KWAME NKRUMAH UNIVERSITY OF SCIENCE AND TECHNOLOGY

COLLEGE OF SCIENCE

DEPARTMENT OF CHEMISTRY

LEVELS OF SOME HEAVY METALS AND PROXIMATE ANALYSES OF COCOA BEANS FROM EASTERN AND CENTRAL REGIONS OF GHANA.

A THESIS PRESENTED TO THE DEPARTMENT OF CHEMISTRY IN PARTIAL FULFILMENT OF THE AWARD OF

MASTER OF PHILOSOPHY DEGREE IN ENVIRONMENTAL CHEMISTRY

BY

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DECLARATION

I do hereby declare that except portions which have been duly cited in the bibliography, this thesis was written by me; from the record of my research work. The work has neither in part or in whole been published by another person nor presented for any degree in the university or elsewhere.

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DEDICATION

I GIVE THANKS TO ALMIGHTY GOD FOR HIS INFINITE MERCIES TO ME FOR HELPING ME COME THROUGH WITH THIS WORK.

This work is dedicated to my wife Miss Diana Quayson and our children Joses Amankwaah Gyimah, Simeonese Amankwaah Gyimah and Anita Amankwaah Kwofie.

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ABSTRACT

In this work total levels of cadmium (Cd), lead (Pb), copper (Cu), iron (Fe), manganese (Mn) and zinc (Zn) were determined in order to evaluate the levels of contamination by these metals of dried cocoa beans from the Eastern and Central Regions of Ghana. Fifty (50) samples comprising of twenty five (25) from each Region and an average of five from one community in five different Districts were analyzed using a Buck Scientific Atomic Absorption Spectrometer after aqua-regia digestion at a temperature of 420^{o}C for one hour twenty minutes.

The determinations were done at wavelengths of 248.3nm, 324.8nm, 228.9nm, 283.3nm, 279.5nm and 213.9nm for Fe, Cu, Cd, Pb, Mn and Zn respectively. Reliability and accuracy of the results were checked by analyses of two reference materials NBS 1571 SRM certified orchard leaves and IAEA-V-10 SRM certified hay powder. Results obtained from these two certified reference materials showed good agreement with values reportedly contained in them. An average range of 0.030 µg/g-0.079µg/g was detected for Cd, 0.020 µg/g-0.070 µg/g for Pb, 10.742-24.620µg/g for Cu, 14.350-39.820µg/g for Fe, 7.116-18.240µg/g for Mn and 29.620-39.990µg/g forZn in all the samples.

All the samples analyzed were found to contain levels of the heavy metals in question in quantities lower than limits set by Codex Alimentarius of 1.000µg/g for cadmium and lead and levels set by US Environmental Protection Agency (US EPA) andrecommended dietary allowance (RDAs) of between 0.900-18.000mg/day for the essential elements set by other reputable institutions. On analyses, the levels of Fe were found to have direct correlation with the age of the cocoa trees from which samples were taken. Thismadeit possible for the age cocoa trees in one of the farms sampled whose age was not available to be predicted. The relationship between iron levels and age can be represented with linear equation with regards to the samples obtained from Asamankese COCOBOD farms. Also the levels of Cu in these samples appeared to have a negative correlation with the age and levels of Fe. Comparing the two Regions, the levels of Fe, Mn, Zn and Pb were found to be higher in the Eastern Region whiles the levels of Cd and Cu were relatively higher in the Central Region than the Eastern Region of Ghana.

Proximateanalyses was done on the samples obtained from COCOBOD farms at Asamankese in the Eastern Region in order to ascertain their nutritional composition and relate them to age because the ages of five out of the six samples were known. This was done using the compositional analyses of Association of Analytical Chemist (AOAC). The data obtained showed a range of 33.93-39.22% fat, 38.15-40.18% carbohydrate, 13.19-14.42% protein, 2.62-2.70% fibre, 3.19-4.11% ash and 2.58-5.14% moisture in all the six samples.

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LIST OF ABREVIATION

SRM	Specified Reference Material
US EPA	United States Environmental Protection Agency
RDA	Recommended Dietary Allowance
COCOBOD	Ghana Cocoa Marketing Board
AOAC	Association of Analytical Chemists
GDP	Gross Domestic Product
US FDA	United States Food and Drugs Administration
TDS	Total Diet Survey
FDA	Food and Drugs Administration
COPAL	Cocoa Producers Alliance
MPL	Maximum Permissible Level
WHO	World Health Organisation
PTWI	Provisional Tolerable Weekly Intake
UL	Upper limit
CRI	Crop Research Institute
CODAPEC	Cocoa National Disease and Pest Control Committee
MIC	Middle Income Status
MDG	Millennium Development Goal
IITA	International Institute of Tropical Agriculture
FAO	Food and Agriculture Organisation
ICCO	International Cocoa Organisation
MOFA	Ministry of Food and Agriculture
CEPS	Custom Excise and Preventive Service
BoG	Bank of Ghana

ISSER	Institute of Statistical, Social and Economic Research
GLSS	Ghana Living Standard Survey
ATP	Adenosine Triphosphate
FNB	Food and Nutrition Board
LDL	Low Density Lipoprotein
CHD	Coronary Heart Disease
ATSDR	Agency for Toxic Substances and Disease Registry
DNA	Deoxyribose Nucleic Acid
PTMI	Provisional Tolerable Monthly Intake
FAO/WAO	Food and Agriculture Organisation/
JECFA	Joint Expect Committee on Food Additives
NTP	National Toxicology Programme
IARC	International Agency for Research on Cancer
PNS	Peripheral Nervous System
CNS	Central Nervous System
NAS/ IOM	National Academy of Science/ Institute of Medicine
CDC	Centre for Disease Control and prevention
IOM/ FNB	Institute of Medicine/ Food and Nutrition Board
MMT	Methylcyclopentadienyl Manganese Tricarbonyl
TOR	Tema Oil Refinery
CEC	Cation Exchange Capacity
ICP-MS	Inductively Coupled Plasma- Mass Spectrometry

CHAPTER ONE

INTRODUCTION

1.1 BRIEF OVERVIEW

Heavy metal contamination is an increasing worldwide environmental concern (Body et al, 1991). Heavy metals can be toxic to humans when they are not metabolized by the body and accumulate in the soft tissues **(**McSheely et al, 2010). It is believed that heavy metals such as lead(Pb) contaminate cocoa beans mainly through adsorption on the shells of the beans from emission from leaded fuel combustion during sun drying and fermentation of the beans (Rankin et al, 2005). Depending on the heavy metal in question, toxicity can occur at levels just above naturally occurring background levels, meaning that consumption of food with a high heavy metal concentration can cause acute or chronic poisoning(McSheely, 2010). Poisoning can result in damaged or reduced mental and central nervous function as well as damage to blood composition, lungs, kidneys, liver, and other vital organs. Long-term exposure to heavy metals may result in slowly progressing physical, muscular, and neurological degenerative conditions as well as cancer(McSheely, 2010; Rankin et al, 2005).

Cocoa has been the main stay of the economies of many West African countries including La Cote d' Ivoire, Ghana, Nigeria and Cameroon(Asare, 2005).It is believed that the cocoa sub-sector in Ghana employs over eight hundred thousand (800,000) smallholder farm families and contributes about 70% -100% of the incomes of these smallholder cocoa farmer's families (Asare, 2005). The sub-sector again is considered as being the backbone of many agrochemical companies, input distributors, licensed cocoa buying companies (Anim-Kwapong and Frimpong, 2005; Asamoah and Baah, 2003), some haulage truck drivers and their owners including carriers. Cocoa contributed 22.4% (463 million US$) of the total foreign exchange earning of Ghana and contributed 63% of the foreign export earnings from agricultural sector in 2002(Anim-Kwapong and Frimpong, 2005).Areport published in the magazine 'African bulletin' on Thursday 2nd September, 2010 quotes Dr. Frank Amoah as having said that cocoa engages over one million farmers, giving 17 to 20 percent of income to small scale farmers. He was also reported to have said that the sub-sector contributes about 5.5% to Ghana's Gross Domestic Product (GDP). At the same conference to adopt a common strategy to really review the position of Ghana and La Cote d' Ivoire in the market with their 60% share in the world production of cocoa, Dr. Amoah was reported again to have said that since 2003, the sub-sector has grown over 30% and represented 37% of foreign currency earnings of the country's national budget in 2004 (African bulletin, 2nd September 2010).

The producer price of the commodity perhaps is a key determinant of the levels of production of the product (Osei, 2007). A 10% increase in the price of the commodity resulted in about 3% increase in the production levels in the short term and about 18% or higher increases in the production levels in ten years' time(Anim-Kwapong and Frimpong, 2005; COCOBOD, 1998).Factors which determine the price of the produce, however, include demands on the world market, levels of production, quality of the beans; how it was handled and levels of contaminants (including heavy metals) in the beans and the nature of the beans exported (Osei, 2007).

A model profile of good cocoa soil is proposed to be deep, well drained, non gravelly top soil over sandy clay loam which contains iron oxide concretions and quartz gravel with average pH of about 5.6 – 7.2(Anim-Kwapong and Frimpong 2005; Ahenkorah, 1981). This indicates that if phytoextraction of heavy metals takes place in cocoa, contamination of cocoa beans with trace levels of iron from the soil is possible.

Heavy metal levels of the biosphere have increased very fast as a result of industrial revolution posing mild to severe environmental problems as damage to land surface and cultivated land pollution(McSheely et al, 2010; Gisberb et al, 2003). Unlike organic compounds, heavy metals are not degradable(Rankin et al, 2005; Gisberb et al, 2003; Aikpokpodion, 2010; Dalman et al, 2006), their removal is the surest way of cleaning them from the surface of cultivated land(Rankin et al, 2005; Gisberb et al, 2003).The metals are not removed from soil as a self purification; they accumulate in reservoirs and enter the food chain(Aikpokpodion 2010; Weichu[3]a and Weichu[3]a, 2003). The common heavy metals with regards to potential hazards and occurrence in contaminated soil include, Zn, Cd, Pb, Cr and Cu(Aikpokpodion, 2010; Alloway, 1995). It is believed that these heavy metals emanate from many sources including anthropogenic pollution, weathering of rocks and metal deposits (Aikpokpodion, 2010; Senesi et al, 1999). Evidence also points to pollution from heavy metal based fungicides applied on cocoa intended for the control of black pod disease(Aikpokpodion, 2010).

1.2 STATEMENT AND JUSTIFICATION OF THE PROBLEM

Contamination of cocoa beans and cocoa products with heavy metals is becoming a key problem in the cocoa industry (Rankin et al, 2005). Fred Accum (1820) was the first person to systematically investigate the widespread contamination of confectionaries with metallic poisons(Rankin et al, 2003). He reported lead chromate contamination in 59 out of 100 sweets studied; 12 contained red lead, 10 Brunswickgreen (Prussian blue and lead chromate). This was attributed to intentional adulteration and leaching from the wrappers labelled with lead compounds (Accum, 1820 in Rankin et al, 2003).

Today however it is believed in certain quarters that industrial activities contribute significantly to lead and heavy metal contamination (Flegal and Smith, 1995; Eghan, 2002; Pirkel et al, 1998; Thomas et al, 1999; Von et al, 2003; Rankin et al, 2005). Information about possible lead and heavy metal contamination of cocoa; the raw material for manufacturing chocolate and other products were made available around the 1970s(Rankin et al, 2005).The search for the possible sources of lead in cocoa therefore begun around the same period (US FDA, 2000; Rankin et al, 2005). Market survey as reported by Nriagu (1990), indicated continued contaminationof food products, especially milk chocolate products and candy bars (Rankin et al, 2005).

In 2000, the United States Food and Drug Administration (FDA) reported 27ng/g lead in milk chocolate, the 4th highest reported for all food items in a Total Diet Survey (TDS)(US FDA, 2000; Rankin et al, 2005). This was corroborated by the 20th Australian TDS where milk chocolate recorded the second highest lead contamination among 65 food products studied (Food Standards Australia New Zealand, 2003; Rankin et al, 2005). In 1997/1998 – New Zealand TDS reported lead concentration of 15ng/g in chocolate biscuits; about three fold higher than those of crackers (5.2ng/g) (Food Standards Australia New Zealand, 2003). In 2005,Dahiya et al reported average lead content of 1.92mg/kg(in a range of 0.05mg-8.3mg/kg) in cocoa powder samples in India(COPAL, 2004a). Onianwa et al(1999) reported average of 310ng/g with the range of 80-880ng/g (Onianwa et al, 1999). This report was confirmed by Cocoa Producers Alliance (COPAL) basedin Nigeria (COPAL, 2004a).

The maximum permissible level (MPL) of lead recently proposed by Codex Alimentarius Commission is 0.1mg/kg for cocoa butter, 1.0mg/kg for cocoa mass and cocoa powder (COPAL, 2004a). The World Health Organization (WHO) set the provisional tolerable weekly intake (PTWI) of lead at 25 µg/kg body weight for children (WHO, 1993), this amounts to 3.6 µg/kg body weight/day.This shows thatcontamination of cocoa with heavy metals is of great concern at leastto many international bodies.

In the years 1979, 1980, and 1982, Knezevic reported the contamination of cocoa with the heavy metals copper (Cu), cadmium (Cd) and lead(Pb)from various countries around the world (Knezevic, 1979; Knezevic, 1980; Knezevic, 1982). Some levels of Cd, Cu and other heavy metals have also been reported in raw cocoa beans by Lee and Low in 1985. They indicated in their work that the metal contentof the various chocolate products decreased with the fraction of cocoa in the products (Lee and Low 1985);suggesting that the source of heavy metal contamination of chocolate product is the cocoa.

Lucas and Musche had already stated this in 1973 when they reported that there was no Pb contamination in the manufacturing process of chocolate products (Lucas and Musche 1973). In 2002 Saracoglu and his colleagues reported that vigorous investigations were being conducted into heavy metal contamination of food samples such as honey, vinegar, lemon juice, sour cream, yoghurt, butter milk, chocolate, cocoa, molasses and other food samples (Saracoglus et al, 2002). The Turkish Authorities after pains taking exercise on this subject put their upper limit values (ULs) for Pb and Cu at 10mg/kg and 30mg/kg respectively (Saracoglus et al, 2002).

Considering the reports enumerated above, the health risk associated with heavy metal contamination, the economic impacts of cocoa cultivation on the lives of many rural dwellers in Ghana and the concern expressed by the then chief executive officer of COCOBOD in 2007about heavy metals (Osei, 2007), it is imperative that the levels of heavy metals in Ghana's cocoa beans are regularly monitored to ascertain the levels at any given time while proper remediation techniques are adopted to avert any 'economic shock' that might arise out of such contaminations.

1.3 OBJECTIVES OF THE STUDY

The main objective of this work is to determine the levels of some heavy metals; Cd, Cu, Fe, Zn, Mn and Pb, in cocoa beans from the Eastern and Central Regions of Ghana and compare these levels with the MPLs set by WHO, Codex Alimentarius Commission, COPAL and other standards set by recognizable bodies around the world.

1.3.1 SPECIFIC OBJECTIVES

Among other things the specific objectives of this work are to

- Investigate the levels of contaminations indried cocoa beans with the heavy metals
    - Cadmium
    - Copper
    - Iron
    - Lead
    - Zinc
    - Manganese

from the Central and Eastern Regions of Ghana.

- Investigate the correlation between age of cocoa trees and the levels of contamination of the heavy metals in the dry cocoa beans.
- Carry out proximate analyses of some of the samples and correlate them to the levels of heavy metal contamination and age of the trees.

CHAPTER TWO

LITERATURE REVIEW

2.1 OVERVIEW

Leiter and Harding in 2004 complained that, other commodities have received much more attention from Social Scientists than Cocoa (Leiter and Harding 2004). They cited Mintz Study of sugar and Paiges Study of Coffee to support their argument(Mintz 1985; Paige 1997 in Leiter and Harding 2004). They contended in their work that commodities grown in the tropics for export raise fundamental question of power, inequality and change in modern world system(Leiter and Harding 2004). Cocoa cannot be an exception; it could perhaps in Ghana become a factor for measuring a Government commitment to many rural dwellers (Asare, 2005). The management of the market; fixation of price and the execution of some other benefits as bonuses coupled with pest and disease control practices(mass spraying) and the period for formal opening and closure of crop seasons are determined by Government. Leiter and Harding believe that cocoa production often benefits from judgment of workers and discretion in adjusting their behaviour(Leiter and Harding, 2004).

This they emphasized as necessary because the crop is disease-prone and sensitive to temperature and moisture variation needed for fermentation and drying of the beans, since thesefactors dictate taste and flavour(Blauner, 1964). The price and bonuses are used as motivating factor which could influence both the amount produced and quality of the beans (Asare, 2005; Clarence-Smith, 1990).

2.2 THE HISTORY OF COCOA IN GHANA

The Bassel Missionaries first introduced cocoa in Ghana in 1857, by planting the seeds they received from Surinam at Akropong (Gordon, 1976b; Grossman-Greene and Bayer, 2009). Unfortunately these seeds could not survive hence they tried again with seeds from Cape Palmas the following year(Maugh, 2007; Grossman-Greene and Bayer, 2009).By 1861 these seeds have turned to ten young trees but only one survived by 1863 due to action of termites and beetles. Pods from this tree were distributed to other Basel mission stations at Aburi, Mampong and Krobo-Odumase in the Eastern Region where most of these plants survived (Grossman-Greene and Bayer, 2009). The Dutch, Swiss, and English though played various roles. Ghanaians believe that it was through the instrumentality of Tetteh Quarshie, a Ga blacksmith from Christainborg that the crop was disseminated and later developed in Ghana (Dand, 1997; Grossman-Greene and Bayer, 2009; Leiter and Harding, 2004). Quarshie is believed to have introduced the crop from Fernando Po to Ghana around 1879. He established cocoa nursery (of about 300 healthy trees) in Mampong-Akwapim and when matured sold pods and seedlings to local farmers (Leiter and Harding, 2004; Grossman-Greene and Bayer, 2009). These trees became the parent trees for Ghana's cocoa industry (Grossman-Greene and Bayer, 2009). From Akwapim, cocoa farming spread to Ashanti, Brong Ahafo, Central and Western Regions, and Ghana exported her first batch of cocoa beans 80 pounds worth in 1891. By 1910-1911 Ghana was the leading producer of cocoa, producing about 40,000 tons per year (Grossman-Greene and Bayer, 2009). This trend continued till after independence in 1957, and the level did follow the upward tradgetory expected(Leiter and Harding, 2004). According to Stephen Hymer, "the industry was developed by Ghanaian capital, Ghanaian enterprises and Ghanaian technology with little help from the colonial government" (Leiter and Harding, 2004; Grossman-Greene and Bayer, 2009).

Cocoa farms in Ghana are mostly small size, on individual or family owned plots rarely exceeding three acres till date;there are no large plantations owned by expatriates, multinationals or corporate entities in Ghana (Grossman-Greene and Bayer, 2009). There are also few but very large plantations, owned by local individuals who have employed caretaker farmers in various parts of the Country where, cocoa production is favourable.Perhaps the area where the colonial government had to work hard to develop the growth of the crop was Ashanti(Leiter and Harding 2004). Men in Ashanti did not engage in farming, the women engaged in subsistence farming; so as an inducement the colonial government established model farms allowing any one who put in 1000 plants the opportunity to buy a Dane gun,one keg of gunpowder and two lead bars(Ake, 1981; Leiter and Harding, 2004). This contributed to the success in the cocoa sector around 1910-1911 as stated above; by 1939, cocoa accounted for about 80% of the country's total exports(Leiter and Harding, 2004).

The country continued to be the leading producer of cocoa, producing about 570,000 tons annually in the mid-1960s(Raffaelli, 1995 and Gordon, 1976b; Leiter and Harding, 2004).This success was without recourse to extension services and other infrastructural development, it is difficult to understand why the British were eager to advance the production of the cash crop yet unwilling to create the necessary conditions for this success to be achieved, Berry in 1992 described the colonial administrators as having "lived on a shoe-string"(Gordon, 1976b; Leiter and Harding, 2004). They posted limited personnel to the sector, yet they were expected to raise enough revenue to cover their administrative cost since they were not prepared to subsidize recurrent or capital cost (Leiter and Harding, 2004). The administrators did not understand that the traditional method of production used by indigenes was well adapted to plentiful supply of land coupled with inadequate labour; they therefore characterized these practices as unskilful, uninventive, crude, neglectful and disorganized hence believed they resulted in the production of poor quality produce leading to low pricing of commodities from Africa in Europe(Hymer, 1971; Hopkins, 1973; Leiter and Harding, 2004). Official policy therefore,wavered between encouraging and limiting export crop production, cocoa production was further confused and constrained with colonial policies, and problems associated with land tenure system; to bring about justice they established a rigid judicial system in Ghana(Berry, 1992; Leiter and Harding, 2004).

In a bid to secure good price for the produce,coastal tradesmen, producers and wealthy farmers staged a boycott from 1937-1938 to as they call it "break the hold European (mainly British) expatriate firms had on the marketing of peasant-produced cocoa overseas" (Howard, 1976; Grossman-Greene and Bayer, 2009). A group of officials who were charged to investigate the drastic decline in cocoa production around 1943 reported that, farmers only collected available crops from the trees without maintaining their farms because they were poorly compensated for their produce. This led to the spread of two major diseases (capsid pest and cocoa swollen shoot virus disease) (Danquah, 2004; Grossman-Greene and Bayer, 2009). It was so serious that the colonial government's report on the Gold Coast in 1947 projected that "if left unchecked, the cocoa industry would disappear in 20years (Danquah, 2003; Grossman-Greene and Bayer, 2009).

The quality of Ghana's cocoa beans is not only the issue of taste but also due to low pesticide use compared with what pertains to other big plantations in other producing countries elsewhere in the world (Leiter and Harding, 2004).Small-holders in Ghana cannot afford many pesticides; they therefore resort to traditional methods of pest control as careful weeding, pruning, and waste disposal(Cox, 1993 in Leiter and Harding, 2004). Besides, the GhanaCOCOBOB monitors the introduction of new pesticides so as to control any possible introduction of new crop contaminants now and then into the industry (Leiter and Harding, 2004).

2.3.IMPORTANCE OF COCOA TO THE ECONOMY OF GHANA

Cocoa positioned itself as Ghana's premier cash and principal means of foreign exchange earnings in the 20th century. It, therefore, became a focal point in many national policies. Nkrumah's government had an ambitious plan of industrializing Ghana and attempted to use cocoa to bankroll his program (Grossman-Greene and Bayer, 2009). Grossman-Greene and Baryer reported that the period of political instability in the country is due in part to sharp decreases in cocoa prices from 1964-65; emanating from pressure to pay interest on international loans and eagerness to increase funding for education and other developmental projects(Woods, 2004; Grossman-Greene and Bayer, 2009). Cocoa continued to follow a downward trend in production levels and by 1978-79 seasons Ivory Coast had replaced Ghana as the Worlds' leading producer of cocoa(Ridler, 1993; Grossman-Greene and Bayer, 2009). Grossman-Greene and Bayer of Tulane University have reported that "as the cost of labour started to increase, government increased its siphoning of cocoa revenue"(Woods, 2004; Grossman-Greene and Bayer, 2009). This indicates that cocoa was the backbone of most of the government developmental projects.

High cocoa production by the nation implies much resources or revenue for the nation to sponsor government policies and projects. Cocoa positioned itself as the main drive for the nation’s economy; pricing for the commodity was therefore a motivating factor for ensuring higher production. Prices were increased from $34 in 1982 to $471 per ton by the government in 1988/89 season. This was further increased to $640 per ton in 1990. Overall production of the commodity by Ghana subsequently increased to 300,000 tons in 1989/90 crop season(Danquah, 2004; Grossman-Greene and Bayer, 2009).

In line with the Structural Adjustment Agreement with the World Bank and the IMF, liberalization of the cocoa sector in 1992/93 season was done with the introduction of private and quasi-private exporting companies; this introduced competition into the sector as reported by Wilcox and Abbott in 2004 (Grossman-Greene and Bayer, 2009). In a World Bank reportby Kurt et al, 2009 and another by Essegby 2009; on “Agribusiness and Innovation Systems in Africa”, the national goal of Ghana in the 2006/2007 season was “ to produce one million metric tons of cocoa by 2010 by increasing from the 700,000 tons levels in 2007”. The Crop Research Institute (CRI) of the COCOBOD was therefore, charged to conduct research into and provide support services to farmers including; distribution of seedlings resistant to CSSV, fertilizers and technical training on farm management practices and in 2008, the COCOBOD was reported to have spent $87,488,569 on CODAPEC free cocoa spraying for cocoa farmers and a further $31,800,000 on solar powered deep wells in farming communities all aimed at boosting farmers’moraleto enhance quality and high levels of cocoa production(Owusu-Amankwah, 2009; Grossman-Greene and Bayer, 2009).

The construction of Ghana's second major hydroelectric power generation dam at Bui is widely believed to have received the financial sponsorship based on some collateralization of the country's cocoa of some kind. The cocoa sector has played significant role in the nation's economic achievements and over the past few years has been the major source of foreign exchange earnings (McKay and Aryeetey, 2004; Begotic et al, 2007; Breisinger et al, 2007; Bulir, 1998). Based on these circumstances the government of Ghana made an announcement on its development vision; declaring the goal of reaching the middle income status (M I C) by 2015 and reducing the number of poor people beyond the Millennium Development Goal (MDG) level, while emphasizing the importance of the cocoa sector by setting target of a million metric ton production by 2010 (Breisinger et al, 2007; Bulir, 1998; IITA, 2007).

While expressing doubts about these goals, sceptics argued that it might not materialize based on the fact that the growth in the cocoa sector is driven by land expansion and increased use of labour rather than by productivity growth (Breisinger et al, 2007; Gockowski, 2007; Vigneri, 2007). They also think increase in production level has direct linkage with price incentive to farmers but not removal of constraints to production and productivity enhancing measures (Vigneri 2007; Teal and Zeitlin, 2006). Once again critics believe COCOBOD's operations have not been efficient enough questioning their expenditure in 2006 as representing about eighty five (85%) percent of total agricultural expenditure for that year in Ghana (Breisinger et al, 2007).

The World Bank,however, believed that cocoa can continue to play an important role in Ghana's economic growth toward MIC status (Breisinger et al, 2007; World Development Report by World Bank, 2007). Again, it is believed that Ghana's cocoa production is below international average, suggesting the potential for productivity driven growth (Breisinger et al, 2007; FAO, 2005; ICCO, 2007)).

New scientific evidence emphasizes health benefits for cocoa consumers which potentially can further boost demand (Breisinger et al, 2007; FAO, 2005).Furthermore, the Government of Ghana has indicated its willingness to carry through its continued liberalization of buying companies to contribute to output and productivity growth (Breisinger et al, 2007; Varangis and Schreiber, 2001; Laven, 2007).Cocoa indeed plays a large role in Ghana's economy and employs many small scale farmers (Breisinger et al, 2007).Cocoa production hit all time high of 3.6 million metric tons in 2005/6 year with West African countries including Ghana accounting for over 70 percent of the world production (ICCO, 2007).

Ghana planned to increase its production by 100,000 tons per annum and due to combination of factors as mass spraying programmes, fertilizer credits, government backed rehabilitation programmes, partial liberalization, establishment of price stabilization policy, higher producer prices; the country has been the most successful of all cocoa exporters (Breisinger et al, 2007; FAO, 2005; Laven, 2007). Cocoa production more than doubled from 395,000 tons in 2000 to 740,000 tons in 2005, contributing 28 percent of agricultural growth in 2006 (Begotic et al, 2007; Breisinger et al, 2007). This makes the sector's performance more impressive following the country's earlier elasticities in production (Abdulai and Rieder, 1995).The boost led to an increase in agricultural GDP from 13.7percent in 2003/2004 to 18.9 percent in 2005/2006 (Breisinger et al, 2007).Producer price rose by about $260 between 2000 and 2006. TheFAO and Ministry of Food and Agriculture(MOFA) estimates, thatachievable yields for cocoa is about 1-1.5 tons per hectare per year; more than double the average yields in2005 (Breisinger et al, 2007; FAO 2005; MOFA, 2007).

In 2005,cocoa beans(24.3%)and cocoa products(3.8 %)together contributed about 28 percent of total exports accounting for about half of agricultural exports (Breisinger et al, 2007).Africa processed on the average 15 percent of cocoa products.However, Ghana's processed cocoa is below Africa's average ranging from 8 to 12 percent. Domestic food industries that use cocoa as raw material are small hence value addition is low limiting its contribution to economic growth (Breisinger et al, 2007). There is, however, an encouraging development, the value of processed beans went up from US$83.6 million in 2004 toUS$152.9 million in 2006 (CEPS, 2006 in Breisinger et al, 2007).

Levy on export tax on cocoa has, however, declined over the years,reducing from 16 percent in 1960s to 12 percent in 1990s and to about 5 percent in 2005(BoG, 2007 and ISSER, 2001 in Breisinger et al, 2007). National poverty reduced from 51.7 percent in 1991 /92 to 39.5 in 1998/99 and then to 28.5 in 2005/2006 (Breisinger et al, 2007).Poverty among cocoa farmers is also believed to have reduced drastically; from 60.1percent or over 281,600 cocoa farmers in 1991/92 to 23.9 percent or 112,000 cocoa farmers in 2006 (Coulombe and Wodon, 2007; Breisinger et al, 2007).

A major problem here is that cocoa production is geographically concentrated and its contribution to poverty reduction is not evenly distributed(Breisinger et al, 2007).From Ghana Living Standard Survey-5 (GLSS-5) about two-thirds (2/3) of the country's cocoa is produced in the forest zone, where rural poverty levels are below the national averageand about 30 percent in the Southern Savanna zone (mainly Brong-Ahafo Region) and the Coastal zone takes the rest (GSS Survey, 2005/2006).

In the North where poverty is endemic, natural conditions are not suitable for cocoa production(Breisinger et al, 2007). The rural household generates only 30 percent of their Agriculture income from cocoa with the rural poor getting about 10 percent of income from cocoa (Breisinger et al, 2007).

2.4.EVIDENCE OF HEAVY METAL CONTAMINATION OF COCOA AND COCOA PRODUCTS

It is believed that Ghana's cocoa production is below the international averages; various steps are being adopted to boost productivity (Breisinger et al, 2007; Varangis and Schreiber, 2001; Laven, 2007). Notable among these include the application of weedicides, pesticides and fungicides, in the control of cocoa related diseases (Laven, 2007). Estimation of crop losses due to capsids is always complicated due to inadequate records and complexity of the losses due to others as fungal and viral drought (Padi and Owusu, 2006). It is, however, estimated that about 25-30 percent of total cocoa produced are lost due to capsids and mealy bugs annually; (Will, 1962; Padi and Owusu, 2006). In 1959, Stapley and Hammond estimated that about 60,000 to 80,000 tons of dry cocoa beans were lost due to capsids alone (Stapely and Hammond, 1959; Padi and Owusu, 2006). This could be up to 75 percent of the yield on the cocoa farm if left unattended to for a period of over three years(Anon, 1951 in Padi and Owusu, 2006). Capsids, also known as marids are recently cited to have the potential of destroying about 100,000 tons of Ghana's cocoa(Owusu-Manu, 1971; Padi and Owusu, 2006). Owusu Manu in 1995 was cited to have stated that "a mean of six capsids per ten trees actually represent a high and damaging population levels(Owusu-Manu, 1995; Padi and Owusu, 2006). Black pod disease is also estimated at 4.9-19 percent in all farms of the country (de Bach, 1964; Dakwa, 1987;

Padi and Owusu, 2006). In 1987, Darkwa reported an outbreak of a more severe disease caused by P. megakarya in the North Western cocoa belt of Ghana (Dakwa, 1987; Padi and Owusu, 2006). It is said that these virulent species were spreading steadily to the South West of Ghana's cocoa belt near the Cote' d' Ivoire border(Opoku et al, 1997; Padi and Owusu, 2006).

Recommendations made for control of these diseases and pest involves the use of copper based fungicicides, with or without metaxyl, at every four weeks interval; about six to seven times a year (Hislop and Park, 1960; Padi and Owusu,2006). These chemicals have a high propensity to end up in the soil and since all heavy metals are largely immobile, they tend to accumulate and persist in soils for a long time (Aikpokpodion et al, 2010).The most commonly reported heavy metals with regards to potential hazards and occurrence are Cd, Pb, Zn, Cr and Cu (Aikpokpodion et al, 2010; Alloway, 1995). Evidence provided by Aikpokpodion et al (2010) suggested contamination of cocoa soils with Pb, Zn, Cd, and Cu.

2.5.POSSIBLE ROUTES OF CONTAMINATION OF COCOA AND COCOA PRODUCTS WITH HEAVY METALS

Contamination of cocoa and cocoa product with heavy metals could be from many sources. It is, however, believed that heavy metals as Pb contaminate cocoa beans mainly through adsorption on the shells of the beans of emission from leaded fuel combustion during sun drying and fermentation of the beans (Rankin et al, 2005).Some evidence alsosuggests that contamination could arise from application of pesticides on the crop in a bid to control pest (Aikpokpodion et al, 2010, Hislop and Park 1960, Padi and Owusu, 2006); other evidence also point to the phytoextraction of the metals from contaminated soil (Aikpokpodion et al, 2010).

2.6. COPPER

2.6.1 IMPORTANCE OF RIGHT LEVELS OF COPPER TO HUMAN LIFE

Copper is believed to be one of the essential trace elements in humans and animals having the redox property of shifting between the cuprous (Cu^{+}) and the cupric (Cu^{2+}) forms. This property enables it to play an important role in reduction reactions giving it an added advantage of scavenging for free radicals in the body(Linder and Hazegh-Azam, 1996; Higdon et al, 2007). The element forms an essential component of many useful enzymes. One of such cuproenzymes, cytochrome *C*- oxidase is responsible for production of cellular energy; it catalyses the reduction of molecular oxygen to water and produces electrical potential for mitochondrion to produce Adenosine Triphosphate (ATP) (Uauy et al, 1998; Higdon et al, 2007). Also lysyl oxidase, another cupro-enzyme is useful for the cross-linking (maturation) of collagen and elastin used in the production of strong and flexible connective tissues helping them to maintain their form as seen in tissues in the heart, blood vessels, and in bone formation(Turnlund, 2006; Higdon et al, 2007). Two other copper based enzymes; ferroxidase I and ferroxidase II (ceruloplasmin) are able to oxidize ferrous iron (Fe^{2+}) to ferric iron (Fe^{3+}), the form suitable for transport by protein transferrins to the site for red blood cell formation(Harris, 1997; Uauy et al, 1998; Higdon et al, 2007). A lot of reactions that take place in the central nervous system are catalysed by cuproenzymes(Higdon et al, 2007).It also aids in the conversion of dopamine to the neurotransmitter neurophrine(Harris, 1997; Higdon et al, 2007).Cytochrome-c-oxidase which is responsible for the synthesis of phospholipids used in making myelin sheath, and the enzyme tyrosinase required for formation of the pigment melanin in giving colour to the hair, skin and eyes(Uauy et al, 1998; Higdon et al, 2007).

This element in the right amount is again useful in making superoxides dismutase (SOD), an antioxidant which catalysesthe conversion of superoxide radicals (ROS) to hydrogen peroxide which is eventually reduced to water(Johnson et al, 1992; Higdon et al, 2007). By binding with copper, ceruloplasmin prevents free copper ions from catalyzing oxidative damage (Higdon et al, 2007). Copper dependent transcriptions factors regulate specific genes; hence copper levels influence the synthesis of proteins by enhancing or inhibiting the transcription of specific genes of which an example is Cu/Zn-SOD (Higdon et al, 2007; Harris, 1997). In fact, adequate copper is required for normal iron metabolism and red blood cell formation; deficiency of iron is found to be common in copper deficient animals(Uauy et al, 1998; Higdon et al, 2007).

Severe copperdeficiency results in heart abnormalities and damage (cardiomyopathy) in some animal species, which differs from artheriosclerotic cardiovascular diseases in humans (FNB, 2001; Higdon et al, 2007). Copper is again believed to play important role in the development and maintenance of the immune system function (Higdon et al, 2007). Nuetropernia (abnormally low numbers of white blood cells) is believed to be a clinical sign for copper deficiency in humans and its effects are more pronounced in infants (Higdon et al, 2007). Infants with menkes disease (a genetic disorder that results in severe copper deficiency) suffer from frequent and severe infections(Percival, 1998; Higdon et al, 2007). This situation is believed to improve significantly after one month of copper supplementation(Heresi et al, 1985; Higdon et al, 2007).

2.6.2 EFFECTS OFHIGH LEVELS OF COPPER

Some scientists have proposed that high levels of copper increase the risk of artherosclerosis by promoting the oxidation of low density lipoprotein (LDL)(Fox, 2000; Higdon et al, 2007). Several studies have indicated that increase in serum copper levels leads to increase in risk of cardiovascular disease(Ford, 2000; Higdon et al, 2007).

A study in the U.S in 4500 men and women at age 30yrs and above over sixteen years period indicated that, 151 participants died from coronary heart disease (CHD). Considering other health risks with copper, the two highest quartiles had a significantly greater risk of dying from CHD (Higdon et al, 2007). Three other case control studies in Europe confirmed similar findings, where 60 patients with chronic heart failure or ischemic heart disease showed serum copper was a predictor of short term outcome (Higdon et al, 2007). Another studies on 4,035 middle aged men reported that high serum copper levels were significantly related to fifty percent (50%) increase in all causes of mortality but not associated with cardiovascular mortality (Higdon et al, 2007).

Symptoms of acute copper toxicity include abdominal pain, nausea, vomiting, and diarrhoea helping to prevent more copper ingestion and absorption (Higdon et al, 2007). This may lead to severe liver damage, kidney failure, coma and death. Long – term exposure on lower doses also leads to liver damage(Ford, 2000; Higdon et al, 2007). The US Food and Nutrition Board (FNB) set the tolerable upper level of intake (UL) of copper at 10mg/day from foods and supplement (FNB, 2001; Higdon et al, 2007).There is, however, evidence to show that the UL of copper 10mg/day may be too high since evidence suggests that men exposed to 7.8mg Cu/day accumulated the copper after 147days affecting their immune function and anti – oxidant status(US EPA, 1987; Heresi et al, 1985; Higdon et al, 2007). Linus Pauling Institute, therefore,recommends RDA (Recommended Dietary Allowance) for copper at 90ug/day for adults to prevent deficiency problems (Higdon et al, 2007). ATSDR reports that long – term exposure to copper dust can irritate the nose, mouth, and eyes and cause headaches, dizziness, nausea and diarrhea at "Minimum value of copper at 1,300ppb" (Turnlund et al, 2005).

2.6.3 METABOLISM AND PHARMACOKINETICS OF COPPER

Copper occurs in drinking water as the cupric ion (Cu^{2+}) complexed with organic ligands; it is however believed that high levels of vitamin C (ascorbic acid) in food adversely affects the absorption and metabolism of copper (ATSDR, 2004). There appears to be an antagonistic relationship between copper and zinc absorption and transport (USEPA, 1987; US EPA, 1997). In humans, copper is absorbed from the stomach and small intestine (Cousins, 1985); about 65 percent of the oral dose of Cu is absorbed from the gastro – intestinal tract (US EPA, 1987; Cousins, 1985; Weber et al, 1969). It rapidly appears in the plasma when administered orally (Strickland et al, 1972). The amount of copper stored in the liver does not affect copper absorption(US EPA, 1987; Bearn and Kunkel, 1955). Pirot in 1996 reported that copper absorption through human skin "in vitro" is not likely to contribute to total copper absorption. Ceruloplasmin binds to copper or zinc and synthesized on membrane – bound polyribosome of liver parenchyma cells.

2.7.CADMIUM; BENEFITS AND HEALTH RISK ON HUMANS.

Cadmium is regarded as a metal with no known nutritional or beneficial effect for human health (Goyer et al, 2004). The metal isdescribed as ubiquitous in nature and present in air, water, and soil (Bearn and Kunkel, 1955). Some level of its exposure is not preventable and is described as a human carcinogen in one way or the other (Goyer et al, 2004; NTP, 2002). The serious aspect is that most carcinogens [eg – cadmium] follow the metabolic pathways of similar essential metals (Goyer et al,2004), because they might have similar binding preference compared with nutritionally essential metals(Goyer et al, 2004; Clarkson, 1986). Mechanism of detoxification of heavy metals as cadmium however is linked to long–term strong and biliary and or urinary excretion.

The metal is known to accumulate in the human pancreas (Clarkson, 1986). Enumerating the factors responsible for its contamination leading to pancreatic cancer, Schwartz and Reis suggested age, smoking, residence in Louisiana, exposure to metal work and pesticide use (Schwartz and Reis, 2000). The last factor applies to cocoa production. The metal is cited to be responsible to cause transdifferentiation of pancreatic cells, increase synthesis of pancreatic DNA and increase in oncogene aeration leading to cancer, hence a plausible carcinogen (Schwartz and Reis, 2000). A problem with pancreatic cancer is that it is usually detected at its advanced and incurable stage (Schwartz and Reis, 2000), accounting for about 28,000 deaths in the U. S. A.in the 1990s (Schwartz and Reis, 2000). Less than five percent of all people diagnosed to have the cancer survive 5years after detection (Schwartz and Reis, 2000; Rosenberg, 1997; Flanders and Foulkes, 1996). Major sources of airborne cadmium are the smelters, burning of fossil fuels and waste materials including the use of phosphate fertilizers and sewage sludge(Yost, 1979; IARC, 1993; Cabrera et al, 1998 and Naqvi et al, 1993;Schwartz and Reis, 2000).

In the soil the principal sources include industrial emissions and fertilizer application which are selectively taken up by edible plants leading to concentrations many times higher than that of the surrounding (Schwartz and Reis, 2000; Naqvi et al, 1993). Similarly many water plants bio accumulates cadmium (Naqvi et al, 1993). In the human body cadmium concentrates in the kidneys, liver, blood forming organs and the lungs resulting most frequently in kidney damage or dysfunctions and metabolic anomalies caused by enzyme inhibitions(eg. excretion of low molecular weight proteins in urine) (Korzun and Heck, 1990). It is believed that the Itai – Itai sickness (bone damage) in Japan is as a result of regular consumption of highly contaminated rice (Korzun and Heck, 1990; Jarup, 2002).It is dangerous to consume regularly foodstuffs with low contamination levels of the metal; however, limit of toxicity of cadmium is not defined,PTMI (provisional tolerable monthly intake) of cadmium set by the Joint FAO/WHO, Expect Committee on Food Additives (JECFA) recently in 2010 established PTMI for cadmium at 25 μg/Kg body weight (WHO, 2010).

High levels of cadmium can lead to disturbances in calcium metabolism and formation of kidney stones, softening of the bones and Osteoporosis may also occur or painful bone fractures (Jarup, 2002). Inhalation exposure of cadmium oxide is also believed to cause acute pneumonitis with pulmonary Oedema which may be lethal; long term exposure also causes lung changes characterized by chronic obstructive airway disease; this can lead to lung cancer and other causes of cancer affirming International Agency for Research on Cancer (IARC) classifying cadmium and its compounds as carcinogenic to humans (Group 1) (IARC, 1993; WHO, 2010).

The metal is believed to be accumulative, with half-life of about 18years (Adelekan and Abegunde, 2011); and it is believed that it can accumulate in the human body for 50years, destroying many important organs and tissues (Forstner, 1995; Wang et al, 2011). Ingesting high levels cause severe irritation of the stomach leading to vomiting and diarrhoea. It is also believed that long term exposure leads to kidney diseases, lung damage and fragile bone (Wang et al, 2011).

The USEPA pegs its ULs at 5ppb;the FDA pegs its UL at 5ppb while the OSHA pegs its ULs at 5mg/m^3 of workplace air (40-hour work/week). Cadmium is believed to disturb calcium metabolism affecting bone tissue and perhaps leading to weakening of bones (Wei and Wei, 2007).

2.8.1 IMPORTANCE OF LEAD IN THE HUMAN BODY

The US EPA sets 15ppb in drinking water as the maximum limit for lead and 0.15mg/m^3 in air (Wang et al, 2011), the metal is classified as toxic having no known nutritional or beneficial effect (Bearn and Kunkel, 1955).

2.8.2 EFFECTS OF LEAD ON HEALTH

Leadis classified as a probable human carcinogen, and affects every organ negatively in the human body (Bearn and Kunkel, 1955; Goyer et al, 2004; Wang et al, 2011; Martin and Griswold, 2009). Long term exposure results in decreased performance in the functioning of the nervous system, weakness in fingers, wrist or ankles, increase in blood pressure and anaemia (Wang et al, 2011). High levels of lead severely damage the brain, kidneys and cause death (Wang et al, 2011). In pregnant women it may lead to miscarriage whiles damaging organs responsible for production of sperms in men (Wang et al, 2011). It is described as a ubiquitous and versatile metal but not essential (Martin and Griswold, 2009; Smirjakova et al, 2005), it damages all organs including the ones mentioned earlier together with the kidneys and blood leading to instant death(Wang et al,2011; Wei and Wei, 2007; Shilu, 1984).

At low levels, haeme synthesis and biochemical processes are affected, psychological and neurobehavioural functions are also impaired (Wei and Wei, 2007; Shilu Smith, 1984; WHO, 1995). It is also believed to cause premature birth or shortening of gravidity, decrease birth weight and retardation in mental development (WHO, 1995).Sometimes even small amount of lead can be toxic especially to children and can be severe (Goldstein, 1992).Chronic lead poisoning leads to neurological disorders as reduced cognitive abilities (low intelligence, poor perception, low learning abilities and poor reasoning); because it affects both the peripheral nervous system (PNS) and the central nervous system (CNS); causing wrist drop (weakening of the extensor muscles of the hand) (Nair, 2011; Sanders et al, 2009). Low levels of lead are associated with decreased neuro-cognitive functioning (Sanders et al, 2009; Tailor, 2005). In adults it can cause insomnia, impotence, chest pain, headache, excess fatigue or hyperactivity, irritability, coma and even death (Nair, 2011). It is also believed to cause nausea, abdominal pain, constipation, vomiting, diarrhoea, weight loss, blue lines along the gums and high blood pressure (Nair, 2011; Sanders, 2009). Children may experience slow growth, staggering, behaviour problems, headache convulsions, drowsiness and confusion. The metal is believed to cause these serious neurological disorders and other problems because it has the ability to pass through the blood-brain barrier mimicking calcium (Sanders et al, 2009). It damages the prefrontal cerebral cortex, hippocampus, and cerebellum leading to the many disorders enumerated including nerve damage and Alzheimer's disease, Parkinson's disease and schizophrenia (Sanders et al, 2009). It interferes with regulatory action of calcium on cell functions; disrupting many intracellular biological activities (Sanders et al, 2009).

2.9.1 IMPORTANCE OF IRON TO THE HUMAN BODY

Iron is classified as nutritionally essential heavy metal (Goyer et al, 2004; Goyer and Clarkson, 2001); forming an essential part of haemoglobin (the red colouring agent of the blood responsible for transporting oxygen throughout the body). It is actually needed in the production of the number of red blood cells required to keep the body in good health (Iron Supplements / health benefits April, 2012). The element is so useful that when red blood cells are being destroyed their iron content is reused in the bone marrow for the production of new red blood cells. It is needed for proper muscle and organ functioning (Iron Supplements / health benefits April, 2012). Children with iron deficiency show difficulty with language, poor motor coordination and balance, poor attention ratings, responsiveness and poor mood swings coupled with poor mental development(Iron Supplements / health benefits April 2012; Nokes et al, 1996). This element forms an integral part of many proteins and enzymes that maintain good health (Iron Supplements / health benefits accessed April 2012). It is needed in the body to form myoglobin (a protein in muscle cells) and is an important co-factor for some enzymes that drive the chemical reaction taking place in the body (Iron Supplements / health benefits accessed April 2012). When the body is fighting against bacterial infection, it sequesters iron in the transporter protein transferrins so that they are not used by the bacteria (Iron Supplements / health benefits accessed April 2012). Lack of iron causes severe tiredness, shortness of breath, decrease in physical performance and learning problems; increasing one's susceptibility to contract diseases (Iron Supplements / health benefits accessed April 2012; Nokes et al, 1996). When this situation persists it leads to anaemia (Iron Supplements / health benefits accessed April 2012).

2.9.2 HEALTH RISK OF HIGH LEVELS OF IRON.

As essential as iron is, it is believed that the metal could be carcinogenic (Goyer et al, 2004; Goyer and Clarkson, 2001). In combination with nitriloacetic acid (an iron chelating agent) it is described as a potential hepatocarcinogen while its inorganic compounds do not cause cancer (Goyer et al, 2004; Sunderman, 1978). It is believed that people with hemochromatosis (iron storage disease) develop hepatic cirrhosis and have a possible risk for hepatocarcinoma (Goyer et al 2004; Cia et al, 1998; NAS/IOM, 2003). Goyer in 2004 indicated that several epidemiological studies havereported a possible correlation between measures of iron status and cancer among people in the general population (Goyer et al,2004; Cia et al, 1978). As people often use dietary supplements and other consumer products as chocolates and other confectionaries, there is the fear that exposure to excess nutritionally essential metals are very eminent and increasingly becoming dangerous (Goyer et al, 2004; Bose et al, 1983; CDC, 1981; CDC, 1982; CDC, 1983; Geffner and Sandler, 1980; McKinney, 1999; Pontifex and Garg, 1985;Trotter 2nd ed, 1985; Yanez et al, 1994). When too much iron accumulates in the body it causes hemochromatosis which may lead to liver cirrhosis, arthritis, diabetes, cardiomyopathy, and problem with hormone production and control (Yanez et al, 1994). The element is also believed to be responsible for oxidative diseases such as Alzhemer's, where high levels of the metal contribute to neurone damage(Yanez et al, 1994).

Though alcohol is known to play significant role in development of cirrhosis the metal also contributes to it in a large extent (Kasper et al, 2005; Bergaonkar, 2003). The most common of the hemochromosis is cirrhosis and liver cancer (Kasper et al, 2005; Bergaonkar, 2003). It is also suggested that elevated levels of iron may increase risk of heart diseases by creating high levels of free radicals that damage the inner lining of arteries (endothelium)(Crowe, 2002). Endothelial dysfunction is central to the development and progression of coronary artery disease(Kasper et al, 2005; Bergaonkar, 2003). The metal is suspected once again to cause conjunctivitis, choroidditis and retinitis when it gets into contact with and or remain in these tissues, while excessive inhalation of dust containing the element could cause lung cancer (Crowe, 2002). A common form of iron overload is seen in hereditary homochromatosis (Kasper et al, 2005; Bergaonkar, 2003).

2.10.1 IMPORTANCE OF ZINC TO THE HUMAN BODY

Zinc is one of the essential minerals present in foods and is used as dietary supplement. It is involved in so many cellular metabolisms and also catalyses activities of over hundred enzymes (COPAL, 2004b; Sandstead, 1994). It plays an important role in immune function (IOM/FNB, 2001; Solomons, 1998), protein synthesis (Solomons, 1998), wound healing (Prasad, 1995),DNA synthesis and cell division (Sandstead, 1994; Solomons, 1998). It supports normal growth and development during pregnancy, child birth and adolescence (Heyneman, 1996; Simmer and Thompson, 1985; Fabris and Mocchegiani, 1995). It is required for sharp sense of taste and smell (Maret and Sandstead, 2006). The body however does not have specialized organs for storage of zinc (Prasad et al, 1997). The US FNB approves RDA of 2mg/day for 0-6month old babies, an average of 6.8mg/day for people below age 18 years and 11mg/day for adults (Sandstead, 1994).

2.10.2 EFFECTS OF ZINC OVERDOSE ON HUMAN HEALTH

High Zinc intake causes nausea, vomiting, loss of appetite, abdominal cramps, diarrhoea and headache (Sandstead, 1994). A report indicates severe nausea and vomiting upon ingestion of 4g of zinc gluconate equivalent to 570mg of elemental zinc in 30minutes (Rink and Gabriel, 2000). Intake of 150 – 450 mg of zinc/ day is believed to cause low copper status altered iron function, reduced immune function and high density of lipoproteins (Lewis and Kokan, 1993). It is also reported to cause reductions in copper-containing enzymes at moderately high zinc level of 60mg/day up to 10 weeks (Sandstead, 1994). For 6.3 years 80mg/day causes significant increases in hospitalization for genitourinary causes suggesting that chronically high levels of zinc affect the urinary physiology negatively (Hooper et al, 1980). Upper limits of zinc are pegged at 40mg/day for adults and 34mg/day for adolescents. Zinc supplements for that matter have the potential to interfere with several types of medications (Johnson et al, 2007; Lomaestro and Baillie, 1995; Pentilla, Hurme and Neuvonen, 1975; Brewer et al, 1993; Wester, 1980).

2.11.1 MANGANESE LEVELS EFFECTS AND USES

Manganese is one of the most abundant heavy metals and exists naturally in the environment but the levels may increase due to activities such as mining, burning of fuels and the use of pesticides and fertilizers on the farm. It is necessary for good health and is regarded as one of the essential elements. Manganese is known to help in bone mineralization, carbohydrate and protein metabolism (Welder, 1994), metabolic regulation and protection of cells from free radicals (Kim and Keeney, 1984). It is present in foods like whole cereals, dried fruits, nuts, and teas at a range of (20-23ppm). The metal was sometimes ago used in an organic compound: methylcyclopentadienylmanganesetricarbonyl (MMT) as an antiknocking agent in fuels (TOR, 2008). A survey conducted by Tema Oil Refinery (TOR) in Ghana indicated that manganese levels have increased along the major highwayscompared with results obtained from a baseline survey conducted earlier (Fitsanakis et al, 2009).

This points to the fact that, the levels in cocoa beans could be due to deposition from fuel combustion and/or phytoextraction by the plant from contaminated soils. The absorption of iron is believed to be dependent on manganese (Freidman et al, 1987). It is, therefore, necessary to maintain adequate levels of manganese than supplementing iron since the levels of manganese is always lower than that of iron because iron supplement causes constipation or gastric upset. It stabilizes blood sugar level and lowers total cholesterol levels (Leach and Harris, 1997).

The element is also useful in controlling/treating menopausal symptoms, menstrual problems, osteoporosis and postpartum depression when using nutrition to treat these problems. It is also useful for normal brain functioning, blood clotting, and DNA synthesis (Leach and Harris, 1997). It is once again believed to activate the enzyme responsible for urine formation (Muszynska et al, 2000). The US FNB sets the RDA levels for manganese at 1.9-2.2mg/day for males between age 11-18 years, 19 years and above males at 2.3mg/day, females 11-18years at 1.6mg/day, 19-50 years at 1.8 - 2.5mg/day and females above 50 years- 1.8mg/day.

2.11.2 EFFECTS OF HIGH LEVELS OF MANGANESE

Excess manganese and iron cause tumour development and can also lead to migraine-headache, Parkinson's disease, frequent menstrual cycle in females (Pal et al, 1999; Aschner and Aschner, 1991), dizziness, depression, mental illness, learning disabilities (Ljung and Vahter, 2007), hypothyroid, high risk of several cancers, edema, liver disease (Keen et al, 1999; Hendler and Rorvik, 2001), chronic nausea, colitis, muscle tremors, diabetes, higher risk of tendon and ligament tears (Pal et al, 1999; Aschner and aschner, 1991).

The US EPA recommends 0.05mg/L as maximum allowable limit in drinking water whiles US FNB sets UL for manganese at 11mg/day for people 19 years and above, 9mg/day for 14- 18 years and 4-8years old pegged at 6mg/day.

2.12REPORTED LEVELS OF HEAVY METALS IN COCOA BEANS FROM SOME PARTS OF GHANA

In 2007, the then chief executive officer of COCOBOB; Mr Isaac Osei, highlighted the need for the country to continue with production of quality produce on the world market. He lamented the possible contamination of the produce with heavy metals among many other problems militating against the bid of the country to continue with the production of quality beans (Osei, I., 2007).

Before this fears, many people had always held the believe that, application of fertilizer remains one of the principal sources of heavy metal contamination of cultivated lands and for that matter plants grown on them. In 2012, COCOBOD in collaboration with a team of researchers from the University of Ghana, Legon worked on the topic 'the Contribution of Fertilizers to heavy metal levels in soils and Cocoa from some Cocoa farms in the Western Region of Ghana'.

The common fertilizers studied were those approved and mostly supplied by COCOBOD for application by farmers including, Cocoa Asaasewura; Sidalco Balanced; Sidalco Potassium Rich; Cocofeed; and Nitrabor (Nartey V. K. et al, 2012).

The report indicated that, continuous application of these fertilizers lead to increase in the heavy metal concentrations above the levels they exist in the natural soils (Nartey V. K. et al, 2012). The levels of the metals;Cu, Pb, Mn, Zn, Ni, Cd, Cr, and Fe were found to be higher in the fertilizer treated soils than in the natural soils (Nartey V. K. et al, 2012). The good news however was that, the impact of this on the levels in the cocoa beans were minimal. This suggests that the beans were safe (Nartey V. K. et al, 2012).

The results (as published in appendix C) indicated that, the approved fertilizers: Nitrabor had low levels of Mn, Cu, Cr and Zn whiles the levels of Fe were found to be high in this fertilizer. Sidalco balance and sidalco potassium rich contains the highest level of Mn, Cu and Zn. Cocofeed and cocoa asaase-wura was found to contain high levels of Fe, Ni, Pb and Cd. However, the levels detected in the fertilizers were within the proposed levels set by the Canadian standards for fertilizers. They suggested

500ppm, 20ppm, 180ppm and 1850ppm for Pb, Cd, Ni and Zn respectively (ATSDR, 1993; FAO/WHO, 2001 in Nartey V. K. et al 2012).

In the soils, Sefwi Asawinso/Nkatieso was reported to have recorded the highest levels of Fe, Zn, Cu, Mn, and Ni. The least levels of these heavy metals were reported by Nartey and his team in soil samples from Wassa Akropong. This observation was attributed to low pH levels. Metals are known to remain adsorbed to soils at high pH (> 7) (Nartey V. K. et al 2012). The report also showed that where the pH of the soil was low (acidic soil), the levels of the heavy metals in the soil was low because continuous application of fertilizer to soils tend to lower the pH since fertilizer contains nitrates and phosphates. This make the heavy metals become soluble and may leach beyond reach of plants or get absorbed by the plants grown on them based on the levels of rainfall (Nartey V. K. et al 2012). This trend was evident in all the fertilizer amended soils and the natural soils of the three areas sampled.

In the cocoa beans, though the levels detected were in good agreement with levels set in fruits and cocoa mass set by Codex as described in literature, a serious observation was made. The levels of the metals detected in the samples on fertilizer amended soils were higher than those obtained on natural soils. Considering Pb, a value of 0.05µg/g was obtained in cocoa nibs from natural soil in Sefwi Asawinso/Nkateiso while 0.07µg/g was obtained from cocoa samples from the same community on fertilizer amended soil. Similarly, Cd value of 0.58µg/g was detected in samples from natural soil from Wassa Akropong whiles 0.71µg/g was detected in fertilizer amended soil from Wassa Akropong (Nartey V. K. et al, 2012). This was attributed to high mobility and solubility of heavy metals at low pH. This phenomenon has the potential of increasing the concentration of these metals in the cocoa beans from fertilizer amended soils.

For copper a high value of 17.80µg/gwas recorded in cocoa samples from Sefwi Asawinso/Nkatieso with the lowest value of 15.73µg/g in Wassa Akropng on fertilizer amended soil. 47.17µg/g zinc was detected in cocoa beans on fertilizer amended soil from Wassa Akropong with the least of 38.96µg/g detected in cocoa samples on fertilizer amended soil from Sefwi Asawinso/Nkatieso. Also 13.05µg/g Mn was recorded in cocoa beans from fertilizer amended soil from Sefwi Asawinso to a high of 33.60µg/g in samples from Wassa Akropong. Furthermore, a least iron level of 28.20µg/g was recorded in beans from Bogoso while the highest of 38.73µg/g was obtained in samples from Wassa Akropong.

In all the analyses, it was obvious that, the levels of the heavy metals in the fertilizer amended soils were higher than in the natural soils except for copper where 19.15µg/g was recorded in natural soils of Sefwi Asawinso as against 17.80µg/g in fertilizer amended soils (Nartey V. K., et al, 2012).

The results show that where pH is high the levels of all the heavy metals except copper were low and vice versa. This is as demonstrated by the pH values obtained for the soil samples in the table 2.1 at Appendix C.

CHAPTER THREE

METHODOLGY

3.1. SAMPLING

Dried cocoa beans were taken from cocoa farmers in five different communities in each of the cocoa growing areas of the two Regions (Central and Eastern) of Ghana. In each of the communities five samples were taken from five different farmers. The communities were selected in such a way as to cover the geographical area of each of the Regions with regards to cocoa production. Some of the cocoa beans were obtained in the form of their fruits (pods); six samples from Assamankese and two from Assin Praso in the West Akim and Assin North District respectively. The beans from these fruits were subjected to fermentation and sun drying until they were fully dried like the others.

The Central Region was divided into five parts the northern, eastern, western, central and the southern where cocoa production is possible because they were at reasonable distance from the sea. The names of the communities were written on sheets of paper in a container and thoroughly mixed. For the Eastern Region Assamankese was pre-selected to represent the southern part of the region due to the special test the samples from the COCOBOD farms were going to be subjected to. The remaining parts of the Eastern Region was subjected the same approach as described for the Central Region.

In the Central Region,the communitiesselected were Agona Swedru in the Agona District, Brakwa in the Assikuma Odobeng Brakwa District, Assin Praso in the Assin North District, Twifo Praso in the Twifo Hemeng Lower Denkyira District and Duaso-Ntoom in the Upper Denkyira West District of the Central Region whiles in the Eastern Region, Assamankese in the West Akim District, Akroso in the Birim south District, Nkawkaw in the Kwahu West District, Kwahu Praso in the Kwahu South District and Adukrom in the Akuapem North District were chosen. The samples obtained from these communites were coded as follows

Table 3.1: The sampling Locations

Region	District	Town Sample Code	Number of Samples
Eastern	West Akim	Assamankese E11Kojo Aggrey, E12 Joseph Opoku, E13Gladys Osain, E14 Emmanuel Oppong, E15Yaw Odaie and E16 Doo Abraham	6
	Birim South	Akroso (E21-25)	5
	Kwahu West	Nkawkaw (E31-E35)	5
	Kwahu South	Kwahu Praso (E41-E45)	5
	Akuapem North	Adukrom (E51-E54)	4
Central	Upper Denkyira	Duaso-Ntoom (C11-C15)	5
	Assin North	Assin Praso (C21-C23)	5
	Twifo Hemang Lower Denkyira	Twifo Praso (C31-C35)	5
	Assikuma Odobeng Brakwa	Brakwa (C41-C45	5
	Agona	Agona Swedru (C51-C55)	5
Total	**10**	**10**	**50**

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The pictures below show some of the farmers and the sites where samples were taken for analyses.

Figure 3.1 Farmers at Duaso-Ntoom in the Central Region of Ghana from whom a sample was obtained (C12)

Figure 3.2 A farmer at Kwahu Praso in the Eastern Region of Ghana from whom samples were obtained (E21).

Again samples were taken from five farmers from each of these communities in the Region except Asanmankese COCOCBOD farms and Adukrom where six and four samples were taken respectively to compensate for the twenty five samples required from the Region. In all fifty (50) samples were taken from the two Regions for preparation and analyses.

Figure 3.5 A Cocoa farm at Assin Praso in the Central Region of Ghana from which cocoa pods were obtained for fermentation and sun drying (C22).

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Figure 3.8 A site in one of the farms at Asamankesse COCOBOD farms in the Eastern Region of Ghana from which samples were taken for fermentation and sun drying.

3.1.1 Study Area

Ghana shares political boundary with Burkina Faso to the North, Togo to the East, La Cote d'Ivoire to the West and Gulf of Guinea to the South. The climate of the country is tropical with two main vegetation; the rain forest and the savannah grassland. The forest is known to support rapid tree plant growth characterised with high temperature and heavy rainfall almost throughout the year. It is divided into rain forest and semi-deciduous forest. Cocoa thrives well in these forest regions of Ghana which covers the South Western and the middle belt of the country comprising of six (6) out of the ten (10) political regions of the country. This work concentrates on two major cocoa producing regions of Ghana (the Eastern and Central Regions).

Eastern Region represents the " the land of birth" for cocoa in Ghana and shares direct political boundary with the Central Region of Ghana which is also considered as one of the most significant cocoa producing Regions of Ghana. The map for selected sites for sampling is shown in Figure 3.10

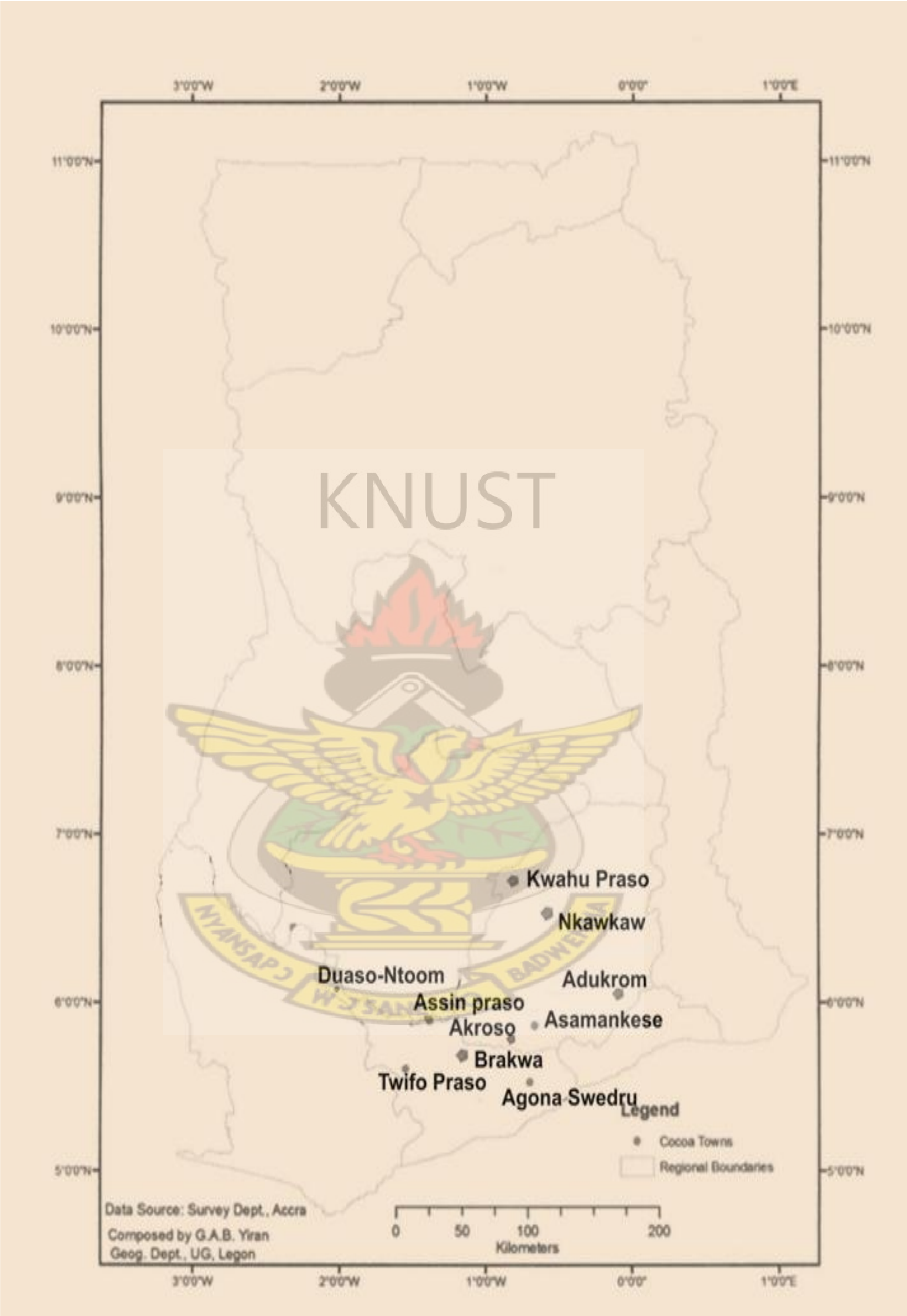

Figure 3.10 Map of Ghana showing the communities from which samples were taken in the Central and Eastern Regions of Ghana.

3.1.2 REAGENTS

- Hydrochloric acid
- Trixonitrate (v) acid (both obtained from Merck Germany)
- Distilled water.
- Petroleum ether *
- Boric acid
- Mixed indicator
- Selenium catalyst
- Anti bumping agent
- Anti foaming agent
- Sodium hydroxide.*

*All chemicals were analytical grade

3.1.3 APPARATUS

- Gallen Kemp Drying Oven
- Buck Scientific Atomic Absorption Spectrometer (model VGP 210);
- Furnace

3.1.4 DRYING OF SAMPLES

Except for the samples obtained from Asamankese COCOBOD farms and two other samples obtained from Assin Praso; all samples obtained from farmers were already dried cocoa beans ready to be sold to purchasing clerks. These eight samples; two from Assin Praso and six from Asamankese COCOBOD farms were obtained in pods. They were opened, and the fresh beans were kept on plantain leaves and fermented for seven days and was sun dried for another seven daysuntil they were dried as the earlier samples. However all the samples were dried again in the Gallen Kemp Drying

Oven at a temperature of sixty degrees (60^oc) for twenty four (24) hours prior to milling (at the Pharmacy Department laboratory at KNUST) to fine powder ready for digestion and subsequent analyses.

3.2. ACID DIGESTION OF SAMPLES

Cocoa samples were collected between 28th November and 5th December 2011; they were dried and milled on the 14th and 15th December 2011 respectively. One gram (1g) of each sample was digested in 30ml aqua-regia (of HCl:HNO_3 in the ratio 3:1) (Rankin et al, 2005) and solution evaporated to about 5ml by heating gradually to and maintained at a temperature of 200^0C for forty-five minutes on a hot plate. The resulting solution is then cooled and made up to the 50ml mark with distilled water and filtered on an acid washed filter paper to avoid clogging during determination in the Buck Scientific Atomic Absorption Spectrophotometer.

Standard solutions the of heavy metals under study were prepared from multi-element standard stock solution (obtained from Inorganic Ventures Inc., USA) in 10% nitric acid and 2% HCl. Single- element standards of most of the elements having very low concentrations were also prepared for calibration. The working standard solutions were all prepared by serial dilution of the stock solution with de-ionized water in 100ml volumetric flask. Each digestion and determination was done in triplicate. Care was also taken to minimize contamination of samples during handling and preparation. All reagents were of analytical grade. Sample containers and apparatus were washed and rinsed thoroughly prior to use. Reagent blanks were prepared and analyzed alongside samples. Concentrations reported in this work are thus actual concentrations of the samples relative to reagent blanks.

3.2.1 BLANKS AND STANDARD REFERENCE MATERIAL

Thirty millilitres (30ml) of the aqua-regia specified above was subjected to the same digestion procedure as done for the samples. Due to the high fat content of cocoa, two certified reference materials with specifications IAEA-V-10 SRM certified Hay powder and NBS 1571 SRM certified orchard leaves were digested under the same conditions and used to assess the efficacy of the method and the reliability of the results obtained.

3.3. INSTRUMENTATION, CONDITIONS AND DETERMINATION

Heavy metal concentrations of the 50 digested samples together with three blanks and the two certified reference materials were determined using the Buck Scientific Atomic Absorption Spectrophotometer (VGP 210); which operates on oxy-acetylene as the carrier gas operating on a pressure of 10psi and fuel pressure of 5psi. Stock standard solutions of Pb, Zn and Cu of concentration 1000mg/L were prepared using their salts (nitrates). For Mn, Cd and Fe their stock standards were prepared using their chlorides. The metals Fe, Cu, Cd, Pb, Mn and Zn were analyzed sequentially at wavelengths of 248.3, 324.8, 228.9, 283.3, 279.5 and 213.9nm respectively after optimization of the instrument with respect to the various metals. Excitation was achieved by the use of Hollow Cathode Lamp (HCL).

3.4. PROXIMATE ANALYSES

This was intended to determine the total protein, fat, carbohydrate, ash and moisture content as a percentage composition of the cocoa beans using the AOAC (1995) approach. The exercise was carried out using the six samples obtained from the COCOBOD farms at Asamankese where the age of the plants from which the samples were taken are known. This provided the basis for comparing the ages of the plants to the levels of nutrients and the levels of metals in them.

3.4.1 DETERMINATION OF ASH CONTENT

A crucible was fire polished, cooled and then weighed. About 2g of sample was weighed with the crucible and burnt in a muffle furnace at 600^0C for two hours to ensure complete ashing. This was removed, cooled in a desicator and reweighed. It was repeated to obtain a constant weight. Percentage ash content was calculated as follows.

%ash content = $\frac{\mathbf{x-y}}{\mathbf{w}} \times 100\%$, where

X= weight of crucible + ash

Y = weight of crucible

W= weight of sample before ashing

3.4.2 DETERMINATION OF MOISTURE CONTENT

Empty crucible was dried in an oven, cooled and weighed. About 2g of the sample was put in this crucible and heated in the oven at 105^0C for 5 hours. The sample was cooled and weighed. The processwas repeated until a constant weight was obtained. The percentage moisture content was calculated as loss in weight of the original sample.

% moisture =$\frac{(B-c)-(D-c)}{A} \times 100\%$

Where

A = weight of sample (g)

B = weight of crucible + sample before oven drying (g)

C = weight of crucible (g)

D = weight of crucible + dry sample after oven drying (g)

3.4.3 TOTAL CRUDE PROTEIN DETERMINATION

Using the Kjedahl method, about 2g of the sample was taken and heated in 25ml concentrated H_2SO_4 in the presence of a selenium catalyst and an anti bumping agent. The mixture was heated until all the carbon and hydrogen were oxidized (indicated by clear solution). The protein nitrogen at this stage was reduced and transformed into ammonium sulphate. The sample solution was transferred into 100ml volumetric flask and topped up to the mark. Twenty five millilitres (25ml) of 2% boric acid was put in a 250ml conical flask and two drops of mixed indicator added. The conical flask and its content were placed under a condenser in such a way that the tip of the condenser is completely immersed in the solution. Ten millilitres(10ml) of the digested sample solution was poured with the aid of a funnel in the steam jacket. Eighteen millilitres (18ml) of 40% NaOH was added to the sample solution in the steam jacket. The stopcock of the funnel was closed to drive liberated ammonia into the collection flask. Steam was forced through the decomposition chamber by shutting the stopcock on the steam trap outlet. The boric acid changed to bluish-green on contact with ammonia. This continued for about 5 minutes. The flask was removed and the content was titrated against 0.1M HCl to the end point (colourless) in duplicate. A blank was prepared using the same amount of all reagents to correct for traces of nitrogen in the reagents. Percentage total nitrogen in the sample was calculated as follows:

$$\% \text{ N} = \frac{100 \times (va - vb) \times Ma \times 0.01401 \times 100}{w \times 100}$$

Where

Va = volume in ml of standard acid used in titration

Vb = volume in ml of standard acid used in blank titration

Ma = Molarity of acid (HCl)

W = wt in gram of sample

% protein = F × % total nitrogen

F = 6.25

3.4.4 CRUDE FIBRE DETERMINATION

About 2g of the sample was defatted using soxhlet extraction technique of AOAC (1984). The defatted sample was put in conical flask after washing and drying. About 0.5g of asbestos was added to the sample in a 750ml Erlenmeyer flask. About 200ml of boiling 1.25% (H_2SO_4) was added to the sample and heated on a hot plate to return the solution immediately to boiling. Care was taken to ensure that the sample did not stick to the walls of the flask. The flask was removed after 30 minutes and the content was immediately filtered on linen cloth and washed with distilled water until washings were no longer acidic (using acid detector). The sample was returned to boiling as above but this time using 1.25% NaOH. The residue after treatment with NaOH was washed with approximately 15ml alcohol and transferred into a dried crucible. It was then put in an oven at 105^0C for one hour, cooled, weighed, and ashed for 30minutes at 600^0C. The sample was then cooled in a desiccator and reweighed. The loss in weight represents the content of fibre, calculated as

$$\% \text{ CRUDE FIBRE} = \frac{loss\ of\ weight\ from\ incineration}{weight\ of sample\ \ before\ \ defatting} \times 100\%$$

3.4.5 CRUDE FAT DETERMINATION

A round bottom flask (250ml) was cleaned and dried in an oven at 105 ^{o}C, cooled and weighed. About 2g of sample was taken and wrapped in a thimble. The thimble with its contentwas put in continuous extraction column with condenser connection. About 200ml of extracting solvent (petroleum ether of boiling point 60-80^{0}C) was put into the flask fitted on the extracting unit. The greater the presence of fresh solvent around the sample, the higher the efficacy of the extraction process. Thevapour of the solventwas condensed as droplets, where it came into contact with the thimble, interacts with sample and get vaporised again. The thimble was removed and solvent salvaged by distillation. The flask and its content were left overnight in an oven at a low temperature (about 30^{o}C) to completely evaporate the solvent leaving the oil. It was weighed to obtain the percentage crude fat calculated as

$$\% \text{ CRUDE FAT} = \frac{\textbf{weightoffat(g)}}{\textbf{weightofsample(g)}} \times 100\%$$

3.4.6 DETERMINATION OF TOTAL CARBOHYDRATE

The total percentage carbohydrate content was determined using the difference method as reported by the AOAC method. The total protein, crude fat, moisture and ash content of the sample were added and subtracted from 100%.The value obtained is the percentage carbohydrate content.

CHAPTER FOUR

RESULTS AND DISCUSSIONS

The results of levels of heavy metals obtained from Eastern and Central Regions of Ghana are presented and discussed in this chapter. Comparison is made with upper limits set by Codex and other recognizable international bodies. The results obtained from the analyses of the SRMs and the samples were as given in Table 4.1-4.3

4.1.0 Quality Assurance and Reliability of Results

The reliability and accuracy of measurement were checked with the determination of the heavy metal levels in the two reference materials: NBS 1571 SRM certified orchard leaves and IAEA- V-10 SRM certified Hay powder. The measured values together with certified or reported values for each reference material were as shown in the tables (4.1 - 4.3).The results showed good agreement with certified values reported after relating them with blanks. Results are as shown tables (4.1-4.3)

Table 4.1:Levels of heavy metals in IAEA –V-10 SRM (Hay Powder) (µg/g)

Metal	Levels observed	Recovery (%)	Reported levels
Cd	0.04 (0.032 – 0.068)	133.33	0.03 (0.02 – 0.053)
Cu	9.90 (9.20 – 10.3)	105.32	9.4 (8.8 – 9.7)
Fe	185.5(175.1 – 189)	99.73	186 (177 – 190)
Mn	48.2. (43.30– 50.40)	102.55	47 (44 -51)
Pb	1.55 (1.42 – 1.51)	96.88	1.6 (0.8 – 1.9)
Zn	23.80 (22.60 – 25.10)	99.17	24 (23 – 25)

Table 4.2: Levels of heavy metals in NBS SRM 1571(orchard leaves)(µg/g)

Metal	Levels observed	Recovery (%)	Reported levels
Cd	0.13±0.03	118.18	0.1 1 ± 0.02
Cu	10.89±0.29	90.75	12.00 ± 1.00
Fe	281.11±9.2	97.00	300.00 ± 20.00
Mn	85.62±2.11	94.09	91.00 ± 4.00
Pb	36.11±5.99	103.17	35.00 ± 3.00
Zn	24.98±2.30	99.92	25.00 ± 3.00

Table 4.3: Average levels of heavy metals (µg/g) in cocoa beans from selected communities in some Districts of Eastern and Central Regions of Ghana.

communities	code	Cd	Pb	Cu	Fe	Mn	Zn
Asamankese	E1	0.0467	0.0416	10.7416	25.8667	7.1167	36.9417
Akroso	E2	0.0490	0.0314	11.7750	39.8200	11.4500	33.1600
Nkawkaw	E3	0.0490	0.0701	13.6400	35.0700	9.8000	37.7400
K Praso	E4	0.0326	0.0553	14.0000	19.7800	18.2400	39.9900
Adukrom	E5	0.0463	0.0403	19.1000	27.3125	8.9250	32.9375
Duaso-Ntoom	C1	0.0350	0.0403	14.7400	19.1100	13.0300	30.0000
As. Praso	C2	0.0740	0.0543	20.1100	14.3500	9.3600	29.6200
T. Praso	C3	0.0320	0.0371	16.2700	22.8900	9.3600	32.7900
Brakwa	C4	0.0670	0.0210	18.6900	25.0700	8.7700	34.2100
Ag. Swedru	C5	0.0300	0.0448	24.6200	30.7000	8.6700	37.3900

Table 4.4:Levels of heavy metals (µg/g) in cocoa beans obtained from selected communities in some Districts of Eastern Region of Ghana

SAMPLES FROM ASAMANKESSE COCOBOD FARMS							
CODE		Cd	Cu	Fe	Mn	Pb	Zn
E11	Kojo Aggrey	0.065±0.000	5.250±0.000	21.400±0.000	4.450±0.050	0.0235±0.001	24.050±0.115
E12	Joseph Opoku	0.040±0.015	8.000±0.150	13.700±0.087	5.350±0.066	0.007±0.001	39.200±0.029
E13	Gladys Osain	0.055±0.003	5.350±0.000	38.300±0.000	6.550±0.132	0.037±0.001	49.600±0.260
E14	Emmanuel Oppong	0.085±0.010	22.700±0.150	14.350±0.150	8.950±0.150	0.0165±0.001	38.800±0.260
E15	Yaw Odaie	0.020±0.015	7.900±0.176	48.700±0.132	8.200±0.100	0.091±0.001	32.800±0.173
E16	Doo Abraham	0.015±0.015	15.250±0.000	18.750±0.050	9.200±0.087	0.075±0.001	37.200±0.144
SAMPLES FROM AKROSO							
CODE		Cd	Cu	Fe	Mn	Pb	Zn
E21		0.020±0.015	6.450±0.000	0.500±0.050	11.300±0.100	0.010±0.001	26.900±0.260
E22		0.090±0.000	11.150±0.000	3.650±0.115	12.250±0.000	0.043±0.008	32.600±0.260
E23		0.065±0.015	16.800±0.150	10.150±0.104	13.300±0.000	0.064±0.001	33.350±0.029
E24		0.030±0.015	11.100±0.000	24.200±0.104	11.300±0.100	0.009±0.001	35.800±0.289
E25		0.040±0.015	12.700±0.150	160.600±0.087	9.100±0.132	0.032±0.001	37.150±0.260
SAMPLES FROM NKAWKAW							
CODE		Cd	Cu	Fe	Mn	Pb	Zn
E31		0.010±0.006	18.200±0.000	22.800±0.087	16.800±0.132	0.080±0.001	39.000±0.173
E32		0.085±0.005	7.500±0.150	57.300±0.173	6.800±0.076	0.078±0.001	37.450±0.289
E33		0.040±0.000	18.300±0.000	4.850±0.173	9.500±0.087	0.081±0.001	39.500±0.087
E34		0.025±0.006	16.850±0.150	38.950±0.173	8.850±0.087	0.055±0.001	36.550±0.087
E35		0.085±0.004	7.350±2.469	51.450±0.150	7.050±0.050	0.057±0.001	36.200±0.050
SAMPLES FROM KWAHU PRASO							
CODE		Cd	Cu	Fe	Mn	Pb	
E41		0.018±0.009	20.000±0.150	27.100±0.087	6.800± 0.150	0.022±0.001	38.800±0.150
E42		0.085±0.001	9.200±0.000	55.200±0.150	7.450±0.132	0.095±0.001	37.500±0.132
E43		0.015±0.001	15.400±0.000	13.250±0.173	12.850±0.100	0.053±0.001	34.150±0.150
E44		0.021±0.001	21.100±0.000	18.650±0.150	11.750±0.100	0.089±0.001	38.750±0.100
E45		0.025±0.001	11.400±0.150	57.300±0.000	52.350±0.100	0.019±0.001	50.750±0.100
SAMPLES FROM ADUKROM							
CODE		Cd	Cu	Fe	Mn	Pb	Zn
E51		0.035±0.000	21.950±0.000	21.650±0.150	14.500±0.100	0.039±0.001	33.850± 0.100
E52		0.020±0.001	19.100±0.150	41.900±0.173	7.100±0.132	0.036±0.001	36.650±0.132
E53		0.060±0.002	17.800±0.000	39.850±0.087	6.650±0.132	0.039±0.001	35.550±0.132
E54		0.070± 0.003	12.250±0.912	5.850 ± 0.076	7.450±0.132	0.048±0.001	25.700±0.132

Table 4.5: Levels of heavy metals (µg/g) in cocoa beans obtained from selected communities in some Districts of Central Regions of Ghana

SAMPLES FROM DUASO-NTOOM						
CODE	Cd	Cu	Fe	Mn	Pb	Zn
C11	0.030±0.003	12.650±0.340	19.750±0.391	8.550± 0.200	0.050± 0.000	28.200±0.132
C12	0.050±0.002	15.800±0.132	16.000±0.444	12.150±0.265	0.003±0.000	30.200±0.250
C13	0.040±0.002	18.350±0.050	10.650±0.397	18.300±0.265	0.070±0.000	34.000±0.132
C14	0.020±0.002	15.400±0.087	19.450±0.100	15.150±0.346	0.047±0.000	31.550±0.050
C15	0.035±0.005	11.500±0.050	29.700±0.100	11.000±0.229	0.033±0.000	26.050±0.202
SAMPLES FROM ASSIN PRASO						
CODE	Cd	Cu	Fe	Mn	Pb	Zn
C21	0.075±0.002	14.250±0.050	17.450±0.265	12.750±0.180	0.050±0.000	27.650±0.200
C22	0.090±0.001	15.150±0.100	3.300±0.087	11.150±0.173	0.050±0.000	27.550±0.304
C23	0.070±0.0023	23.000±0.050	23.550±0.100	11.150±0.278	0.095±0.000	32.000±0.229
C24	0.065±0.002	18.050±1.198	7.950± 0.391	13.600±0.000	0.022±0.000	32.200±0.265
C25	0.070±0.001	30.100±0.100	19.500±0.436	11.150±0.200	0.055± 0.000	28.700±0.200
SAMPLES FROM TWIFO PRASO						
CODE	Cd	Cu	Fe	Mn	Pb	Zn
C31	0.005±0.005	15.250±0.050	18.550± 0.05	13.950±0.126	0.068±0.000	33.900± 0.05
C32	0.040±0.010	21.750±0.050	13.850±0.265	7.700±0.229	0.042±0.000	34.300±0.000
C33	0.030±0.013	15.650±0.350	3.000± 0.100	11.000±0.300	0.013±0.000	33.200±0.236
C34	0.020±0.015	14.850±0.100	41.550±0.050	7.200±0.100	0.002±0.000	32.650±0.493
C35	0.065±0.022	13.850±0.087	37.500±0.132	6.950 ± 0.260	0.061±0.000	29.900±0.000
SAMPLES FROM BRAKWA						
CODE	Cd	Cu	Fe	Mn	Pb	Zn
C41	0.095± 0.005	18.300±0.029	19.350±0.100	8.600 ± 0.050	0.028±0.000	33.150±0.260
C42	0.090± 0.002	21.850±0.050	23.850±0.208	9.300 ±0.200	0.026±0.000	35.000±0.260
C43	0.090± 0.005	21.900±0.000	38.300±0.050	8.950 ± 0.229	0.005±0.000	38.150±0.312
C44	0.035±0.023	15.250±0.050	17.750±0.150	7.500 ± 0.350	0.045±0.000	30.700±0.087
C45	0.025±0.008	16.150±0.029	26.100±0.397	9.500 ± 0.433	0.002±0.000	34.050±0.409
SAMPLES FROM AGONA SWEDRU						
CODE	Cd	Cd	Fe	Mn	Pb	Zn
C51	0.045± 0.005	41.950±0.100	43.700±8.834	5.400 ± 0.173	0.081±0.000	57.900±0.087
C52	0.025± 0.009	21.850±0.050	23.050±0.346	10.500±0.304	0.008±0.000	32.150±0.132
C53	0.005± 0.009	19.050±0.087	22.000±0.100	13.550±0.000	0.093±0.000	29.400±6.077
C54	0.025± 0.015	22.900±0.087	33.150±0.346	6.700 ± 0.250	0.038±0.000	36.150±0.361
C55	0.050± 0.010	17.350±0.029	31.600±0.100	7.200 ± 0.361	0.004±0.000	31.350±0.161

4.2.0 Levels of heavy metals in the cocoa beans

4.2.1 Cadmium Levels

A mean cadmium concentration of 0.046µg/g was obtained from all the samples. From the table of results (Table 4.4) the highest detected level of cadmium of 0.095 µg/g was recorded in Brakwa District in the Central Region; the least value of 0.010µg/g was detected in Nkawkaw in the Kwahu west District of the Eastern Region of Ghana. However on the town to town averages, Assin Praso recorded the highest level followed by Brakwa with Twifo Praso recording the lowest average value as shown on the graph. The value recorded in some of the communities were close to the maximum permissible levels of 0.100µg/g in fruits/cocoa butter and chocolate but were far below the limit set by Codex in cocoa mass and cocoa powder of 1.0 µg/g (Rankin et al, 2005; COPAL, 2004b).

Also the levels detected in this work are far lower than the levels detected in samples (cocoa nibs) from Sefwi Asawinso, Bogoso and Wassa Akropong where the highest value of 0.710µg/g was recorded in the work published by Nartey and his group in 2012 (Nartey et al 2012).

The levels obtained however, comparefavourably with the level set in plant parts at 0.l00µg/g fresh weight. The European -Union in 2006 conference on cocoa proposed for adoption, a level of 0.8µg/g. Though in this work the shells which many believe act as the surface for strong attachment of heavy metals were not taken away from the nibs, the levels detected were far below the maximum levels proposed by those international bodies. The beans were not deshelled because the Codex and Japanese method for processing the beans does not require deshelling of the beans.

It is believed that levels of cadmium in soils range from 0.010-7.000µg/g (Sandstead, 1994). This metal is contained in phosphate fertilizers in trace amounts and might be absorbed by plants grown with the use of these fertilizers (Clarkson, 1986; Flanders and Foulkes, 1996; IARC 1993; Yost,1979; Cabrera, 1993). The levels detected in the samples used suggest low levels of sulphate/nitrate fertilizer use by the farmers from whom the samples were taken. For cadmium, its concentration in tropical soils is very low due to cation exchange capacity (CEC) of most tropical soils (IOM/ FNB, 2001). Most metals are held in soil colloids and dead plants and animal remains and are prevented from entering into solution making it inaccessible to roots of plants (IOM FNB, 2001).

Another important source of the element is the use of pesticides. In cocoa production spraying is done throughout the year due to many diseases and/or pests. This may lead to accumulation by the plant leading to toxicity. It is believed, however, that it accumulates more in the leaves than seeds (Solomons, 1998; Prasad, 1995). In this work the levels detected in the whole beans are not very high and cannot pose any significant risk.

The graph for levels of cadmium in cocoa beans obtained from the Eastern Region and Central Regions is as Follows:

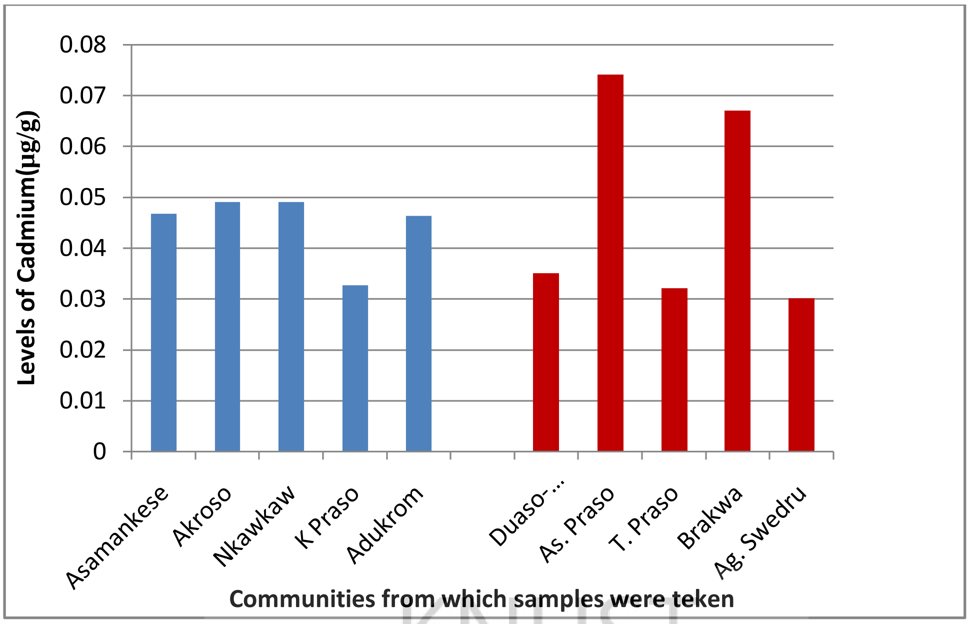

Figure 4.1: graph of average levels of cadmuim (µg/g) in cocoa beans from the Eastern and Central Regions of Ghana

From the graph it is clear that the averages from some of the communities in the Central Region far exceed the levels of the Eastern Region. This suggest more use of fertilizer (the most probable source of this metal in the soil) in the Central Region than the Eastern Region. Central Region is one of the prominent cocoa producing Regions of Ghana after Western and Ashanti Regions.

The average levels of the cadmim in the cocoa beans from the two regions campared with codex levels is as represented below.

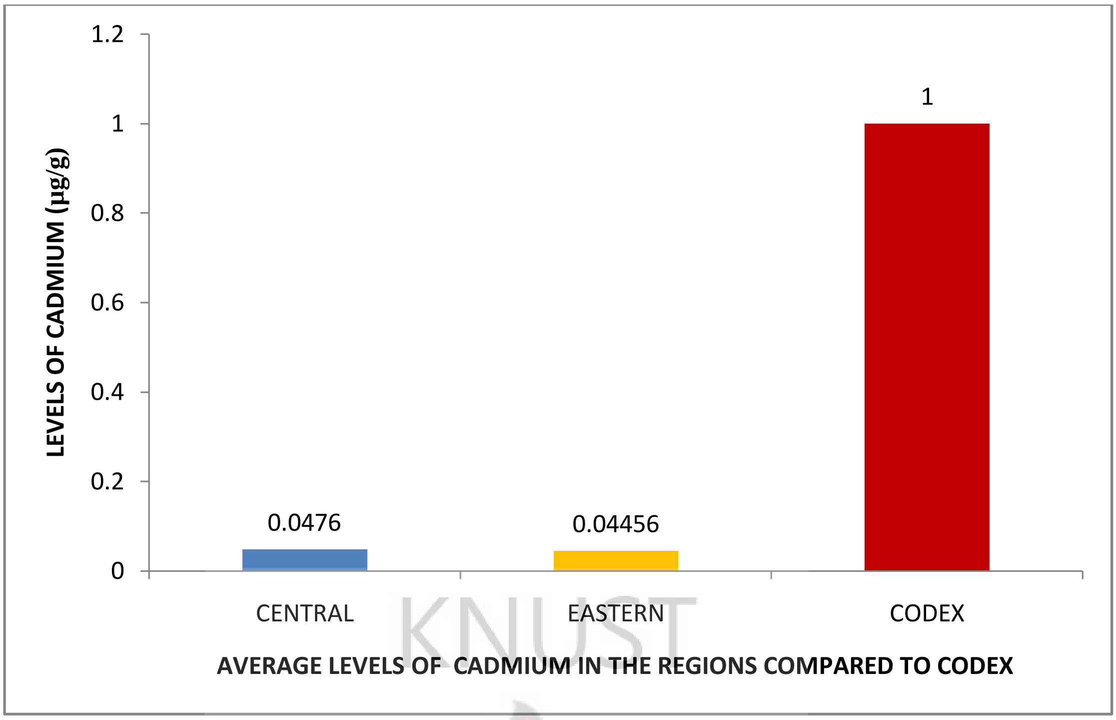

Figure 4.2: Average levls of cadmium from Eastern and Central Regions in relationship with Codex limit in Cocoa beans.

4.2.2 Lead Levels

A mean lead concentration of 0.0436µg/g was detected in all the samples with values ranging from the least of 0.002µg/g in cocoa beans from Brakwa in the Esikuma Odobeng Brakwa District of the Central Region to the highest of 0.0945µg/g from Kwahu Praso in the Eastern Region. Also on the town to town averages, Nkawkaw recorded the highest average, with Kwahu Praso and Assin Praso following closely, whiles Brakwa recorded the lowest average level of the metal. Besides these extremes, the levels of the metal were found to be quite uniform. The levels werebelow the Codex alimentaruis' maximum level of 0.100µg/g in fruits and vegetables and 1.000µg/g maximum permissible level for cocoa powder and cocoa mass. The levels reported here were however higher than Rankin et al's report of 0.005µg/g in cocoa nibs from Nigeria using ICP–MS (Rankin et al 2005). The levels were higher, but very close to the maximum level detected by Nartey and his team of researchers who reported 0.07µg/g in cocoa nibs from Wassa Akropong (Nartey et al, 2012).

Lead is one of the most toxic metals affecting almost all organs in the body negatively (Bean and Kunkel, 1955; Goyer et al, 2004; Smith, 1984). Cocoa products are considered to have relatively high levels of lead compared to other similar food products (Dahiya et al, 2005). Increase in lead concentrations in soils and subsequently in foods may be due to the many applications of the metal in paints, car batteries and in making antiknocking agents in fuels. This many believe have a high possibility of ending up in the soil from deposits of exhaust fumes and other activities. Though the use of leaded fuel has been stopped in Ghana, the metal is not biodegradable and may persist in the environment for a long time. Also due to the porous nature of the West African borders, smuggling of leaded fuel across the borders is very possible.

In the soil, the metal sticks to soil colloids and organic matter; and its mobility and fate depends on soil pH, type and content of the organic matter (Heyneman, 1996).

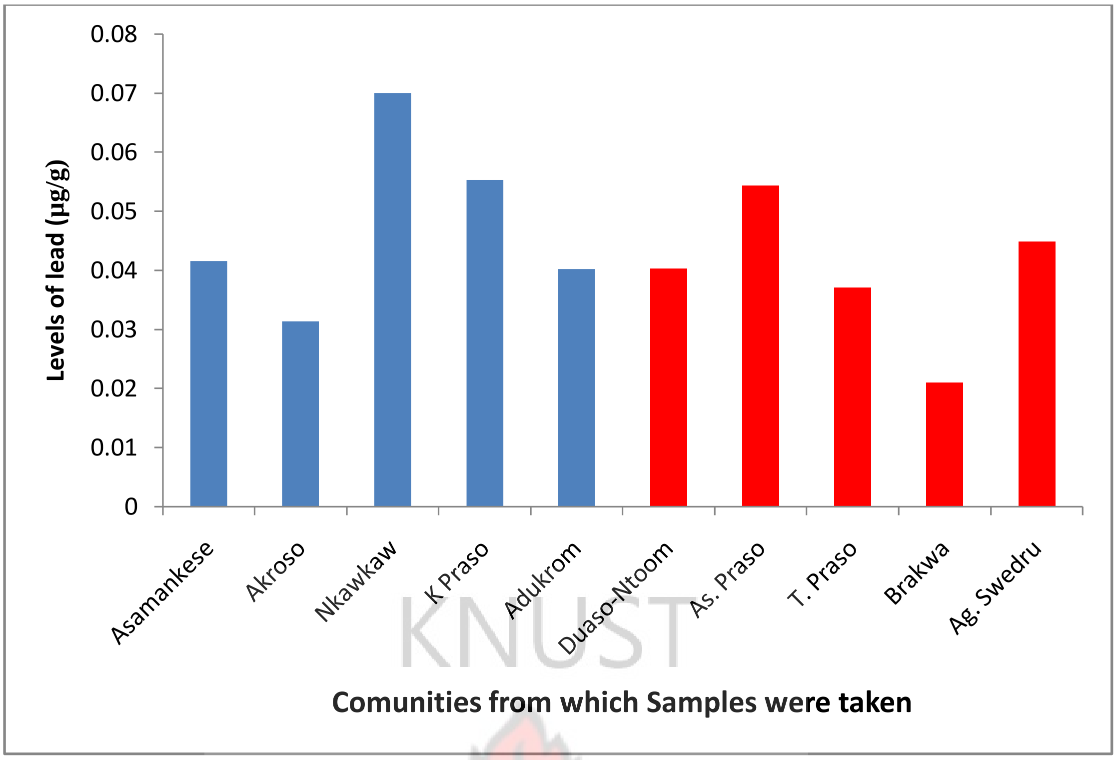

Figure 4.3: Graph for average levels of lead in cocoa beans from the Eastern and Central Regions of Ghana

From the graph, one can observe that the levels of lead were higher in most of the samples from the Eastern Region than in the Central Region. This is probably due to the position of Eastern Region on the map of Ghana. The Region has high vehicular traffic linking Greater Accra to Ashanti, Brong–Ahafo, Northern, Upper West, Upper East Regions and neighbouring Burkina Faso. Vehicles from Greater Accra to all these destinations and or the other way round passes through the Eastern Region. This shows that if the main source of this metal in the soil is the use of leaded fuel together with other commercial activities requiring the use of fuel, Eastern Region stands more exposed than all the other regions of the country hence the levels observed.

Also the people in the region are more involved in farming where weedicides and pesticides used in the production of vegetables and other produce. The region is also closer to many industries which burn a lot of fuel.

Considering the levels of cadmium and lead there appears to be an interesting relationship between them with regards to their levels as shown in the graphs in Fig4.3 below.

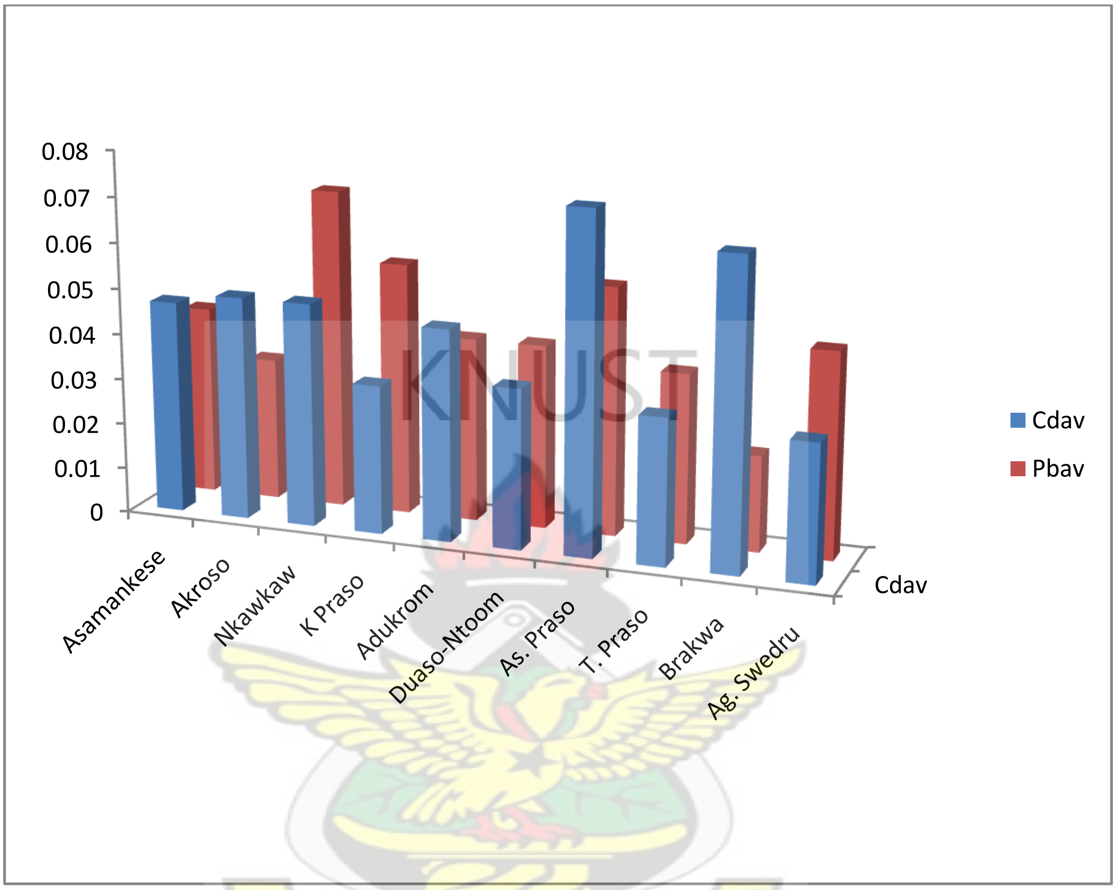

Fig 4.4: Relationship between levels of cadmium and lead in the cocoa beans from the Eastern and Central Regions of Ghana.

Thegraph shown above in figures 4.3reveals that, lead and cadmium vary inverselyto each other in terms of their levels in the samples. This relationship is clearly shown in all the averages of the Eastern Region, whiles the trend is not very pronounced in some of the samples from the Central Region.

The average levels of Lead in the two region in relationship with codex levels is as presented below.

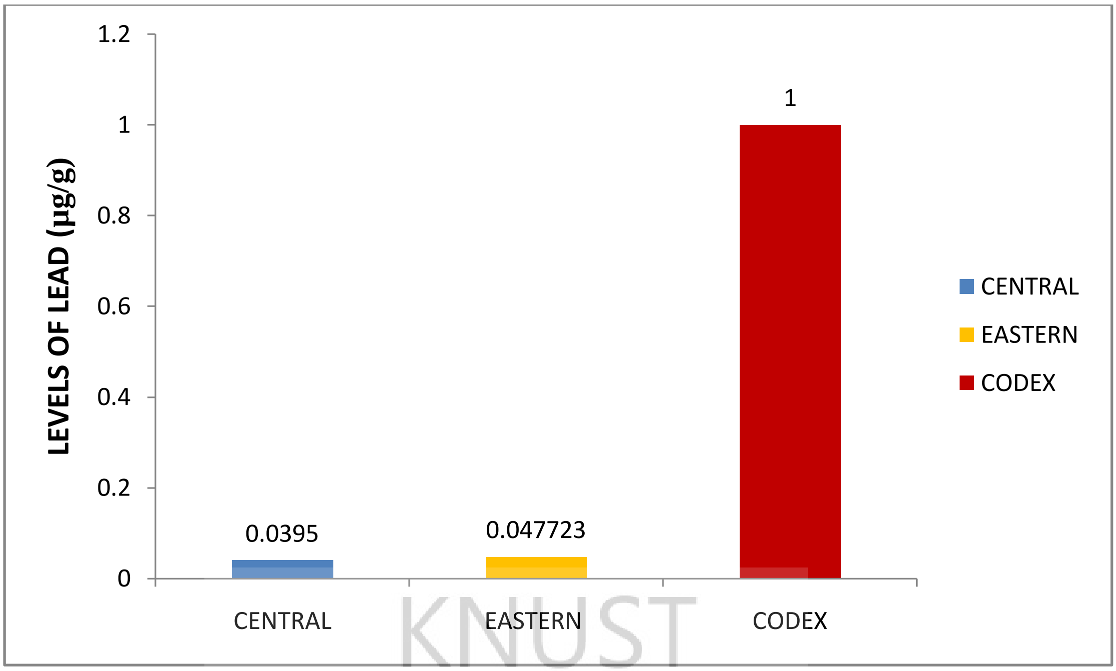

Figure 4.5: Average levls of cadmium from Eastern and Central Regions in relationship with Codex limit in Cocoa beans.

4.3 Copper levels

The United States Food and Nutrition Board(US FNB) has set the upper limit(UL) of copper at 10mg/day whiles Linus Pauling Institute suggests an recommended dietary allowance(RDA) level of 900.000µg/day for adults. In this work a mean copper level of 16.550µg/g was detected in the samples with the least value of 5.250µg/g in Asamankese COCOBOD farms located in the West Akim District of the Eastern Region specifically Kojo Aggrey farms; the highest value of 41.950µg/g was detected in the beans from Agona Swedru in the Central Region. The levels agree well with the average town to town levels. Following closely on the average levels to Agona Swedru are levels detected in the beans from Assin Praso and Adukrom while Asamankese recorded the lowest level as shown in the graph at Figure 4.4. These values observed were far lower than the RDA value of 900µg/day for adults as recommended by Linus Pauling Institutes and the 10mg/day set by US FNB (Food and Nutrition Board) (FNB, 2001)

This shows that the level of copper in the samples can not pose any health risk to humans. The metal is one of the essential minerals in foods. The levels are higher compared with the other toxic metals because it is used in pesticides and fungicides to control the black pod disease. The levels in the two regions are as shown in Figure 4.6

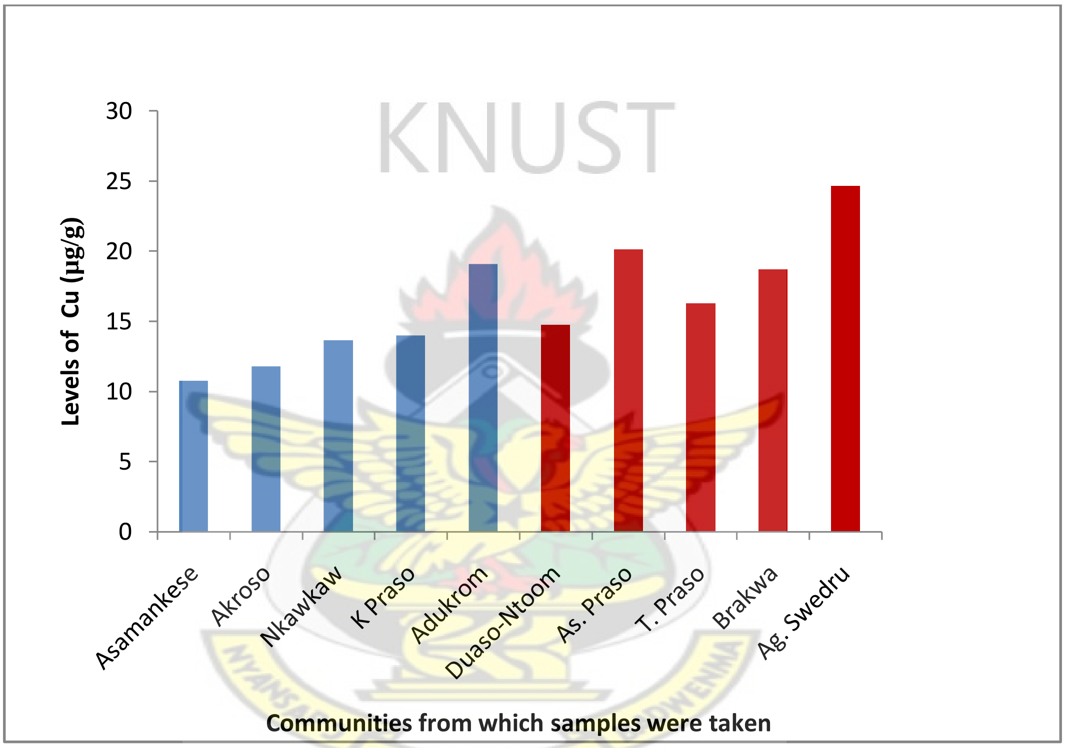

Figure 4.6 Average levels of Cu in cocoa beans sampled from Eastern and Central Regions of Ghana.

Considering the graph fig 4.4, the levels obtained in Agona Swedru is about two and half times higher than the levels obtained in the Asamankesse COCOBOD farms in the Eastern Region. It has been outlined in this work that high levels of iron suppress the levels of copper in the samples. Asamankesse is closer to one of the highest levels of iron deposite in Ghana,(Kibi), than most of the other communities sampled. The levels of copper in the samples from Asamankesse therefore confirm the observation that high iron levels suppress the levels of copper uptake by the plants.

Also it is evident from this work and another done by a team of researchers led by Nartey V. K. in 2012 that while all the other metal levels are increasing based on low pH, the levels of copper show a decrease. The levels detected in the samples in this work is in good agreement with levels detected in the work done by Nartey and his team of researchers who reported highest value of 17.800µg/g in the samples from Sefwi Asawinso with the highest pH.

Besides the above,the farms at Asamankesse act as one of the research farms for COCOBOD where new chemicals for controlling certain disease pests are tested. This means that the farms may not have been using only the copper based chemicalin controlling the black pod disease since there is the possibility of applying other chemicals for the same purpose. It is therefore not surprising that the levels of copper in the samples from the COCOBOD farms are lower than all the other samples obtained from other parts of the two regions.

4.4. Iron levels

For iron, a mean level of 27.420µg/gwas detected with a range of 0.500µg/g as the least value recorded in Akim Akroso in the Birim South District of the Eastern Region. The highest value of 160.60µg/g was also recorded at Akroso in the Birim South District. Also a high average level of the metal was recorded at Akroso following closely are the levels recorded at Nkawkaw, Agona Swedru, Adukrom, Asamankese with the lowest average level recorded at Assin Praso in the Assin North District in the Central Region.

The levels of the metal detected in the samples compare very well with levels detected by Nartey and his team of researchers except in one of the samples from Akroso. Nartey and his team of researchers reported a maximum value of 38.730µg/g which compares very well with all the values reported in this work.

The levels of iron detected in the Eastern Region were higher than values reported in the Central Region probably due to the fact that the Eastern Region is known to hold one of the prominent and promising deposits of iron ores in the country precisely the Kibi area.

It is believed that acute toxicity of the metal can occur at 20-60µg/Kg body weight. On the other hand, 8mg/day iron levels is set as recommended dietary allowance(RDA) for males at age 19years and above,14-18years males require 11mg/day, 0-6months require – 0.27mg/day for both males and females, 7–12months require 11mg/day for both males and females, for children between ages 9-13years, males require 7mg/day while females require 8mg/day. However, for adolescents between 14-18years who are females, they require 15mg/day and 19–50years females requires 18mg/day. Females 51 years and older require 8mg/day. For expectant mothers they require 27mg/day whiles, nursing mothers below and at age 18 require 10mg/day and those above 18years require 9mg/day.

Comparing the levels detected in this work with these established levels, it can be said that values observed are far below the recommended dietary allowance(RDA) average values of between 15-10mg/day and the ULs (tolerable upper limits) of 45mg/day set by the US FNB (US FNB 2001).

Graph for the average levels in the various communities are as presented in figure 4.8 and 4.9.

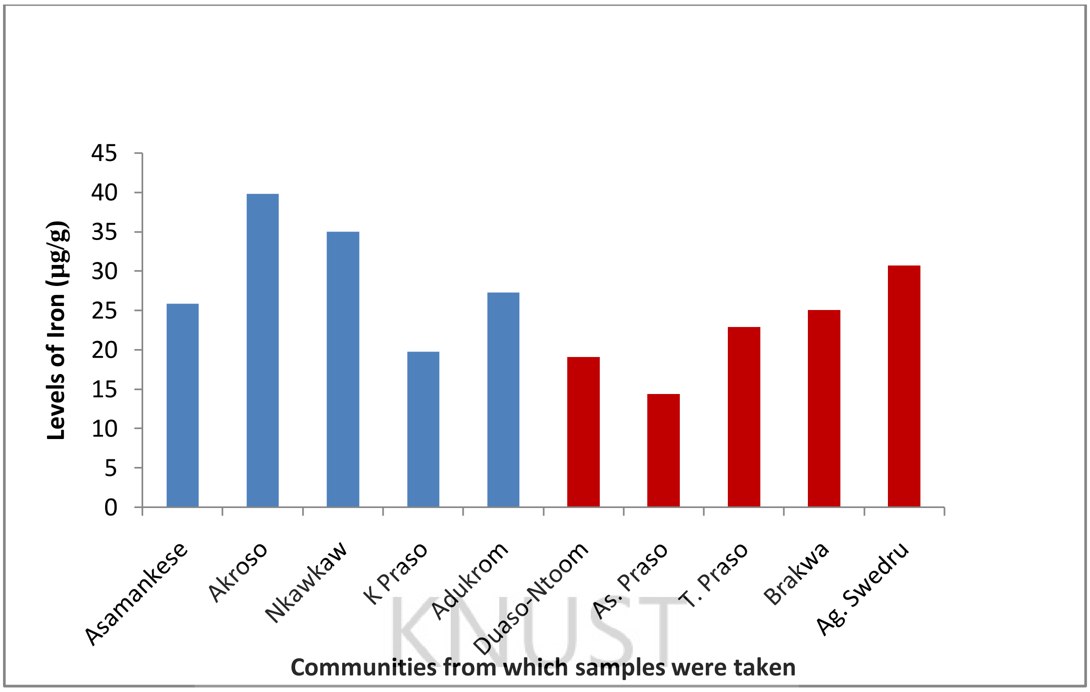

Figure 4.7: Average levels of iron in cocoa beans samples from Central and Eastern Region of Ghana

4.5. Levels of Manganese

The levels of manganese obtained in this work range from 4.450µg/g in the sample obtained from Kojo Aggrey farm at Asamankesse COCOBOD farms in the Eastern Region in the West Akim District to a high value of 52.35µg/g in one of samplesat Kwahu Praso inthe Kwahu South District of the Eastern Region. Consideringaverages, Kwahu Praso recorded the highest followed by Duaso-Ntoom, Akroso and the lowest obtained at Asamankese in the Eastern Region. The mean manganese level detected was 10.698±6.750ug/g. Apart from the two extremes, the levels detected were around the mean value.

Overdose of manganese is problematic though the mineral plays a lot of important roles as described in literature. Whiles the US EPA recommends 0.05mg/g as the maximum allowable limit their "sister" institution, US FNB set the ULs for manganese at 10mg/day for people at age 19yrs and above whiles 9mg/day is set for those between ages 14–18years. Also the requirement for 4–8years old has been fixed at 6mg/day. Again the RDA for manganese has been pegged at 1.8-2.3mg/day for adults (19 + years) for foods, water and supplements. The good news is that the levels detected in this work fall far below the levels set by the various institutions. This therefore points to the fact that cocoa produced by these communities does not pose any health risk and are safe for consumption with regards to manganese content.

The averages for the various communities recorded in this work as shown on the graph is in good agreement with the levels of manganese detected by Nartey and his team in cocoa nibs from the three communities, Bogoso, Sefwi Asawinso and Wassa Akropong. In theirwork, a high level of 33.600µg/g was detected in Wassa Akropong with the lowest of 13.050µg/g detected in Sefwi Asawinso.

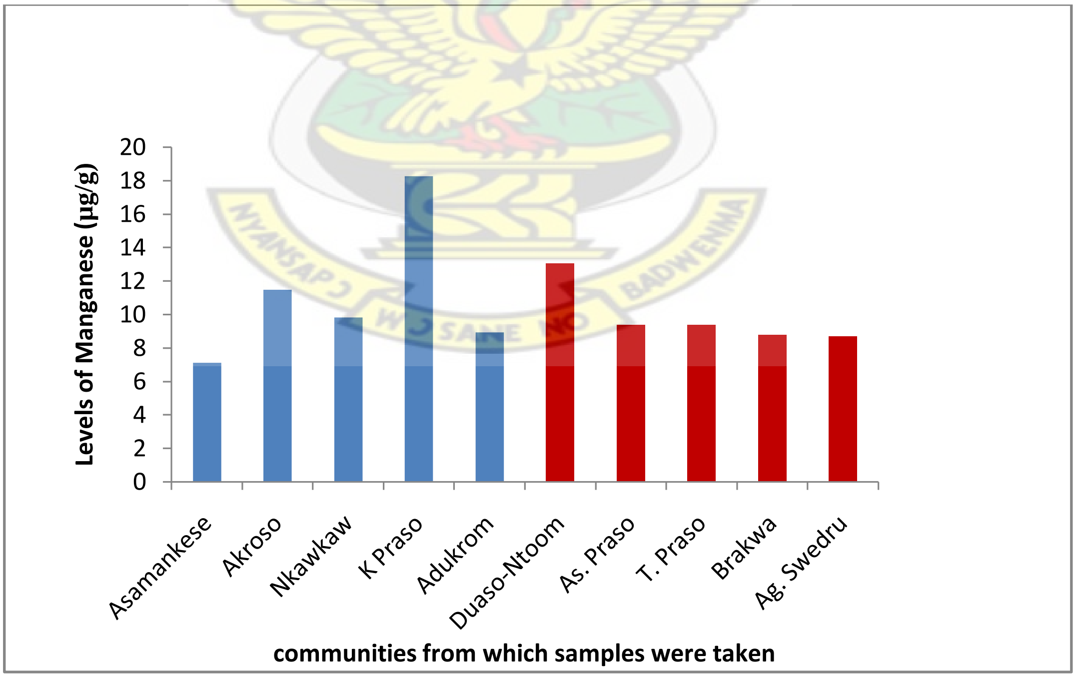

Figure 4.8: Average levels of manganese in the cocoa samples from the Eastern and Central Regions.

4.6 Levels of Zinc

The RDA for Zinc has been pegged at 12 – 15mg/day and the UL is set at 40mg / day on all foods, water and supplements. In this work a mean value of 34.558±6.13µg/g zinc was detected; with a range of 24.05µg/g least value recorded at Kojo Aggrey farms at Asamankese COCOBOD cluster of farms at the West Akim District of the Eastern Region. A high value of 50.785µg/g was recorded at Kwaku Praso in the Kwahu South District of the Eastern Region.

The values recorded from the Central Region appeared to be very close to the mean value whiles those in the Eastern Region were dispersed. On the average, Kwahu Praso recorded the highest value followed by Agona Swedru, Nkawkaw, Asamankese with the lowest average recorded at Assin Praso. The levels in the Central Region were generally lower than values in the Eastern Region. However the levels detected once again were far lower than the RDA's set for this element suggesting that there is no risk of contamination of the cocoa beans with Zinc.

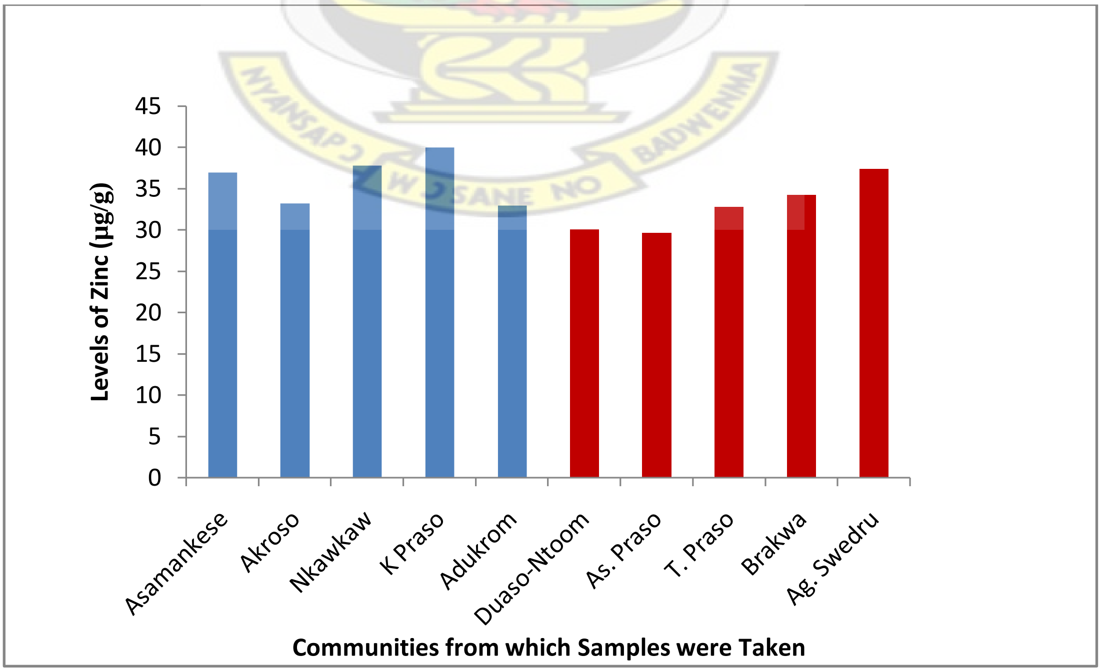

Figure 4.9: Average levels of zinc in cocoa beansfrom the Central and Eastern Regions of Ghana

The levels detected in the samples in this work, with the highest of 39.99µg/g as shown in the graph were once again in good agreement with levels detected by Nartey and his group, where the highest value of 47.17µg/g was detected in cocoa samples from Wassa Akropong.

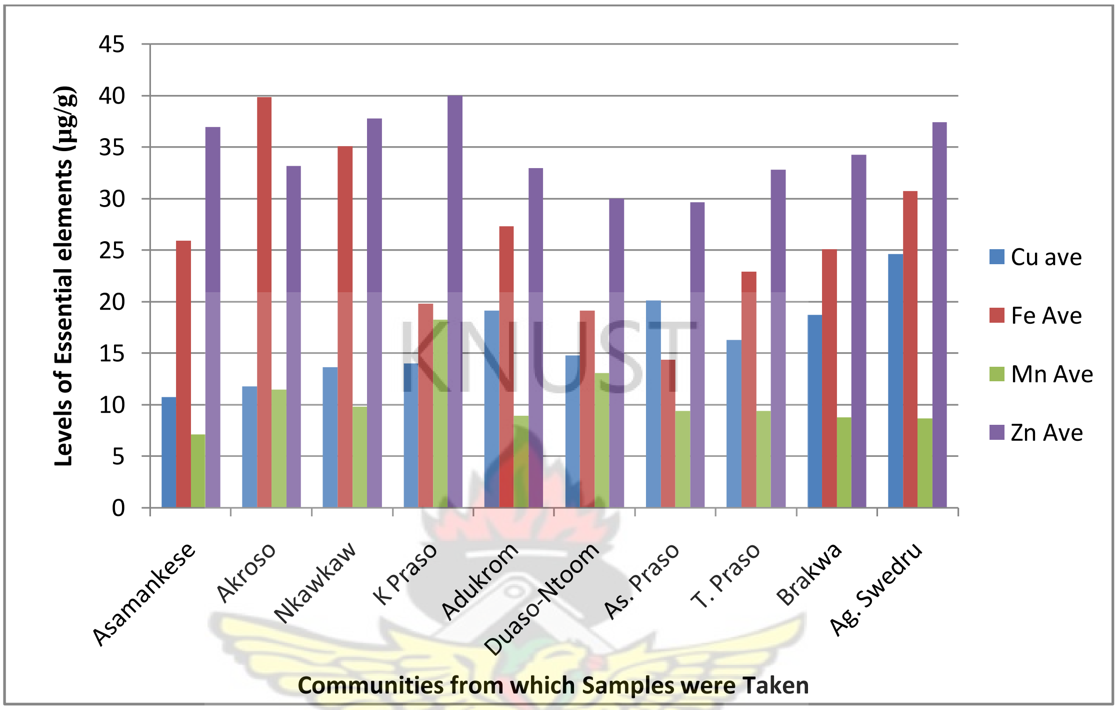

Figure 4.10: Average levels of essential elements in the cocoa samples from Central and Eastern Regions of Ghana.

From the graph, it is clear that the levels of zinc and iron were relatively higher in the two regions than the other metals. In the Eastern Region as can be observed from the graph, the levels of most of the metals were generally higher than in the Central Region except copper and cadmium which varied inversely with iron levels. The levels of zinc and iron also appear to vary inversely with each other in most of the samples from theEasternRegion; as have been buttressed by the graph in figure 4.11.

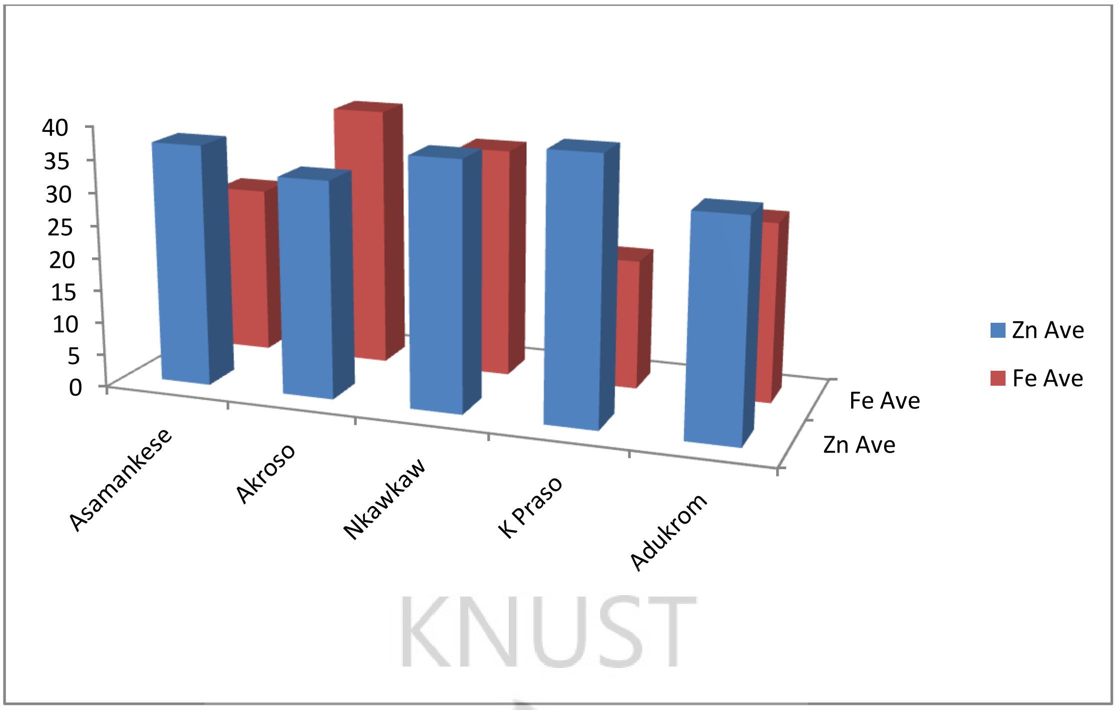

Figure 4.11 AverageLevels of iron and zinc in cocoa beans from the Eastern Region.

4.7. TRENDS OF METAL LEVELS IN SAMPLES FROM ASAMANKESE COCOBOD FARMS

The levels of the heavy metals detected in the samples at Asamankese COCOBOD farms show direct collaboration with the observations made earlier on. The levels of iron and zinc were very high compared with the other essential elements. Copper and manganese levels are inversely proportional to each other; where copper levels are high, manganese showed a reduction and the other way round. Except in samples obtained from Yaw Oddae farms and Emmanuel oppong farms whose age was not known, the levels of copper appear to be declining with age increase. The levels of iron however, showed the opposite trend; it increases with age of the plant. This could be, so, because Asamankese is closer to one of the promising deposits of iron; Kibi. High levels of iron tend to suppress the manganese and zinc levels.

Table 4.6: Levels of heavy metals in the age tagged samples of Asamankese COCOBOD farms.

Farm Sampled	CODES	Cd	Pb	Cu	Fe	Mn	Zn	AGE(yrs)
Doo Abraham	E16	0.015	0.075	15.250	18.750	9.200	37.200	12
Joseph Opoku	E12	0.040	0.007	8.000	13.700	5.350	39.200	13
Kojo Aggrey	E11	0.065	0.0235	5.250	21.140	4.950	24.040	22
Yaw Odaie	E15	0.020	0.0905	7.900	48.700	8.200	32.800	27
Gladys Osain	E13	0.055	0.037	5.150	38.300	6.550	49.600	39
Emmanuel Oppong	E14	0.085	0.0165	22.700	14.350	8.950	38.800	-

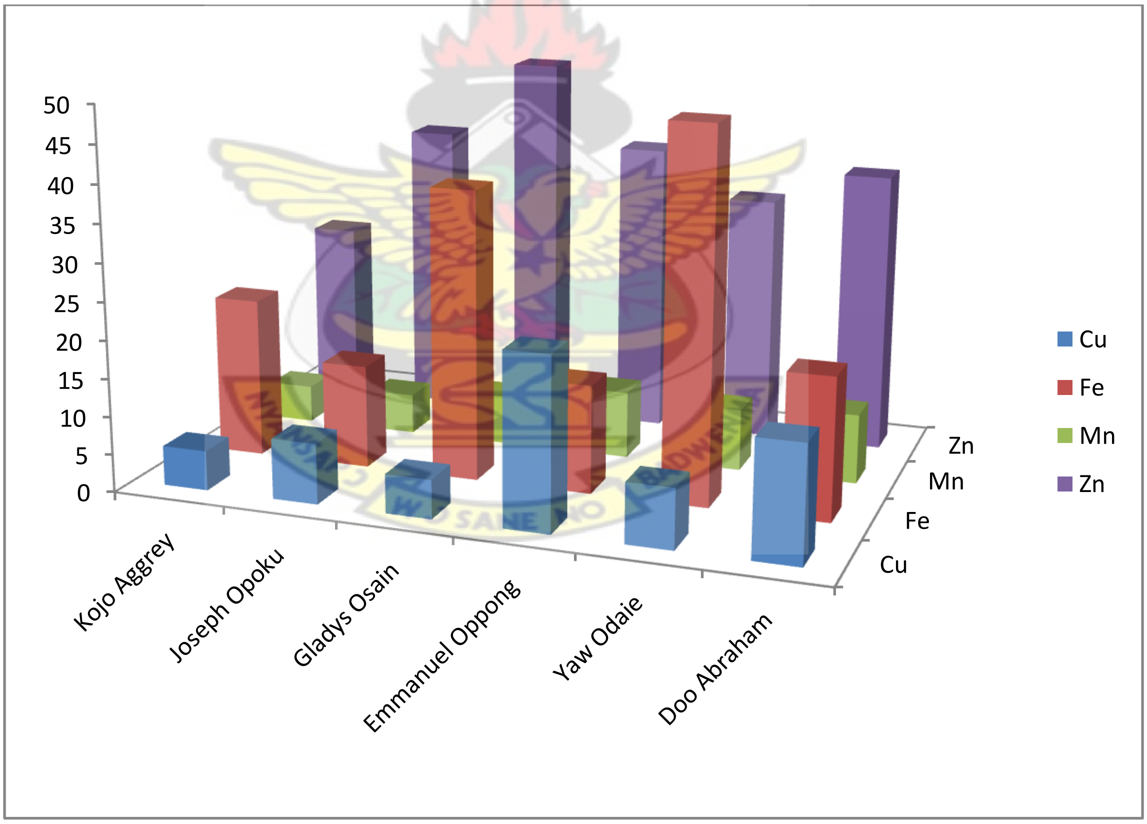

Figure 4.12 Levels of essential elements in the cocoa beans from Asamankese COCOBOD farms.

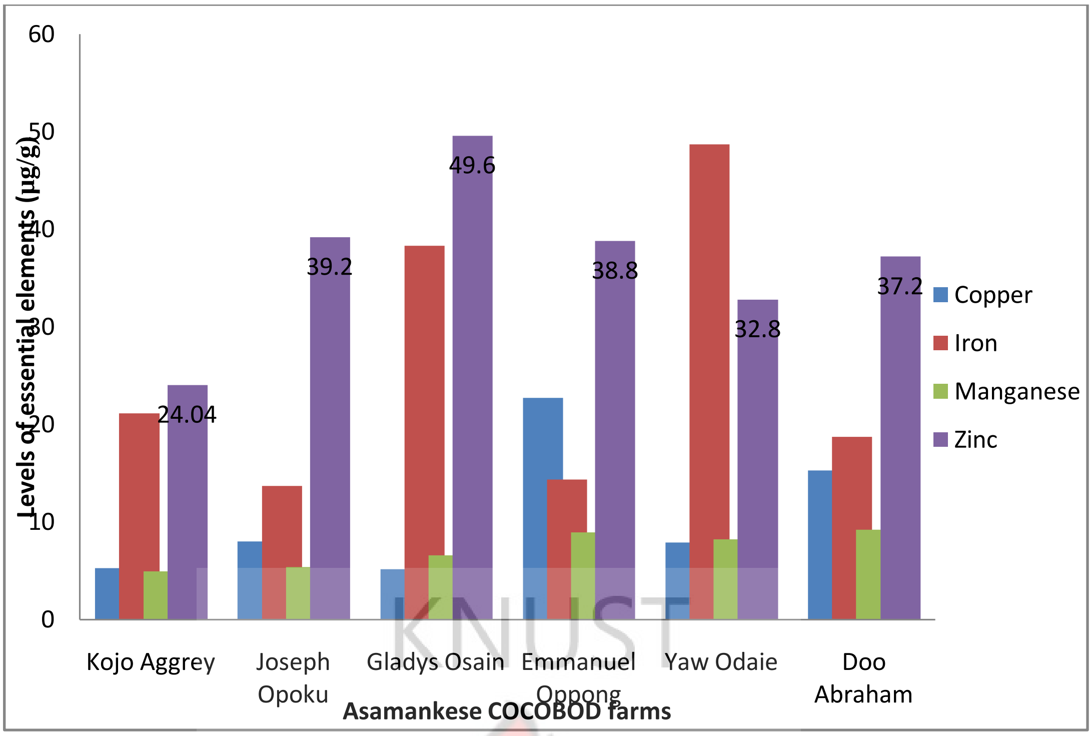

Figure 4.13: A bar graph showing the levels of the essential elements in the age tagged samples from Asamankese COCOBOD farms.

From the graphs, in figures 4.10 and 4.11, it is clear that levels of iron and zinc were relatively higher than the other essential elements. Copper and iron levels were inversely proportional to each other in all the farms. Also, levels of manganese were very low and show slight increases in levels with increases in levels of zinc.

The levels of zinc were higher than all the other metals in all the samples except in the cocoa beans from Yaw Odaie. This may be due to the fact that certain factors (pH, solubility in soil solution and colloids, morbidity etc) of the cocoa growing soils from which the samples were obtained favours the release of zinc, iron and copper in this levelsobserved.

This observation is supported by the fact that low soil pH increases the mobility of metals and increases their ability to go into solution. This leads to high levels of thesemetals available for absorption by plants grown on them (Narteyet al, 2013).

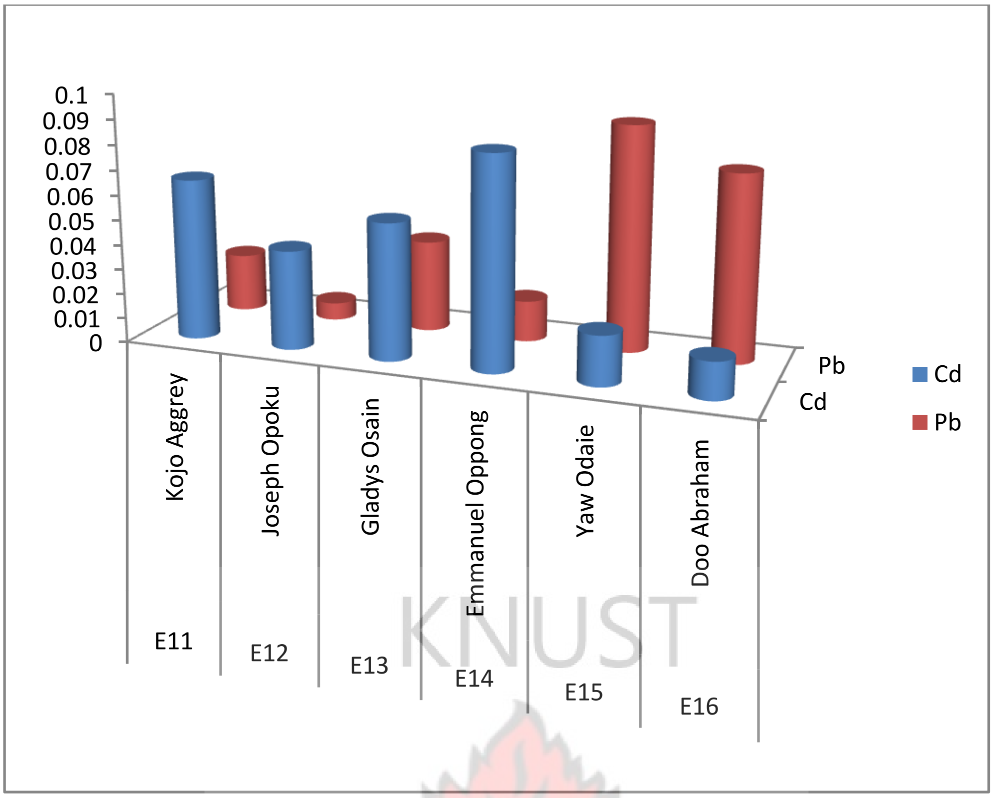

Figure 4.14 Levels of lead and cadmium (μg/g) in samples from Asamankese COCOBOD farms.

The levels of lead and cadmium follow the same trend in the samples from Kojo Aggrey, Joseph Opoku and Gladys Osain farms, but show dramatic departure from this initial trend and point to different directions in the samples from Emmanuel Oppong, Yaw Oddie and Doo Abraham farms confirming the observations made in the earlier samples involving the averages of the two regions as shown in Figure 4.12.

Lead and cadmium levels in these samples do not show any relationship with age of plants from which the samples were obtained. The levels of lead and cadmium in these samples may depend on other factors but not age.

Considering the other metals, more interesting trends were observed as shown in the diagram below.

Figure 4.15 Trends of levels of heavy metals with age of trees from which samples were taken in Asamankese COCOBOD farms.

From figure 4.15, the levels of iron are in direct proportionality with age of the sample suggesting that the age of the cocoa trees in Emmanuel Oppong farms is perhaps some where closer to but lower than 13years. The levels of copper from the graph vary inversely with age and for that matter Iron. Manganese levels in the samples also appear to be in direct proportionality with zinc. From the graph zinc appears to vary directly withiron and age with regards to samples from Kojo Aggrey, Joseph Opoku and Gladys Osain farms. Zinc shows direct relationship with increase in age of the plants from which the samples were taken. This observation confirms those made earlier on where the levels of zinc were over and above all the other essential elements studied.

From the graph, manganese and copper levels show regression as age increases. All soil conditions held constant, it will not be out of place to predict the low levels of manganese and copper whiles levels of iron and zinc can be predicted to be high while age of plants increase.

However, among the most important factors which contribute significantly to the levels of all heavy metals in the soil are the, levels of these heavy metals in fertilizers and other chemicals applied in the bid of controlling diseases and pest. Natural levels of these metals in the soil and most importantly the pH of the soil which determines the availability, mobility and the levels of absorption by plants grown on the soils, are also other factors.

The relationship between the levels of Copper, Iron and age of the sample is further elaborated with the regression graph, fig 4.16.Using the expression of the linear graph, the ageof cocoa trees from which samples were obtained in Emmanuel Oppong farms with regards to the iron levels was 9.0038years.

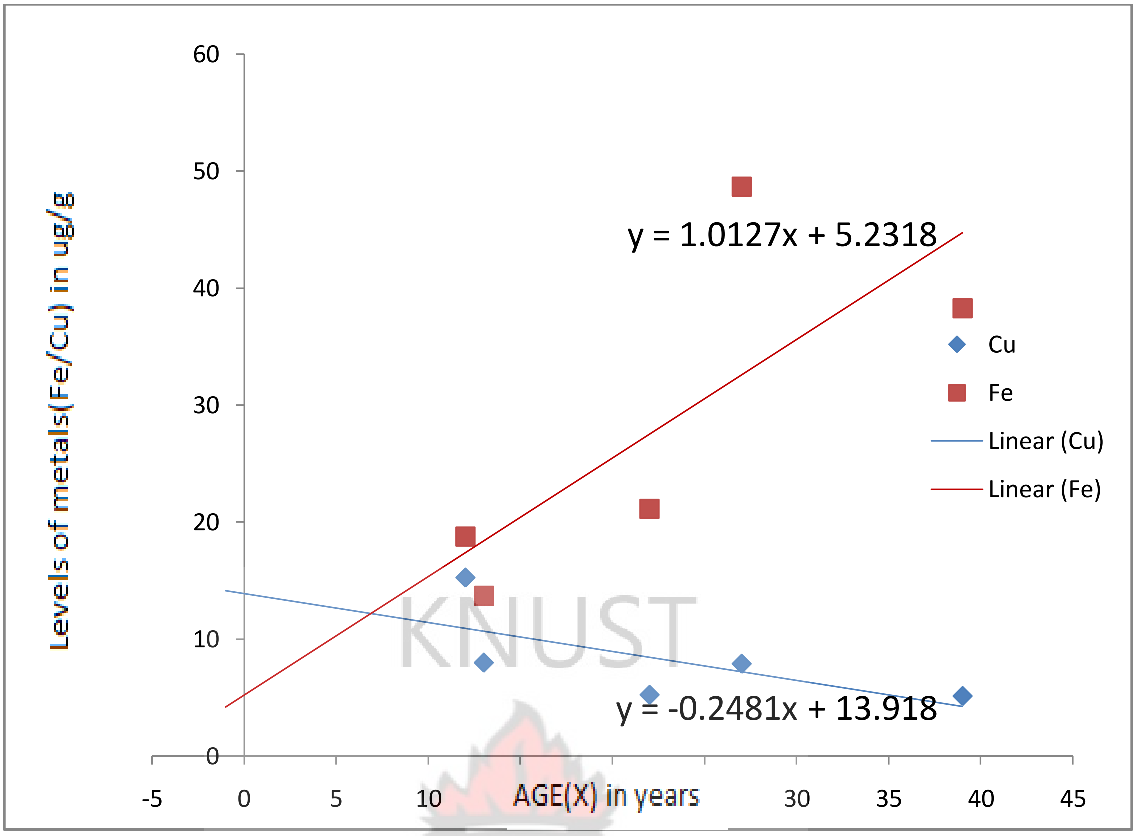

Fig. 4.16:Relationship between age of cocoa plant, levels of copper and iron in samples from Asamankese COCOBOD farms.

From the graph it is clear that the levels of the metals are not a perfect direct one with age of the plants from which the samples were taken. Other factors as levels of the metals in the soil, soil pH and other environmental factors which were not studied as part of this work may have contributed significantly to the observations made.

4.8. PROXIMATE ANALYSIS

Proximate analysis was conducted for six samples obtained from COCOBOD farms in Asamankese in the West Akim District of the Eastern Region. Results obtained were as shown in Table 4.6.

Table 4.7 Results of Proximate Analysis of Cocoa beans from Asamankese COCOBOD farms.

FARMS SAMPLED	Code	%MOISTURE	%PROTEIN	%FAT	% FIBRE	% ASH	% CARBOHYDRADTE	AGE(yrs)(of cocoa plants)
Doo Abraham	E16	4.260	13.190	36.630	2.635	3.575	39.710	12
Joseph Opoku	E12	3.400	13.720	38.425	2.665	3.665	38.125	13
Kojo Aggrey	E11	5.140	14.020	33.930	2.630	4.105	40.175	22
Yaw Odae	E15	3.510	14.420	36.625	2.620	4.030	38.795	27
Gladys Osain	E13	2.985	14.190	36.850	2.520	3.750	39.705	39
Emmanuel Oppong	E14	2.580	14.170	39.215	2.695	3.190		

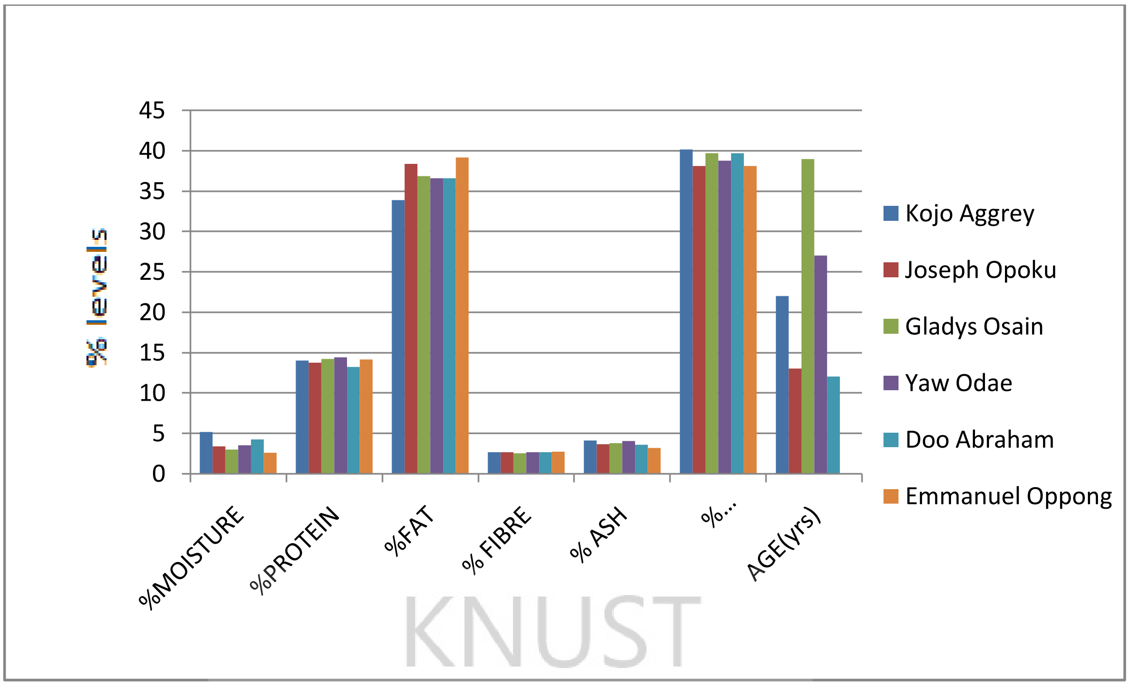

Figure 4.17 (a): Percentage Nutritional values in samples

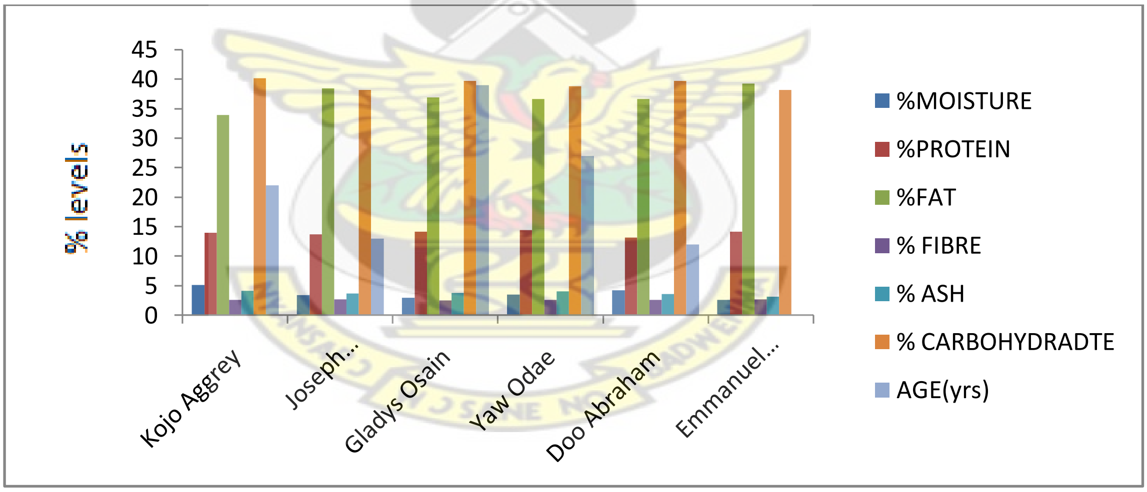

Figure 4.17(b): Percentage Nutritional levels in cocoa samples from Asamankese COCOBOD farms.

4.8.1 Discussions on Proximate Values.

The low moisture content obtained from the analysis as shown in table 4.6 is very appreciable considering the fact that the samples were dried in an oven prior to milling and determination. Samples from Kojo Aggrey farms had the highest percentage moisture of 5.14% whiles those from Emmanuel Oppong had the lowest level of 2.58%.The average moisture content determined for all the samples was 3.66458%.

An average protein of 13.95% was determined in all the samples. Samples from Yaw Oddie farms had the highest percentage protein of 14.42% with the lowest of 13.19% protein in those from Doo Abraham farms.

For fat, an average value of 36.95% was obtained in all the samples with the highest of 39.215% obtained in samples from Emmanuel Oppong farms whiles the lowest value of 33.93% was determined in those from Kojo Aggrey farms.

An average fibre level of 2.63% was detected in the samples. Samples from Emmanuel Oppong farms had the highest level of 2.695% whilesa least of 2.52% was obtained in those from Gladys Osain farms. The values in all the samples were however very close to each other. The levels compare well with established limits; suggesting that cocoa can be use as food for controlling constipation.

The ash content in a beverage is attributed to its mineral content. An average of 3.719% was determined with the highest value of 4.105% in the samples from Kojo Aggrey farms whiles the beans from Emmanuel Oppong farms recorded the lowest of 3.19%. The values obtained were very close to each other and were not far from limits set for beverages indicating that cocoa is a good source of minerals.

For carbohydrate an average of 39.110% was detected. The samples from Kojo Aggrey Aggrey farms recorded the highest value of 40.173% whiles the lowest value of 38.125% was recorded in samples from Joseph Opoku farms.

The levels of the various nutrients had no established correlation with the age of the samples and the levels of heavy metals in them.

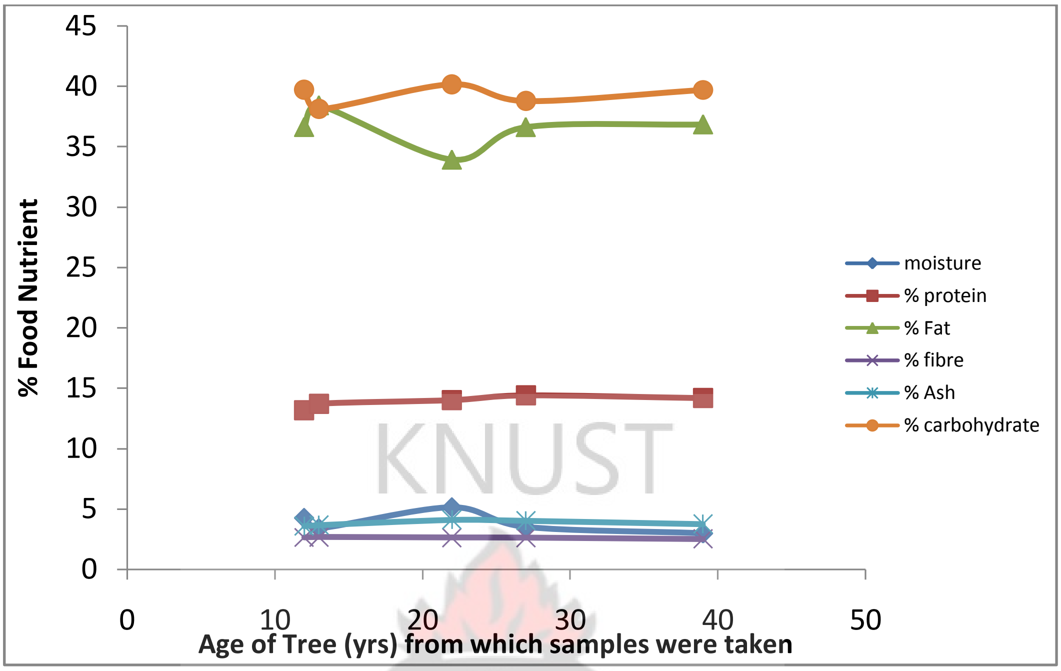

Figure 4.18: Variation of the age of plants from which samples were taken with various food nutrients.

Though no trend was established between age of plant and most of the food nutrients, there appears to be a reduction in the percentage moisture levels with increase in age of plants as shown in fig. 4.18and emphasised below.

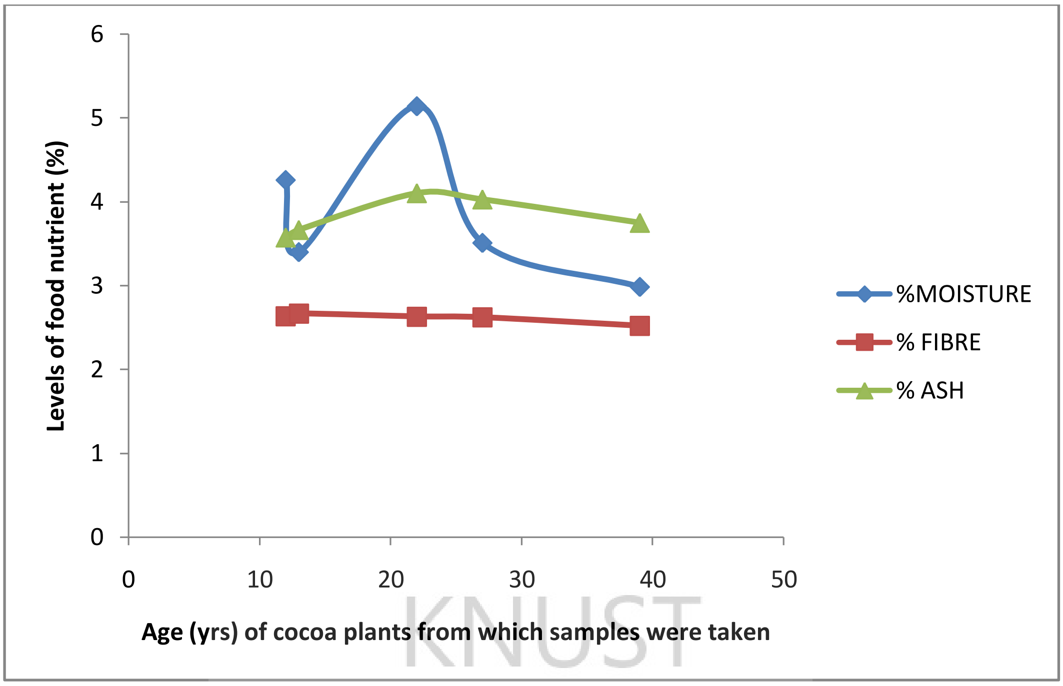

Figure 4.19 Trend of variation of some food nutrient with age of plant from which samples were taken.

From fig. 4.19, the highest moisture level was recorded at age 22 of cocoa plant but showed reductions in most cases with increase in age of plant. Fibre also showed a slight decrease with increase in age of plant. Ash levels showed no specific trend with age of plant.

Also there is an interesting relationship between the percentage fat and that of carbohydrate as a function of time as demonstrated in fig. 4.18 above. They do not show any correlation with age of the plants; however their percentage levels vary inversely to each other. As one is increasing the other will be reducing.Once again, protein showed no observable correlation with the age of plants from whichsamples were taken as shown in Fig. 4.18.

With the heavy metals, the following observation as demonstrated by the graph was made.

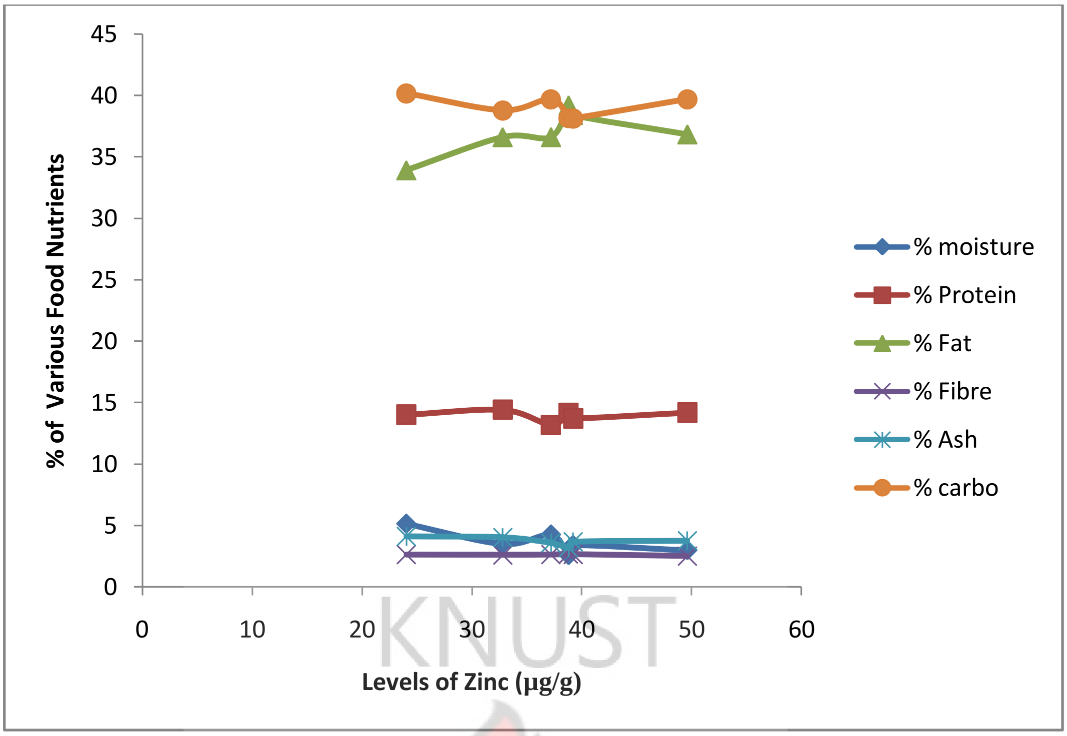

Figure 4.20 A chart showing variation of levels of zinc with various food nutrients in the samples from Asamankese COCOBOD farms.

Moisture shows adecrease in levels as the level of zinc increases in the samples. The other food nutrients do not show any clear relationship with the levels of zinc. However, carbohydrate and fat, the two food nutrients which were of very high percentages in the samples continue to show levels which point to opposite directions asobserved in figure 4.18. The only difference between the trends observed in figure 4.18 and 4.20 in terms of carbohydrate and fat is the directions they point to.

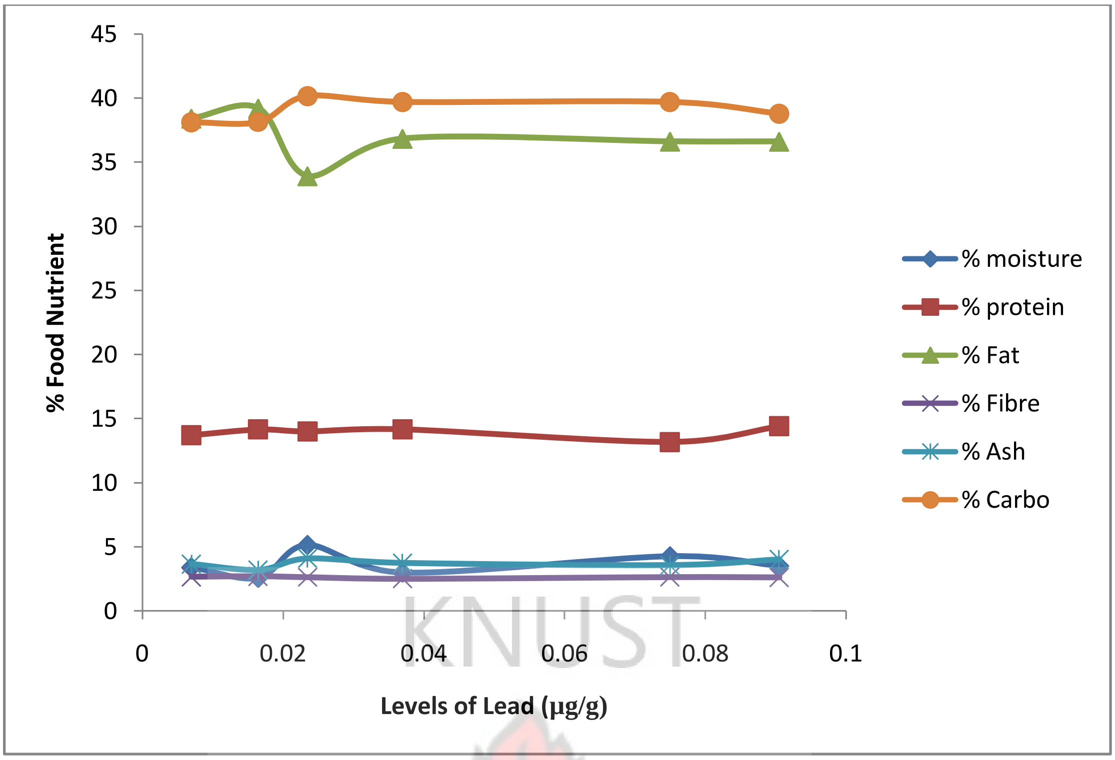

Figure 4.21 A chart showing the variation of lead with percentage food nutrients in the samples obtained from Asamankese COCOBOD farms in the Eastern Region.

From fig. 4.21, there is no clear relationship between any of the food nutrients detected in the samples and the levels of lead detected. Fat and carbohydrate showed inverse variation with each other.

CHAPTER FIVE

CONCLUSIONS AND RECOMMENDATIONS

5.1.0 CONCLUSIONS

The levels of cadmium, lead, copper, iron, manganese and zincanalyzed with the Buck Scientific AAS were found to be below the Codex levels and tolerable upper limit(UL) set by other reputable institutions such as the US EPA, EU, US FNB and suggested RDAs by Linus Pauling institute of medicine at the Oregon State University. The levels detected in the beans compare well with levels detected in samples from other parts of the country reported by other researchers.

The reliability of the analyses and for that matter the results were checked with the analysis of standard reference materials, NBS 1571 SRM certified orchard leaves and IAEA-V-10 SRM certified Hay Powder. Results obtained were found to be in good agreement with values reported on them.The results obtained from the samples show that the levels of the two relatively toxic metals (lead and cadmium) were very low and were negatively correlerated. The trend is as shown on the graph indicated by figures 4.3 and 4.10.

As the concentration of lead increases, that of cadmium shows a decreases and vice versa. It is therefore important to study the chemistry of this trend carefully making sure that any measures taken to reduce one does not lead to the eventual enhancement of the other in the soil and for that matter the cocoa beans.

Comparing the levels of the metals in the two regions, it is clear that the levels of cadmium were higher in the Central Region compared with those in the Eastern

Region while the Opposite is true for lead confirming their negative correlation with each other discussed earlier.

The levels of copper were higher in the Central Region than in the Eastern Region whiles the levels of iron, manganese and zinc were generally higher in the Eastern Region compared with the Central Region.The relationship between iron and age of cocoa plant from which samples were obtained for analyses can be represented by the linear equation $y = 0.99x – 5.\ 18$; where y = age and x = levels of iron. The linear relationship however, does not sum up the entire trends observed in this work since it is clear from literature and the discussions that other factors might have contributed significantly to the levels of the metals observed in the samples.

The levels of the essential elements were found to be far below the RDAs and the tolerable upper limits(ULs) suggested by various reputable institutions. Similarly manganese and iron levels affected each other. High iron levels correlate with low levels of manganese. The levels of heavy metals detected in the age tagged samples in Asamankese COCOBOD farms appear to affirm all observations made.

However, the levels of iron in the samples show a perfect and direct correlation with age of plants from which samples were taken. Using the iron content, the age of the plants from which samples were taken from Emmanuel Oppong farmswhich was not available during sampling can be predicted. The levels of copper showed negative correlation with age of the plants from which samples were obtained and for that matter iron; indicating that the levels of copper and iron correlate negatively to each other in the samples. Levels of manganese and zinc showed no specific trend with agejust as the levels of the other metals in the sample from Asamankese COCOBOD farms.

The fibre content in the samples obtained from the COCOBOD farms in Asamankese appear to be relatively uniform; with ash and moisture content relatively low. The levels of the nutrients; fat, protein and carbohydrate were relatively high; showing that cocoa is a very useful beverage. It is encouraged that it is taken because of its high levels of essential elements such as iron, copper, zinc and manganese coupled with its nutritional facts as presented in table 4.6. Levels of fat and carbohydrate showed that they correlate negatively to each other though the two nutrients were relatively higher in the samples than all the other nutrients.

No established trend was observed between the nutrient levels and the levels of the metals in the beans studied except moisture which showed a decrease with increasing zinc concentration. There was no correlation between age of the samples and the levels of the nutrients analyzedexcept moisture content which showed a decrease with age of plant from which samples were taken.

5.2.0 RECOMMENDATIONS

From the analyses, it is clear that, cocoa is a very nutritious beverage; it contains very useful essential elements which need to be constantly monitored in order to ascertain their levels at any point in time. Also it is very difficult from this work to pin point the exact sources of these essential and toxic metals in the cocoa beans. There is therefore the need for further research on soil parameters such as pH, CEC, Morbidity, levels of the metals in soil solutions, their characterization and effects of other environmental activities such as mining, industrial and other activities on the levels of these heavy metals in these cocoa beans.

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APPENDICES

APPENDIX A: RAW AND TREATED RESULTS ON HEAVY METALS IN COCOA SAMPLES (μg/g) FROM EASTERN AND CENTRAL REGIONS OF GHANA

LEVELS OF IRON IN SAMPLES OBTAINED FROM THE EASTERN REGION OF GHANA

Sample code	Fe*	Fe	Fe	Fe		Fe**	f1	F2	F3		stds	av std		code	
e11	**0.827**	0.825	0.828	0.828		21.400	21.400	21.4	21.4		0.000	0.070		codex	
e12	**0.673**	0.672	0.672	0.675		13.700	13.750	13.6	13.75		0.087			e1	25.867
e13	**1.165**	1.163	1.166	1.166		38.300	38.300	38.3	38.3		0.000			e2	39.820
e14	**0.686**	0.687	0.687	0.684		14.350	14.500	14.35	14.2		0.150			e3	35.070
e15	**1.373**	1.373	1.375	1.371		48.700	48.800	48.75	48.55		0.132			e4	40.050
e16	**0.774**	0.773	0.775	0.774		18.750	18.800	18.75	18.7		0.050			e5	34.300
														e6	27.313
e21	**0.409**	0.407	0.411	0.409		0.500	0.500	0.55	0.45		0.050	0.092			
e22	**0.472**	0.474	0.473	0.473		3.650	3.850	3.65	3.65		0.115				
e23	**0.602**	0.601	0.601	0.600		10.150	10.200	10.05	10		0.104				
e24	**0.883**	0.881	0.881	0.885		24.200	24.200	24.05	24.25		0.104		Eastern.		
e25	**3.611**	0.610	0.613	0.610		160.600	10.650	10.65	10.5		0.087				
e31	**0.855**	0.854	0.854	0.857		22.800	22.850	22.7	22.85		0.087	0.151			
e32	**1.545**	1.547	1.544	1.544		57.300	57.500	57.2	57.2		0.173				
e33	**0.496**	0.498	0.495	0.495		4.850	5.050	4.75	4.75		0.173				
e34	**1.178**	1.180	1.177	1.177		38.950	39.150	38.85	38.85		0.173				
e35	**1.428**	1.429	1.426	1.429		51.450	51.600	51.3	51.45		0.150				
e41	**0.941**	0.940	0.943	0.940		27.100	27.150	27.15	27		0.087	0.112			
e42	**1.503**	0.504	0.504	0.501		55.200	5.350	5.2	5.05		0.150				
e43	**0.664**	0.666	0.663	0.663		13.250	13.45	13.150	13.150		0.173				
e44	**0.772**	0.773	0.770	0.773		18.650	18.8	18.500	18.650		0.150				
e45	**1.545**	1.543	1.546	1.546		57.300	57.3	57.300	57.300		0.000				

code	Fe*	Fe	Fe	Fe		Fe**	f1	F2	F3		stds	av std		code	
e51	**0.832**	0.833	0.833	0.830		21.650	21.8	21.650	21.500		0.150	0.122			
e52	**1.237**	1.239	1.236	1.236		41.900	42.1	41.800	41.800		0.173				
e53	**1.196**	1.195	1.198	1.195		39.850	39.9	39.900	39.750		0.087				
e54	**0.516**	0.515	0.515	0.517		5.850	5.9	5.750	5.850		0.076				
e01	**0.399**	0.397	0.400	0.400		0	0	0	0		0.000				

LEVELS OF COPPER IN SAMPLES OBTAINED FROM THE EASTERN REGION OF GHANA

Sample code	Cu	Cu*	Cu	Cu		Cu**	Cu1	Cu2	Cu3		stds	av stds		code	value
e11	0.409	**0.410**	0.409	0.412		5.250	5.250	5.250	5.250		0.000	0.081		codex	
e12	0.467	**0.465**	0.464	0.464		8.000	8.150	8.000	7.850		0.150			e1	10.742
e13	0.411	**0.412**	0.411	0.414		5.350	5.350	5.350	5.350		0.000			e2	11.640
e14	0.761	**0.759**	0.758	0.758		22.700	22.850	22.700	22.550		0.150			e3	13.640
e15	0.465	**0.463**	0.461	0.461		7.900	8.050	7.850	7.700		0.176			e4	15.420
e16	0.609	**0.610**	0.609	0.612		15.250	15.250	15.250	15.250		0.000			e5	17.775
e21	0.433	**0.434**	0.433	0.436		6.450	6.450	6.450	6.450		0.000	0.060			
e22	0.527	**0.528**	0.527	0.530		11.150	11.150	11.150	11.150		0.000				
e23	0.643	**0.641**	0.640	0.640		16.800	16.950	16.800	16.650		0.150			Eastern.	
e24	0.526	**0.527**	0.526	0.529		11.100	11.100	11.100	11.100		0.000				
e25	0.561	**0.559**	0.558	0.558		12.700	12.850	12.700	12.550		0.150				
e31	0.668	**0.669**	0.668	0.671		18.200	18.200	18.200	18.200		0.000	0.554			
e32	0.457	**0.455**	0.454	0.454		7.500	7.650	7.500	7.350		0.150				
e33	0.670	**0.671**	0.670	0.673		18.300	18.300	18.300	18.300		0.000				
e34	0.641	**0.642**	0.644	0.641		16.850	16.850	17.000	16.700		0.150				
e35	0.451	**0.452**	0.454	0.541		7.350	7.350	7.500	11.700		2.469				

Sample code	Cu	Cu*	Cu	Cu		Cu**	Cu1	Cu2	Cu3		stds	av stds		code	value
e41	0.704	**0.705**	0.707	0.704		20.000	20.000	20.150	19.850		0.150	0.060			
e42	0.488	**0.489**	0.488	0.491		9.200	9.200	9.200	9.200		0.000				
e43	0.612	**0.613**	0.612	0.615		15.400	15.400	15.400	15.400		0.000				
e44	0.726	**0.727**	0.726	0.729		21.100	21.100	21.100	21.100		0.000				
e45	0.535	**0.533**	0.532	0.532		11.400	11.550	11.400	11.250		0.150				
e51	0.743	**0.744**	0.743	0.746		21.950	21.950	21.950	21.950		0.000	0.266			
e52	0.689	**0.687**	0.686	0.686		19.100	19.250	19.100	18.950		0.150				
e53	0.660	**0.661**	0.660	0.663		17.800	17.800	17.800	17.800		0.000				
e54	0.570	**0.550**	0.540	0.540		12.250	13.300	11.800	11.650		0.912				
e01	0.304	**0.305**	0.304	0.307		0.000	0.000	0.000	0.000		0.000				

LEVELS OF MANGANESE (µg/g) IN SAMPLES FROM THE EASTERN REGION OF GHANA															
Sample code	***Mn****	**Mn**	**Mn**	**Mn**		**Mn****									
E01	***0.009***	***0.008***	***0.010***	***0.009***		Mn**	mn1	mn2	Mn3		stds	ave stds		averages	value
E11	***0.098***	0.098	0.099	0.097		4.450	4.500	4.450	4.400		0.050	0.597		codex	
E12	***0.116***	0.117	0.118	0.011		5.350	5.450	5.400	0.115		3.066			e1	7.117
E13	***0.140***	0.141	0.138	0.141		6.550	6.650	6.400	6.600		0.132			e2	11.450
E14	***0.188***	0.187	0.186	0.191		8.950	8.950	8.800	9.100		0.150		Eastern.	e3	9.800
E15	***0.173***	0.174	0.174	0.171		8.200	8.300	8.200	8.100		0.100			e4	18.240
E16	***0.193***	0.193	0.192	0.194		9.200	9.250	9.100	9.250		0.087			e5	8.925
E21	***0.235***	0.236	0.236	0.233		11.300	11.400	11.300	11.200		0.100	0.066			
E22	***0.254***	0.253	0.255	0.254		12.250	12.250	12.250	12.250		0.000				
E23	***0.275***	0.274	0.276	0.275		13.300	13.300	13.300	13.300		0.000				
E24	***0.235***	0.236	0.236	0.233		11.300	11.400	11.300	11.200		0.100				
E25	***0.191***	0.192	0.193	0.188		9.100	9.200	9.150	8.950		0.132				
E31	***0.345***	0.346	0.347	0.342		16.800	16.900	16.850	16.650		0.132	0.086			
E32	***0.145***	0.146	0.145	0.146		6.800	6.900	6.750	6.850		0.076				
E33	***0.199***	0.199	0.198	0.200		9.500	9.550	9.400	9.550		0.087				
E34	***0.186***	0.186	0.188	0.184		8.850	8.900	8.900	8.750		0.087				
E35	***0.150***	0.148	0.151	0.151		7.050	7.000	7.050	7.100		0.050				
E41	***0.145***	0.144	0.143	0.148		6.800	6.800	6.650	6.950		0.150	0.126			
E42	***0.158***	0.159	0.160	0.155		7.450	7.550	7.500	7.300		0.132				
E43	***0.266***	0.268	0.267	0.263		12.850	13.000	12.850	12.700		0.150				
E44	***0.244***	0.245	0.245	0.242		11.750	11.850	11.750	11.650		0.100				
E45	***1.056***	1.055	1.059	1.054		52.350	52.350	52.450	52.250		0.100				
E51	***0.299***	0.296	0.300	0.301		14.500	14.400	14.500	14.600		0.100	0.124			
E52	***0.151***	0.152	0.149	0.152		7.100	7.200	6.950	7.150		0.132				
E53	***0.142***	0.143	0.144	0.139		6.650	6.750	6.700	6.500		0.132				
E54	***0.158***	0.159	0.160	0.155		7.450	7.550	7.500	7.300		0.132				

LEVELS OF ZINC (μg/g) IN SAMPLES FROM THE EASTERN REGION OF GHANA

Sample code	***Zn****	**Zn**	**Zn**	**Zn**											
E01	***0.048***	***0.047***	***0.045***	***0.052***		zn**	zn1	zn2	zn3		stds	av stds		code	av levels
E11	***0.529***	0.528	0.530	0.529		24.050	24.050	24.050	23.850		0.115	0.140		codex	
E12	***0.832***	0.830	0.831	0.836		39.200	39.150	39.150	39.200		0.029			e1	36.942
E13	***1.040***	1.041	1.042	1.037		49.600	49.700	49.700	49.250		0.260			e2	33.160
E14	***0.824***	0.823	0.827	0.822		38.800	38.800	38.800	38.500		0.173			e3	37.740
E15	***0.704***	0.703	0.705	0.704		32.800	32.800	32.800	32.600		0.115			e4	39.990
E16	***0.792***	0.791	0.794	0.791		37.200	37.200	37.200	36.950		0.144			e5	32.938
E21	***0.586***	0.587	0.588	0.583		26.900	27.000	27.000	26.550		0.260	0.219			
E22	***0.700***	0.701	0.702	0.697		32.600	32.700	32.700	32.250		0.260				
E23	***0.715***	0.714	0.713	0.718		33.350	33.350	33.350	33.300		0.029				
E24	***0.764***	0.766	0.765	0.761		35.800	35.950	35.950	35.450		0.289				
E25	***0.791***	0.793	0.791	0.789		37.150	37.300	37.300	36.850		0.260				
														Eastern	
E31	***0.828***	0.829	0.827	0.828		39.000	39.100	39.100	38.800		0.173	0.150			
E32	***0.797***	0.799	0.798	0.794		37.450	37.600	37.600	37.100		0.289				
E33	***0.838***	0.839	0.840	0.835		39.500	39.600	39.600	39.150		0.260				
E34	***0.779***	0.778	0.777	0.782		36.550	36.550	36.550	36.500		0.029				
E35	***0.772***	0.770	0.771	0.775		36.200	36.150	36.150	36.150		0.000				
E41	***0.824***	0.823	0.825	0.824		38.800	38.800	38.800	38.600		0.115	0.162			
E42	***0.798***	0.799	0.796	0.796		37.500	37.600	37.600	37.200		0.231				
E43	***0.731***	0.730	0.732	0.731		34.150	34.150	34.150	33.950		0.115				
E44	***0.823***	0.821	0.822	0.826		38.750	38.700	38.700	38.700		0.000				
E45	***1.063***	1.065	1.066	1.058		50.750	50.900	50.900	50.300		0.346				
E51	***0.725***	0.726	0.723	0.726		33.850	33.950	33.950	33.700		0.144	0.137			
E52	***0.781***	0.780	0.780	0.783		36.650	36.650	36.650	36.550		0.058				
E53	***0.759***	0.758	0.761	0.758		35.550	35.550	35.550	35.300		0.144				
E54	***0.562***	0.562	0.561	0.560		25.700	25.750	25.750	25.400		0.202				

LEVELS OF CADMIUM IN SAMPLES FROM THE EASTERN REGION OF GHANA

code	**Cd***	Cd	Cd	Cd		Cd**	Cd1	Cd2	Cd3		stds	av stds		code	av levels
e11	**0.018**	0.017	0.017	0.020		0.065	0.065	0.065	0.065		0.000	0.010		e1	0.047
e12	**0.013**	0.015	0.012	0.012		0.040	0.055	0.040	0.025		0.015			e2	0.049
e13	**0.016**	0.015	0.015	0.017		0.055	0.055	0.055	0.050		0.003			e3	0.049
e14	**0.022**	0.024	0.023	0.023		0.085	0.100	0.095	0.080		0.010			e4	0.033
e15	**0.009**	0.011	0.008	0.008		0.020	0.035	0.020	0.005		0.015			e5	0.046
e16	**0.008**	0.007	0.010	0.007		0.015	0.015	0.030	0.000		0.015			codex	0.100
e21	**0.009**	0.008	0.011	0.008		0.020	0.020	0.035	0.005		0.015	0.012			
e22	**0.023**	0.022	0.022	0.025		0.090	0.090	0.090	0.090		0.000			eastern.	
e23	**0.018**	0.020	0.017	0.017		0.065	0.080	0.065	0.050		0.015				
e24	**0.011**	0.010	0.013	0.010		0.030	0.030	0.045	0.015		0.015				
e25	**0.013**	0.015	0.012	0.012		0.040	0.055	0.040	0.025		0.015				
e31	**0.007**	0.006	0.006	0.090		0.010	0.010	0.010	0.415		0.234	0.066			
e32	**0.022**	0.024	0.021	0.021		0.085	0.100	0.085	0.070		0.015				
e33	**0.013**	0.012	0.012	0.015		0.040	0.040	0.040	0.040		0.000				
e34	**0.010**	0.030	0.009	0.009		0.025	0.130	0.025	0.010		0.065				
e35	**0.022**	0.021	0.024	0.021		0.085	0.085	0.100	0.070		0.015				
e41	**0.009**	0.009	0.008	0.009		0.018	0.024	0.022	0.008		0.009	0.023			
e42	**0.022**	0.024	0.021	0.021		0.085	0.100	0.085	0.070		0.015				
e43	**0.008**	0.010	0.007	0.007		0.015	0.030	0.015	0.000		0.015				
e44	**0.009**	0.009	0.009	0.009		0.021	0.027	0.026	0.009		0.010				
e45	**0.010**	0.030	0.009	0.009		0.025	0.130	0.025	0.010		0.065				
e51	**0.012**	0.011	0.011	0.014		0.035	0.035	0.035	0.035		0.000	0.010			
e52	**0.009**	0.010	0.008	0.008		0.020	0.030	0.020	0.005		0.013				
e53	**0.017**	0.019	0.018	0.014		0.060	0.075	0.070	0.035		0.022				
e54	**0.019**	0.018	0.019	0.020		0.070	0.070	0.075	0.065		0.005				
e01	**0.005**	0.004	0.004	0.007		0.000	0.000	0.000	0.000		0.000				

LEVELS OF LEAD (µg/g) IN SAMPLES OBTAINED FROM THE EASTERN RGION

Sample code	**Pb***	Pb	Pb	Pb		Pb**	Pb1	Pb2	Pb3		stds	av stds		code	av levels
e11	**0.052**	0.054	0.051	0.051		0.024	0.024	0.023	0.023		0.001	0.001		codex	0.100
e12	**0.019**	0.018	0.018	0.021		0.007	0.006	0.006	0.008		0.001			e1	0.042
e13	**0.079**	0.081	0.078	0.078		0.037	0.038	0.036	0.037		0.001			e2	0.031
e14	**0.038**	0.037	0.040	0.037		0.017	0.016	0.017	0.016		0.001			e3	0.070
e15	**0.186**	0.185	0.185	0.188		0.091	0.090	0.090	0.092		0.001			e4	0.055
e16	**0.155**	0.157	0.154	0.154		0.075	0.076	0.074	0.075		0.001			e5	0.040
e21	**0.025**	0.022	0.027	0.026		0.010	0.008	0.011	0.011		0.001	0.003			
e22	**0.090**	0.080	0.080	0.110		0.043	0.037	0.037	0.053		0.009				
e23	**0.132**	0.131	0.131	0.134		0.064	0.063	0.063	0.065		0.001				
e24	**0.023**	0.025	0.022	0.022		0.009	0.010	0.008	0.009		0.001				
e25	**0.069**	0.068	0.071	0.068		0.032	0.031	0.033	0.032		0.001				
														Eastern	
e31	**0.165**	0.164	0.164	0.167		0.080	0.079	0.079	0.081		0.001	0.001			
e32	**0.161**	0.163	0.160	0.160		0.078	0.079	0.077	0.078		0.001				
e33	**0.166**	0.165	0.165	0.168		0.081	0.080	0.080	0.082		0.001				
e34	**0.115**	0.116	0.117	0.112		0.055	0.055	0.056	0.054		0.001				
e35	**0.119**	0.118	0.118	0.120		0.057	0.056	0.056	0.058		0.001				
e41	**0.050**	0.040	0.040	0.060		0.023	0.017	0.017	0.028		0.006	0.002			
e42	**0.194**	0.196	0.193	0.193		0.095	0.095	0.094	0.094		0.001				
e43	**0.110**	0.111	0.109	0.110		0.053	0.053	0.052	0.053		0.001				
e44	**0.182**	0.184	0.181	0.181		0.089	0.089	0.088	0.088		0.001				
e45	**0.042**	0.044	0.041	0.041		0.019	0.019	0.018	0.018		0.001				
e51	**0.082**	0.084	0.081	0.081		0.039	0.039	0.038	0.038		0.001	0.001			
e52	**0.076**	0.078	0.075	0.075		0.036	0.036	0.035	0.035		0.001				
e53	**0.083**	0.085	0.081	0.081		0.039	0.040	0.038	0.038		0.001				
e54	**0.101**	0.103	0.100	0.100		0.048	0.049	0.047	0.048		0.001				

LEVELS OF IRON (μg/g) IN SAMPLES OBTAINED FROM THE EASTERN REGION

Sample code	Fe*	Fe	Fe	Fe		Fe**	f1	F2	F3		stds	av std			code	
e11	**0.83**	0.83	0.83	0.83		21.40	21.40	21.40	21.40		0.00	0.07			codex	
e12	**0.67**	0.67	0.67	0.68		13.70	13.75	13.60	13.75		0.09				e1	25.87
e13	**1.17**	1.16	1.17	1.17		38.30	38.30	38.30	38.30		0.00				e2	39.82
e14	**0.69**	0.69	0.69	0.68		14.35	14.50	14.35	14.20		0.15				e3	35.07
e15	**1.37**	1.37	1.38	1.37		48.70	48.80	48.75	48.55		0.13				e4	40.05
e16	**0.77**	0.77	0.78	0.77		18.75	18.80	18.75	18.70		0.05				e5	34.30
															e6	27.31
e21	**0.41**	0.41	0.41	0.41		0.50	0.50	0.55	0.45		0.05	0.09				
e22	**0.47**	0.47	0.47	0.47		3.65	3.85	3.65	3.65		0.12					
e23	**0.60**	0.60	0.60	0.60		10.15	10.20	10.05	10.00		0.10					
e24	**0.88**	0.88	0.88	0.89		24.20	24.20	24.05	24.25		0.10			Eastern.		
e25	**3.61**	0.61	0.61	0.61		160.6	10.65	10.65	10.50		0.09					
e31	**0.86**	0.85	0.85	0.86		22.80	22.85	22.70	22.85		0.09	0.15				
e32	**1.55**	1.55	1.54	1.54		57.30	57.50	57.20	57.20		0.17					
e33	**0.50**	0.50	0.50	0.50		4.85	5.05	4.75	4.75		0.17					
e34	**1.18**	1.18	1.18	1.18		38.95	39.15	38.85	38.85		0.17					
e35	**1.43**	1.43	1.43	1.43		51.45	51.60	51.30	51.45		0.15					
e41	**0.94**	0.94	0.94	0.94		27.10	27.15	27.15	27.00		0.09	0.11				
e42	**1.50**	0.50	0.50	0.50		55.20	5.35	5.20	5.05		0.15					
e43	**0.66**	0.67	0.66	0.66		13.25	13.45	13.15	13.15		0.17					
e44	**0.77**	0.77	0.77	0.77		18.65	18.80	18.50	18.65		0.15					
e45	**1.55**	1.54	1.55	1.55		57.30	57.30	57.30	57.30		0.00					
e51	**0.83**	0.83	0.83	0.83		21.65	21.80	21.65	21.50		0.15	0.12				
e52	**1.24**	1.24	1.24	1.24		41.90	42.10	41.80	41.80		0.17					
e53	**1.20**	1.20	1.20	1.20		39.85	39.90	39.90	39.75		0.09					
e54	**0.52**	0.52	0.52	0.52		5.85	5.90	5.75	5.85		0.08					
e01	**0.40**	0.40	0.40	0.40		0.00	0.00	0.00	0.00		0.00					

CENTRAL REGION VALUES

LEVELS OF MANGANESE (µg/g) OBTAINED FROM SAMPLES FROM THE CENTRAL REGION OF GHANA

Sample code	**Mn***	**Mn**	**Mn**	**Mn**			mn**									
C01	***0.03***	***0.029***	***0.028***	***0.033***		***C0de***	Mn**	Mn	Mn	Mn		stds	ave stds		code	av values
C11	***0.201***	0.2	0.203	0.2		**C11**	8.55	8.55	8.75	8.35		0.200	0.261		c1	13.03
C12	***0.273***	0.274	0.275	0.27		**C12**	12.2	12.3	12.35	11.85		0.265			c2	11.96
C13	***0.396***	0.397	0.398	0.393		**C13**	18.3	18.4	18.5	18		0.265			c3	9.36
C14	***0.333***	0.336	0.335	0.328		**C14**	15.2	15.4	15.35	14.75		0.346			c4	8.77
C15	***0.25***	0.25	0.252	0.248		**C15**	11	11.1	11.2	10.75		0.229			c5	8.67
C21	***0.285***	0.28	0.284	0.291		**C21**	12.8	12.6	12.8	12.9		0.180	0.166			
C22	***0.253***	0.25	0.255	0.254		**C22**	11.2	11.1	11.35	11.05		0.173				
C23	***0.253***	0.251	0.257	0.251		**C23**	11.2	11.1	11.45	10.9		0.278				
C24	***0.302***	0.301	0.3	0.305		**C24**	13.6	13.6	13.6	13.6		0.000				
C25	***0.253***	0.256	0.251	0.252		**C25**	11.2	11.4	11.15	10.95		0.200				
C31	***0.309***	0.311	0.305	0.313		**C31**	14	14.1	13.85	14		0.126	0.203			
C32	***0.184***	0.187	0.183	0.182		**C32**	7.7	7.9	7.75	7.45		0.229				
C33	***0.25***	0.255	0.248	0.247		**C33**	11	11.3	11	10.7		0.300				
C34	***0.174***	0.173	0.17	0.179		**C34**	7.2	7.2	7.1	7.3		0.100				
C35	***0.169***	0.171	0.17	0.166		**C35**	6.95	7.1	7.1	6.65		0.260				
C41	***0.202***	0.2	0.201	0.205		**C41**	8.6	8.55	8.65	8.6		0.050	0.252			
C42	***0.216***	0.219	0.214	0.215		**C42**	9.3	9.5	9.3	9.1		0.200				
C43	***0.209***	0.207	0.212	0.208		**C43**	8.95	8.9	9.2	8.75		0.229				
C44	***0.18***	0.184	0.181	0.175		**C44**	7.5	7.75	7.65	7.1		0.350				
C45	***0.22***	0.224	0.223	0.213		**C45**	9.5	9.75	9.75	9		0.433				
C51	***0.138***	0.135	0.134	0.145		**C51**	5.4	5.3	5.3	5.6		0.173	0.218			
C52	***0.24***	0.243	0.241	0.236		**C52**	10.5	10.7	10.65	10.15		0.304				
C53	***0.301***	0.3	0.299	0.304		**C53**	13.6	13.6	13.55	13.55		0.000				
C54	***0.164***	0.163	0.167	0.162		**C54**	6.7	6.7	6.95	6.45		0.250				
C55	***0.174***	0.175	0.178	0.169		**C55**	7.2	7.3	7.5	6.8		0.361				

<u>LEVELS OF ZINC(µg/g) IN SAMPLES OBTAINED FROM THE CENTRAL REGION</u>

Zn *	**Zn**	**Zn**	**Zn**	**Sample Code**											
0.097	***0.096***	***0.1***	***0.095***	***C01***		Zn**	zn1	zn2	Zn3		stds	av std		averages	values
0.661	0.663	0.662	0.658	**C11**		28.2	28.35	28.1	28.15		0.132	0.153		c1	30
0.701	0.7	0.699	0.704	**C12**		30.2	30.2	29.95	30.45		0.250			c2	29.62
0.777	0.774	0.779	0.778	**C13**		34	33.9	33.95	34.15		0.132			c3	32.79
0.728	0.727	0.73	0.727	**C14**		31.55	31.55	31.5	31.6		0.050			c4	34.21
0.618	0.616	0.617	0.62	**C15**		26.05	26	25.85	26.25		0.202			c5	37.39
														codex	
0.65	0.653	0.649	0.648	**C21**		27.65	27.85	27.45	27.65		0.200	0.240			
0.648	0.644	0.647	0.653	**C22**		27.55	27.4	27.35	27.9		0.304				
0.737	0.735	0.736	0.74	**C23**		32	31.95	31.8	32.25		0.229				
0.741	0.742	0.738	0.743	**C24**		32.2	32.3	31.9	32.4		0.265				
0.671	0.674	0.67	0.669	**C25**		28.7	28.9	28.5	28.7		0.200				
0.775	0.774	0.777	0.774	**C31**		33.9	33.9	33.85	33.95		0.050	0.156			
0.783	0.782	0.786	0.781	**C32**		34.3	34.3	34.3	34.3		0.000				
0.761	0.762	0.759	0.763	**C33**		33.2	33.3	32.95	33.4		0.236				
0.75	0.751	0.753	0.766	**C34**		32.65	32.75	32.65	33.55		0.493				
0.695	0.694	0.698	0.693	**C35**		29.9	29.9	29.9	29.9		0.000				
0.76	0.762	0.757	0.761	**C41**		33.15	33.3	32.85	33.3		0.260	0.266			
0.797	0.799	0.794	0.798	**C42**		35	35.15	34.7	35.15		0.260				
0.86	0.861	0.856	0.863	**C43**		38.15	38.25	37.8	38.4		0.312				
0.711	0.712	0.713	0.708	**C44**		30.7	30.8	30.65	30.65		0.087				
0.778	0.775	0.774	0.785	**C45**		34.05	33.95	33.7	34.5		0.409				
1.255	1.226	1.227	1.222	**C51**		57.9	56.5	56.35	56.35		0.087	1.363			
0.74	0.742	0.741	0.737	**C52**		32.15	32.3	32.05	32.1		0.132				
0.685	0.681	0.684	0.89	**C53**		29.4	29.25	29.2	39.75		6.077				
0.82	0.827	0.821	0.812	**C54**		36.15	36.55	36.05	35.85		0.361				
0.724	0.726	0.725	0.719	**C55**		31.35	31.5	31.25	31.2		0.161				

LEVELS OF IRON (μg/g) IN SAMPLES OBTAINED FROM THE EASRERN REGION

code	Fe*					Fe**	Fe1	Fe2	Fe3		stds				
c11	**0.621**	0.616	0.624	0.623		19.75	19.300	19.950	20.000		0.391	0.286		code	av values
c12	**0.546**	0.540	0.548	0.550		16	15.500	16.150	16.350		0.444			C1	19.11
c13	**0.439**	0.434	0.441	0.442		10.65	10.200	10.800	10.950		0.397			c2	14.35
c14	**0.615**	0.619	0.612	0.614		19.45	19.450	19.350	19.550		0.100			c3	22.89
c15	**0.820**	0.824	0.817	0.819		29.7	29.700	29.600	29.800		0.100			c4	25.07
														c5	30.7
c21	**0.575**	0.573	0.576	0.576		17.450	17.150	17.550	17.650		0.265	0.256			
c22	**0.292**	0.295	0.290	0.291		3.300	3.250	3.250	3.400		0.087				
c23	**0.697**	0.699	0.696	0.696		23.550	23.450	23.550	23.650		0.100				
c24	**0.385**	0.380	0.388	0.387		7.950	7.500	8.150	8.200		0.391				
c25	**0.616**	0.610	0.619	0.619		19.500	19.000	19.700	19.800		0.436				
c31	**0.597**	0.600	0.596	0.595		18.550	18.500	18.550	18.600		0.050	0.119			
c32	**0.503**	0.501	0.504	0.504		13.850	13.550	13.950	14.050		0.265				
c33	**0.286**	0.288	0.285	0.285		3.000	2.900	3.000	3.100		0.100				
c34	**1.057**	1.060	1.056	1.055		41.550	41.500	41.550	41.600		0.050				
c35	**0.976**	0.977	0.977	0.974		37.500	37.350	37.600	37.550		0.132				
c41	**0.613**	0.615	0.612	0.612		19.350	19.250	19.350	19.450		0.100	0.181			
c42	**0.703**	0.700	0.701	0.701		23.850	23.500	23.800	23.900		0.208				
c43	**0.992**	0.995	0.991	0.990		38.300	38.250	38.300	38.350		0.050				
c44	**0.581**	0.588	0.577	0.578		17.750	17.900	17.600	17.750		0.150				
c45	**0.748**	0.743	0.75	0.751		26.100	25.650	26.250	26.400		0.397				
c51	**1.100**	1.000	1.300	1.300		43.700	38.500	53.75	53.85		8.834	1.963			
c52	**0.687**	0.681	0.691	0.689		23.050	22.550	23.3	23.3		0.433				
c53	**0.666**	0.670	0.663	0.665		22.000	22.000	21.9	22.1		0.100				
c54	**0.889**	0.885	0.892	0.89		33.150	32.750	33.35	33.35		0.346				
c55	**0.858**	0.860	0.857	0.857		31.600	31.500	31.6	31.7		0.100				
c01	**0.226**	0.230	0.225	0.223											

LEVELS OF COPPER (µg/g) IN SAMPLES OBTAINED FROM THE CENTRAL REGION

code	Cu1	**Cu***	Cu2	Cu3		Cu**	Cu1	Cu2	Cu3		std	avstd			
c11	0.453	**0.451**	0.445	0.457		12.65	12.85	12.35	13		0.340	0.132		averages for towns.	
c12	0.515	**0.514**	0.516	0.511		15.8	15.95	15.9	15.7		0.132			c1	14.74
c13	0.565	**0.565**	0.566	0.564		18.35	18.45	18.4	18.35		0.050			c2	20.11
c14	0.507	**0.506**	0.506	0.505		15.4	15.55	15.4	15.4		0.087			c3	16.27
c15	0.428	**0.428**	0.429	0.427		11.5	11.6	11.55	11.5		0.050			c4	18.69
														c5	24.62
c21	0.481	**0.483**	0.484	0.484		14.25	14.25	14.3	14.35		0.050	0.300			
c22	0.502	**0.501**	0.502	0.499		15.15	15.3	15.2	15.1		0.100				
c23	0.657	**0.658**	0.658	0.659		23	23.05	23	23.1		0.050				
c24	0.558	**0.559**	0.559	0.600		18.05	18.1	18.05	20.15		1.198				
c25	0.801	**0.800**	0.801	0.798		30.1	30.25	30.15	30.05		0.100				
c31	0.502	**0.503**	0.503	0.504		15.25	15.3	15.25	15.35		0.050	0.127			
c32	0.632	**0.633**	0.633	0.634		21.75	21.8	21.75	21.85		0.050				
c33	0.512	**0.511**	0.512	0.500		15.65	15.8	15.7	15.15		0.350				
c34	0.496	**0.495**	0.496	0.493		14.85	15	14.9	14.8		0.100				
c35	0.476	**0.475**	0.475	0.474		13.85	14	13.85	13.85		0.087				
c41	0.565	**0.564**	0.566	0.565		18.3	18.45	18.4	18.4		0.029	0.032			
c42	0.634	**0.635**	0.635	0.636		21.85	21.9	21.85	21.95		0.050				
c43	0.635	**0.636**	0.637	0.636		21.9	21.95	21.95	21.95		0.000				
c44	0.504	**0.503**	0.505	0.503		15.25	15.4	15.35	15.3		0.050				
c45	0.522	**0.521**	0.523	0.522		16.15	16.3	16.25	16.25		0.029				
c51	1.037	**1.037**	1.035	1.036		41.95	42.05	41.85	41.95		0.100	0.070			
c52	0.634	**0.635**	0.635	0.636		21.85	21.9	21.85	21.95		0.050				
c53	0.579	**0.579**	0.578	0.577		19.05	19.15	19	19		0.087				
c54	0.656	**0.656**	0.655	0.657		22.9	23	22.85	23		0.087				
c55	0.544	**0.545**	0.546	0.546		17.35	17.4	17.4	17.45		0.029				
c01	0.196	**0.198**	0.198	0.197											

LEVELS OF CADMIUM(µg/g) IN SAMPLES OBTAINED FROM THE CENTRAL REGION

code	Cd*					Cd**	Cd1	Cd2	Cd3		stds	av stds		code	av levels
c11	**0.0026**	0.0025	0.0023	0.003		0.03	0.025	0.005	0.06		0.028	0.018		codex	0.1
c12	**0.003**	0.0031	0.0028	0.0031		0.05	0.055	0.03	0.065		0.018			c1	0.035
c13	**0.0028**	0.0026	0.0027	0.0031		0.04	0.03	0.025	0.065		0.022			c2c	0.074
c14	**0.0024**	0.0021	0.0026	0.0025		0.02	0.005	0.02	0.035		0.015			c3	0.032
c15	**0.0027**	0.0026	0.0029	0.0026		0.035	0.03	0.035	0.04		0.005			c4	0.067
														c5	0.03
c21	**0.0035**	0.0038	0.0034	0.0033		0.075	0.09	0.06	0.075		0.015	0.014			
c22	**0.0038**	0.0036	0.0041	0.0037		0.09	0.08	0.095	0.095		0.009				
c23	**0.0034**	0.0035	0.0031	0.0036		0.07	0.075	0.045	0.09		0.023				
c24	**0.0033**	0.003	0.0035	0.0034		0.065	0.05	0.065	0.08		0.015				
c25	**0.003**	0.0029	0.003	0.0031		0.07	0.045	0.055	0.065		0.010				
c31	**0.0021**	0.0021	0.0022	0.002		0.005	0.005	0	0.01		0.005	0.013			
c32	**0.0028**	0.003	0.0027	0.0027		0.04	0.039	0.025	0.045		0.010				
c33	**0.0026**	0.0027	0.0025	0.0026		0.03	0.035	0.015	0.04		0.013				
c34	**0.0024**	0.0027	0.0023	0.0022		0.02	0.035	0.005	0.02		0.015				
c35	**0.0033**	0.0031	0.0032	0.0036		0.065	0.055	0.05	0.09		0.022				
c41	**0.0039**	0.0043	0.0046	0.0043		0.095	0.115	0.12	0.125		0.005	0.013			
c42	**0.0038**	0.0037	0.0036	0.0041		0.09	0.085	0.07	0.115		0.023				
c43	**0.0038**	0.0043	0.0043	0.004		0.09	0.115	0.105	0.11		0.005				
c44	**0.0027**	0.0026	0.0025	0.003		0.035	0.03	0.015	0.06		0.023				
c45	**0.0025**	0.0028	0.0027	0.002		0.025	0.04	0.025	0.03		0.008				
c51	**0.0029**	0.0028	0.0032	0.0027		0.045	0.04	0.05	0.045		0.005	0.009			
c52	**0.0025**	0.0027	0.0026	0.0022		0.025	0.035	0.02	0.02		0.009				
c53	**0.0021**	0.002	0.0022	0.0021		0.005	0	0	0.015		0.009				
c54	**0.0025**	0.0028	0.0024	0.0023		0.025	0.04	0.01	0.025		0.015				
c55	**0.003**	0.0028	0.0032	0.003		0.05	0.04	0.05	0.06		0.010				
c01	**0.002**	0.002	0.0022	0.0018		0	0	0	0		0.000				

LEVELS OF LEAD (µg/g) IN SAMPLES FROM THE CENTRAL REGION

code	**Pb***					Pb**					stds	av std		code	value
c11	**0.119**	0.121	0.118	0.118		0.05	0.05	0.05	0.05		0	2.884E-18		c1	0.0403
c12	**0.024**	0.026	0.023	0.023		0.0025	0.0025	0.0025	0.0025		1E-18			c2	0.0543
c13	**0.158**	0.16	0.157	0.157		0.0695	0.0695	0.0695	0.0695		0			c3	0.0371
c14	**0.112**	0.114	0.111	0.111		0.0465	0.0465	0.0465	0.0465		8E-18			c4	0.021
c15	**0.085**	0.087	0.084	0.084		0.033	0.033	0.033	0.033		5E-18			c5	0.0448
														codex	0.1
c21	**0.119**	0.121	0.118	0.118		0.05	0.05	0.05	0.05		0	4.249E-18			
c22	**0.119**	0.121	0.118	0.118		0.05	0.05	0.05	0.05		0			central.	
C23	**0.208**	0.210	0.207	0.207		0.0945	0.0945	0.0945	0.0945		2E-17				
c24	**0.063**	0.065	0.062	0.062		0.022	0.022	0.022	0.022		4E-18				
c25	**0.129**	0.131	0.128	0.128		0.055	0.055	0.055	0.055		0				
c31	**0.155**	1.056	1.053	1.053		0.068	0.5175	0.5175	0.5175		1E-16	2.489E-17			
c32	**0.102**	0.104	0.101	0.101		0.0415	0.0415	0.0415	0.0415		5E-18				
c33	**0.045**	0.047	0.044	0.044		0.013	0.013	0.013	0.013		0				
c34	**0.023**	0.025	0.022	0.022		0.002	0.002	0.002	0.002		0				
c35	**0.141**	0.143	0.14	0.14		0.061	0.061	0.061	0.061		8E-18				
c41	**0.074**	0.076	0.073	0.073		0.0275	0.0275	0.0275	0.0275		0	0.0369504			
c42	**0.071**	0.073	0.710	0.710		0.026	0.026	0.346	0.346		0.1848				
c43	**0.029**	0.031	0.028	0.028		0.005	0.005	0.005	0.005		1E-18				
c44	**0.108**	0.110	0.107	0.107		0.0445	0.0445	0.0445	0.0445		8E-18				
c45	**0.023**	0.025	0.022	0.022		0.002	0.002	0.002	0.002		0				
c51	**0.181**	0.183	0.180	0.180		0.081	0.081	0.081	0.081		0	3.824E-18			
c52	**0.035**	0.037	0.034	0.034		0.008	0.008	0.008	0.008		2E-18				
c53	**0.205**	0.207	0.204	0.204		0.093	0.093	0.093	0.093		2E-17				
c54	**0.095**	0.097	0.094	0.094		0.038	0.038	0.038	0.038		0				
c55	**0.027**	0.029	0.026	0.026		0.004	0.004	0.004	0.004		0				
c01	**0.019**	0.021	0.018	0.018		0	0	0	0		0				

TREATED RESULTS

Table 4.4: Levels of heavy metals (µg/g) in cocoa beans obtained from selected communities in some Districts of Eastern Region of Ghana

SAMPLES FROM ASAMANKESSE COCOBOD FARMS							
CODE		Cd	Cu	Fe	Mn	Pb	Zn
E11	Kojo Aggrey	0.065±0.000	5.250±0.000	21.400±0.000	4.450±0.050	0.0235±0.001	24.050±0.115
E12	Joseph Opoku	0.040±0.015	8.000±0.150	13.700±0.087	5.350±0.066	0.007±0.001	39.200±0.029
E13	Gladys Osain	0.055±0.003	5.350±0.000	38.300±0.000	6.550±0.132	0.037±0.001	49.600±0.260
E14	Emmanuel Oppong	0.085±0.010	22.700±0.150	14.350±0.150	8.950±0.150	0.0165±0.001	38.800±0.260
E15	Yaw Odaie	0.020±0.015	7.900±0.176	48.700±0.132	8.200±0.100	0.091±0.001	32.800±0.173
E16	Doo Abraham	0.015±0.015	15.250±0.000	18.750±0.050	9.200±0.087	0.075±0.001	37.200±0.144
SAMPLES FROM AKROSO							
CODE		Cd	Cu	Fe	Mn	Pb	Zn
E21		0.020±0.015	6.450±0.000	0.500±0.050	11.300±0.100	0.010±0.001	26.900±0.260
E22		0.090±0.000	11.150±0.000	3.650±0.115	12.250±0.000	0.043±0.008	32.600±0.260
E23		0.065±0.015	16.800±0.150	10.150±0.104	13.300±0.000	0.064±0.001	33.350±0.029
E24		0.030±0.015	11.100±0.000	24.200±0.104	11.300±0.100	0.009±0.001	35.800±0.289
E25		0.040±0.015	12.700±0.150	160.600±0.087	9.100±0.132	0.032±0.001	37.150±0.260
SAMPLES FROM NKAWKAW							
CODE		Cd	Cu	Fe	Mn	Pb	Zn
E31		0.010±0.006	18.200±0.000	22.800±0.087	16.800±0.132	0.080±0.001	39.000±0.173
E32		0.085±0.005	7.500±0.150	57.300±0.173	6.800±0.076	0.078±0.001	37.450±0.289
E33		0.040±0.000	18.300±0.000	4.850±0.173	9.500±0.087	0.081±0.001	39.500±0.087
E34		0.025±0.006	16.850±0.150	38.950±0.173	8.850±0.087	0.055±0.001	36.550±0.087
E35		0.085±0.004	7.350±2.469	51.450±0.150	7.050±0.050	0.057±0.001	36.200±0.050
SAMPLES FROM KWAHU PRASO							
CODE		Cd	Cu	Fe	Mn	Pb	
E41		0.018±0.009	20.000±0.150	27.100±0.087	6.800± 0.150	0.022±0.001	38.800±0.150
E42		0.085±0.001	9.200±0.000	55.200±0.150	7.450±0.132	0.095±0.001	37.500±0.132
E43		0.015±0.001	15.400±0.000	13.250±0.173	12.850±0.100	0.053±0.001	34.150±0.150
E44		0.021±0.001	21.100±0.000	18.650±0.150	11.750±0.100	0.089±0.001	38.750±0.100
E45		0.025±0.001	11.400±0.150	57.300±0.000	52.350±0.100	0.019±0.001	50.750±0.100
SAMPLES FROM ADUKROM							
CODE		Cd	Cu	Fe	Mn	Pb	Zn
E51		0.035±0.000	21.950±0.000	21.650±0.150	14.500±0.100	0.039±0.001	33.850± 0.100
E52		0.020±0.001	19.100±0.150	41.900±0.173	7.100±0.132	0.036±0.001	36.650±0.132
E53		0.060±0.002	17.800±0.000	39.850±0.087	6.650±0.132	0.039±0.001	35.550±0.132
E54		0.070± 0.003	12.250±0.912	5.850 ± 0.076	7.450±0.132	0.048±0.001	25.700±0.132

Table 4.5: Levels of heavy metals (µg/g) in cocoa beans obtained from selected communities in some Districts of Central Regions of Ghana

SAMPLES FROM DUASO-NTOOM						
CODE	Cd	Cu	Fe	Mn	Pb	Zn
C11	0.030±0.003	12.650±0.340	19.750±0.391	8.550± 0.200	0.050± 0.000	28.200±0.132
C12	0.050±0.002	15.800±0.132	16.000±0.444	12.150±0.265	0.003±0.000	30.200±0.250
C13	0.040±0.002	18.350±0.050	10.650±0.397	18.300±0.265	0.070±0.000	34.000±0.132
C14	0.020±0.002	15.400±0.087	19.450±0.100	15.150±0.346	0.047±0.000	31.550±0.050
C15	0.035±0.005	11.500±0.050	29.700±0.100	11.000±0.229	0.033±0.000	26.050±0.202
SAMPLES FROM ASSIN PRASO						
CODE	Cd	Cu	Fe	Mn	Pb	Zn
C21	0.075±0.002	14.250±0.050	17.450±0.265	12.750±0.180	0.050±0.000	27.650±0.200
C22	0.090±0.001	15.150±0.100	3.300±0.087	11.150±0.173	0.050±0.000	27.550±0.304
C23	0.070±0.0023	23.000±0.050	23.550±0.100	11.150±0.278	0.095±0.000	32.000±0.229
C24	0.065±0.002	18.050±1.198	7.950± 0.391	13.600±0.000	0.022±0.000	32.200±0.265
C25	0.070±0.001	30.100±0.100	19.500±0.436	11.150±0.200	0.055± 0.000	28.700±0.200
SAMPLES FROM TWIFO PRASO						
CODE	Cd	Cu	Fe	Mn	Pb	Zn
C31	0.005±0.005	15.250±0.050	18.550± 0.05	13.950±0.126	0.068±0.000	33.900± 0.05
C32	0.040±0.010	21.750±0.050	13.850±0.265	7.700±0.229	0.042±0.000	34.300±0.000
C33	0.030±0.013	15.650±0.350	3.000± 0.100	11.000±0.300	0.013±0.000	33.200±0.236
C34	0.020±0.015	14.850±0.100	41.550±0.050	7.200±0.100	0.002±0.000	32.650±0.493
C35	0.065±0.022	13.850±0.087	37.500±0.132	6.950 ± 0.260	0.061±0.000	29.900±0.000
SAMPLES FROM BRAKWA						
CODE	Cd	Cu	Fe	Mn	Pb	Zn
C41	0.095± 0.005	18.300±0.029	19.350±0.100	8.600 ± 0.050	0.028±0.000	33.150±0.260
C42	0.090± 0.002	21.850±0.050	23.850±0.208	9.300 ±0.200	0.026±0.000	35.000±0.260
C43	0.090± 0.005	21.900±0.000	38.300±0.050	8.950 ± 0.229	0.005±0.000	38.150±0.312
C44	0.035±0.023	15.250±0.050	17.750±0.150	7.500 ± 0.350	0.045±0.000	30.700±0.087
C45	0.025±0.008	16.150±0.029	26.100±0.397	9.500 ± 0.433	0.002±0.000	34.050±0.409
SAMPLES FROM AGONA SWEDRU						
CODE	Cd	Cd	Fe	Mn	Pb	Zn
C51	0.045± 0.005	41.950±0.100	43.700±8.834	5.400 ± 0.173	0.081±0.000	57.900±0.087
C52	0.025± 0.009	21.850±0.050	23.050±0.346	10.500±0.304	0.008±0.000	32.150±0.132
C53	0.005± 0.009	19.050±0.087	22.000±0.100	13.550±0.000	0.093±0.000	29.400±6.077
C54	0.025± 0.015	22.900±0.087	33.150±0.346	6.700 ± 0.250	0.038±0.000	36.150±0.361
C55	0.050± 0.010	17.350±0.029	31.600±0.100	7.200 ± 0.361	0.004±0.000	31.350±0.161

APPENDIX B: RESULTS FROM PROXIMATE ANALYSES

PROXIMATE RESULT OF SAMPLES OBTAINED FROM COCOBOD FARMS AT ASSAMANKESE IN THE WEST AKIM DISTRICT OF THE EASTERN REGION

ASH													
SAMPLE CODES	**Wt of crucible (g)**	**Wt of crucible + sample (g)**	**Wt of crucible + dry sample (g)**	**Wt of sample taken (g)**	**Wt of moisture (g)**	**% ASH**	**Average %ash**	**Age of sample (yrs)**		code	average	age(yrs)	stds
										e16	3.575	12	0.08
E15	21.131	23.197	21.213	2.067	0.083	4	***4.03***	***27(1984)***		e12	3.665	13	0.08
E15	20.230	22.290	_	2.060	0.084	4.06		***27(1984)***		e11	4.105	22	0.08
E13	19.732	21.770	19.807	2.038	0.075	3.7	***3.75***	***39(1972)***		e15	4.030	27	0.04
E13	18.499	20.524	_	2.025	0.078	3.8		***39(1972)***		e13	3.750	39	0.07
E16	18.166	20.199	18.237	2.033	0.072	3.52	***3.58***	***12(1999)***		e14	3.190	_	0.08
E16	18.248	20.278	_	2.029	0.074	3.63		***12(1999)***					
E11	18.723	20.768	18.805	2.046	0.083	4.05	***4.11***	***22(1989)***					
E11	18.729	20.767	_	2.039	0.085	4.16		***22(1989)***					
E12	19.677	21.708	19.750	2.031	0.073	3.61	***3.67***	***13((1988)***					
E12	19.724	21.753	_	2.029	0.076	3.72		***13(1988)***					
E14	19.554	21.612	19.618	2.058	0.064	3.13	***3.19***	_					
E14	19.486	21.535	_	2.049	0.067	3.25		_					

MOISTURE DETERMINATION

sample	Wt of crucible (g)	Wt of crucible + sample (g)	Wt of crucible + dry sample (g)	Wt of sample taken (g)	Wt of moisture (g)	% moisture	Average moisture value	Age of sample (yrs)		stds code	stds values	age(yrs)	% moisture
E15	43.646	45.671	45.596	2.025	0.075	3.7	***3.51***	***27(1984)***		e15	0.269	27	3.51
E15	43.284	45.318	45.250	2.034	0.068	3.32		***27(1984)***		e13	0.049	39	2.99
E13	38.721	40.803	40.741	2.082	0.062	2.95	***2.99***	***39(1972)***		e14	0.212	_	2.58
E13	39.012	41.090	41.027	2.078	0.063	3.02		***39(1972)***		e12	0.339	13	3.4
E16	21.798	23.848	23.760	2.050	0.088	4.29	***4.26***	***12(1999)***		e16	0.042	12	4.26
E16	21.861	23.911	23.825	2.050	0.087	4.23		***12(1999)***		e11	0.071	22	5.14
E11	23.729	25.772	25.668	2.043	0.104	5.09	***5.14***	***22(1989)***					
E11	22.9214	24.961	24.855	2.039	0.106	5.19		***22(1989)***					
E12	48.849	50.982	50.915	2.134	0.068	3.16	***3.4***	***13((1988)***					
E12	46.779	44.130	48.802	2.100	0.077	3.64		***13(1988)***					
E14	42.078	44.109	44.074	2.053	0.056	2.73	***2.58***	_					
E14	42.098	44.158	44.109	2.060	0.050	2.43		_					

FAT

SAMPLE	Wt of flask	Wt of flask + fat	Wt of sample taken	Wt of fat	% Fat	*Average % fat*	*Age of sample*
E15	118.2320	118.9680	2.0213	0.7360	36.41	***36. 625***	***27(1984)***
E15	119.2410	119.9830	2.0143	0.7420	36.84		***27(1984)***
E13	123.3280	124.0820	2.0439	0.7540	36.89	***36. 85***	***39(1972)***
E13	124.2480	124.9970	2.0348	0.7490	36.81		***39(1972)***
E16	121.5460	122.2880	2.0192	0.7420	36.75	***36.63***	***12(1999)***
E16	122.4840	123.2220	2.0214	0.7380	36.51		***12(1999)***
E11	183.8900	184.5830	2.0411	0.6930	33.95	***33.93***	***22(1989)***
E11	146.8430	147.5320	2.0321	0.6890	33.91		***22(1989)***
E12	118.2020	118.9930	2.0570	0.7910	38.45	***38.415***	***23((1988)***
E12	119.3040	120.0900	2.0481	0.7860	38.38		***23(1988)***
E14	123.2930	124.0940	2.0430	0.8010	39.21	***39.215***	_
E14	122.4860	123.2850	2.0374	0.7990	39.22		_

CRUDE FIBRE

SAMPLE	Wt of crucible + asbestos + fibre (g)	Wt of crucible + asbestos (g)	Wt of sample taken	Wt of fibre	% fibre	*Average % fibre*	*Age of sample*
E15	18.2461	18.1938	2.0213	0.0523	2.59	***2.62***	***27(1984)***
E15	18.2884	18.2351	2.0142	0.0533	2.65		***27(1984)***
E13	19.2441	19.1932	2.0439	0.0509	2.49	***2.52***	***39(1972)***
E13	20.2341	20.1831	2.0348	0.0510	2.55		***39(1972)***
E16	22.4231	22.3703	2.0192	0.0528	2.61	***2.635***	***12(1999)***
E16	22.4112	22.3574	2.0214	0.0538	2.66		***12(1999)***
E11	21.3641	21.3110	2.0411	0.0531	2.60	***2.63***	***22(1989)***
E11	31.4882	21.4341	2.0321	0.0541	2.66		***22(1989)***
E12	20.4849	20.4307	2.0570	0.0542	2.63	***2.665***	***13((1988)***
E12	20.5641	20.5089	2.0481	0.0552	2.70		***13(1988)***
E14	20.8641	20.8096	2.0430	0.0545	2.67	***2.695***	_
E14	22.8486	22.7931	2.0374	0.0555	2.72		_

PROTEIN

SAMPLE	INITIAL READING (cm^3)	FINAL READING (CM^3)	TITRE VALUE (CM^3)	AVERAGE TITRE (CM^3)	WT OF SAMPLE TAKEN	*% PROTEIN*	*AGE OF SAMPLE*
E15	0.00	3.45	3.45		2.0346	***14.42***	***27(1984)***
E15	3.45	7.00	3.55	3.50			***27(1984)***
E13	7.00	10.50	3.50		2.0358	***14.19***	***39(1972)***
E13	10.50	13.90	3.40	3.45			***39(1972)***
E16	13.90	17.25	3.35		2.0417	***13.94***	***12(1999)***
E16	17.25	20.70	3.45	3.40			***12(1999)***
E11	0.00	3.40	3.40		2.0249	***14.05***	***22(1989)***
E11	3.40	6.80	3.40	3.40			***22(1989)***
E12	6.80	10.15	3.35		2.0423	***13.72***	***13((1988)***
E12	10.10	13.50	3.35	3.35			***13(1988)***
E14	13.50	15.90	3.40		2.0391	***14.17***	_
E14	16.90	20.40	3.50	3.45			_

CARBOHYDRATE DETERMINATION

SAMPLE	AGE	% CARBOHYDRATE
Kojo Aggrey (E11)	22	40.175
Joseph Opoku(E12)	13	38.125
Gladys Osain(E13)	39	39.705
Emmanuel Oppong(E14)	_	38.150
Yaw Odaie(E15)	27	38.795
Doo Abraham(E16)	12	39.710

Zn(µg/g)	%MOISTURE	%PROTEIN	%FAT	% FIBRE	% ASH	% CARBOHYDRADTE
24.040	5.140	14.020	33.930	2.630	4.105	40.175
32.800	3.510	14.420	36.625	2.620	4.03	38.795
37.200	4.260	13.190	36.630	2.635	3.575	39.710
38.800	2.580	14.170	39.215	2.695	3.190	38.150
39.200	3.400	13.720	38.425	2.665	3.665	38.125
49.600	2.985	14.190	36.850	2.520	3.750	39.705

Pb	%MOISTURE	%PROTEIN	%FAT	% FIBRE	% ASH	% CARBOHYDRADTE
0.007	3.400	13.720	38.425	2.665	3.665	38.125
0.0165	2.580	14.170	39.215	2.695	3.190	38.150
0.0235	5.140	14.020	33.930	2.630	4.105	40.175
0.037	2.985	14.190	36.850	2.520	3.750	39.705
0.075	4.260	13.190	36.630	2.635	3.575	39.710
0.0905	3.510	14.420	36.625	2.620	4.030	38.795

APPENDIX C: RESULTS FROM NARTEY AND HIS TEAMS' WORK

Table 2.1 Mean Soil pH values

Sample location	Soil type	pH values
Sefwi Asawinso/Nkatieso	**NS**	**6.45**
	FS	**5.90**
Wassa Akropong	**NS**	**4.21**
	FS	**3.87**
Bogoso	**NS**	**5.43**
	FS	**5.01**

NS: Natural soil

FS: Fertilizer amended soil

Table 2.2 : mean values of heavy metal levels (µg/g) in natural soils (NS) and fertilizer amended soils (FS)

Sampling town	Soil type	Cu	Mn	Ni	Cd	Cr	Pb	Zn	Fe
Sefwi A/N	NS	8.14±0.01	233.40±9.20	20.60±1.30	ND	5.25±4.80	2.38±0.01	14.50±5.50	8600.00±1000
	FS	11.30±3.60	287.00±61.90	29.70±4.40	ND	8.00±7.00	2.60±0.30	14.40±0.60	7890.00±1880
Wassa Akropong	NS	2.01±0.47	28.80±2.03	5.71±0.06	ND	12.80±2.63	1.12±0.16	2.01±0.25	1659.80±440
	FS	2.82±0.22	14.10±2.90	7.03±1.62	ND	19.60±0.40	1.52±0.55	1.99±0.05	2500.00±230
Bogoso	NS	2.77±0.35	46.80±14.40	5.99±0.44	ND	13.60±0.57	1.32±0.41	2.43±0.83	2410.00±180
	FS	3.25±0.53	57.40±8.24	6.27±1.05	ND	13.00±1.20	1.76±0.36	2.76±0.17	2052.00±18

Sourced: (Nartey et al, 2012)

Table 2.3: Mean values of heavy metals levels in cocoa nibs of cocoa from natural soils (NS) and fertilizer amended soils (FS) (µg/g)

Sampling town	Soil type	Cu	Mn	Ni	Cd	Cr	Pb	Zn	Fe
Sefwi A/N	NS	19.15±5.59	25.30±9.76	0.25±0.13	0.13±0.01	ND	0.05±0.07	33.60±1.27	28.75±7.28
	FS	17.80±3.11	13.05±2.05	0.18±0.01	0.41±0.31	ND	0.07±0.04	38.96±7.14	36.75±2.76
Wassa Akropong	NS	11.70±2.59	26.33±3.71	0.38±0.05	0.43±0.26	ND	0.07±0.05	43.97±1.39	38.50±10.41
	FS	15.73±5.43	33.60±7.89	0.27±0.07	0.71±0.13	ND	0.16±0.02	47.17±9.63	38.73±10.80
Bogoso	NS	16.25±3.24	25.60±5.52	0.32±0.04	0.58±0.25	ND	0.07±0.14	44.35±1.06	29.33±5.67
	FS	16.95±2.05	24.75±6.57	0.32±0.12	0.54±0.12	ND	0.07±0.04	43.65±1.91	28.20±5.87

Sourced: (Nartey et al, 2012)