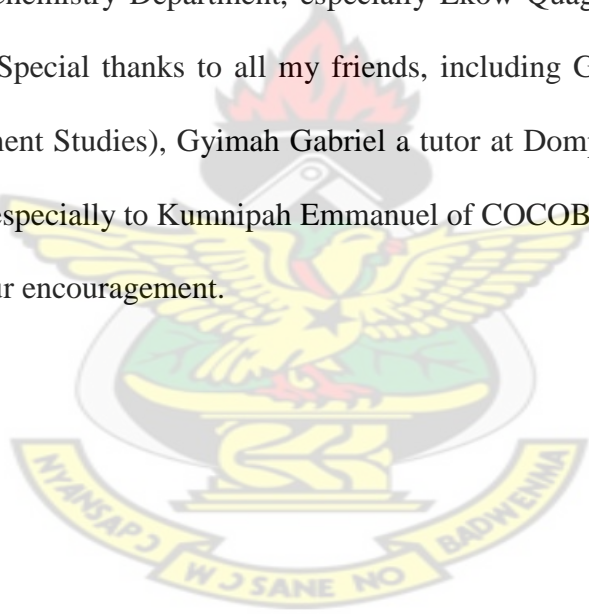NAME:
     (HEAD OF DEPARTMENT)

DEDICATION

This work is dedicated to God Almighty, my parents Mr. & Mrs. Brenya of Ahnwiaso-Adansi, my Wife Alberta Kyei Durowaa and my Children, Samuel and Isaac.
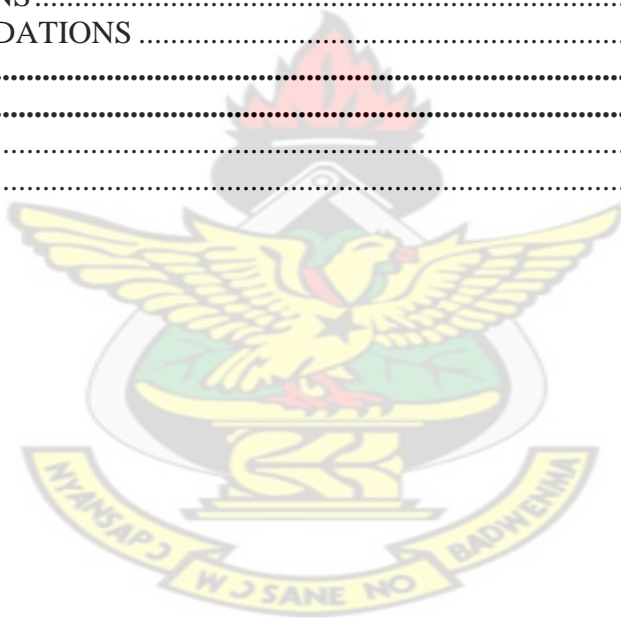
ACKNOWLEDGEMENT

ABSTRACT

The use of organochlorine pesticides for agricultural purposes has been banned for over 25 years now in some developing nations like Ghana. However, there are evidences of their continuous usage in many developing nations, such as Ghana, due to inadequate regulation and management on the production, trade and use of these chemicals. In addition, not much work has been done on organochlorine pesticides (OCPs) residues and metals in soils and beans from cocoa farms in Ghana. This study conducted an investigation into the occurrence and levels of organochlorine pesticide residues and metals in soils and cocoa beans from ten inorganic farms at Kade. Soil and cocoa beans samples were also collected from an organic cocoa farm from Kade to serve as a control. The soil samples were analysed for Al, As, Ca, K, La, Mn, Na, V, Fe, Cu, Zn, Pb, Cr, Ni, Cd and Co, using Instrumental Neutron Activation Analysis (INAA) and Atomic Absorption Spectrophotometer (AAS). The pesticide residues in the collected soil and beans samples were determined by gas chromatography with electron capture detector (GC-ECD). The metal pollution levels in the soil samples were quantified using pollution load index and geoaccumulation Index. In addition, the mean concentrations of Al, As, Ca, V, Fe, Cu, Zn, Pb, Cr, Ni, Cd and Co in the inorganic soils were below their respective concentrations in the control soil samples. However, the mean concentrations of K, La, Mn and Na in the inorganic cocoa farm soil samples were significantly ($p<0.05$) higher than the measured mean concentrations in the control samples. The generally low concentrations of the elements in the soil samples reflected in the overall pollution indices of the studied farms. The pollution load index (PLI) and geoaccumulation index analyses of the soil data revealed that the soils at Kade cocoa farms were not polluted with the measured elements. The low PLI values for all the inorganic farms (<1) may suggest that the agricultural activities in Kade have little impacts on the soil so far as the sixteen examined elements are concerned. The results from this study also show that the concentrations of Ca, Mg, Pb, Cr, Cd, Al, Co, As, La, K and V in the cocoa beans samples were less than the machine detection limits of 0.001 mg/kg. However, the mean detected concentrations of Fe, Mn, Zn and Ni in the cocoa beans samples collected from the inorganic cocoa farms were relatively higher than the measured amounts in the control samples. The recorded concentrations of Fe, Mn, Zn, Cu and Ni in the cocoa beans samples do not pose any health threat to consumers since they were all within the permissible levels of WHO and FAO.

The study identified no organochlorine pesticide (OCPs) residue in the cocoa beans from Kade. In general, sixteen different pesticide residues were detected in the soil samples. These included the derivatives of HCH, DDT and its metabolites, aldrin, dieldrin, heptachlor, trans-heptachlor epoxide, cis-heptachlor epoxide, trans-nanochlor, and trans-chlordane. The total DDT and total HCH levels in the soils of each sampling site were lower than 200ng/g stipulated by WHO/FAO. The residue levels of HCHs and DDTs measured in the soils of this study would have little risk to ecological environment and human health. The results indicated that past agricultural application of OCPs might be the major source of OCP residues in the soils. The low concentrations or non-detectable levels of aldrin, dieldrin, heptachlor, trans-heptachlor epoxide, cis-heptachlor epoxide, trans-nanochlor, and trans-chlordane, indicate a possible phasing out of these persistent organic pollutants.

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CHAPTER ONE

INTRODUCTION

1.1 BACKGROUND

Trace elements [e.g. copper (Cu), zinc (Zn), iron (Fe), manganese (Mn), molybdenum (Mo), boron (B), cobalt (Co), nickel (Ni), lead (Pb), cadmium (Cd), chromium (Cr), arsenic (As), and selenium (Se)] are defined as elements that are present at low concentrations ($mgkg^{-1}$ or less) in most soils, plants, and living organisms (He *et al*., 2005; Basta *et al*., 2005).

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 and heavy metals (e.g, Cu, Zn, Pb and Cd) are of environmental concern because of their tendency to cause contamination in soil, water, and food chains (Webber, 1981; Kremser and Schnug, 2002; Henry *et al.,* 2004). He *et al.* (2005) reported 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.

Inputs of trace elements and heavy metals through human activities have been increasing since the last century (Dampare *et al*., 2006). Trace elements may enter the agro ecosystem through both natural and anthropogenic processes (Campus, 2003). Soil inherits trace elements and heavy metals from its parent materials. Anthropogenic activities that may contribute variable amounts of trace elements and heavy metals to the agro ecosystem are the application of fertilizers,

organic manures, industrial and municipal wastes, irrigation, and wet or dry deposits (He *et al*., 2005).

The use of metal-containing substances in agriculture has increased significantly to sustain crop production. Application of trace elements such as Cu, Zn, Fe, Mn, and B that are essential to plant growth is now a common practice for correcting deficiencies of these elements in soils (Martens and Westermann, 1991).

In recent times, the use of pesticides, and their mode of application including their abuse especially in agriculture have been of much concern to environmental scientists (Essumang *et al*., 2009). Alongside their uses are also the residual effect of these pesticides and particularly their replicating effect on human health. Many chemicals including fungicides, pesticides, and herbicides contain Cu, Zn, Fe, Mn, and As (Essumang *et al*., 2009). Some trace and heavy metals such as Cd and Pb may enter the soil as impurities of fertilizers (Campus, 2003; He *et al*., 2005). Mortvedt and Beaton (1995) reported that, phosphorus fertilizers are sources of heavy metals in the agricultural systems. On the average, phosphate rock contains 11, 25, 188, 32, 10, and $239 mgkg^{-1}$ of As, Cd, Cr, Cu, Pb and Zn, respectively (Mortvedt and Beaton, 1995). He *et al*. (2005) observed that, Cu, Zn, Pb, and As can be accumulated in the soils if metal-containing chemicals are frequently used. For instance, repeated use of phosphate fertilizers such as triple superphosphate may result in accumulation of these elements and increase the contamination potential, especially of Cd, in the soil (He *et al*., 2005).

When a soil is contaminated with heavy metals, microorganisms in the soil are the first living organisms to be subjected to their impacts; trace elements (especially heavy metals) decrease microbial biomass by directly killing or biochemically disabling organisms in soil (Domsch, 1984; He *et al*., 2005).

According to He *et al*. (2005) trace elements from agro ecosystems may get into the environment through crop harvest, losses by leaching, surface runoff, and gaseous emission (only for Se, As, and Hg). Plants require an adequate supply of trace elements or micronutrients for their normal physiological and biochemical functions. However, an excessive supply of trace elements, especially heavy metals, results in toxicity to plants (Masoni *et al*., 1996; Fageria *et al*., 2002).

Increased anthropogenic inputs of trace elements and heavy metals in soils have received considerable attention, since transport of the metals may result in increased levels of trace elements in the ground water and surface water (Moore Jr. *et al.,* 1998). Moore Jr. *et al*. (1998) reported that, soils receiving repeated applications of inorganic manures, fungicides, and pesticides exhibited high concentrations of extractable metals and subsequently resulted in increased heavy metal concentrations in runoff.

This study assesses the levels of some trace and heavy elements (copper, zinc, iron, manganese, molybdenum, boron, cobalt, nickel, lead, cadmium, chromium, arsenic, mercury and selenium); and some pesticide residues (organochlorine and organaphosphorous) in soils and cocoa beans from selected cocoa farms at Kade.

1.2 PROBLEM STATEMENT

Ghana is the second largest cocoa producer in the world after Côte d'Ivoire (Fairtrade Foundation, 2011). Cocoa is susceptible to attacks by black pod disease, cocoa swollen shoot virus (CSSV), and insect pests such as cocoa capsids (*Distinthiella theobromae* and *Salbeligella singularis*). For instance, by the early 1980s Ghana's cocoa production dwindled significantly and this was attributed to several factors including widespread cocoa diseases (PAN, 2001).

In Ghana, pests and disease management in cocoa production has been heavily dependent on chemicals. For instance, the government initiated mass spraying (mainly with lindane, heptachlor, DDT/DDE, dieldrin and aldrin pesticide) campaign to control capsids between 1959 and 1962 (PAN, 2001). In 2001, the government again introduced mass cocoa spraying programme to combat black pod disease and control capsid. According to Ghana News Agency report, Sarpong-Akosa (2001), the country has increased its cocoa production levels to more than 500,000 tons; an all time high since 1965 levels. This has been attributed to the free Government-sponsored mass spraying of cocoa farms with pesticides (Sarpong-Akosa, 2001).

In recent times, emphasis has been placed on the use of fertilizers and insecticides in cocoa production (Photius, 2004). The focus of repetitive chemical (fertilizers, insecticides and pesticides) use in cocoa production is for economic gains. The fate of the environment with respect to potential pollution (with trace elements and other agrochemical residues) of the agroecosystem and other ecosystems needs to be assessed. Therefore, trace elements and chemical residues surveillance within the agricultural sector (especially cocoa farms) is

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imperative. This study, therefore, determines the extent of pollution of the cocoa farms with potentially toxic elements and organochlorine pesticide residues.

In Ghana, trace elements and heavy metals assessments in the environment have mainly concentrated on the mining (Nyarko *et al*., 2006; Serfor-Armah *et al*., 2006) and other industrial sectors (Affum *et al*., 2008). Little literature and data exist on the contribution of trace elements, heavy metals, and pesticide residues pollution of the soil resulting from cocoa production activities. Kade, is a major cocoa growing area in Ghana where various agrochemicals (including fertilizers and pesticides) have been extensively used on cocoa farms.

Kade is in the Kwaebibirem district (Figure 1) and is located in the south-western corner of the Eastern Region of Ghana. Kwaebibirem district is bounded on the West by the Birim north district, on the East by East Akim municipality, on the south east by Suhum Kraboa Coaltar District, to the South by West Akim municipality, and on the South-west by the Birim South District.

Organophosphorus (OP) and organochlorine (OC) pesticides have been used in Ghana for more than forty years, both for agricultural and public health purposes (Essumang *et al*., 2009). Hence, the need for their continuous monitoring.

1.3   OBJECTIVES OF THE STUDY

Main objective:

The main objective is to determine the levels of some metals and pesticide residues in soils and cocoa beans from farms in Kade, area of the Eastern Region of Ghana.

Specific objectives:

1. To measure the concentrations of some metals [copper (Cu), zinc (Zn), iron (Fe), manganese (Mn), vanadium (V), sodium (Na), cobalt (Co), nickel (Ni), lead (Pb), cadmium (Cd), chromium (Cr), arsenic (As), potassium (K), aluminium (Al), lanthanium (La) and magnesium (Mg)] in soils and cocoa beans samples from some inorganic and organic cocoa farms at Kade.

2. To determine the concentrations of some organochlorine pesticide residues [derivatives of hexachlorocyclohexane (HCH), dichlorodiphenyltrichloroethane (DDT), aldrin, dieldrin, heptachlor, trans-heptachlor epoxide, cis-heptachlor epoxide, trans-nanochlor, and trans-chlordane) in soils and cocoa beans from selected inorganic cocoa farms at Kade.

1.4   JUSTIFICATION OF THE STUDY

Organochlorine pesticides (OCs) are among the agrochemicals that have been used extensively for long periods in Ghana (Ntow, 2001; Darko *et al*., 2008; Bempa *et al*., 2011). Many of these OCs and their metabolites have been implicated in a wide range of adverse human and environmental effects including reproduction and birth defects (Edwards, 1987), Immune system dysfunction, endocrine disruptions, and cancer (WWF, 1999). Residues and metabolites of many pesticides are very stable, with long half lives in the environment (UNEP, 2002). The persistent

nature of pesticide residues and metals in the environment may pose the problem of chronic toxicity to animals and humans via air, water and foods intake. In view of potential toxic and persistent nature of some pesticides, there is the pressing need for their control and monitoring in the environment (Bempa *et al*., 2011).

The use of organochlorine pesticides for agricultural purposes has been banned for about 25 years now in the developed world and some developing nations including Ghana. However, there are evidences of their continuous usage in many developing nations, like Ghana, due to inadequate regulation and management on the production, trade and use of these chemicals (Darko and Acquaah, 2007; Darko *et al*., 2008; Bempa *et al*. 2011). Studies have shown that DDT is still in its highest concentration in biota of some developing countries that have banned the use of OCs (Doong *et al*., 2000; Zhang *et al*., 2002). Many other recent works have indicated the presence of OC residues in surface waters, sediments, biota and vegetations in Africa (Ntow, 2005; Dem *et al*., 2007; Ize-Iyamu *et al*., 2007). These studies did confirm the presence of pesticides in all these environmental samples (FAO/WHO, 1998).

In Ghana, there is very limited data and studies on pesticide residues in quality cocoa beans (Botchway, 2000), crops and sediments (Ntow, 2001, 2005; Ntow *et al*., 2006; Darko and Aquaah, 2007). The inhabitants of Kade are predominately cocoa farmers who use pesticides in their farming activities. In spite of the high usage of agrochemicals in the area, no published work is available on the levels of pesticide residues and metal contaminants in the cocoa beans and soils. Also, judging by the large usage of pesticides coupled with low perception of the

effects of these chemicals among Ghanaians (Amoah *et al*., 2006), there is the need to monitor the levels of these hazardous chemical in the soils and cocoa beans of the Kade area.

According to Kannan *et al*. (1995) and Darko *et al*. (2008) the determination of pesticide residues and metals levels in soil and cocoa beans may give indication of the extent of soil and beans contamination that will help in understanding the behaviour and fate of these persistent agrochemicals. This study, therefore, seeks to provide baseline information on levels of pesticide residues and some metals levels in soils and cocoa beans that will assist in a scientific assessment of the impact of agrochemicals on public health and the environment in Ghana.

CHAPTER TWO

LITERATURE REVIEW

2.1   COCOA PRODUCTION IN GHANA

Ghana is one of the major producers of cocoa in the world. The crop contributed about 3.4% to total gross domestic product annually and an average of 29% to total export revenue between 1990 and 1999 (Anon., 2001) and 22% between 2000 and 2002 (Dormon *et al*., 2004). Since the mid-1980s, production levels have risen gradually to an average of 400,000 tons during the late 1990s (Abekoe *et al*., 2002), which still is considerably less than the production levels attained in the mid-1960s. The decrease in production in the early 1980s was attributed by government to adverse weather conditions that led to widespread bush fires, destroying many cocoa farms (Anon., 1999).

Generally, yields of cocoa are lower in Ghana than in other major producing countries. Whilst the average cocoa yield in Malaysia is 1800 kg ha^{-1} and 800 kg ha^{-1} in Ivory Coast, it is only 360 kg ha^{-1} in Ghana (Dormon *et al*., 2004). 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. In 1999, the government adopted a development strategy with the objective of improving the performance of the cocoa sector.

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Under this strategy, production levels were expected to reach 700,000 tons by the year 2010 (Dormon *et al*., 2004).

In addition, since 2001 the government has mass-sprayed all cocoa farms under the Cocoa Diseases and Pests Control programme at no direct cost to the farmer. Since 2003, the government has also started an interest-free credit scheme called the Cocoa 'Hi-Tech' Programme, which is aimed at increasing productivity by providing fertilizers and pesticides (Dormon *et al*., 2004). In its first year, 50,000 farmers benefited from this programme, a number that increased to 100,000 one year later.

Traditional export crops have played an important role in the development of many African countries by generating foreign exchange earnings, government revenues, and household incomes. Dependence on a few export commodities has often made these countries vulnerable to international price volatility, however, and a continued deterioration of agricultural commodities' terms of trade has reinforced the divergence in economic development between primary-commodity-producing countries and manufacturing and service exporters (UNCTAD, 2005).

Ghana is a prime example, where favourable external conditions and internal reforms have led to a surge in traditional exports. Ghana has regained its top position among the world's leading cocoa producers and exporters, and the sector has played an important role in the nation's recent economic growth (McKay and Aryteey, 2004; Bogetic *et al*. 2007). In the light of these circumstances, the Government of Ghana has extended its development vision and recently declared the goals of reaching middle-income (MIC) status by 2015 and further reducing the

number of poor people beyond the level required by the first Millennium Development Goal. This will require doubling per capita income from the current US$450 to US$1,000 by 2015. While the Government of Ghana stresses the need for diversifying the nation's economic structure, it also emphasizes the important role of the cocoa sector and has set the target of achieving one million metric tons of cocoa output by 2010 (NDPC, 2005; IITA , 2007).

Cocoa has historically been a key economic sector and a major source of export and fiscal earnings (McKay and Aryteey, 2004). In recent years, cocoa production has more than doubled, from 395,000 tons in 2000 to 740,000 tons in 2005, contributing 28 percent of agricultural growth in 2006—up from 19 in 2001 (Bogetic *et al*., 2007). The boost in production has led to an increase of cocoa's share in agricultural GDP from 13.7 percent in 2000-2004 to 18.9 percent in 2005/2006 (Breisinger *et al*., 2008).

Cocoa accounts for about half of agricultural exports, including forestry and fishery. In comparison, the two major non-traditional agricultural export commodities, palm oil and fruits, together account for only about 4 percent of total agricultural exports (Breisinger *et al*., 2008).

Linkages of cocoa production to other sectors of the economy, including cocoa processing (cocoa milling and cocoa butter production), other food industries (beverages, bakery, chocolate products), and trade, transportation, and other marketing activities, offer additional potential for growth. However, the share of low income, cocoa-producing countries in cocoa processing remains low (Breisinger *et al*., 2008).

Ghana continues to levy an export tax on cocoa that contributes directly to government incomes. The importance of this income source has declined, however, coming down from an average of 16 percent in the 1960s and 12 percent in the 1990s to about 5 percent in 2005 (BoG, 2007; Breisinger *et al*., 2008). Additional cocoa-related income tax revenues come from the nearly half-million cocoa-producing households.

2.2   PESTICIDES

Pesticides are agents   used   to destroy   pests. The purposes of pesticide use are to increase the production of food and to promote public health; in practice they are also used for aesthetic reasons. Among the pests attacking agricultural crops are insects, weeds, rodents, birds, and disease-causing organisms including fungi and bacteria.

The use of pesticides over the years has made it possible to increase crop yields and food production (Aikpokpodion *et al*., 2010). However, intensive use of pesticides results in some environmental problems such as contamination of soil and underground water. When pesticides are applied to destroy pests and pathogens, only 15% of the applied amount hits the target, with the remaining 85% being distributed in the soil and air (Leonila, 2002). The soil is the main matrix for pesticide disposition and the bulk of pesticide residues are generally confined to the upper 5cm of the top soil (Leonila, 2002). Pesticide residue in the soil can move from the surface when they dissolve in runoff water, or percolate down through the soil, and eventually reach the groundwater (FAO, 2000). Most farmers are only interested in protecting their crops from ravages by pests in order to get good harvest but have little concern for the detrimental effects of these pesticides on the soil environment (Aikpokpodion *et al*., 2010).

2.3   TRACE METALS

Trace elements that   have been extensively studied in the last decade include copper (Cu), zinc (Zn), iron (Fe), manganese (Mn), molybdenum (Mo), boron (B), cobalt (Co), nickel (Ni), lead (Pb), cadmium (Cd), chromium (Cr), arsenic (As), and selenium (Se). Cu, Zn, Fe, Mn, Mo, and B are essential to the normal growth of plants, Cu, Zn, Fe, Mn, Mo, Co and Se are essential to the growth and   health of animals and human beings, Cu, containing elements that have been often reported to cause contamination of soil, water, and food chains. Some plants can tolerate and accumulate   much higher concentrations of trace elements such as Cu, As, and Cd than regular plant (Jiang *et al*., 2004; Yang *et al*., 2004).

Trace elements enter an agro ecosystem through both natural and anthropogenic processes. Soil inherits trace elements from its parent materials. Some soils have been found to have a high background of some trace elements, which are toxic to plants and wild life, due to extremely high concentrations of these elements in the parent materials (He *et al*., 2005). Anthropogenic processes include inputs of trace elements through use of fertilizers, organic manures, and industrial and municipal wastes, irrigation, and wet or dry deposits. These processes contribute variable amounts of trace elements to the agro ecosystem. Accumulation of trace elements, especially heavy metals, in the soil has potential to restrict the soil's function, cause toxicity to plants, and contaminate the food chain. In recent years, it has also been found that heavy metals from point and non-point sources impair water systems, causing lesions and deformation in fish (Henry *et al*., 2004).

2.3.1 Trace elements in agro ecosystems

The normal abundance of an element in the earth material is commonly referred to by the geochemist as back-ground, and for any particular element this value, or range of values is likely to vary according to the nature of the materials (He *et al*., 2005). Trace elements in soil are derived from parent materials and anthropogenic inputs. In remote or mountain areas where impacts of human activity are relatively small, trace elements in soil are mainly inherited from parent materials, whereas in urban areas or agricultural land with a long history of crop production, the concentrations of trace elements in soil can be higher than those found in the parent materials. For instance, Cu concentrations in some citrus grove soils in Florida have been found to be as high as several hundreds mg Kg^{-1}, or 10–20 times greater than the background level, due to repeated use of Cu-containing fungicides/ pesticides/ herbicides for sustaining citrus production (Alva, 1992).

Inputs of trace elements through human activities have increased since the last century (Grzebisz *et al*., 2002; He *et al*., 2005). Both industrial and agricultural operations contribute to the elevation of trace metals in soil. The smelter-related industries often act as point sources of metals, which enter agro ecosystems by dry and wet deposit or use of industrial byproducts. Use of metal-containing substances in agriculture has significantly increased to sustain crop production. Application of trace elements such as Cu, Zn, Fe, Mn, and B that are essential to plant growth is now common practice for correcting deficiencies in these elements (Fageria *et al*., 2002). Many chemicals including fungicides, pesticides, and herbicides contain Cu, Zn, Fe, Mn, and As. Some trace metals such as Cd and Pb enter the soil as impurities of fertilizers (He *et al*., 2005).

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Some fertilizers contain trace amounts of trace elements. Phosphorus (P) fertilizers such as triple superphosphates and calcium/magnesium superphosphates are source of phosphate rock. Some P fertilizers can have Cd concentrations of 450 mg/Kg and they are banned for use in agriculture in an increasing number of countries (Mortvedt and Beaton, 1995). In the USA, the trace elements Cu, Zn, B, Fe, and Mn were purposely added to regular blend fertilizers to meet the demand of plant growth for these elements (He *et al*., 2005). These fertilizers are important sources of trace elements for crops growing in soils subject to severe deficiency in these elements, such as sandy soils, peaty soil, and calcareous soils.

Most of the metal-containing chemicals are used for curing or preventing diseases of apple, citrus, grape, cherry, and peach. In old orchids of grape, citrus, and apple, Cu, Zn, Pb, and As have substantially accumulated in the soils due to repeated use of the metal-containing chemicals (He *et al*., 2005).

2.3.2   Outputs of trace elements from agro ecosystems

Outputs of trace elements from agro ecosystems include crop harvest, losses by leaching, surface runoff, and gaseous emission. Crop harvest accounts for a big proportion of the output of trace elements, although the precise amounts of metal removal vary greatly with the type of soil, crop variety, and climate conditions. For most fine texture soil, leaching of trace elements is limited because of the strong binding of these elements with soil colloids, whereas for sandy soils, especially under acidic conditions, leaching can be an important output (He *et al*., 2005). Surface runoff losses of trace elements are often   associated with transport of particulates that contain adsorbed trace elements and organic-metal complexes. Relatively few studies have been

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conducted to quantify surface runoff losses of trace elements. Gaseous losses are important only for Se, As, and Hg (He *et al*., 2005).

Some volatile organic Se and As compounds are formed in plants and emitted from plant leafs. Leaf emission has been reported to be an important pathway of Se output. Mercury can be converted into methyl-Hg through microbial activity and emitted from the soil (He *et al*., 2005).

2.4   SOIL

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 and pesticides, organic manures, disposal of urban and industrial wastes, as well as mining and smelting processes (Alloway, 1990; Brumelis *et al.*, 1999). Findings from many studies on soil samples have reported high concentrations of heavy metals which are released into the environment (Moral *et al.*, 2005). 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 (Moral *et al.*, 2005).

2.5   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 process enables researchers to evaluate the pollution status of any vicinity of interest. The standards and guidelines establish the threshold concentrations of the pollutants

above which they may pose danger to the environment. These standards and guidelines may be national or internationally generated by a body of repute comprising experts of the field.

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 1 contains tentative soil quality criteria for some metals.

Table 1: 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 for harmful effects on human health or the environment and requiring further investigation.
[3] Limiting value for heavily polluted soil requiring remedial investigations and cleanup.
Source: VROM (1983)

2.6   APPLICATION OF CHEMOMETRICS TO ANALYSIS OF SOIL POLLUTANTS

The understanding of the dynamics of pollution indicator parameters in an area has been enhanced with the application of basic and advanced statistical methods. In recent times, multivariate statistical methods such as principal component analysis (PCA) and cluster analysis (CA) are being used in the treatment of pollution data (Hussain *et al*., 2008; Zhang *et al*, 2009;

Mostert *et al*., 2010). The application of different multivariate statistical techniques helps in the interpretation of complex data to better understand the environmental and ecological status of the studied areas. It also allows the identification of possible factors that influence environmental systems and offers a valuable tool for reliable environmental management (Simeonov *et al*., 2003; Zhang *et al*., 2009).

Many studies related to these methods have been carried out. For example, Vega *et al*. (1998) and Zhang *et al*. (2009) used PCA and CA to classify sampling sites and identified the latent pollution sources. According to the above researches, it can be concluded that these methods could be used to assess the relationships between variables and possible pattern in distribution of measured data. Computer software programmes such as SPSS, STATISTICA, SAS and MINITAB can be used to explore environmental pollution data using PCA and CA.

2.6.1   Cluster analysis (CA)

According to Vega *et al*. (1998) and Mostert *et al*. (2010), cluster analysis is an unsupervised pattern recognition technique that uncovers intrinsic structure or underlying behaviour of a data set without making prior assumptions about the data, in order to classify the objects of the system into categories or clusters based on their nearness or similarity. Cluster analysis (CA) is used to develop meaningful aggregations, or groups, of entities based on a large number of interdependent variables. The resulting clusters of objects exhibit high internal (within-cluster) homogeneity and high external (between clusters) heterogeneity (Vega *et al*., 1998).

Of all cluster analysis, hierarchical agglomerative cluster is the most common approach. Hierarchical agglomerative cluster analysis indicates groupings of samples by linking inter-sample similarities and illustrates the overall similarity of variables in the data set (Vega *et al*., 1998). In hierarchical cluster analysis the distance between samples is used as a measure of similarity. There are two types of cluster analysis: R- and Q-modes (Hussain *et al*., 2008). The R-mode CA can be used to assess the affinity among environmental parameters or variables, and ultimately the sources and processes with which they are associated (Hussain *et al*., 2008). Q-mode CA is also used to group sampling sites. Hierarchical agglomerative cluster analysis can be performed by first normalizing a given data set by means of techniques such as complete linkage (furthest neighbour), average linkage (between and within groups), weighted pair-group and Ward's methods. Using squared Euclidean distances as a measure of similarity, a dendrogram is generated defining clusters. Cluster analysis uses all the variance or information contained in the original data set (Vega *et al*., 1998).

2.6.2   Principal component analysis (PCA)

PCA is a powerful tool applied to reduce the dimensionality of a data set by explaining the correlation among a large set of variables in terms of a small number of underlying factors or principal components, while retaining as much as possible the variability presented in the given dataset (Vega *et al*., 1998). This reduction is achieved by transforming the dataset into a new set of variables – the principal components (PCs), which are orthogonal (non-correlated) and are arranged in decreasing order of importance.

Mathematically, the PCs are computed from covariance or other cross-product matrix, which describes the dispersion of the multiple measured parameters to obtain Eigenvalues and eigenvectors. Principal components are the linear combinations of the original variables and the eigenvectors. The characteristic roots (Eigenvalues) of the PCs are a measure of their associated variances, and the sum of Eigenvalues coincides with the total number of variables. Correlation of PCs and original variables and the sum of Eigenvalues coincides with the total number of variables (Vega *et al*., 1998). Correlation of PCs and original variables is given by loadings, and individual transformed observations are called scores. The R-mode and Q-mode are the two types of PCA.

2.7   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 Tomlinson *et al*. (1980), indices enable quality of the environment to be easily understood by non-specialist. They are also used to compare the pollution status of different areas of the environment (Tomlinson *et al*., 1980; Boamponsem, 2011).

2.7.1   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 (El-Sammak and Abdul-Kassim, 1999). 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 (Tomlinson *et al*, 1980; El-Sammak and Abdul-Kassim, 1999; Adomako *et al*.,

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2008). The CF of an element is the ratio of its concentration in sample to the background/ baseline concentration.

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 (Tomlinson *et al*., 1980). Pollution Load Index value of 1 indicates heavy metal load close to the background level, and value above 1 indicates pollution (Tomlinson *et al*., 1980; Cabrera *et al*., 1999; Boamponsem *et al*., 2011).

2.7.2 Geoaccumulation Index

The geoaccumulation index (Igeo) has been used since the late 1960s, and has been widely employed in European trace metal studies (Yaqin *et al*., 2008). Originally used for bottom sediments, it has been successfully applied to the measurement of soil pollution (Cabrera *et al*., 1999; Grzebisz *et al.*, 2002; Yaqin *et al*., 2008, Okweye *et al*., 2009). The Igeo values enable the assessment of pollution by comparing current and pre-industrial concentrations, although it is not always easy to reach pre-industrial sediment layers (Yaqin *et al*., 2008). Geoaccumulation Index is calculated using the formula;

$$IGEO = \frac{\log_2 Cn}{1.5(Bn)}$$

Where Cn is the measured concentration of the element in soil or sediment,

Bn is the geochemical background value and 1.5 is a constant.

The constant 1.5 allows for analyses of natural fluctuations in the content of a given substance in the environment and to detect very small anthropogenic influences (Teng *et al*., 2004; Lokeshwari and Chandrappa, 2007; Yaqin *et al*., 2008).

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The equation indicates that the index will be affected by the content of the samples and the geochemical background values. The world average shale, Earth's crust, and the world average soil are some of the materials often used to provide background values (Turekian and Wedepohl, 1961; Karbassi *et al*., 2008; Yaqin *et al*., 2008). The world average shale concentrations of elements of interest are either directly measured in texturally equivalent uncontaminated sediments or size fractions or taken from literature (Teng *et al*., 2004).

The geoaccumulation index consists of 7 grades or classes (Grzebisz *et al*., 2002; Lokeshwari and Chandrappa, 2007; Yaqin *et al*., 2008). Class 7 is an open class and comprises all values of the index higher than class 6. The elemental concentrations in class 7 may be hundredfold greater than the geochemical background value (Teng *et al*., 2004; Lokeshwari and Chandrappa, 2007; Yaqin *et al*., 2008; Boamponsem *et al*., 2010).
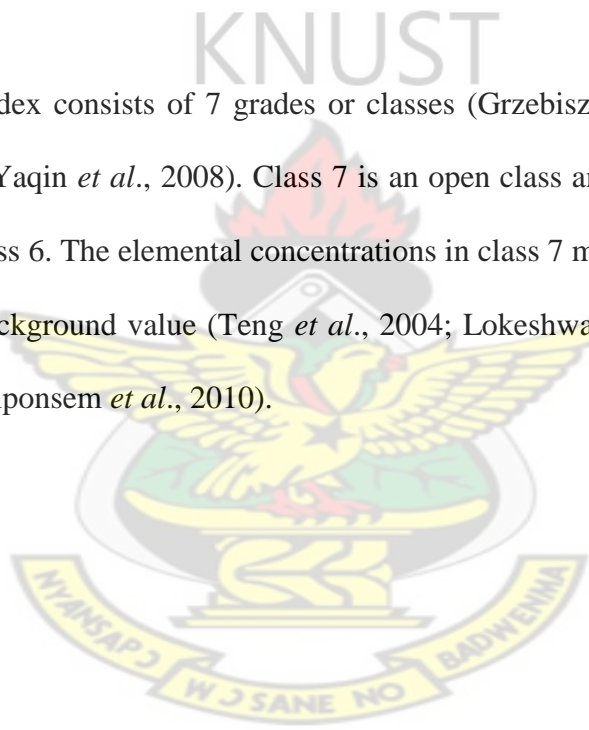
CHAPTER THREE

MATERIALS AND METHODS

3.0   THE STUDY AREA

Kade is in the Kwaebibirem district (Figure 1) and is located in the south-western corner of the Eastern Region of Ghana, between altitudes 1 degree O^0W and O degree 35^0E and Longitudes 6 degrees 22^0N and 5 degrees 75^0S. Kwaebibirem district is bounded on the West by the Birim north district, on the East by East Akim municipality, on the south east by Suhum Kraboa Coaltar District, to the South by West Akim municipality, and on the South-west by the Birim South District (Figure 1) (Kwaebibirem District Assembly, 2006)
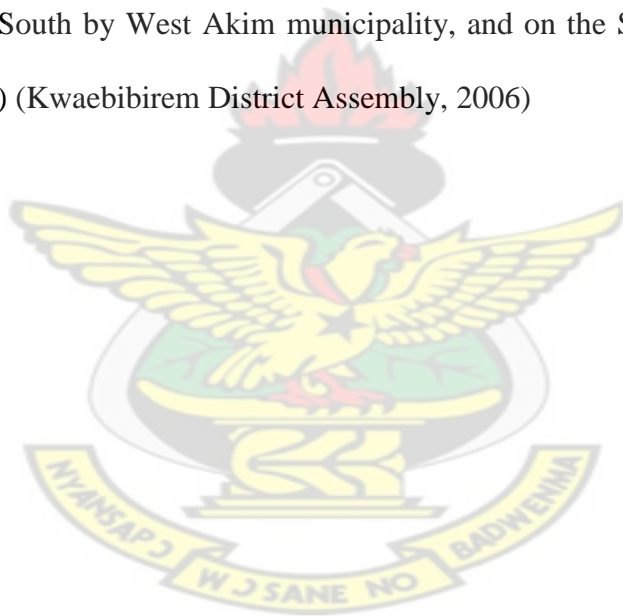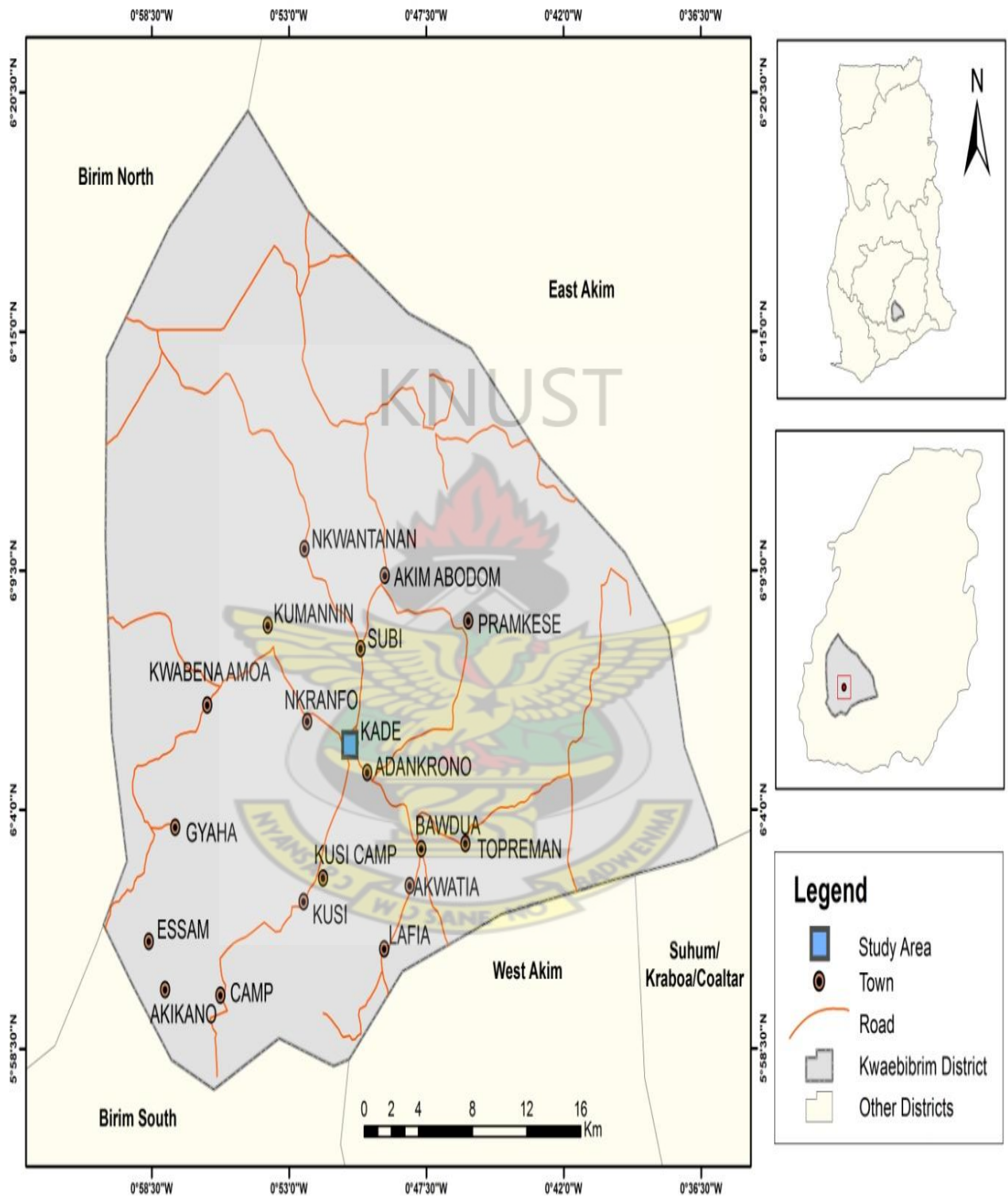
Figure 1. Map of Kwaebibirem district showing the study area.

3.1   SOIL AND COCOA BEANS SAMPLING

Soil and cocoa beans samples were randomly taken from ten inorganic farms and one organic cocoa farm from Kade, in the Eastern region of Ghana (Figure 2). Samples were taken once every month between September and December 2010. The soil and cocoa beans samples from the designated sampling points were collected using the methods of Uwah *et al*. (2009) and Owusu-Ansah *et al*. (2010). A total of, 44 soil samples and 44 cocoa beans samples were collected from the study area. The soil samples were kept in polyethylene bags which had been rinsed with 1M HCl and dried and transported to the laboratory. The Cocoa beans samples were air dried for a period of 21 days before they were packaged in a polyethylene bags for elemental and residual analyses.
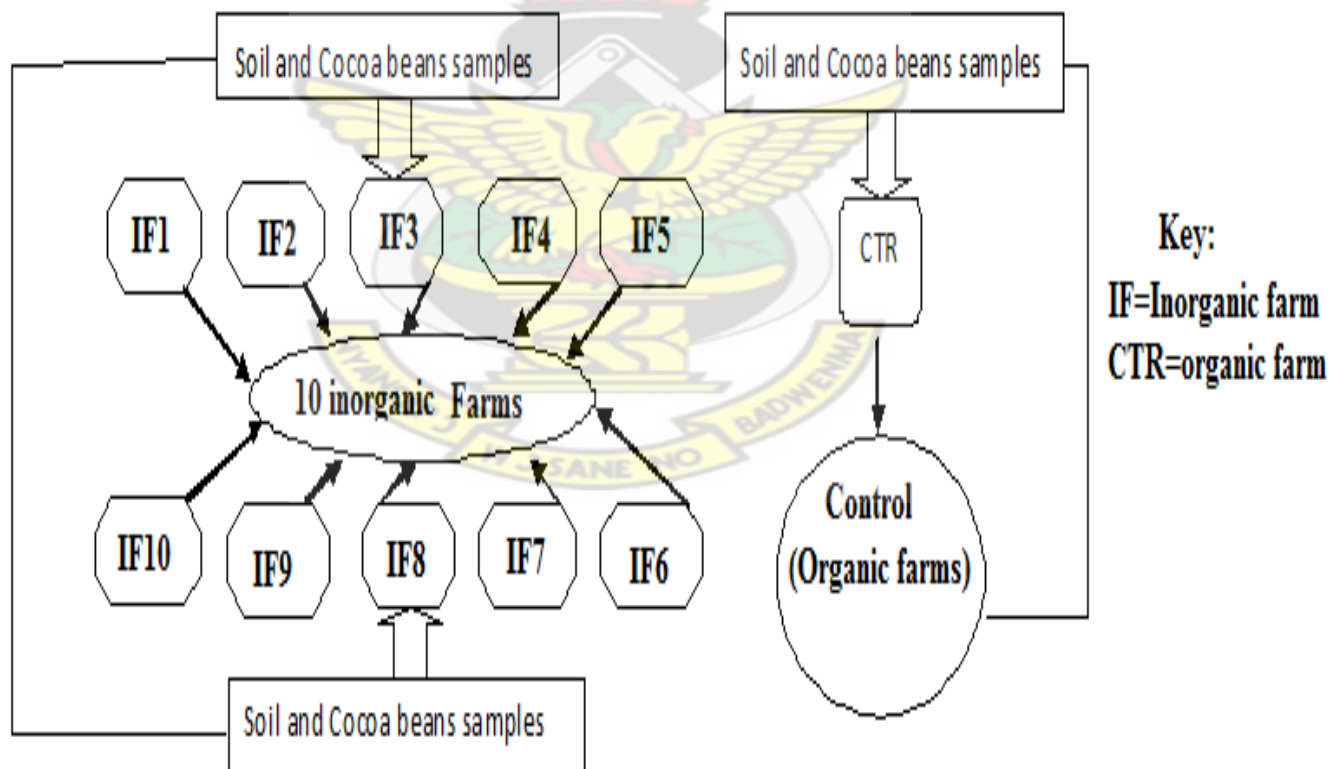
Figure. 2 Sampling design

3.1.1 Soil samples preparation for INAA

The soil samples were disaggregated dried in a dry and dust-free place at room temperature of 37^0C for 3 days and ground. The samples were sieved using 2mm mesh, homogenized and packed in polyethylene bags and stored in the laboratory until analysis. At the Instrumental Neutron activation Analysis (INAA) laboratory, about 0.1g of each soil sample was weighed onto different polythene films wrapped and heat-sealed. Six replicate sub-samples were prepared for each sample, put into polyethylene irradiation capsules and heat-sealed for irradiation and analysis.

3.1.2 Determination of elements concentration in soils using INAA

The soil samples and standards were irradiated using Ghana Research Reactor-1 (GHARR-1) facility at the National Nuclear Research Institute Laboratory of Ghana Atomic Energy Commission (GAEC). GHARR-1 reactor (miniature neutron source) operated at power rating of 15 kW with a thermal neutron flux of 5.0 x $10^{11}ns^{-1}cm^{-2}$ by means of pneumatic transfer systems which operated at a pressure of 1.723 bars, the samples were transferred into the inner irradiation sites. The scheme for irradiation was chosen according to the half-lives of the elements of interest. The soil and standards were short irradiated for 10 s. At the end of each irradiation, the samples were returned from the reactor and allowed to cool down until the level of activity was within the acceptable limit for handling. The irradiated samples were placed on top of the detector and counts were accumulated for pre-selected time to obtain the spectra intensities. Ten minutes counting time was chosen for short and medium irradiations as done by Tando *et al*. (2009) and Boamponsem *et al*. (2010).

The qualitative and quantitative measurements of elements in soil samples were performed using a PC-based gamma ray spectroscopy consisting of n-type high purity germanium (HPGe) detector model GR 2518 (Canberra industries Inc.), HV power supply model 3103, amplifier model 2020, an 8K Ortec multi-channel buffer (MCB) emulation software card and a Pentium II computer for spectrum and data evaluation and analysis. The detector had a relative efficiency of 25% to NaI detector and operated on a bias voltage of (–ve) 3000V with a resolution of 1.8keV for ^{60}Co gamma-ray energy of 1332 keV. The MCB card was used to obtain the spectra intensities of the samples. Microsoft windows based software MAESTRO was used for spectrum analysis (i.e., qualitative and quantitative analyses). The nuclear data which was used for the determination of the various elements in this study was based on procedures used by Dampare *et al.* (2006), Adomako *et al.* (2008), Tando *et al.* (2009) and Boamponsem *et al.* (2010).

3.1.3 Determination of elements concentration in soils and cocoa beans using AAS

Replicates of soil and cocoa beans samples from each sampling site were acid digested for the determination of Fe, Cu, Pb, Cr, Zn, Ni, Cd and Co. The acid digestion methods which were used for soil and beans samples were according to the GAEC acid digestion protocol as described by Sood *et al.* (2004). Samples were digested by weighing 0.4g of each in Teflon tubes. Exactly 4ml of concentrated nitric acid (HNO_3) was slowly added to the content. The tubes were closed and placed in stainless steel bombs. The bombs were placed on a hot plate and heated at 150ºC for about 22 minutes and then allowed to cool to room temperature before carefully opening the bombs to release pressure. The samples were transferred into graduated polypropylene tubes and the Teflon tubes rinsed 3 times with distilled water and added to the content of the polypropylene

tube. The content was diluted to the 50ml mark of the tube with distilled water and mixed thoroughly.

A Varian AA-240FS AAS was used to determine the levels of all the elements of interests. All reagents used were of analytical grade and equipment pre-calibrated appropriately with standard solutions prior to measurement. Replicate analyses were carried out for each determination to ascertain reproducibility and quality assurance. Reference Standard for the elements of interest blanks and repeats or duplicates of the samples were digested the same way as the actual samples. These served as internal positive controls. The reference standards used were from fluka analytical Sigma Aldrich Chemie GmbH, product of Switzerland.

3.1.4 Determination of pesticide residues in soils and cocoa beans

The dried soil and cocoa beans samples were separately milled and this step was carried out two times for each sample to achieve better extracts. About 20 g of each ground sample was transferred into 250 mL Erlenmeyer flask. The samples were subsequently prepared for the determination of organochlorine pesticides residues in each sample. The methods which were used for studied compounds were based on GAEC standard protocols. For example, for the extraction of lindane, 100 mL of chloroform was added to each cocoa beans sample. Erlenmeyer flasks were then placed on a shaker at a go for 4 to 6 hours to allow full penetration of solvent followed by 5 minutes motionless state. Using Buchner funnel and filter paper the samples were filtrated. The solvent was evaporated using a rotary vacuum evaporator. In order to remove co-extractives from the analyte, the extracts were cleaned up using pre-conditioned C-18 Solid Phase Extraction bond columns and residues recovered by adding hexane. The residual contents were poured into separately labeled sample tubes to desired volume for Gas Chromatography

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(GC) analysis. The samples were analysed for lindane and other compounds residue at the GAEC GC laboratory. Detection limit of the GC was determined for lindane by the successive dilution of the standard mixed pesticide solution, followed by injection into the GC-column, for which the retention time was recorded. Then 1μL of each cleaned up test samples were injected into the GC. The residue was identified by comparing the retention time of sample peaks with that of the standards.

The United Nations Environmental programme (UNEP) Standard Mix reference material was used for the analysis. This is a mix standard for the determination of α-HCH, *ß*-HCH, ɣ-HCH, δ-HCH, O,P'-DDD dichlorodiphenyldichloroethane; P,P'-DDE- dichlorodiphenyldichloroethylene ; O, P'-DDE, O, P'-DDT, P, P'-DDT, aldrin, dieldrin, heptachlor, trans-heptachlor epoxide, cis-heptachlor epoxide, trans-nanochlor, and trans-chlordane. The standard was serially diluted (with factors: 5, 10, 20, 50, 100, 200 respectively) and the retention times determined for each concentration using the GAEC GC. The calibration curves were then constructed for the analysis of the pesticide residues in the soil and cocoa beans samples.

3.2   VALIDATION OF ANALYTICAL METHODS

The reference material, International Atomic Energy Agency (IAEA) -SOIL-7, was used for quality control test and quantitative analyses. Six replicate samples each with a mass of 0.1 g of the standard was weighed and heat-sealed in a similar manner as the soil. The accuracy of the INAA analytical method was evaluated using IAEA-405 (Trace elements and methyl mercury in

estuarine sediment) as certified reference material. The analytical values of the reference material obtained from this study were compared with the actual values (in ppm).

3.3   STATISTICAL ANALYSES AND CALCULATION OF POLLUTION INDICES

3.3.1 Statistical analyses

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 Spearman's and Pearson's correlation methods of the SPSS software. Cluster analysis (CA) and principal component analysis (PCA), and charts (line and bar graphs) for soil and cocoa beans data were performed using SPSS version 16 software. The data were normalized using Ward's method of linkage with squared Euclidean distance as a measure of similarity (Vega *et al*., 1998; Zhang *et al*., 2009). Cluster analysis in R-mode was performed on all the examined elements in cocoa beans and soil samples. Q-mode CA was used to define groups (clusters) of sampling sites in terms of the studied elements (Chandrasekhram *et al*., 2001; Hussain *et al*., 2008).

3.3.2.   Calculation of pollution indices

The pollution Load Index (PLI) and Geoaccumulation Index (Igeo) were computed for the soil data using MINITAB software (Adomako *et al*., 2008; Karbassi *et al*., 2008; Boamponsem *et al*., 2010; Bhuiyan *et al*., 2010).

The soil pollution status of the studied sites was quantified using the Pollution Index Factor (PIF) approach as described by Freitas and Nobre (1997) and Nyarko *et al*. (2004). The equation used is given by;

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

Where 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).

According to Bhuiyan *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).

Pollution load index (PLI) is an empirical index which provides a simple, comparative means for assessing the level of trace elements pollution (Tomlinson *et al*., 1980). Pollution Load Index was therefore used to find out the mutual pollution effect of the trace elements on each of the sampling sites. The PLI values were calculated as the nth root of the product of the n CF (Tomlinson *et al*., 1980; Adomako *et al*., 2008; Boamponsem *et al*., 2010):

$$PLI = \sqrt[n]{CF1 X CF2 X CF3 X \ldots X CFn}$$

Geoaccumulation Index (Igeo) approach was used to quantify the degree of anthropogenic contamination in soils. Geoaccumulation indices for the trace elements in each sampling site was calculated using the equation:

$$IGEO = \frac{\log_2 Cn}{1.5(Bn)}$$

Where Cn is the concentration of the element in soil samples and Bn is the geochemical background concentration of the metal (n) in the world average shale (Karbassi *et al*., 2008; Bhuiyan *et al*., 2010). Factor 1.5 is the background matrix correction factor due to lithospheric effects.

The geoaccumulation index consists of 7 grades or classes (Grzebisz et *al*., 2002; Lokeshwari and Chandrappa, 2007; Yaqin *et al*., 2008) [Table 2]. The intensity of each element pollution in the soils was designated using the classes presented in Table 2.

Table 2. The seven classes of geoaccumulation indices

IGEO value	IGEO Class	Intensity of pollution
<0	1	Practically unpolluted
>0-1	2	Unpolluted to moderately polluted
>1-2	3	Moderately polluted
>2-3	4	Moderately to strongly polluted
>3-4	5	Strongly polluted
>4-5	6	Strongly to very strongly polluted
>5	7	Very strongly polluted

CHAPTER FOUR

RESULTS

4.1   METALS LEVEL IN SOILS

Metal levels and pesticide residues were determined in soils and cocoa beans from Kade in the

Eastern Region of Ghana between September, 2010 to December, 2010. The metal

concentrations were determined using INAA and AAS techniques. The validity of the techniques

was determined by analyzing certified reference materials. The values compare favourably well

with the recommended values for the examined elements with bias less than 7% for all the

analytical methods. The precision was calculated as a percentage relative standard deviation

(%RSD) of six replicate samples of the prepared standards, and was found to be less than 6%.

The sampling sites from the ten inorganic cocoa farms were designated IF1, IF2, IF3, IF4, IF5,

IF6, IF7, IF8, IF9 and IF10 respectively, while the organic farm sampling site was designated

Control.

The mean concentration of the studied elements in the soil samples collected from the ten

inorganic cocoa farms and an organic farm (control) are presented in Table 3. and Table 4. The

mean Al concentration in the soil samples from the inorganic farms ranged from 8117.69 ±

240.93 to 116636.17 ± 300.96 mg/Kg. Inorganic farm 2 (IF2) soil samples had the highest mean

As concentration of 17.99 ± 1.15 mg/Kg whereas the lowest level was recorded at IF9 of 7.20 ±

0.81. Seven inorganic farms (IF1, IF4 to IF9) had mean As concentrations lower than the

measured concentration reported for the organic farm (control). The sampling point IF3 had the

highest mean Ca concentration of 474.06 ± 31.26 mg/Kg, and sampling point IF7 recorded the

lowest concentration of 102.69 ± 11.02 mg/Kg. In general, seven inorganic farms (IF1, IF6-10) had mean Ca concentrations lower than the recorded value (259.62 ± 29.86) for the organic cocoa farm.

With the exception of IF9, all the inorganic cocoa farms had mean K concentration in soil samples higher than the measured level (5448.34 ± 182.89 mg/Kg) in the control soils. The highest mean K concentration in soil of 10573.95 ± 287.56 mg/Kg was recorded at IF2 and the lowest level of 4898.42 ± 199.84 mg/Kg was reported at IF9.

All the inorganic cocoa farms soil samples had mean La, Mn and Na concentrations greater than the measured amounts in the control soil samples. The lowest and highest mean concentrations for La, Mn and Na are 6.12 ± 0.14 and 18.66 ± 1.33; 52.50 ± 3.50 and 347.22 ± 14.69; 243.84 ± 5.12 and 461.77 ± 6.81 respectively. All the inorganic cocoa farm soils recorded mean V concentration mg/Kg less than the measured amount (135.84 ± 6.24) in the control soil samples except sampling points IF2 and IF3 which had 146.16 ± 8.16 and 146.57 ± 6.35 respectively.

Table 3. Mean elemental composition of soils from ten inorganic cocoa farms (mg/kg) in kade determined by INAA method.

Sample site	Al	As	Ca	K
IF1	8117.69±240.93	10.19±0.87	255.79±17.62	7909.08±234.65
IF2	113346.19±278.09	17.99±1.15	383.64±26.87	10573.95±287.56
IF3	116636.17±300.96	12.28±1.14	474.06±31.26	10344.54±285.78
IF4	78794.28±290.83	10.19±0.89	226.37±19.86	7621.99±273.69
IF5	72681.88±255.67	10.68±1.08	299.18±2.39	7184.89±238.54
IF6	63788.46±199.61	8.26±0.82	123.21±10.22	5661.12±184.97
IF7	57106.69±206.87	9.15±0.81	102.69±11.02	6462.49±219.23
IF8	79634.87±221.02	8.59±0.77	250.39±18.67	5576.73±206.73
IF9	63259.82±196.35	7.20±0.81	215.68±19.96	4898.42±199.84
IF10	71855.00±223.08	14.72±1.04	178.3±12.37	8503.84±251.74
Control	80635.31±246.33	12.07±0.81	259.62±29.86	5448.34±182.89
Sample site	La	Mn	Na	V
IF1	18.66±1.33	279.04±15.10	395.02±7.67	113.53±6.32
IF2	6.32±0.46	52.50±3.50	461.77±6.81	146.16±8.16
IF3	8.78±0.87	247.81±17.01	384.87±6.26	146.57±6.35
IF4	10.96±1.54	298.64±15.84	394.54±6.47	105.23±6.98
IF5	6.12±0.14	209.89±1.18	421.89±6.58	96.03±6.95
IF6	7.49±0.46	223.22±18.99	262.42±5.82	79.07±5.51
IF7	8.17±0.41	287.41±10.78	313.41±5.52	73.09±4.83
IF8	6.68±0.11	347.22±14.69	312.65±5.46	80.64±4.38
IF9	10.32±0.64	296.23±11.66	243.84±5.12	89.35±5.63
IF10	15.38±1.59	125.34±8.54	372.11±6.11	93.21±5.17
Control	3.62±0.91	17.05±1.29	239.23±4.84	135.84±6.24

The mean Fe concentrations in soils from the inorganic farms ranged from 145.79 ± 5.22 mg/Kg in IF6 to 151.38 ± 7.82 mg/Kg in IF4 (Table 4.). With the exception of IF4, all the sampling sites had mean Fe concentrations slightly lower than the recorded mean value (151.19 ± 4.87) for the control soil samples. All the reported mean Cu and Zn concentrations in the soil samples were lower than the recorded concentrations in the control soil samples. The highest mean Cu concentration of 10.8 ± 0.21 mg/Kg was measured in soil samples from IF2, whereas the lowest value of 6.39 ± 0.47 mg/Kg was recorded at IF9. The inorganic farm sampling points IF10 and

IF7 had the highest and lowest mean Zn concentrations of 4.09 ± 0.04 mg/Kg and 2.44 ± 0.03 mg/Kg respectively.

Soil samples from the inorganic cocoa farm sampling point IF10 and IF6 recorded the highest and lowest mean Pb concentrations of 4.49 ± 0.03 mg/Kg and 2.49 ± 0.02 mg/Kg respectively. However, inorganic cocoa farms sampling points   IF3, IF5, IF6, IF7 and IF9 had mean Pb levels less than the measured value (3.29 ± 0.01 mg/Kg) of the control soil samples.

All the soil samples from the ten inorganic cocoa farms recorded mean Cr and Ni concentrations lower than the reported amounts in the control soil samples (Table 4.). The mean Cr and Ni concentrations in the soils from the inorganic cocoa farms ranged from 1.92 ± 0.09 mg/Kg in IF6 to 4.03 ± 1.62 mg/Kg in IF10, and 2.27 ± 0.04 mg/Kg in IF6 to 5.59 ± 0.04 mg/Kg in IF10 respectively.

All the inorganic cocoa farms had mean Cd concentrations slightly lower than the measured amount (0.2 ± 0.05 mg/Kg) in the control soil samples, with the exception of soil samples from IF2, IF3, IF4, IF5 and IF7. IF9 and IF4 recorded the highest and lowest mean Cd concentrations of 0.307 ± 0.01 mg/Kg and 0.107 ± 0.02 mg/Kg respectively. All the soil samples from the inorganic cocoa farms recorded mean Co concentrations lower than the measured level (1.56 ± 0.04 mg/Kg) in the control soil samples, except sampling point IF2 which had 1.72 ± 0.06 . The soil samples from the inorganic farms had lowest mean Co concentration of 0.83 ± 0.03 and highest mean Co concentration of 1.72 ± 0.06 mg/Kg.

Table 4. Mean elemental composition of soils from inorganic cocoa farms (mg/kg) in Kade determined by the AAS method.

Sample site	Fe	Cu	Zn	Pb
IF1	148.95± 0.01	8.72 ± 0.55	2.6 ± 0.03	3.91 ± 0.02
IF2	148.3 ± 7.30	10.8 ± 0.21	3.43 ± 0.07	3.92 ± 0.03
IF3	147.84 ± 6.71	10.59 ± 0.63	3.09 ± 0.03	2.59 ± 0.02
IF4	151.38 ± 7.82	9.01 ± 0.49	3.01 ± 0.01	3.61 ± 0.02
IF5	148.1 ± 4.20	8.73 ± 0.32	3.51 ± 0.04	3.28 ± 0.04
IF6	145.79 ± 5.22	7.25 ± 0.27	2.49 ± 0.04	2.49 ± 0.02
IF7	146.41 ± 2.91	7.01 ± 0.47	2.44 ± 0.03	3.17 ± 0.02
IF8	147.38 ± 5.44	7.51 ± 0.36	2.85 ± 0.01	4.19 ± 0.04
IF9	149.86 ± 7.01	6.39 ± 0.47	3.37 ± 0.06	3.09 ± 0.03
IF10	147.98 ± 6.24	10.07 ± 0.31	4.09 ± 0.04	4.49 ± 0.03
Control	151.19 ± 4.87	13.21 ± 0.56	5.05 ± 0.03	3.29 ± 0.01
Sample site	Cr	Ni	Cd	Co
IF1	2.55 ± 0.17	2.43 ± 0.51	0.187 ± 0.05	1.52 ± 0.02
IF2	2.84 ± 0.09	3.45 ± 0.62	0.293 ± 0.03	1.72 ± 0.06
IF3	2.45 ± 1.41	3.1 ± 0.59	0.293 ± 0.05	1.31 ± 0.02
IF4	2.5 ± 0.82	2.92 ± 0.36	0.307 ± 0.01	1.24 ± 0.04
IF5	2.21 ± 1.72	4.64 ± 1.05	0.253 ± 0.04	0.99 ± 0.03
IF6	1.92 ± 0.09	2.27 ± 0.04	0.2 ± 0.06	0.83 ± 0.03
IF7	2.48 ± 0.14	2.72 ± 0.02	0.24 ± 0.01	1.03 ± 0.04
IF8	2.4 ± 0.02	3.03 ± 0.46	0.16 ± 0.04	0.94 ± 0.01
IF9	2.73 ± 0.01	3.76 ± 0.02	0.107 ± 0.02	0.93 ± 0.02
IF10	4.03 ± 1.62	5.59 ± 0.04	0.187 ± 0.01	1.03 ± 0.02
Control	4.69 ± 1.09	6.1 ± 1.07	0.2 ± 0.05	1.56 ± 0.04

4.1 SOIL POLLUTION QUANTIFICATION USING CONTAMINATION FACTOR (CF), POLLUTION LOAD INDEX (PLI) AND GEOACCUMULATION INDEX (IGEO)

The results of the contamination factors calculated for each sampling point using the world average shale values reported by Turekian and Wedepohl (1961), Adomako *et al*. (2008) and Karbassi *et al*. (2008), presented in Table 5. All the sampling sites had Al CF values less than unity except for IF2 and IF3 and IF8. Only sampling point IF2 recorded As CF value (1.38) slightly above 1. Soil samples from IF2, IF3 and control had V CF values slightly above 1

while the rest of the sites recorded V CF values less than 1. Only soil samples from IF4 recorded

Cd CF value slightly higher than 1, all the rest of the sites had Cd CF values less than 1. All the

soil samples from the sampling sites including the control recorded CF values for the metals Ca,

K, La, Mn, Na, Fe, Cu, Zn, Pb, Cr, Ni, and Co, less than 1.

The resultant Pollution Load Index (PLI) of the sixteen studied metals is presented in Figure 3.

In general all the sampling points recorded PLI values less than 1. The ranking of the sampling

sites with respect to the PLI variations is as follows;

IF3>IF2>IF10>IF4>IF5>IF1>IF8>IF9> IF7>Control>IF6

All the sampling sites recorded geoaccumulation indices less than zero (Table 5).
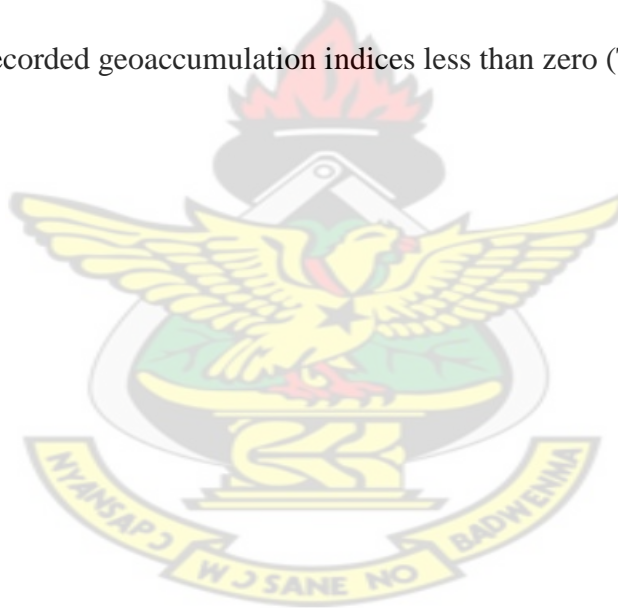
Table 5. Contamination factors of metals in soil samples from study area at Kade

	IF1	IF2	IF3	IF4	IF5	IF6	IF7	IF8	IF9	IF10	Control
CF_{Al}	0.10	1.42	1.46	0.98	0.91	0.80	0.71	1.00	0.79	0.90	0.10
CF_{As}	0.78	1.38	0.94	0.78	0.82	0.64	0.70	0.66	0.55	1.13	0.93
CF_{Ca}	0.01	0.02	0.02	0.01	0.01	0.01	0.00	0.01	0.01	0.01	0.01
CF_{K}	0.30	0.40	0.39	0.29	0.27	0.21	0.24	0.21	0.18	0.32	0.20
CF_{La}	0.20	0.07	0.10	0.12	0.07	0.08	0.09	0.07	0.11	0.17	0.04
CF_{Mn}	0.33	0.06	0.29	0.35	0.25	0.26	0.34	0.41	0.35	0.15	0.02
CF_{Na}	0.04	0.05	0.04	0.04	0.04	0.03	0.03	0.03	0.03	0.04	0.02
CF_{V}	0.87	1.12	1.13	0.81	0.74	0.61	0.56	0.62	0.69	0.72	1.04
CF_{Fe}	0.0032	0.0031	0.0031	0.0032	0.0031	0.0031	0.0031	0.0031	0.0032	0.0031	0.0032
CF_{Cu}	0.19	0.24	0.24	0.20	0.19	0.16	0.16	0.17	0.14	0.22	0.29
CF_{Zn}	0.03	0.04	0.03	0.03	0.04	0.03	0.03	0.04	0.04	0.04	0.05
CF_{Pb}	0.20	0.20	0.13	0.18	0.16	0.12	0.16	0.21	0.15	0.22	0.16
CF_{Cr}	0.03	0.03	0.03	0.03	0.02	0.02	0.03	0.03	0.03	0.04	0.05
CF_{Ni}	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CF_{Cd}	0.63	0.97	0.97	1.03	0.83	0.67	0.80	0.53	0.37	0.63	0.67
CF_{Co}	0.08	0.09	0.07	0.07	0.05	0.04	0.05	0.05	0.05	0.05	0.08
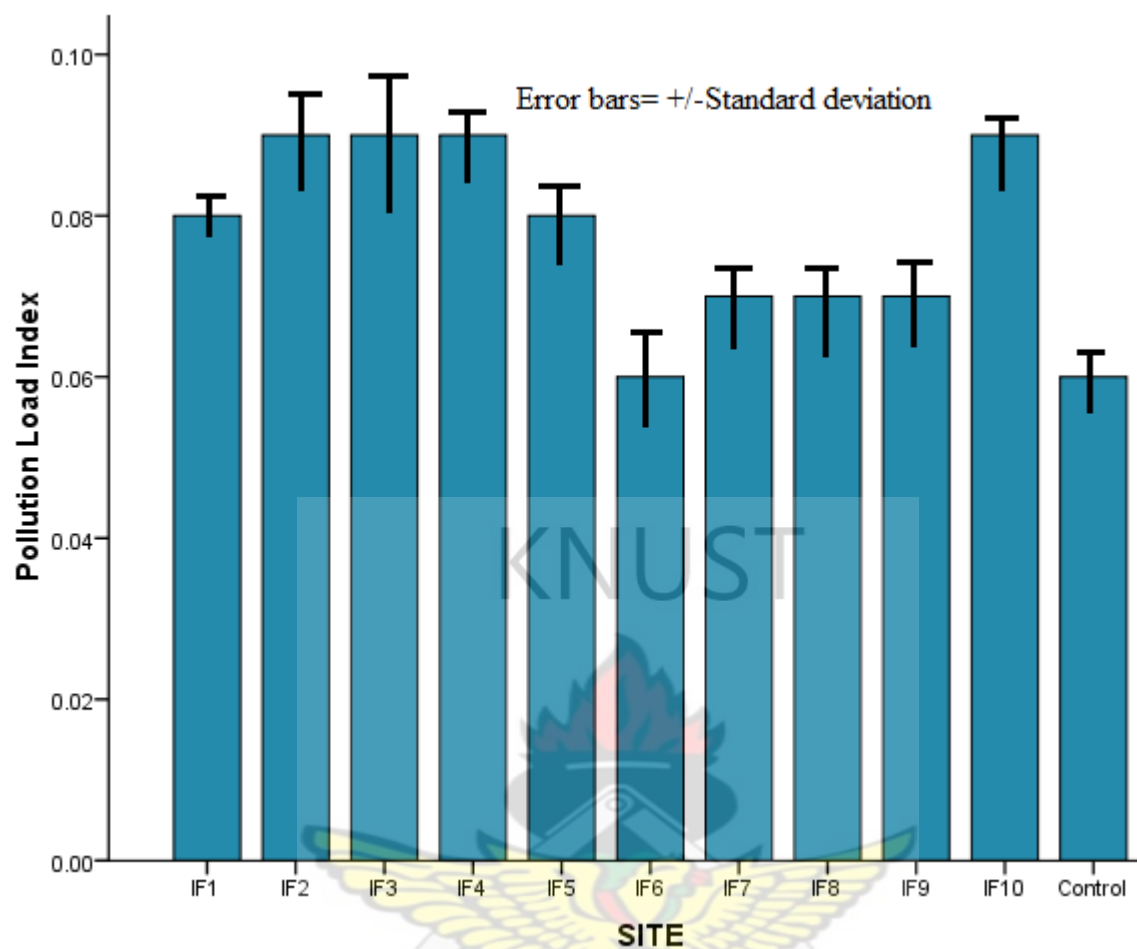
Figure 3. PLI variations in soil samples taken from different indicated sites at Kade

Table 6. Geoaccumulation indices of soils from the indicated sites at Kade

	IF1	IF2	IF3	IF4	IF5	IF6	IF7	IF8	IF9	IF10	Control
$IGEO_{Al}$	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
$IGEO_{As}$	0.172	0.214	0.186	0.172	0.175	0.156	0.164	0.159	0.146	0.199	0.184
$IGEO_{Ca}$	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
$IGEO_{K}$	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
$IGEO_{La}$	0.031	0.019	0.023	0.025	0.019	0.021	0.022	0.020	0.024	0.029	0.013
$IGEO_{Mn}$	0.006	0.004	0.006	0.006	0.006	0.006	0.006	0.007	0.006	0.005	0.003
$IGEO_{Na}$	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001
$IGEO_{V}$	0.035	0.037	0.037	0.034	0.034	0.032	0.032	0.032	0.033	0.034	0.036
$IGEO_{Fe}$	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
$IGEO_{Cu}$	0.046	0.051	0.050	0.047	0.046	0.042	0.042	0.043	0.040	0.049	0.055
$IGEO_{Zn}$	0.010	0.012	0.011	0.011	0.013	0.009	0.009	0.011	0.012	0.014	0.016
$IGEO_{Pb}$	0.066	0.066	0.046	0.062	0.057	0.044	0.055	0.069	0.054	0.072	0.057
$IGEO_{Cr}$	0.010	0.011	0.010	0.010	0.008	0.007	0.010	0.009	0.011	0.015	0.017
$IGEO_{Ni}$	0.013	0.018	0.016	0.015	0.022	0.012	0.014	0.016	0.019	0.024	0.026
$IGEO_{Cd}$	-5.324	-3.969	-3.969	-3.755	-4.444	-5.160	-4.575	-5.875	-7.076	-5.324	-5.160
$IGEO_{Co}$	0.021	0.027	0.014	0.011	-0.001	-0.009	0.001	-0.003	-0.004	0.001	0.023

4.2 COMPARISON BETWEEN METAL LEVELS IN ORGANIC AND INORGANIC FARMS

The results of the one sample t-test of the mean metals concentrations in soil samples from the organic (control) and inorganic cocoa farms are presented in Table 7. The results showed that, there were significant ($P<0.05$) differences between the mean of the inorganic and the control concentrations for the metals; K, La, Mn, Na, V, Fe, Cu, Zn, Cr, Ni and Co. However, differences in the mean concentrations of Al, As, Ca, Pb and Cd, between the inorganic cocoa farms and the control soil samples were not statistically significant ($p>0.05$).

Table 7. T-test comparison of elemental composition of organic (control) and inorganic cocoa farm sites

Element	t-value	df	Sig.	Mean Difference
Al	-0.85	9	0.419	-8113.21
As	-1.10	9	0.298	-1.15
Ca	-0.24	9	0.814	-8.69
K	3.31	9	0.009	2025.37
La	4.77	9	0.001	6.27
Mn	7.80	9	0.000	219.68
Na	5.25	9	0.001	117.02
V	-4.05	9	0.003	-33.55
Fe	-5.88	9	0.000	-2.99
Cu	-9.40	9	0.000	-4.60
Zn	-11.88	9	0.000	-1.96
Pb	0.88	9	0.404	0.18
Cr	-11.74	9	0.000	-2.08
Ni	-8.29	9	0.000	-2.71
Cd	1.13	9	0.286	0.02
Co	-4.46	9	0.002	-0.41

4.3 RELATIONSHIPS BETWEEN METALS IN INORGANIC COCOA FARMS SOILS

Table 8 summarizes the results of the preliminary analysis of the associations between the studied elements in the soils samples from the inorganic farms using Spearman's Rho method. The results showed that some of the elements were positively associated with each other since their correlation coefficients were statistically significant ($p<0.05$). Some of the elements such as Al, As, Ca, V, Fe, Cu, Cr, Ni, and Co were also negatively associated with each other at the significant 0.05 level.

Table 8 also gives the results of the subsequent analyses of the relationship between the studied elements in the soil samples, using principal component analysis (PCA). Four principal

components were extracted with Eigenvalues > 1, explaining 86.8% of the total variance in the

soil dataset. The first PC, accounting for 46.358% of the total variance was positively correlated

with As, Ca, K, Na, V, Cu, Cd, and Co. The second PC, explaining 20.191% of the total variance

was correlated primarily with As, Mn, Zn, Pb, Cr and Ni. The third PC, accounting for 12.853%

of the total variance, was weighted on Al, La and Pb. The fourth PC, accounting for 7.407% of

the total variance positively correlated with Fe.

Table 8. Correlation matrix of elements in soils

| Element	Al	As	Ca	K	La	Mn	Na	V	Fe	Cu	Zn	Pb	Cr	Ni	Cd
Al	1														
As	0.511	1													
Ca	0.603	0.51	1												
K	0.506	.874*	.728*	1											
La	-.650*	0.026	-0.174	0.104	1										
Mn	-0.401	-.880*	-0.27	-.650*	0.057	1									
Na	0.288	0.778*	0.613	0.827*	0.077	-0.55	1								
V	0.513	.697*	0.893*	0.892*	0.04	-0.481	.706*	1							
Fe	-0.029	0.039	0.235	0.119	0.355	0.142	0.287	0.299	1						
Cu	0.523	0.888*	0.706*	0.961*	0.13	-.672*	0.847*	0.830*	0.173	1					
Zn	0.388	0.569	0.293	0.353	0.09	-0.587	0.363	0.259	0.32	0.504	1				
Pb	-0.148	0.426	-0.057	0.162	0.405	-0.223	0.39	-0.007	0.271	0.289	0.438	1			
Cr	0.065	0.552	-0.038	0.334	0.507	-0.478	0.212	0.109	0.207	0.419	0.741*	0.670*	1		
Ni	0.218	0.418	0.076	0.178	0.096	-0.482	0.256	-0.007	0.14	0.333	0.937*	0.437	0.725*	1	
Cd	0.511	0.524	0.455	0.709*	-0.256	-0.334	0.717*	0.581	0.138	0.660*	-0.011	-0.143	-0.146	-0.114	1
Co	0.157	0.691*	0.609	0.796*	0.244	-0.444	0.763*	0.840*	0.336	0.697*	0.057	0.279	0.152	-0.165	0.528

*. Correlation is significant at the 0.05 level (2-tailed).

Table 9. Varimax component matrix of 4 factor model explaining 86.8% of the total

variance for soil dataset

	Component			
Element	PC1	PC2	PC3	PC4
Al	0.438	0.265	-0.789	0.007
As	0.812	0.509	0.005	-0.249
Ca	0.740	0.040	-0.373	0.360
K	0.956	0.205	-0.030	-0.046
La	0.048	0.141	0.882	0.218
Mn	-0.576	-0.548	0.070	0.456
Na	0.868	0.213	0.086	0.071
V	0.916	0.023	-0.132	0.236
Fe	0.180	0.157	0.213	0.875
Cu	0.897	0.363	-0.033	0.001
Zn	0.176	0.946	-0.129	0.187
Pb	0.137	0.567	0.558	0.047
Cr	0.129	0.847	0.382	-0.024
Ni	-0.029	0.953	-0.078	0.043
Cd	0.761	-0.168	-0.279	-0.026
Co	0.899	-0.088	0.289	0.117
Eigenvalue	7.417	3.231	2.056	1.185
% of Variance	46.358	20.191	12.853	7.407
Cumulative %	46.358	66.55	79.402	86.809

The results of the cluster analysis (CA) using Wards method and squared Euclidean distance is given by Figure 4. Four distinct groups or clustered were seen. Cluster 1 contains only Al, whereas Cluster 2 contains Zn, Cr, Pb, Ni, Cd, Co, As, Cu, and La. The members of cluster 3 are Ca, Na, V, Fe and Mn. The last cluster, 4 has only K as its member.
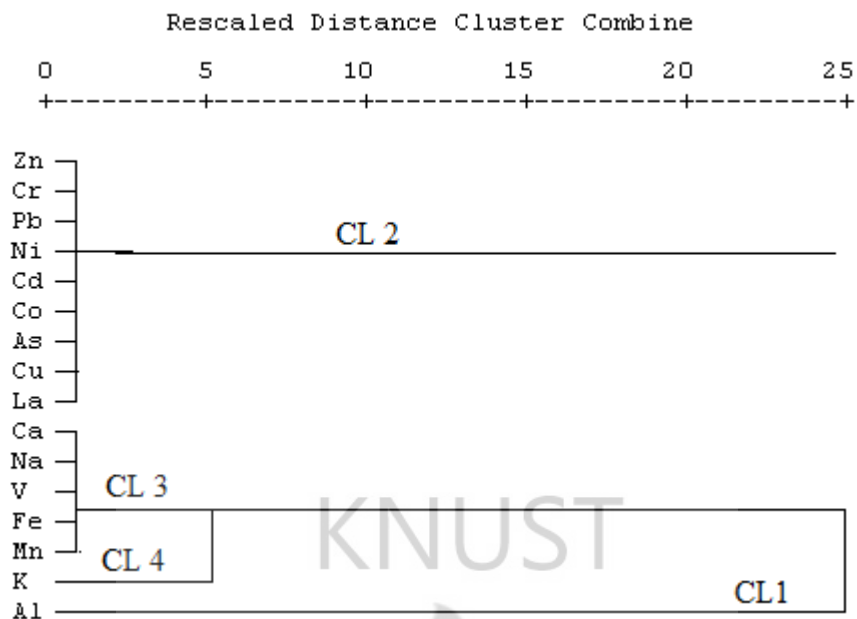
Figure 4. Dendrogram of metals level in soils from the study area at Kade

4.5   PESTICIDE RESIDUES LEVEL IN SOIL SAMPLES

The results from the gas chromatography (GC) analysis of the mean concentrations of the organochlorine pesticide residues in soils from the studied cocoa farms are presented in Table 10. No organochlorine pesticide residue was detected in the cocoa beans samples. In general, sixteen different pesticide residues were detected in the soil samples. These included the derivatives of Hexachlorocyclohexane (HCH)[α-HCH, *ß*-HCH, ɣ-HCH and δ-HCH], dichlorodiphenyltrichloroethane (DDT) [O, P'-DDD-dichlorodiphenyldichloroethane ; P, P'-DDE – dichlorodiphenyldichloroethylene ; O, P'-DDE, O, P'-DDT and P, P'-DDT], aldrin, dieldrin, heptachlor, trans-heptachlor epoxide, cis-heptachlor epoxide, trans-nanochlor, and trans-chlordane.

The total DDT (sum of *O, P'*-DDD, *O, P'*-DDT, *P, P'*-DDT, *P, P'*- DDE and O, P'-DDE) and total HCH (sum of *α*-HCH, *ß*-HCH, ɣ-HCH, and *δ*-HCH) of the soil samples are also presented in Table 10.

Table 10. Pesticide residue in soil samples taken from the indicated organic (control) and inorganic cocoa farm sites

Compound	IF1	IF2	IF3	IF4	IF5	IF6	IF7	IF8	IF9	IF10	CONTROL
α-HCH	0.001	0.001	<0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001
β-HCH	0.001	0.001	<0.001	<0.001	0.001	<0.001	<0.001	0.001	0.001	0.001	0.001
ɣ-HCH	0.002	0.002	<0.001	0.002	0.002	0.001	0.001	0.001	0.001	0.002	0.003
δ-HCH	0.021	0.008	0.001	0.006	0.026	0.013	0.024	0.010	0.011	0.012	0.002
ALDRIN	0.008	0.002	<0.001	0.006	0.006	0.001	0.001	0.001	0.001	0.003	0.002
DIELDRIN	0.004	0.002	<0.001	<0.001	0.002	<0.001	<0.001	0.004	0.005	0.001	<0.001
HEPTACHLOR	0.023	0.017	0.002	0.016	0.022	0.013	0.015	0.016	0.018	0.020	0.017
TRANS-HEPTACHLOR E	<0.001	<0.001	<0.001	0.001	0.002	<0.001	0.007	0.001	0.001	0.001	0.001
CIS-HEPTACHLOR E	0.004	<0.001	<0.001	<0.001	0.000	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
TRANS-NANOCHLOR	0.001	0.002	<0.001	0.001	0.003	<0.001	<0.001	0.001	0.004	<0.001	<0.001
TRANS-CHLORDANE	0.004	<0.001	<0.001	0.003	0.023	<0.001	<0.001	0.004	0.007	<0.001	<0.001
O, P'-DDD	0.006	0.005	0.001	<0.001	0.001	<0.001	<0.001	0.002	<0.001	0.001	0.001
O, P'-DDT	0.001	0.001	<0.001	0.002	0.001	0.001	<0.001	<0.001	<0.001	0.001	0.001
P, P'-DDT	0.006	0.003	<0.001	0.003	0.003	0.003	<0.001	0.001	0.003	0.004	<0.001
P, P'- DDE	0.001	0.001	<0.001	<0.001	0.002	0.001	<0.001	0.001	0.004	0.001	0.001
O, P'-DDE	0.014	0.014	0.001	<0.001	<0.001	0.002	<0.001	<0.001	<0.001	0.029	0.008
TOTAL DDT	0.028	0.024	0.002	0.005	0.007	0.007	0.000	0.004	0.007	0.036	0.011
TOTAL HCH	0.025	0.012	0.001	0.009	0.03	0.015	0.026	0.013	0.014	0.016	0.007

The detected concentration of *α*-HCH and *ß*-HCH in the soil samples were all 0.001 mg/Kg. No α-HCH was detected in soil samples from IF3. No *ß*-HCH was also detected in the soil samples from IF3, IF4, IF6 and IF7. All the detected lindane (ɣ-HCH) in the soil samples from the inorganic cocoa farms was lower than the measured concentration (0.003 mg/Kg) in the control.

The average lindane concentration in the soils samples from inorganic farms ranged from 0.001 to 0.002 mg/Kg. No lindane pesticide residue was detected in soil samples from IF3.

δ-HCH pesticide residues were detected in all the soil samples from iorganic farms and the concentrations were higher than the detected concentration (0.02 mg/Kg) in the control samples, except IF3. The sampling site IF5 recorded the highest concentration (0.026 mg/Kg) of δ-HCH. Aldrin pesticide residues were detected in all the soil samples from the study area except sampling site IF3. The highest aldrin concentration of 0.008 mg/kg in the soil samples was identified at IF1. However, four inorganic farms had mean aldrin concentration of 0.001 mg/kg, lower than the detected concentration (0.002 mg/Kg) in the control samples.

The detected average dieldrin concentration in the soil samples ranged from 0.001 to 0.005 mg/kg. No dieldrin was detected in soil samples from IF3, IF4, IF6, IF7 and the control. Heptachlor was detected in all the soil samples including that of the control. The order of the detected mean heptachlor concentration in all the sampling sites was in the sequence;
IF1>IF5 >IF10>IF9>IF2=control>IF4=IF8>IF7>IF6>IF3.

Trans-heptachlor epoxide residues were detected in soil samples from IF4, IF5, IF7-10 and the control. The highest trans-heptachlor epoxide concentration of 0.007 mg/Kg in the soil samples was detected at IF7 and the lowest identified level of 0.001 mg/Kg was found at IF4, IF8-10 and the control site. Cis-heptachlor epoxide was detected in only soil samples from IF1 and IF4 with concentrations 0.004 mg/Kg and 0.001 mg/Kg respectively. No trans-nanochlor and trans-chlordane pesticide residues were detected in the soil samples from the control site. No trans-

nanochlor pesticide residue was also detected in soil samples from IF3, IF6, IF7 and IF10. The trans-chlordane pesticide residues in soil samples from IF3, IF3, IF6, IF7 and IF10 were below the detection limit. The detected trans-nanochlor and trans-chlordane pesticide residues in the soil samples ranged from 0.001 to 0.004 mg/Kg and 0.003 to 0.007 mg/Kg respectively.

O, P'-DDD pesticide residues were identified in all the soil samples from the sampling sites except IF4, IF6, IF7 and IF9. O, P'-DDT was detected in soil samples from IF1-2, IF4-6, IF10 and the control site. P, P'-DDT was identified in all the soil samples except those from IF3, IF7 and the control sites. P, P'- DDE was detected in all the soil samples except those collected from IF 3-4, and IF7 sampling sites. O, P'-DDE was also detected in all the soil samples except those collected from IF7 IF4-5, and IF7-9 sampling sites. In general the mean measured concentrations of O, P'-DDD, O, P'-DDT, P, P'-DDT, P, P'- DDE and O, P'-DDE were between 0.001 and 0.006 mg/Kg, 0.001 and 0.002 mg/Kg, 0.001 and 0.006 mg/Kg, 0.001 and 0.004 mg/Kg, 0.001 and 0.026 mg/Kg respectively

The highest total DDT concentration of 0.036 mg/Kg was recorded at IF 10 while the lowest amount of <0.001 occurred at IF7. The highest total HCH level of 0.026 mg/Kg and the least concentration of 0.001 mg/Kg were recorded at IF7 and IF3 respectively.

4.5   METALS LEVEL IN COCOA BEANS

The mean concentrations of the elements determined in cocoa beans samples (beans and husk) are presented in Table 11. The mean concentrations of Fe, Mn, Zn and Ni in the beans samples collected from the inorganic cocoa farms were relatively higher than the measured amounts in

the control (organic farm) samples. However, the mean concentration (1.11 mg/Kg) of Cu in the control beans samples was slightly higher than the recorded amount (1.044 mg/Kg) in the inorganic cocoa samples.

Table 11. Metals levels in cocoa beans (mg/Kg)

Element	Inorganic farm		organic farm	
	Beans	Husk	Beans	Husk
Fe	4.860	5.956	3.920	2.320
Mn	0.800	3.616	0.654	2.492
Cu	1.044	0.348	1.110	0.308
Zn	0.840	1.004	0.672	0.532
Pb	<0.01	<0.01	<0.01	<0.01
Cr	<0.06	<0.06	<0.06	<0.06
Ni	0.328	0.304	0.180	<0.01
Cd	<0.002	<0.002	<0.002	<0.002
Co	<0.005	<0.005	<0.005	<0.005
As	<0.001	<0.001	<0.001	<0.001

CHAPTER FIVE

DISCUSSION

5.0   METAL CONCENTRATIONS IN SOILS AND BEANS FROM COCOA FARMS

All the elements (Al, As, Ca, K, La, Mn, Na, V, Fe, Cu, Zn, Pb, Cr, Ni, Cd and Co) were within their respective levels in world average shale soils reported by Turekian and Wedepohl (1961). [Appendix 1]. Also, the levels of these elements were within the permissible levels proposed by Kloke (1979) and Kabata-Pendias and Pendias (1984).   The concentrations of As, Cd, Cr, Co, Cu, and Ni in the soil samples were all within the reference value for "good" soil quality suggested by VROM (1983) [Table 1]. The levels of Cu, Zn, Co, and Cr in the soil samples were also all less than normal values reported by Bowen (1979).

In addition, the mean concentrations of Al, As, Ca, V, Fe, Cu, Zn, Pb, Cr, Ni, Cd and Co in the inorganic farm soils were below their respective concentrations in the control soil samples. This may suggest that the use of the agrochemicals in these cocoa farms have little impact on the concentrations of Al, As, Ca, V, Fe, Cu, Zn, Pb, Cr, Ni, Cd and Co in the soils. However, the mean concentrations of K, La, Mn and Na in the inorganic cocoa farm soil samples were significantly ($p < 0.05$) higher than the measured mean concentrations in the control samples. This may suggest that the agrochemicals used in these farms may contain significant amount of K, La, Mn and Na.

Table 12. Comparison of the concentrations of pesticide residues in this study and different studies.

Location/tolerance limit	Sampling period	Sample type	Total DDT	Total HCH	Lindane	Aldrin	Dieldrin	Reference
Kade	2010	soil Cocoa beans	ND-0.036 mg/kg ND	<0.001-0.026 mg/kg ND	ND-0.002 mg/kg ND	<DL -0.008 mg/kg ND	ND - 0.005 mg/kg ND	This study
FAO/WHO maximum acceptable limit for human consumption	-	food	200 ng/g	-	-	-	-	FAO/WHO (1998)
Chinese quality standards (CLASS I)	-	soil	50 ng/g	50 ng/g	-	-	-	Hu *et al*. (2009)
Twifo Praso district, Ghana	2008	Cocoa beans	-	-	ND	-	-	Owusu-Ansah *et al*. (2010)
Lake Bosomtwi, Ghana	2008	Sediment	4.41±1.54ng/g	-	0.126 ng/g	0.065	0.072ng/g	Darko *et al*. (2008)
		fish (*Tilapia zilli*)	3.645±1.81ng/g	-	-	-	0.035ng/g	
Accra Metropolis, Ghana	2007-2011	fruits and vegetable	<0.01 µg/g-0.11 µg/g		-		-	Bempah *et al*. (2011)
Akumadan, Ghana	2001	Sediment	0.46± 0.2 µg/kg (DDE)	0.96± 0.1 µg/kg	-		-	Ntow (2001)
LakeVictoria, Uganda	2003–2007	Sediment	4.24±3.83 µg/kg	2.80±2.00 µg/kg	-	0.22–15.96 µg/kg	3.80±3.55 µg/kg	Wasswa *et al*. (2011)
Tanzania	2004	Sediment soil	700 µg/kg 500 µg/kg	132 µg/kg 60 µg/kg	- -	- -	- -	Kishimba *et al*. (2004)
Vikuge, Tanzania	2004	soil	282,000 mg/kg	63,000 mg/kg	-	-	-	Kishimba *et al.* (2004)
Awash valley, Ethiopia	-	soil	22-230 ng/g	1-45 ng/g	-	<10 ng/g	<0.07-2 ng/g	Westbom *et al*. (2008)
Chao Phraya River Basin, Thailand	2009	soil	ND	29.9 ± 1.3 µg/g	-	-	-	Keithmaleesatti *et al*. (2009)
Yinchuan,China	2008	soil	92.1 µg/kg	7.98 µg/kg	-	-	-	Wang *et al*. (2009)
Romania	2001	soil	226.9 ± 157.2	28.4 ± 33.7 µg/kg	-	-	-	Covaci *et al*. (2001)
Nanning, China	2002	soil	63–1050.7 ng/g	2.7–130.6 ng/g	-	-	-	Cai *et al*. (2008)
Beijing, China	2007	soil	7.84 ng/g	0.85 ng/g	-	-	-	Hu *et al*. (2009)
Xinghua Bay, China	2009	soil	20.18 ng/g	2.82 ng/g	-	-	-	Zhang *et al*. (2011)
Central Germany	1995	soil	23.7–173 ng/g	4.60–11.50 ng/g	-	-	-	Cai *et al*. (2008)

ND: Not detected   DL: Detection limit

The measured concentrations of Cr, Co, Cu, and Zn in the soils of inorganic farms were lower than the average reported value by Dampare *et al*, (2006) in some agricultural soils in Ghana. The concentrations of As in the soils were within the research findings of Boamponsem (2011) on some agricultural soils in the Tarkwa area. The mean concentrations of Cd in the soils from Kade were lower than the report of Boamponsem (2011). However, the concentrations of As and V in Kade were higher than the measured concentrations reported by Dampare *et al*. (2006) and Boamponsem (2011) in some agricultural soils in Ghana. This could be due to the agricultural activities or the geology of the area.

The generally low concentrations of the elements in the soil samples reflected in the overall pollution Indices of the studied farms. The pollution indices of the elements in this study agree with the findings of Boamponsem (2011) in agricultural soils. The pollution load index (PLI) and geoaccumulation index analyses of the soil data have revealed that the soils of Kade cocoa farms were not polluted. The low PLI values for all the inorganic farms (less than 1.0) may suggest that the agricultural activities in Kade have little impacts on the soil as far as the sixteen examined elements were concerned.

The results from this study have also shown that the concentrations of Ca, Mg, Pb, Cr, Cd, Al, Co, As, La, K and V in the cocoa beans samples were less than the detection limits (MDL). However, the mean detected concentrations of Fe, Mn, Zn and Ni in the cocoa beans samples collected from the inorganic cocoa farms were relatively higher than the measured amounts in the control (organic farm) samples. This suggests that the agrochemicals used in these studied farms may contain Fe, Mn, Zn and Ni. However, the level of concentrations of Fe, Mn, Zn, Cu

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and Ni in the cocoa beans samples does not pose any health hazard to consumers since they are all within the permissible levels stipulated by FAO/WHO (1998). This implies that cocoa beans from Kade are not laden with these potentially toxic elements.

5.1 PESTICIDE RESIDUES IN SOILS AND COCOA BEANS

The study showed no organochlorine pesticide (OCPs) residue in the cocoa beans from the cocoa farms. In general, sixteen different pesticide residues were detected in the soil samples (including the control). These organochlorine pesticides have also been identified in similar studies in agricultural soils in other parts of Africa (Kishimba *et al*., 2004; Westbom *et al*., 2008).

The detected OCPs in the soils include the derivatives of HCH, DDT and its metabolites, aldrin, dieldrin and chlordane compounds. The measured concentrations of the individual pesticides were all lower than some of the similar published studies in Africa (Kishimba *et al*., 2004; Westbom *et al*., 2008), Asia (Hu *et al*., 2009; Keithmaleesatti *et al.,* 2009; Wang *et al*., 2009, Zhang *et al*., 2011) and Europe (Covaci *et al*., 2001) [Table 5]. The detection of lower levels of DDT than its metabolite and DDE, in the samples implies that the presences of these contaminants in the farms might be due to past usage of the pesticides on the farms.
This finding agrees with that of Darko *et al*. (2008) who studied organochlorine pesticides in the fish and sediments of Lake Bosomtwi, in Ghana.

The total DDT and HCH levels in the soils of each sampling site were lower than permissible levels (Hu *et al*., 2009) and reported values of other recent studies in Ghana (Darko *et al*., 2008; Ntow, 2001) [Table 5.0]. The residues of HCHs and DDTs measured in the soils of this study

will have little risk to ecological environment and human health. This indicates that, sources of HCHs and DDTs mainly originated form historical application rather than new input, suggesting the efficient management by Ghana Government in restricting the application of HCHs and DDTs. The low concentrations or non-detectable levels of aldrin, dieldrin, heptachlor, trans-heptachlor epoxide, cis-heptachlor epoxide, trans-nanochlor, and trans-chlordane, indicate a possible phasing out of these persistent organic pollutants.

This study agrees with that of Owusu-Ansah *et al*. (2010) that the following factors may have contributed to the low levels of pesticide residues in the sampled cocoa beans:

- Soil characteristics such as pH, temperature, clay fraction, moisture content, and particularly organic matter content also influence the uptake of pesticides by plants.

- The type of pesticide, the pesticide formulation, the method of application, and the mode of action affect plant uptake. Once absorbed by the plant a pesticide can be metabolized and is lost.

- Biological degradation as a result of microbial metabolism of pesticides, and is often the main source of pesticide degradation in soils. It occurs when fungi, bacteria, and other microorganisms in the soil use pesticides as food or other energy source, or consume the pesticides along with other sources of food or energy. Soil organic matter content, moisture, temperature, aeration, and pH all affect microbial degradation.

- Pesticides applied on leaves to crop residues are subject to interception by the plant material. These pesticides remain on the plant surface until they are removed by intercepted rainfall. The wash-off of these pesticides will amend the pesticide load in the

soil and thus will alter the amount of pesticide available for movement by runoff and sediment.

5.2 SOURCE IDENTIFICATION OF ELEMENTS

The significant correlation ($p<0.05$) between some of the elements might show that they come from a common origins (Table 8). Further analyses of the soil data with PCA and CA suggest that the elements might come from four main sources. The first source mainly contributing to As, Ca, K, Na, V, Cu, Cd, and Co levels in the soils might be due to agrochemicals (fertilizers and pesticides). The second source mainly responsible for As, Mn, Zn, Pb, Cr and Ni levels in the soils is likely to be from the parent rock materials (due to the geology of the area). The main source of Al, La and Pb in the soils might be due to both agricultural activities and natural. The presence of iron in the soils is likely to be from other non-point sources.
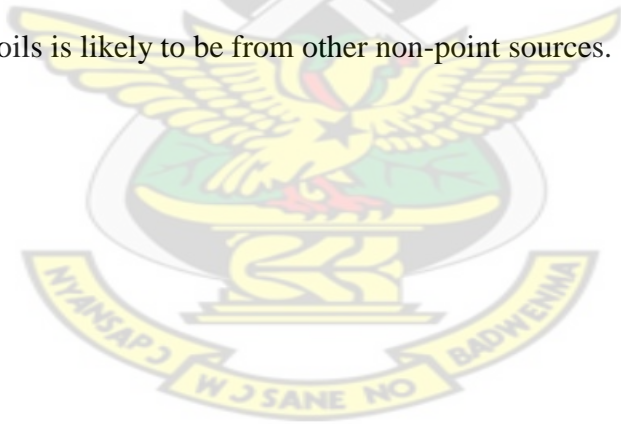
CHAPTER SIX

CONCLUSIONS AND RECOMMENDATIONS

6.0   CONCLUSIONS

The following conclusions can be deduced from the outcome of this research:

The mean concentrations of the elements; Al, As, Ca, K, La, Mn, Na, V, Fe, Cu, Zn, Pb, Cr, Ni, Cd and Co in the soils were mostly within their respective levels in world average soils as suggested by Bowen (1979), Dampare *et al*., 2006; VROM (1983) and Turekian and Wedepohl (1961). In addition, the mean concentrations of Al, As, Ca, V, Fe, Cu, Zn, Pb, Cr, Ni, Cd and Co in the inorganic soils were below their respective concentrations in the control soil samples. However, the mean concentrations of K, La, Mn and Na in the inorganic cocoa farm soil samples were significantly ($p<0.05$) higher than the measured mean concentrations in the control samples.

The generally low concentrations of the elements in the soil samples were reflected in the overall pollution Indices of the studied farms. The pollution load index (PLI) and geoaccumulation index analyses of the soil data have shown that the soils of Kade cocoa farms were not polluted with the measured elements. The low PLI values for all the inorganic farms (less than 1.0) may suggest that the agricultural activities in Kade have little impacts on the soil as far as the sixteen examined elements are concerned.

The results from this study have also shown that the concentrations of Ca, Mg, Pb, Cr, Cd, Al, Co, As, La, K and V in the cocoa beans samples were less than the machine detection limits (MDL).

However, the mean detected concentrations of Fe, Mn, Zn and Ni in the cocoa beans samples collected from the inorganic cocoa farms were relatively higher than the measured amounts in the control (organic farm) samples. The recorded concentrations of Fe, Mn, Zn, Cu and Ni in the cocoa beans samples do not pose any health threat to consumers since they were all within the permissible levels provided by FAO/WHO (1986).

The study detected no organochlorine pesticide (OCPs) residues in the cocoa beans from Kade. In general, sixteen different pesticide residues were detected in the soil samples (including the control). These included the derivatives of HCH, DDT and its metabolites, aldrin, dieldrin, heptachlor, trans-heptachlor epoxide, cis-heptachlor epoxide, trans-nanochlor, and trans-chlordane. The residual of HCHs and DDTs measured in the soils of this study will have little risk to ecological environment and human health. The results indicated that past agricultural application of OCPs was the major source of OCP residues in the soils. The low concentrations or non-detectable levels of aldrin, dieldrin, heptachlor, trans-heptachlor epoxide, cis-heptachlor epoxide, trans-nanochlor, and trans-chlordane, indicate a positive phasing out of these persistent organic pollutants.

This research serves as a reference for future studies on the assessment of the levels of toxic metals and persistent organic pesticides in the study area. It is envisaged that the results of this study will enrich the discussion and understanding of the fate of agrochemicals in the environment, especially pesticides.

6.1   RECOMMENDATIONS

Based on the results and conclusions of this study, the following recommendations have been made:

1. Further investigations should be conducted into other pesticide residues (e.g; organophosphorus) in soils and cocoa beans from the study area.

2. A monitoring system of the water bodies (surface and ground water) in the study area should be established by environmental protection agency to enhance early detection of specific areas susceptible to any metal or pesticide residue contamination due to farming activities.

3. Further studies should be carried out by other students or routine checkup of pesticide residue in the study area.
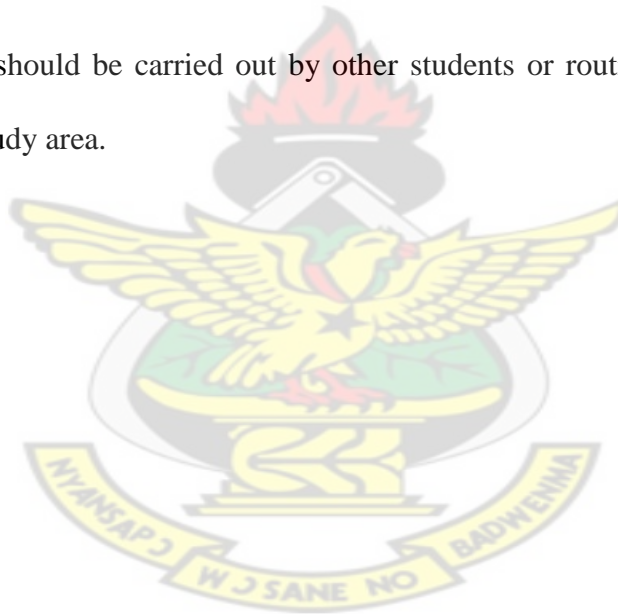
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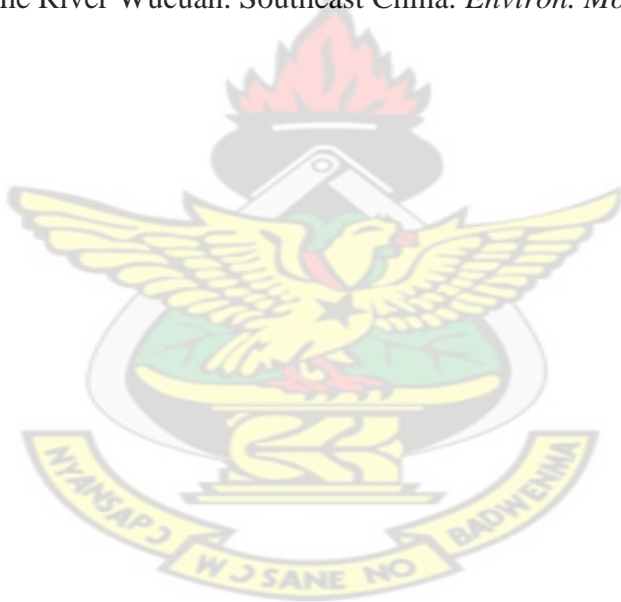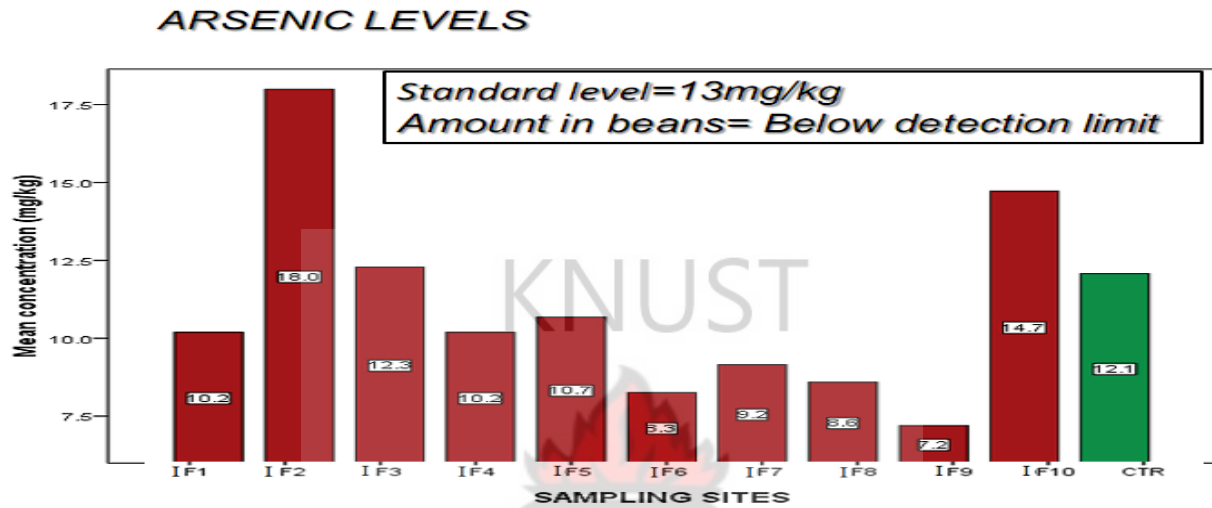
APPENDICES

Appendix 1:

World average concentrations (ppm) of monitored elements in shale.

Metal	Concentration (mg/kg)
Fe	47200
Mn	850
Cu	45
Zn	95
Ca	22100
Mg	15000
Pb	20
Cr	90
Ni	68
Cd	0.3
Al	80000
Co	19
As	13
La	92
K	26600
V	130

Source: Turekian and Wedepohl (1961)

Appendix 2:

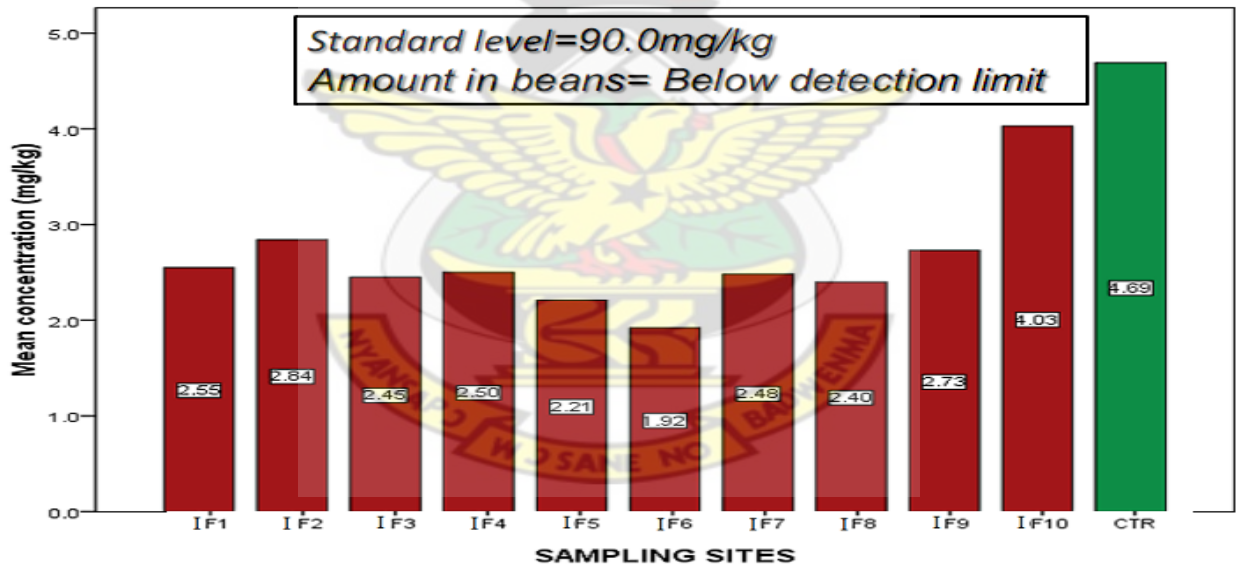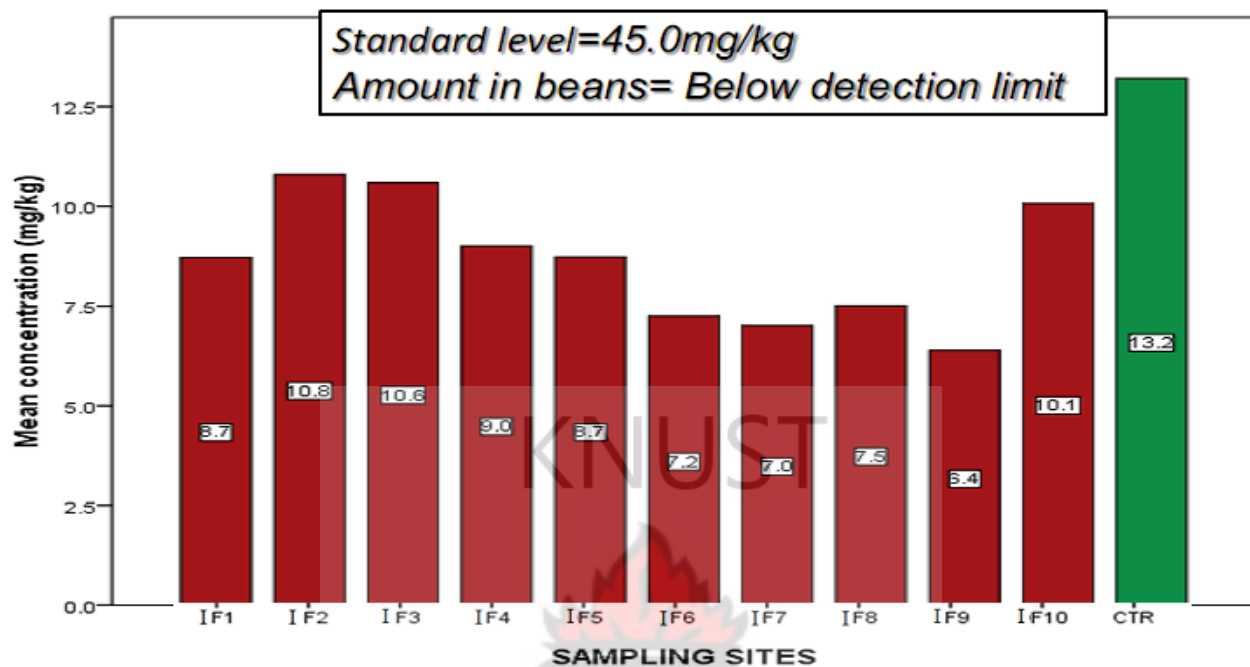Comparison of metals levels in soil samples: Standard (World average shale values)

ARSENIC LEVELS

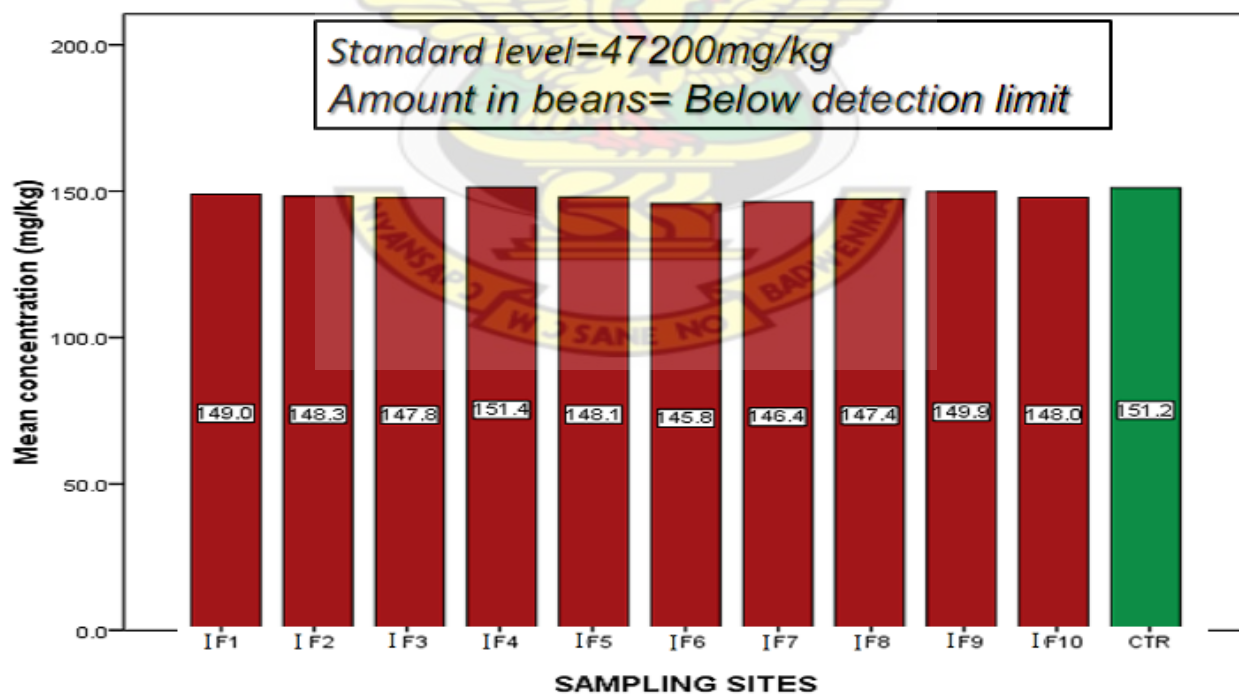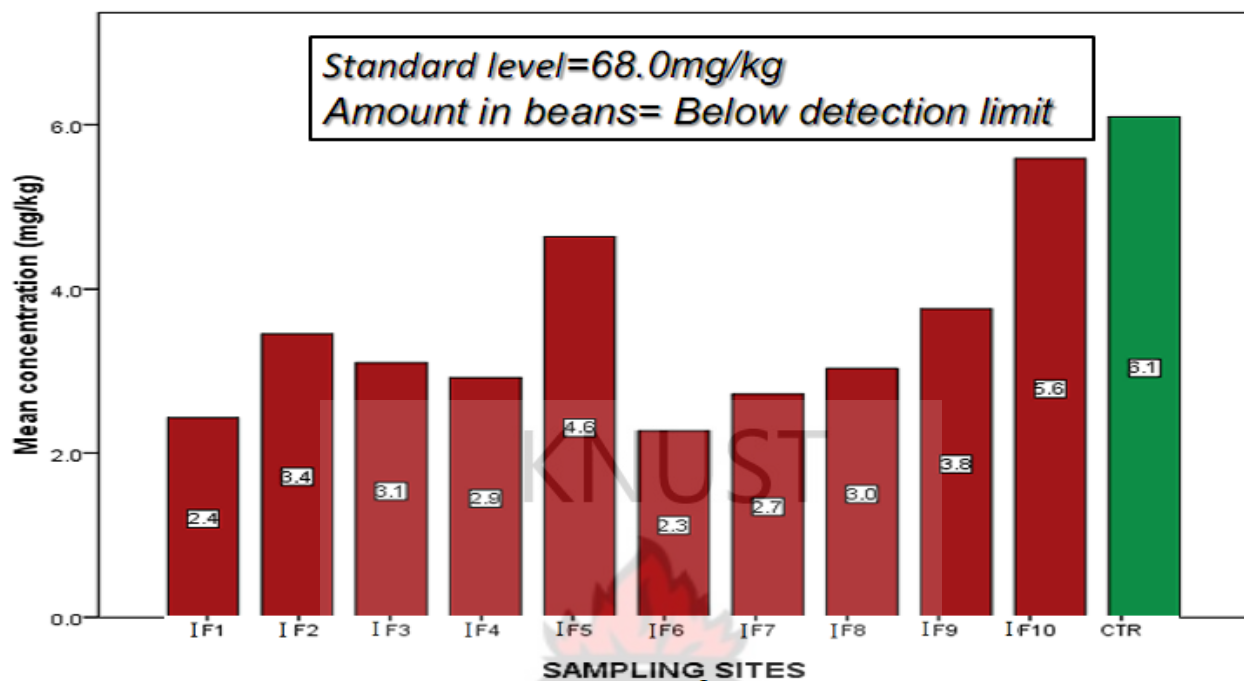Standard level=13mg/kg
Amount in beans= Below detection limit

Cadmium

Standard level=0.3mg/kg
Amount in beans= Below detection limit

Cobalt

Standard level=19.0mg/kg
Amount in beans= Below detection limit

Chromium

Standard level=90.0mg/kg
Amount in beans= Below detection limit

Copper

Standard level=45.0mg/kg
Amount in beans= Below detection limit

Iron
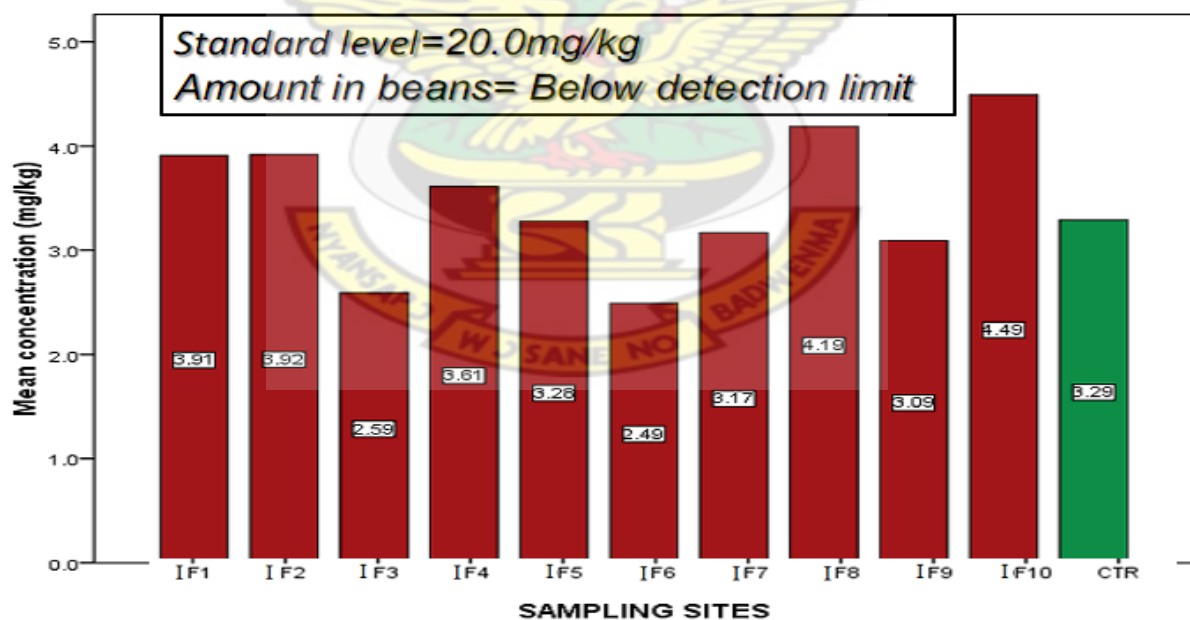

Standard level=47200mg/kg
Amount in beans= Below detection limit

Nickel

Standard level=68.0mg/kg
Amount in beans= Below detection limit

Lead

Standard level=20.0mg/kg
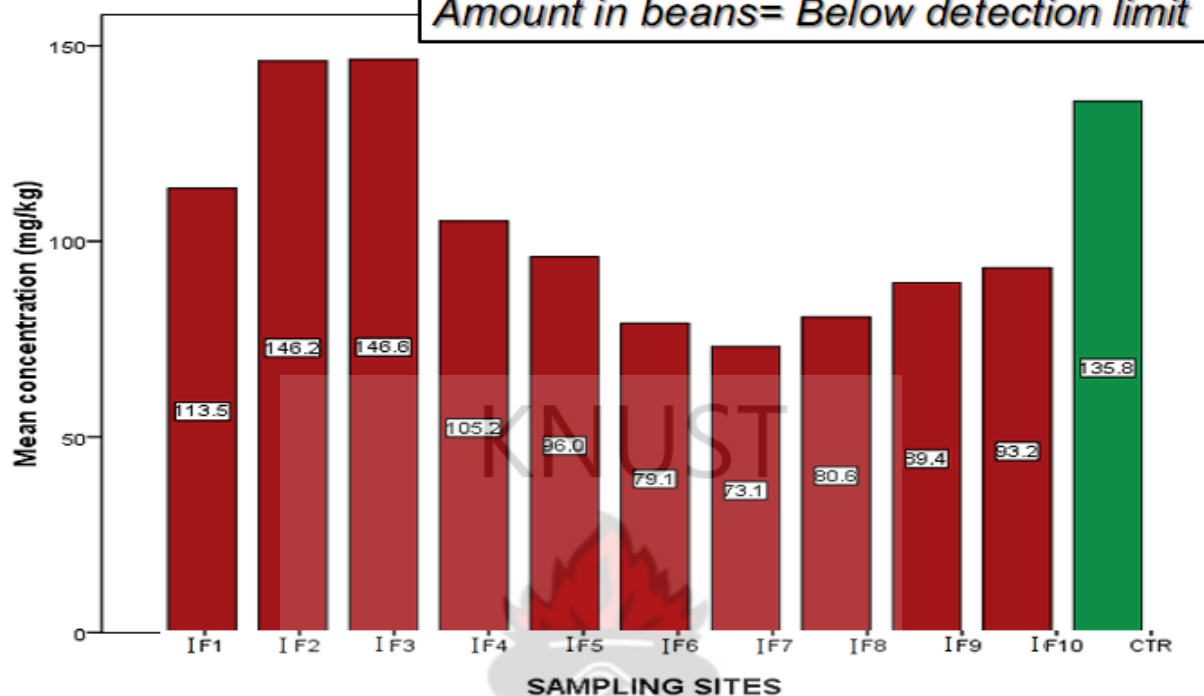Amount in beans= Below detection limit

Vanadium

Standard level=130.0mg/kg
Amount in beans= Below detection limit

Zinc

Standard level=95.0mg/kg
Amount in beans= Below detection limit