PESTICIDE USE AND PESTICIDE RESIDUES IN DRINKING WATER, SOIL AND COCOA BEANS IN THE DORMAA WEST DISTRICT OF GHANA

BY

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DECLARATION

I hereby declare that except for references of other people's work which have been cited and duly acknowledge, this work is the result of my own research and initiative conducted under supervision, and that this thesis has neither in whole nor in part been presented for an award of a degree elsewhere.

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ABSTRACT

Pesticide residue levels in drinking water, soils and cocoa beans were assessed in four cocoa growing communities in the Dormaa West District of Ghana to assess the levels of pesticides contamination. In all 127 samples were collected between December 2014 and February 2015 from sixteen (16) selected cocoa farms and six (6) selected control sites. The samples were extracted and analyzed for organochlorine and synthetic pyrethroids, and organophosphate pesticide residues using the Gas chromatography equipped with electron capture detector (ECD) and pulse flame photometric detector (PFPD), respectively. Some water and soil physico-chemical properties were also determined to evaluate the quality of drinking water and soils using standard procedures. Two hundred and forty (240) cocoa farmers were randomly selected and interviewed using a structured questionnaire. Information on the types, sources, methods of pesticides application, operational habits and common health related issues with pesticides usage were sought. The results obtained showed that samples analyzed from the various sites contained measurable levels of the studied pesticides. The organochlorine pesticide residues found in all the samples were aldrin, dieldrin, lindane, p,p´-DDT, endosulfan-sulfate, alpha-endosulfan, beta-hexachlorocyclohexane, methoxychlor, and heptachlor, with heptachlor (from non-detectable (ND)-0.04 µg/L), dieldrin (ND-0.02 mg/kg) and lindane (0.03-0.05 mg/kg) occurring most frequently in water, soil and cocoa beans, respectively. The organochlorine residue concentrations ranged from ND-0.05 µg/L, ND-0.05 mg/kg and ND-0.06 mg/kg for water, soil and cocoa beans, respectively. In addition, the organophosphate pesticide residues recorded in the samples analyzed were diazinon, chlorpyrifos, pirimiphos-methyl and profenofos, with chlorpyrifos occurring most frequently in water, soil and cocoa beans at respective concentration range of ND-0.06 µg/L, ND-0.04 mg/kg and ND-0.42 mg/kg. The synthetic pyrethroids pesticide residues recorded were fenvalerate, deltamethrin, cypermethrin, bifenthrin, permethrin, lambda-cyhalothrin, allethrin and cyfluthrin, with allethrin (ND-0.05 µg/L), lambda-cyhalothrin (ND-0.03 mg/kg) and cypermethrin (0.02-0.05 mg/kg) occurring most frequently in water, soil and cocoa bean samples, respectively. The synthetic pyrethroids residues concentrations ranged from ND-0.07 µg/L, ND-0.06 mg/kg and ND-0.06 mg/kg for water, soil and cocoa beans samples respectively. The occurrence of the pesticides indicates a recent or previous use in the study area. The

results of the physico-chemical properties of water sampled were in ranges; temperature (25.9-27.9 ºC), pH (5.18-5.82), EC (98.0-198.0 µS/cm), TDS (46.3-65.5 mg/L), TSS (4.00-70.0 mg/L), Turbidity (2.29-63.6 NTU), NO_3 (2.20-5.90 mg/L), NH_3 (0.18-1.25 mg/L), PO_4^{3-} (0.67-0.77 mg/L), Na^+ (11.8-18.6 mg/L) and K^+ (2.29-4.45 mg/L). The physico-chemical properties of soil were in ranges; pH (7.35-8.49), EC (203-251 µS/cm), % OC (1.38-6.25), % OM (2.38-10.8), % N (1.64-2.13), phosphorous (0.63-2.47 mg/kg), potassium (0.35-0.85 ppm), NH_4^+ (34.8-45.0 mg/L), NO_3 (25.7-40.6 mg/L), % sand (50.8-67.8), % clay (11.7-25.0), and % silt (9.96-24.3). Commonly applied pesticides by cocoa farmers in the study area included; diazinon, chlorprifos-ethyl, acetamiprid, endosulfan, dichlorodiphenyltrichloroethane (DDT), imidacloprid, fenvalerate, permethrin, aldrin, cupric-hyroxide, cuprous-hydroxide, cuprous-oxide, bifenthrin, promecarb, thiamethoxam, metalaxyl cuprous oxide, chlopyrifos, cypermethrin, lambda-cyhalothrin, deltamethrin and cuprous oxide + metalaxyl. Sources of pesticides used by farmers were agrochemical retailers, fellow farmers and the government of Ghana cocoa mass spraying agents. Majority of cocoa farmers' sprayed their farms using the blanket spraying method with few using the spot spraying method. Farmers' exhibited habits such as eating, drinking, smoking, chewing, talking, not wearing protective cloths, using their mouth to remove blockages from sprayer nozzles, stirring pesticides with their bare hands, among others, during pesticides spraying. Most of the farmers experienced symptoms such as watery eyes, headaches, dizziness, skin irritation, cough, chest pain, body weakness, itching eyes, among others, during and after spraying. The results showed high risk exposure of cocoa farmers to toxicity and health hazards of pesticides usage. The physico-chemical parameters recorded in the drinking water sources were within the World Health Organization (WHO) permissible limits for potable water except turbidity, nitrate, ammonia and pH at some sampled sites. Comparing the mean values of pesticide residues found in drinking water, soils and cocoa beans analyzed with the maximum residue limit (MRLs) adopted by the WHO, US EPA and EU, respectively, shows that water, soils and cocoa beans samples from some sampled sites were contaminated and thus could be harmful if the trend is not checked. In view of the damaging effects of pesticide on human health and the environment, regular monitoring and analysis of pesticide residues in the study area is recommended. It is

also recommended that farmers should be educated on the appropriate use of pesticides to avoid health hazards.

DEDICATION

I wish to dedicate this thesis to my mum Dorcas Yeboah who has for years upheld the zeal of educating our family and without whose unique financial and maternal care I would never have come this far. I will also wish to extend this dedication to my siblings Edmond Korang and Beatrice Asantewaa Dartey for their love, care and prayers towards the successful completion of this research.

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LIST OF ABBREVIATIONS

ADI	Acceptable Daily Intake
ADI	Acceptable Daily Intake
ADP	Agricultural Development Programme
ANOVA	Analysis of Variance
ATSDR	Agency for Toxic Substances and Disease Registry
COCOBOD	Ghana Cocoa Board
CODAPEC	Cocoa Diseases and Pest Control Programme
CODEX	Codex Alimentarius Commission
CRIG	Cocoa Research Institute of Ghana
CSSVD	Cocoa swollen shoot virus Disease
DDD	Dichlorodiphenyldichloroethane
DDE	Dichlorodiphenylethane
DDT	Dichlorodiphenyltrichloroethane
EPA	Environmental Protection Agency
EU	European Union
FAO	Food and Agricultural organization
GC	Gas Chromatograph
GC-ECD	Gas Chromatograph with Electron Capture Detector
GC-MS	Gas Chromatograph with Mass Spectrometer
GPS	Global Positioning System
HCH	Hexachlorocyclo Hexane
ICCO	International Cocoa Organization
ISSER	Institute of Statistical, Social and Economic Research
LCB	Licensed cocoa buying companies
LOD	Limit of Detection
MOFA	Ministry of Food and Agriculture
MRL	Maximum Residue Levels

ND	Not Detected
NOAEL	No Observable Adverse Effect Level
OCP	Organochlorine Pesticide
OP	Organophosphate pesticides
SPSS	Statistical Package for the Social Sciences
TDS	Total Dissolved Solids
UV	Ultraviolet
WHO	World Health Organization

CHAPTER ONE

1.0 INTRODUCTION

1.1 Background

Agriculture has been the key player in Ghana's economic growth and development since independence (Mahrizal *et al.*, 2014). In 2013, the sector contributed 21.3% to the country's Gross Domestic Product and made up 20% (US$ 2,709 million) of the total foreign exchange earnings (ISSER, 2014). Additionally, the sector employs about 41.5% of the economically active population in Ghana (Ghana Statistical Service, 2013).

Cocoa (*Theobroma cacao*) is the major agricultural export commodity and the main cash crop in Ghana with over one hundred years of history (Anim-Kwapong and Frimpong, 2004). The crop contributes substantially to the national economy in terms of foreign revenue earnings, employment and domestic incomes (Ayenor *et al.*, 2007; Anang, 2011). In 2013, earnings from cocoa constituted approximately 16.48% (US$ 2,267.3 million) of total agriculture export receipts (ISSER, 2014). It is believed that the cocoa sector in Ghana employs over eight hundred thousand (800,000) smallholder farm families and about 1.5 million hectares of land is used in the cultivation (Anim-Kwapong and Frimpong, 2004; Danso-Abbeam *et al.*, 2014). For these farmers, the sector contributes about 70-100% of their annual household income (Appiah, 2004).

Unfortunately, Ghana's cocoa production has over the years faced major challenges. Among these challenges is the incidence of insect pests and diseases which has been recognized as a major cause of declining yields in cocoa production (Ayenor *et al.*,

2007; Ntiamoah and Afrane, 2008), with adverse consequences for the country's economy. The application of synthetic pesticide has been a measure to control pest and disease in order to increase cocoa yields in Ghana (Dankyi *et al.*, 2014). In 1959 and 1962, the Government of Ghana initiated a nationwide cocoa mass spraying campaign mainly with lindane, heptachlor, DDT, dieldrin and aldrin to control capsids (Antwi-Agyakwa, 2013). Additionally, the Government has, since 2001/2002 cocoa season, instigated a nationwide Cocoa Disease and Pest Control (CODAPEC) programme dubbed 'mass spraying', which provides free spraying on all cocoa farms using recommended synthetic insecticides and fungicides against capsids and blackpod disease, respectively (Dormon *et al.*, 2007; Ntiamoah and Afrane, 2008; Danso-abbeam *et al.*, 2014). However, considering the regular and repeated nationwide application of pesticides under the CODAPEC programme, in addition to individual applications done by cocoa farmers throughout cocoa seasons, there is a concern on the impact of the pesticides on residual levels in soil, cocoa bean and water sources.

Despite the positive roles pesticides play in keeping pest and disease below their economic injury level, their use has often been associated with unintended environmental and human health consequences (Dankyi *et al.*, 2014; Owombo *et al.*, 2014). In most developing countries, these consequence have often been severe due to misuse and overuse of pesticides instigated by ignorance or lack of safety concerns, as well as a general lack of effective regulations on chemical usage (Fianko *et al.*, 2011). The contamination of the natural environment with pesticides has been shown to be of major concern by many researchers because of their toxicity and threat to human, soil, water, animal and plant health (Afful *et al.*, 2010; Fianko *et al.*, 2011). Soil contamination by pesticides is consequently a critical environmental problem as it

poses a significant impact to soil microflora and microfauna, as well as the ecosystem (Bentum *et al.,* 2006; Braschi *et al.,* 2011). These chemicals are also able to infiltrate into surface water as well as groundwater. The presence of pesticides in the soil subsequently enter the human food web through plants and constitute risk to the ecosystem as they tend to bio-accumulate and can be transferred from one food to another causing acute or chronic toxicity in humans after consumption (Ortiz-hernández *et al.,* 2011). In recent years, several human acute and chronic illnesses have been associated with low doses of pesticides exposure (Mostafalou and Abdollahi, 2012; Gill and Garg, 2014). In addition, studies have also shown that a significant amount of applied pesticides ends up in soils, sediments, water, crops, meat, fish and human fluids (Ntow, 2001; Darko and Acquaah, 2007; Darko *et al.,* 2008; Bempah and Donkor, 2011; Bempah *et al.,* 2011; Tutu *et al.,* 2011; Kuranchie-Mensah *et al.,* 2012).

In Ghana, several works (Botchway, 2000; Bentum *et al.,* 2006; Owusu-Ansah *et al.,* 2010; Apau and Dodoo, 2011; Agyen, 2011; Frimpong *et al.,* 2012d; Frimpong *et al.* 2012c), on pesticide residues in the cocoa industry have focused mainly on organochlorines, which are banned for use in crop production, with little information on the residual levels of organophosphates and synthetic pyrethroids which are approved for agricultural purposes. This study, therefore, was carried out in the Dormaa West District (known to be one of the major cocoa growing areas in Brong Ahafo Region) to determine the levels of organophosphates and synthetic pyrethroids, in addition to organochlorines pesticides in water sources, soils and cocoa beans from cocoa farms.

1.2 Problem statement

There has been a significant use of pesticides in Ghana particularly in cocoa production (Dormon *et al.*, 2007; Dankyi *et al.*, 2014). The high usage has been mainly as a result of a government policy of free pesticide spraying on cocoa farms, in an effort to curb declining yields caused by pests and diseases and to prevent the use of unapproved or banned pesticide on cocoa farms. However, the scale of cocoa farming, the frequency, mode of application and intensity of usage, coupled with the indiscriminate use of banned and unapproved pesticides in the cocoa industry may result in large physical volumes of pesticides in the environment. This leads to pollution of natural resources such as water, soil, plant as well as air (Dankyi *et al.*, 2014). Pesticides that get into the environment may persist for a significant time after their application, because of their toxicity, high persistence, long range transport, lipophilic, bio-accumulative nature and non-degradability into non-toxic forms (Bempah *et al.*, 2011; Agbeve *et al.*, 2014).

Pesticides reaching the soil after spraying may affect soil quality by disturbing soil organism such as earthworms, microbes and natural enemies which acts as decomposers (Ntiamoah and Afrane, 2008). This decreases soil microbial biomass by directly killing or influencing activities such as behaviour, reproduction and metabolism of organism which may permanently impair and alter the closely interactive ecosystem (Aktar *et al.*, 2009; Gill and Garg, 2014). These residues also have the potential to cause toxicity to plants, their product and contaminate the food chain when taken up by plant roots and leaves from soils, air and other nutrient solutions. Additionally, pesticides residue in soils has the tendency to pollute groundwater and surface water through losses by leaching and surface runoffs, respectively (Singh and Mandal, 2013; Gill and Garg, 2014). Most cocoa farms in

Ghana are close to active drinking water sources that are, hence, exposed to pesticides pollution as a result of the farming processes and agrochemical applications. Increased accumulation of these chemicals in the food chain may pose serious health hazards when they are not metabolized by the body and accumulate in the soft tissues (Akan *et al.*, 2013; Agbeve *et al.*, 2014). Exposure to pesticides compounds through food and drinking water are reported to affect thyroid function, and cause low sperm count in males, birth defects, increased in testicular cancer, reproductive and immune malfunction, endocrine disruptions, cancers, immunotoxicity, neurobehavioral and developmental disorders (Mesnage *et al.*, 2010; Tanner *et al.*, 2011; Cocco *et al.*, 2013; Gill and Garg, 2014).

This has led to the prescription of tolerance Maximum Residue Limits (MRLs), and Acceptable Daily Intake (ADI) as well as No Observable Adverse Effect Level (NOAEL) for various pesticides in food (including cocoa beans), soil and drinking water, especially by the Codex Alimentarius Commission (CODEX), the World Health Organisation (WHO) (Sosan *et al.*, 2008) and other designated authorities (Bateman, 2009). In view of the strict enforcement of the MRLs harmonization, export of cocoa beans from Ghana in particular to its main partners in Europe and Japan are liable to possible rejections if prohibited substances are found in the product or at levels above the MRLs. The rejection of cocoa beans as a result of high level of prohibited substances will threaten the livelihood of smallholder farmers, thereby worsening unemployment and poverty as well as the foreign income earning of the country.

A study of pesticide concentrations and their distribution in drinking water sources, soils of cocoa farms and cocoa beans in the Dormaa West District, an area in the

Brong Ahafo Region which is known for cocoa production was therefore imperative in order to ascertain whether or not the levels of the pesticides were above the maximum contamination levels. This thesis, sought to assess the levels of pesticide contamination in drinking water, soils and cocoa beans in the study area to assist in a scientific assessment of the impacts of pesticides on public health, agriculture and the environment.

1.3 General objective

The aim of this study was to investigate pesticide residue levels in drinking water, soils and cocoa beans from selected cocoa farms in the Dormaa West District.

1.3.1 Specific objectives

1. To assess the physico-chemical properties of water and soil from the selected cocoa farms.
2. To assess the levels of pesticide residues in drinking water, soils and cocoa beans in the District.
3. To assess the types, the sources and methods of pesticide application by cocoa farmers in the Dormaa West District.
4. To assess the operational habits and common health related issues associated with the usage of pesticides by farmers.

1.4 Hypothesis

Alternate hypothesis (H_1): Drinking water sources, soils and cocoa beans from cocoa farms in the Dormaa West District are contaminated with pesticide residues as a result of pesticide use by farmers.

1.5 Research questions

- What are the physico-chemical properties of the soil and water samples from the study area?
- What are the levels of pesticide residues in soils, cocoa beans and drinking water sources from the study area?
- What are the types, sources and modes of application of pesticides used to control cocoa pest and disease by farmers in the study area?
- What are the operational habits and common health related issues of the usage of pesticides by farmers?

1.6 Justification

The Dormaa West District is generally an agrarian economy (Ghana Statistical Service, 2014). The majority of its inhabitants are predominantly cocoa farmers who use pesticides in the control of pest and diseases, hence, with likely impact on the quality of drinking water sources in and around cocoa farms, soils and cocoa beans produced from the area. In spite of the high usage of agrochemical in the area, little is known on the types of pesticides used and levels of their residue in water sources, soils and cocoa beans from cocoa farms in the District. In view of the public health significance of pesticides residues and the uncertainty that exits regarding the long term effects of low dose exposure to these pesticides to human and the environment, it was relevant to assess their levels in the environment to protect health. It was against this background that this study sought to address this concern and provide data on the types of pesticide used by cocoa framers and levels of their residues in water, soils and cocoa beans from some selected cocoa producing communities of the District to complement the available data on pesticide usage and residue levels in Ghana.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 Cocoa production and its importance to Ghana's Economy

Cocoa production in Ghana is focused nearly exclusively in the forest agro-ecological zones of the country namely; Ashanti Region, Brong-Ahafo Region, Central Region, Eastern Region, Western Region, and Volta Region, where climatic conditions are ideal for its production. Currently, the main cocoa producing region is the Western Region and supplies more than half (56.5%) of the total annual cocoa crop (World Bank Report, 2011).

Production of cocoa in Ghana increased from 340,562 t in 2001/02 to 496,846 t in 2002/03 and over 700,000 t in 2003/04 (Anim-Kwapong and Frimpong, 2004). According to the World Bank Report (2011), cocoa production in Ghana picked up, reaching a peak of 740,000 Mt in the 2005/2006 season. Additionally, production levels increased from an estimated average of 903,646 Mt in 2011 to an estimated average of 1 million Mt in 2012 (COCOBOD, 2012).

In Ghana, the crop occupies a key position in the country's economy in terms of domestic income, source of revenue for the provision of socio-economic, infrastructure and foreign exchange generation. The cocoa sector in Ghana employs about 800,000 smallholder families (i.e. 60% of total agricultural labour), with average farm holdings ranging from 0.4 hectare to 4.0 hectare (Appiah, 2004; Anim-Kwapong and Frimpong, 2004). For these smallholder farmers, cocoa contributes about 70-100% of their annual household incomes. In addition, other stakeholders like chemical companies, input distributors and licensed cocoa buying companies (LCB's)

also depend largely on cocoa for markets for their products, employment and income (Asamoah and Baah, 2003; Anim-Kwapong and Frimpong, 2004)

Sales of cocoa beans have been one of the major foreign exchange earners to Ghana throughout the years. Cocoa contributed more than 1 billion dollars in foreign exchange receipt in 2006, representing 27% of total export. In 2009-10, Ghana exported more than half a million tons of cocoa beans, generating over US$1.6 billion in foreign exchange. Additionally, the cocoa industry contributed approximately 16.48% (US$ 2,267.3 million) of total agriculture export receipts in 2013 (ISSER, 2014). Due to the importance of cocoa to the economy, the Government of Ghana has prioritized cocoa as a commodity crop and aims to increase its production (Frimpong *et al.*, 2007). To this end, the government has over the years been implementing policies aimed at reforming the cocoa sector in an attempt to boost production.

2.2 Cocoa Pests and Diseases in Ghana

The cocoa tree and its pod can be attacked by different species of insect pests, fungal diseases and rodents. The major insect pests and diseases of cocoa in Ghana are the mirids (Capsids) locally known as '*akate*', the *Phytophthora* pod rot, commonly called 'black pod' and the swollen shoot virus, also known locally as '*cocoa sasabro*' (Ayenor *et al.*, 2007). Lesser constraints are imposed by organisms, such as termites, mealy bugs (*planococcus and stictococcus species*), stem borers, pod borers/feeders, parasitic mistletoes, leaf defoliators, nematode parasites (*meliodogyne*), etc. (Padi *et al.*, 2002; Danso-Abbeam *et al.*, 2014).

2.3 Use of pesticides to control cocoa pests and diseases in Ghana

Since the 1950's, the main methods of control recommended by Cocoa Research Institute of Ghana (CRIG) for cocoa pests and diseases has been the application of

chemical pesticides (Owusu-Manu, 2001; Sarfo, 2013). In the early 1950s, excellent mirid control was achieved with dichlorodiphenyltrichloroethane (DDT) (as Arkotine) applied to resting sites of the insects as stem paint (Antwi-Agyakwa, 2013). However, the discovery of lindane as gamma BHC (Gammalin 20) and the introduction of application equipment by industry, revolutionized mirid control in the 1950's (Bentum *et al.,* 2006). Between 1959 and 1962, the Government of Ghana through a cocoa extension spraying scheme, sprayed cocoa farms for farmers free of charge (mainly with lindane, heptachlor, DDT, dieldrin and aldrin (trade name Aldrex 40) pesticide to control capsids occurring in Ghana (Adjinah and Opoku, 2010; Frimpong *et al.*, 2012d).

According to Antwi-Agyakwa (2013), in the 1970s DDT and other organochlorines were banned from usage in the production of cocoa due to their high persistence and the enormous residual effect they had on the soil and non-target organisms. This period saw the screening of a number of carbamates, organophosphates and synthetic pyrethroids leading to the recommendation of propoxur (Unden 200 EC) as an alternative to lindane in cocoa production in Ghana. In the late 1990s, imidacloprid (Confidor 200SL) was introduced to gradually replace lindane and propoxur as evidence began to emerge that resistance was being built against them. In addition, a cocktail of pirimiphos-methyl and bifenthrin as Axtellic Talstar and Promecarb-carbamult insecticides were introduced alongside Confidor, but carbamult was later banned from use on cocoa (Antwi-Agyakwa, 2013). Afterwards, pest and disease control was left to cocoa farmers who bought their own pesticides and equipment. Pesticides such as nicotine, dimethrin, malathion, dioxocarb, cypermethrin, copper sulphate, kokotine, apeco, perenox, didimac 25, basudin, brestan, among others were

being used to control insect pest and disease on cocoa in Ghana (Owusu-Ansah *et al.*, 2010; Frimpong *et al.*, 2012d; Sarfo, 2013).

In order to regulate pesticides usage among cocoa farmers and to increase cocoa production, the Ghana Government since 2001/2002 cocoa season, has instigated a nationwide Cocoa Disease and Pest Control (CODAPEC) programme, dubbed 'mass spraying'. This provides free spraying on all cocoa farms in Ghana using recommended synthetic insecticides and fungicides against capsids and blackpod disease, respectively (Dormon *et al.*, 2007; Adjinah and Opoku, 2010). Eight fungicide types, Ridomil Gold 66 plus WP (Cuprous oxide + mefenoxam), Metalm 72 plus WP (Cuprous oxide + metalaxyl), Nordox 75 WG (Cuprous oxide), Funguran-OH WP (Cupric Hydroxide), Champion WP (Cupric hydroxide) and Kocide 2000 WP (Cupric Hydroxide), Fungikill WP (Cupric hydroxide + metalaxyl) and Agro-Comet WP (Cuprous oxide + metalaxyl) were recommended for spraying against the black pod disease (Adjinah and Opoku, 2010). Similarly, three insecticide types, Confidor (Imidacloprid), Akate Master (Bifenthrin) and Actara (Thiamethoxam) were recommended for use against mirids (Adjinah and Opoku, 2010). Nonetheless, some farmers use the approved pesticides in addition to unapproved pesticides for cocoa production in Ghana.

2.4 Fate processes of pesticides in the Environment

Pesticide introduced into the environment by application, a disposal or a spill, is influenced by many processes (Tiryaki and Temur, 2010). These processes determine a pesticide's persistence, movement, if any and its ultimate fate. The fate processes can have both positive and negative influences on pesticide's effectiveness or its impact on the environment. They can move a pesticide to the target area or destroy its

potentially harmful residues. Sometimes they can be detrimental, leading to reduced control of a target pest, injury of non-target plants and animals and environmental damage (Duttweiler and Malakhov, 1977; Arnold and Briggs, 1990; Waite *et al.*, 2002). Of particular concern today is the movement of pesticides into ground water and increased accumulation in the food chain. However, different soil characteristics (pH, clay, sand, organic matter, etc.), pesticides characteristics (water solubility, tendency to adsorb to the soil, persistence, its resistance to being broken-down over time, etc.), climatic factors, application methods and different handling practices of pesticides for instance can promote or prevent each process (Braschi *et al.*, 2011). An understanding of the fate processes ensures that applications are not only effective but are also environmentally safe. Fate processes of pesticides in the environment could be grouped into four major types: (I) adsorption, where pesticides are bound with soil; (II) degradation, i.e. pesticides break down, (III) transfer processes, i.e. pesticides are moved away from an application area, and (IV) Absorption, i.e. pesticides taken up by plants and animals. These physical and chemical properties of pesticides determine their environmental risk.

2.4.1 Adsorption

Pesticides and other organic molecules in the soil can be adsorbed by soil particles. Pesticides adsorption is the adhesion or attraction of pesticides to soil particles similar to iron filings or paper clips sticking to a magnet (Sangchan, 2012). The degree of adsorption between the soil and pesticides influences the bioactivity, leachability, and degradability of these chemicals in a given environment, and affects their distribution through the soil profile (Fishel, 2003). The amount of adsorption in the soil depends on the type of soil and its holding potential, the soil characteristics (temperature, pH, moisture content, organic matter content, particle size, etc.), the characteristics of the

pesticides (molecular structure, electrical charge, solubility, etc.) and its concentration in the soil water (Dao and Lavy, 1978; Wauchope and Myers, 1985). Soils high in organic matter or clay are more adsorptive than coarse and sandy soils. This is because there are more particle surface area with clay or organic soil (Fishel, 2003; Sangchan, 2012). Additionally, less pesticide is adsorbed onto wet soils than dry soils because water molecules compete with the pesticide for the binding sites. Pesticides strongly adsorbed to soil particles usually remain in the root zone, where they can be absorbed by plants or degrade. Weakly adsorbed pesticides move down through the soil profile with rain or irrigation water contaminating ground and surface water. Adsorption is particularly important because it influences whether other processes are able to affect pesticides; for example, soil microorganisms cannot degrade pesticides while they are adsorbed (Fishel, 2003).

2.4.2 Degradation

Pesticide degradation is the breakdown of pesticides in the environment. Pesticides half-life measures the rate at which degradation occurs. A pesticide with a long half-life is described as persistent. In general, the longer the half-life, the greater the potential for pesticide movement (Tiryaki and Temur, 2010). Pesticide degradation is usually beneficial as pesticide-destroying reactions change most pesticide residues in the environment to non-toxic or harmless compounds (Fishel, 2003). However, degradation is detrimental when a pesticide is destroyed before the target pest has been controlled. Three general types of pesticide degradation are microbial/biological, chemical and photochemical degradation.

Microbial degradation is the breakdown of pesticides by fungi, bacteria and other micro-organisms that use pesticides as a food source (Sangchan, 2012). It is the most

common type of pesticide breakdown. This is a very important process by which soil microbes or aquatic microbes can detoxify chemicals (Solaimalai *et al.,* 2004) However, the formation of a more toxic chemical may result from the microbial degradation process. Chemicals that are highly water soluble can biodegrade, but those with low water solubility usually will not. Most microbial degradation of pesticides occurs in the soil. The rate of microbial degradation in soil is affected by moisture, temperature, aeration, pH and the amount of organic matter. This is because of their direct influence on microbial growth and activity (Sangchan, 2012). A factor that can influence microbial degradation is the frequency of pesticide application. Rapid microbial degradation is more likely when the same pesticide is used repeatedly in a field as repeated applications can stimulate the build-up of organisms that are effective in degrading the chemical (Solaimalai *et al.,* 2004).

Chemical degradation is the breakdown of pesticides by processes that do not involve living organisms. Chemical processes including hydrolysis, oxidation-reduction and ionization are responsible for degradation and transformation of pesticides in soils and water, usually through the presence of excess acidity or alkalinity, and is therefore related to pH (Sangchan, 2012). As soil pH becomes extremely acidic or alkaline, microbial activity usually decreases, but such conditions may result in increased chemical degradation (Fishel, 2003). Among these, hydrolysis, a breakdown process in which the pesticide reacts with water, is stressed as the major process. Hydrolysis is sensitive to temperature and is pH-dependent. Many organophosphate and synthetic pyrethroids pesticides are particularly susceptible to hydrolysis under alkaline conditions. Some are actually broken down within a matter of hours when mixed with alkaline water. The rate of hydrolysis may be slower under acidic to neutral conditions (Fishel, 2003).

Photochemical degradation is the breakdown of pesticides by ultraviolet or visible light, particularly sunlight (Sangchan, 2012). Pesticides on foliage, on soil, in water and even in the air can be destroyed by this process. Factors that influence this kind of degradation include intensity of the sunlight, length of exposure, characteristics of the application site such as soil type, organic matter content, soil pH, sorption to soil, depth of the chemical in soil and water, sensitizers, vegetation cover, application method, and the physical and chemical properties of the formulated pesticide (Fishel, 2003; Solaimalai *et al.*, 2004).

2.4.3 Transfer/Transport

Pesticide transfer is sometimes essential for pest control as some pesticides need to circulate for effective utilization. Too much movement, however, can move a pesticide away from the target pest, leading to reduced pest control, contamination of surface water and groundwater, and injury to non-target species, including humans (Arnold and Briggs, 1990). Pesticides can be transferred through natural processes such as volatilization, runoff, absorption and leaching.

Volatilization is the process through which pesticides are converted from the solid or liquid phase to gas (Sangchan, 2012). Once volatilized, a pesticide can move in air currents away from the treated surface (Osunbitan *et al.*, 2014). Vapour pressure is an important factor in determining pesticide volatility. The higher the vapour pressure, the more volatile the pesticide is. In contrast, a pesticide tightly adsorbed to soil particles is less likely to volatilize (Laprade, 2002), therefore, soil conditions such as texture, organic matter content and moisture can influence pesticide volatilization (Fishel, 2003). Environmental factors such as high temperature, low relative humidity, wet soil and air movement tend to also increase volatilization. Compounds that are

both highly volatile and highly soluble in water may become groundwater contaminants. Chemicals that are highly volatile but not very water soluble are more likely to be lost to the atmosphere, and less likely to leach into groundwater. Volatilization can result in reduced control of the target pest because less pesticide remains at the target site (Fishel, 2003).

Run-off is the movement of water over the land surface or a sloping surface rather than through the soil. Runoff occurs when water application is applied faster than it can infiltrate the soil (Osunbitan *et al.,* 2014). The amount and severity of pesticides in runoff water is a function of site-related factors such as the slope of the land and moisture content of the soil. Climatic factors such as temperature, the amount and timing of rainfall relative to the pesticide application are also of influence (Osunbitan *et al.,* 2014). Other factors to note are the pesticide-water-soil interactions such as the solubility and adsorptivity of the pesticide, the erodibility and the texture of the soil. In general, pesticide losses in runoff are most likely to occur when a heavy or sustained rainfall follows soon after a pesticide is applied (Fishel, 2003). Steep slopes, wet soils and poor vegetative cover all contribute to high levels of run-off. Certain physical and chemical properties of the pesticide, such as how quickly it is absorbed by plants or how tightly it is bound to plant tissue or soil, are also important. Some pesticides are so tightly adsorbed that they will remain attached to particles of soil and organic matter even when these solids are suspended in run-off water (Sangchan, 2012).

Leaching is the downward movement of pesticides in water through the soil rather than over the surface. Pesticide leaching depends in parts on the pesticide's chemical and physical properties (solubility, adsorption, volatility, degradation, dissociation,

evaporation and rainfall) (Kordel and Kleim, 1992). For example, a pesticide held strongly/tightly to soil particles by adsorption is less likely to be leached (Osunbitan *et al.*, 2014). Solubility is another factor that affects the leaching of pesticides. A pesticide that dissolves readily in water is said to be highly soluble and can move with water in the soil. Additionally, the persistence, or longevity, of a pesticide also influences the likelihood of leaching (Kordel and Kleim, 1992). According to Laprade (2002) and Osunbitan *et al.* (2014), a pesticide that is rapidly broken down by a degradation process is less likely to leach because it may remain in the soil only for a short time. However, the longer the compound lasts before break down, the longer it is subject to the forces of leaching. If a pesticide is highly volatile and not very water soluble, it is likely to be lost to the atmosphere, and less will be available for leaching. Soil factors that influence leaching include soil type, soil moisture content and availability, soil pH, texture, organic matter present and microbial community (Fishel, 2003). These factors influence leaching because of their effect on pesticide adsorption (Arnold and Briggs, 1990). Soil permeability (how readily water moves through the soil) is also important. The more permeable a soil is the greater is its potential for pesticide to leach down the soil profile (Laprade, 2002). A sandy soil, for example, is much more permeable than clay. The method and rate of application and the amount and timing of water a treated area receives after application can also influence pesticide leaching. Typically, the closer the time of application to a heavy or sustained rainfall, the greater the likelihood that leaching of some pesticides will occur (Laprade, 2002). Pesticides leaching down the soil profile is of great concern both in relation to the potential for a chemical to move through the soil and contaminate groundwater and pesticide efficiency. A slow transport through soil and subsoil materials may result in an increased content of pesticides in the groundwater. A

certain amount of pesticide leaching may be essential for control of a target pest. Too much leaching, however, can lead to reduce pest control, injury of non-target species and ground water contamination (Osunbitan *et al.*, 2014).

2.4.4 Absorption

Absorption or uptake of pesticides is the movement of pesticides into plants and animals and the storage of the chemical or its degradation product within the tissues of that organism (Tangahu *et al.*, 2011). Absorption of pesticides by target and non-target organisms is influenced by environmental conditions and by the physical and chemical properties of the pesticide and the soil. Once absorbed by plants, pesticides may be broken down or they may remain in the plant until tissue decay or harvest. Pesticide build-up can cause long-term damage or death (Fishel, 2003). It can also build up in the food chain: a process called bio-magnification. Bio-magnification results in much greater exposures in organisms at the top of the food chain. Bio-magnification of persistent pesticides in food chains was one of the reasons for banning organochlorine pesticides such as DDT (Solaimalai *et al.*, 2004). Bioaccumulation and bio-magnification also occur in aquatic systems. Fishes, for example, are affected when their water habitats or food sources are contaminated. The extent of damage to the fish depends not only on the properties of the pesticide but also on the species of fish, its age, size and its position in the food chain (Fishel, 2003).

2.5 Consequence of the use of pesticides

Pesticides which are used for preventing or destroying pests and diseases are having more negative impact on our environment when compared to its desired action. Pesticides are carried by wind to other areas, thereby, causing air pollution. Some

pesticides also cause water pollution while others are persistent organic pollutants which contribute to soil contamination (Deepa *et al.,* 2011).

2.5.1 Soil contamination

A major fraction of the pesticides that is used for agriculture and other purposes accumulates in the soil, whose impact may endure for decades and adversely affect soil conservation (Gill and Garg, 2014). Pesticides enter the soil via spray drift during foliage treatment, wash-off from treated foliage and wrong disposal of left over spray solution, sprayer wash water and containers. Pesticides residue in the soil can be directly toxic to soil arthropods and soil microorganisms. This results in a negative impact on their activities (i.e. behaviour, metabolism, reproduction and decomposition) which permanently impairs and alters the soil microbial diversity and microbial biomass, eventually leading to the disturbance in soil ecosystem and loss of soil fertility (Handa *et al.*, 1999; Sofo *et al.*, 2012; Gill and Garg, 2014). Reinecke and Reinecke (2007) reported that earthworms were influenced detrimentally due to chronic and intermittent exposures to chlorpyrifos and azinphos methyl, respectively.

According to Hussain *et al.* (2009) and Munoz-Leoz *et al.* (2011), pesticides in soils may also adversely affect the soils vital biochemical reactions including nitrogen fixation, nitrification, and ammonification by activating/deactivating specific soil microorganisms and/or enzymes involved in the processes. The insecticides DDT, methyl-parathion and especially pentachlorophenol have been shown to interfere with legume-rhizobium chemical signaling. Reduction of this symbiotic chemical signaling result in reduced nitrogen fixation and thus, reduced crop yields (Rockets, 2007).

Pesticides that reach the soil may also disturb local metabolism or can alter the soil enzymatic activity (Gonod *et al.*, 2006; Floch *et al.*, 2011). Soil, in general, contains

an enzymatic pool which comprises of free enzymes, immobilized extracellular enzymes and enzymes excreted by (or within) microorganisms that are indicators of biological equilibrium including soil fertility and quality (Mayanglambam *et al.*, 2005; Hussain *et al.*, 2009). Degradation of both pesticides and natural substances in soil is catalysed by this enzymatic pool (Floch *et al.*, 2011; Kizilkaya *et al.*, 2012).

Glover-Amengor *et al.* (2008) and Nuertey *et al.* (2007) in their study on the effect of excessive use of pesticides on biomass and microorganisms in oil palm and vegetable agro-ecosystems in Ghana, observed that pesticides inhibit bacterial population resulting in inhibited nitrification and blockage of other soil microorganisms of both organic and inorganic constituents in the soil, hence, decreasing the soil fertility. It was also revealed that pesticide application had a higher effect on fungal population.

2.5.2 Contamination of water

Pesticide residues in water are a major concern as they pose a serious threat to biological communities including humans (Gill and Garg, 2014). According to Carvalho (2006) and Camargo and Alonso (2006), massive use of pesticides has caused serious contamination of aquifers and surface water bodies, decreasing the quality of water for human consumption. Pesticides applied in the environment can get into water bodies (surface and groundwater) via drift during pesticide spraying, by runoff from treated area, by eroding soil, atmospheric fallout, wrong disposal of pesticide waste, accidental spillage or through neglect, washing of spray equipment after spray operation and percolation or leaching through the soil profile (Papendick *et al.*, 1986; Deepa *et al.*, 2011; Singh and Mandal, 2013). Once pesticides enter water bodies, they have a potential to cause harmful effects on human health when consumed, on aquatic organisms, and can cause disruptions of the aquatic ecosystems.

In Italian forests, indiscriminate use of pesticides and its active metabolites has led to the contamination of water bodies possibly affecting the health of aquatic biota fishes and amphibians (Trevisan *et al.,* 1993). Studies by the UK government showed that pesticide concentrations exceeded those allowable for drinking water in some samples of river water and groundwater (Bingham, 2007). Similarly, water samples from rivers in the intensive cocoa growing areas in the Ashanti and Eastern Regions of Ghana have been found to contain lindane and endosulfan (Acquaah, 1997). Also, studies by Darko *et al*. (2008), Kuranchie-Mensah *et al*. (2012) and Gbeddy *et al.* (2015) have reported on the occurrences of organochlorine pesticides in water samples from Lake Bosomtwi, Densu river basin and Volta Lake in Ghana, respectively.

2.5.3 Contamination of air

Pesticides can contribute to air pollution. This occurs when pesticides suspended in the air during and after application as particles are carried by wind to other areas potentially causing contamination (Deepa *et al.,* 2011). The presence of pesticides in air can be caused by a number of factors including spray drift, volatilization from the treated surfaces, through wind erosion of contaminated soil particles, and aerial application of pesticides (Tiryaki and Temur, 2010; Gill and Garg, 2014). Pesticides in air pose a threat to wildlife, the environment (as droplets settle down on soils and water bodies far away from the site of application of the pesticide) and human health when inhaled (Tiryaki and Temur, 2010). According to Armstrong *et al.* (2013), organophosphorus (OP) pesticides were identified from environmental samples of air following agricultural spray applications in California and Washington (USA). Similarly, Adu-Kumi *et al.* (2012) and Hogarh *et al*. (2014) have reported on the occurrence of organochlorine pesticides (OCPs) in air samples from Ghana.

2.5.4 Health effects

Pesticides can enter the human body by direct contact with chemicals, through food especially fruits and vegetables, contaminated water or polluted air (Ye *et al.*, 2013). Both acute and chronic diseases can result from pesticide exposure, as described below.

Acute illness

Acute illness generally appears a short time after contact or exposure to the pesticide. Pesticide drift from agricultural fields, exposure to pesticides during application and intentional or unintentional poisoning, generally leads to the acute illness in humans (Dawson *et al.,* 2010; Lee *et al.*, 2011). An acute illness is generally regarded as an illness that occurs within the few days after exposure, usually less than two weeks. Headaches, body aches, skin irritation, respiratory problems, skin rashes, poor concentration, nausea, fatigue, diarrhoea, vomiting, throat and lung irritation, dizziness, impaired vision, cramps and panic attacks are symptoms that can occur due to acute pesticide poisoning (Pan-Germany, 2012; Gill and Garg, 2014). The severity of the symptoms associated with pesticide poisoning is due to the toxicity of the chemical, mode of action, mode of application, the length/duration and magnitude of exposure, the type of pesticide, dose, timing, and the susceptibility of the exposed individual (Xavier *et al.,* 2004; Lioy, 2006). The Northern Presbyterian Agricultural Services (NPAS) (2012) reported that the most common acute illness experienced by Ghanaian farmers during and after the application of pesticides included irritation, headache, general body weakness, difficulty in breathing and dizziness. Similarly, farmer's field surveys carried out by Clarke *et al.* (1997), Gerken *et al.* (2001), Mensah *et al.* (2004) and Horna *et al*. (2008) in Ghana, identified headache, general weakness, dizziness, body pains, skin irritation, nausea, sneezing, abdominal pains,

vomiting, fever, blurred vision, cough, itchy or watery eyes, stomach ache, breathing difficulties, burning sensations and diarrhoea as acute poisoning symptoms through pesticides application.

Chronic illness

Continued exposure to sub-lethal quantities of pesticides for a prolonged period of time (years to decades), results in chronic illness in humans (Pan-Germany, 2012). Symptoms are not immediately apparent and manifest at a later stage. Farm workers and their families experience the greatest exposure to agricultural pesticides through direct contact with the chemical. However, the general population is also affected especially due to contaminated food and water or pesticides drift from the fields (Deepa *et al.,* 2011; Pan-Germany, 2012). Chronic diseases that are linked to prolonged pesticides exposure by various studies are cancer, including childhood and adult brain cancer, renal cell cancer, lymphocytic leukaemia C (LL) and prostate cancer (Shim *et al.,* 2009; Heck *et al.,* 2010; Xu *et al.,* 2010; Band *et al.,* 2011; Cocco *et al.,* 2013), neurodegenerative diseases including parkinson disease, alzheimer disease (Elbaz *et al.,* 2009; Hayden *et al.,* 2010; Tanner *et al.,* 2011), cardio-vascular disease including artery disease (Andersen *et al.,* 2012), diabetes (Type 2 Diabetes) (Song *et al.,* 2010; Lee *et al.,* 2011), reproductive disorders (Figà-Talamanca, 2006; Harley *et al.,* 2008), birth defects (Winchester *et al.,* 2009; Mesnage *et al.,* 2010), hormonal imbalances including infertility, menstrual disturbance, adrenal gland exhaustions, early menopause and breast pain (Xavier *et al.,* 2004), and respiratory diseases (asthma, chronic obstructive pulmonary disease (COPD)) (Chakraborty *et al.,* 2009; Hoppin *et al.,* 2009; Ye *et al.,* 2013). In Ghana, NPAS (2012) reported that fifteen farmers died from suspected pesticides poising in the Upper East Region in late 2010 and further explained that most of these death resulted from poor storage of

pesticides, which seeped into food stocks. According to Gerken *et al*. (2001) three Ghanaian children died after consuming fruits containing high residues of carbamates in March 1999.

2.6 Impact of pesticide residues in cocoa beans on the cocoa economy in Ghana

The indiscriminate use of pesticides may also have dire consequences for cocoa exports since Ghana's major cocoa beans partners, Japan and the European Union, have expressed concern about the levels of pesticide residues in cocoa beans and its products. In view of this, Japan and the European Union have been evaluating the safety of residues in cocoa beans and establishing maximum residue limits (MRLs) to help ensure that pesticides are not overused and that any residue is safe for human consumption (Bateman, 2009). In view of the strict enforcement of the MRLs harmonization in Japan and Europe over the years, export of cocoa beans and its product from Ghana is therefore likely to face a bleak future if the residual levels in any cocoa beans and its products from Ghana are found liable or exceeds this legislation. According to Sarfo (2013), a 2,000 tonne shipment of cocoa to Japan from Ghana was rejected in 2006, due to the detection of illegal insecticides residues. The rejection of cocoa could reduce foreign earnings, accruing from cocoa exports. Also, this will threaten the livelihood of smallholder farmers by affecting their income, thereby, worsening unemployment and poverty in the areas where cocoa is grown.

2.7 Studies on pesticide residues in cocoa bean, water and cocoa growing soils

Botchway (2000) detected lindane in exportable cocoa beans collected from selected cocoa growing districts in the middle belt of Ghana and the two shipping ports at Tema and Takoradi. The concentration in mg/kg was about 10% of maximum residue level of 0.1 mg/kg permitted by Codex Alimentarious Commission. The results of the

research indicated that Ghana's exportable cocoa beans were of no immediate danger of being rejected by importing countries due to the presence of lindane pesticide residues. In a similar study, Apau and Dodoo (2011) confirmed the presence of lindane residue in cocoa beans in the Central Region of Ghana. The concentration range was 0.06-3.32 mg/kg with a mean residue value of 0.411 mg/kg. The study revealed that the concentrations of lindane in cocoa beans were below FAO/WHO 1998 recommended maximum residue limit of 1 mg/kg. However, Owusu-Ansah *et al.* (2010) detected no concentration of lindane in 20 cocoa pods samples analyzed for lindane residue from five communities within the Twifo- Praso District in the Central Region.

In another study, Daanu (2011) reported pesticides contamination of cocoa beans from Asukese and its environs in the Eastern Region of Ghana. The average pesticides detected were aldrin (0.11 mg/kg), p,p´-DDD (0.01 mg/kg), p,p´-DDE (0.02 mg/kg), p,p´-DDT (0.03 mg/kg), endosulfan-sulphate (0.001 mg/kg), beta-endosulfan (0.0003 mg/kg), alpha-endosulfan (0.01 mg/kg), chlorpyrifos (0.02 mg/kg), dimethoate (0.02 mg/kg), ethophosphos (0.01 mg/kg), fenitrothion (0.08 mg/kg), malathion (0.02 mg/kg), parathion (0.01 mg/kg), profenofos (0.01 mg/kg), fenvalerate (0.06 mg/kg), deltamethrin (0.0003 mg/kg), cypermethrin (0.02 mg/kg) and permethrin (0.01 mg/kg). The result from the study however, revealed that the mean concentrations of aldrin and fenvalerate were above their various EU MRL set for cocoa beans.

Additionally, Boakye (2012) detected pesticides in cocoa beans sampled from the Brong Ahafo and Ashanti regions of Ghana. Chlorpyrifos exhibited the highest concentrations of 10.55 mg/kg for samples from Mim in the Brong Ahafo Region and 9.81 mg/kg for samples from Offinso in the Ashanti Region. The lowest pesticide

concentration of 0.01 mg/kg was recorded for endosulfan I for samples from Sankore in the Ashanti Region and for beta-HCH which had a value of 0.01 mg/kg for samples from Offinso, Apagya, Juaso and New Edubiase. The results of the study revealed that 50% and 45% of the pesticides residues detected in the Brong Ahafo and Ashanti Region, respectively were above their EU allowable limit for cocoa beans.

Similarly, Aikpokpodion *et al.* (2012a) assessed the concentrations of diazinon and endosulfan in cocoa beans obtained from three cocoa ecological zones in Nigeria. The results of the study showed that mean total endosulfan residue in cocoa beans obtained from selected cocoa plantations in Ondo, Cross River and Ogun State were 1.06 mg/kg, 0.99 mg/kg and 1.03 mg/kg respectively. Additionally, the concentration range in mg/kg dry weight for diazinon in cocoa beans from Ondo state was non-detected to 0.17 mg/kg with an average value of 0.12 mg/kg. Furthermore, Aikpokpodion *et al.* (2012b) reported the presence of DDT and its metabolites in Nigerian cocoa beans. The study revealed that the mean total DDT residue in cocoa beans obtained from selected cocoa plantations in Ondo, Cross River and Ogun States were 0.44 mg/kg, 0.99 mg/kg and 0.24 mg/kg, respectively. The study however concluded that the concentrations of DDT in most of the beans were below the European Union maximum residue limit of 0.50 mg/kg set for DDT in cocoa beans.

Frimpong *et al.* (2012d) detected organochlorine pesticide residues in cocoa beans samples collected randomly from two cocoa storage stations located in Tema and Takoradi, cities of Ghana. The concentration values in µg/kg dry weight from the study were: beta-HCH (ND-0.01); lindane (ND-0.02); delta-HCH (ND-0.01); aldrin (ND-0.02); dieldrin (ND-0.04); endrin (ND-0.01); gamma-chlordane (ND-0.02); alpha-endosulfan (ND-0.10); beta-endosulfan (ND-0.10); endosulfan sulphate (ND-

0.10); p,p´-DDT (ND-0.01); p,p´-DDD (ND-0.01) and p,p´-DDE (ND-0.01). The study concluded that none of the detected organochlorine pesticide residues did exceed their various maximum residue limits. In another study, Frimpong *et al.* (2012b) assessed the residue levels of organophosphate pesticides in cocoa beans ready for export from two main cocoa storage warehouses located in Tema and Takoradi cities in Ghana. The results of the study indicated that there were appreciable amounts of pirimiphos-methyl (29.5 µg/kg), dimethoate (22.3µg/kg), malathion (20.6 µg/kg), chlorpyrifos (50.2 µg/kg) and fenitrothion (93.8 µg/kg) in the cocoa bean samples. The findings of the study further revealed that the residue levels of all organophosphate pesticides detected were below both the EU and Japanese maximum residue limits set for cocoa beans, with the exception of methamidophos, chlorpyrifos, malathion and profenofos. It was concluded that the presence of these pesticides in the cocoa beans indicate the extensive use of these organophosphates pesticides in Ghana.

In addition, Frimpong *et al.* (2012a) analyzed dried cocoa beans samples ready for export from two main cocoa storage warehouses located in Tema in the Greater Accra region and Takoradi in the Western region of Ghana for selected synthetic pyrethroids pesticides. The ranges of concentration, reported in µg/kg dry weight were allethrin (ND-28.0), bifenthrin (ND-32.0), fenpropathrin (5.0-47.0), lambda-cyhalothrin (ND-38.0), permethrin (ND-105.0), cyfluthrin (ND-42.0), cypermethrin (ND-58.0), fenvalerate (ND-32.0) and deltamethrin (ND-68.0). They asserted that none of the detected synthetic pyrethroids pesticides' average residue concentrations did exceed the European Union or Japanese Maximum Residue Limits in cocoa beans produced in Ghana. However, allethrin, cypermethrin and fenvalerate average residues concentrations were revealed to be at the borderline of the Japanese MRLs.

Bentum *et al.* (2006) reported that lindane and propoxur pesticide residues were present in soils to which these pesticides had already been applied. The findings revealed the concentrations range of 2.1 to 15.4 mg/kg for lindane and 1.71 to 7.95 mg/kg for propoxur respectively. It was further indicated that both the extracted lindane and propoxur residues correlated negatively with soil pH, cation exchange capacity, moisture content, and organic carbon. Propoxur however was found to correlate positively with the amount of clay in the soil but there was no significant correlation between the amount of clay and the extracted lindane concentration.

Agyen (2011) conducted an investigation into the occurrence and levels of organochlorine pesticide residues in soils and cocoa beans from cocoa farms in Kade. The study identified no organochlorine pesticides (OCPs) in the cocoa beans from Kade but generally, sixteen different pesticide residues were detected in the soil samples. These included the derivatives of HCH, DDT and its metabolites, aldrin, dieldrin, heptachlor, trans-heptachlor epoxide, cis-heptachlor epoxide, trans-nanochlor, and trans-chlordane. The study revealed that the total DDT and total HCH levels in the soils of each sampling site were lower than 200 ng/g stipulated by WHO/FAO. The study further indicated that past agricultural application of OCPs might be the major source of OCP residues in the soils.

In another study, Aiyesanmi and Idowu (2012) assessed the contamination levels of cocoa farm soils by organochlorine pesticides within the Central Senatorial District of Ondo State, Nigeria. Organochlorine compounds detected at varied concentrations included endosulfan I and endosulfan II occurring most frequently with highest concentrations of 350.10 mg/kg and 3.55 mg/kg respectively. Other organochlorine compounds detected were heptachlor, heptachlor epoxide, aldrin, deldrin, isomers of

benzene hexachloride: α-BHC, β-BHC, δ-BHC, and Y-BHC (lindane). The concentrations of the organochlorine pesticides (mg/kg) measured in the soil samples also showed significant correlation ($p < 0.05$) with the total organic matter contents of the soil. In another study, Okoya *et al.* (2013a) in studying the concentration of organochlorine compounds in soils of major cocoa plantations in Ondo State of Nigeria showed that soils of the study area were contaminated by organochlorine compounds (OCCs) in varied degree which ranged from ND to 40.55 ± 1.54 µg/g.

Sosan *et al.* (2008) analyzed domestic water sources for insecticide residues in selected cocoa growing communities of south-western part of Nigeria. It was revealed that the sources of drinking water had been contaminated with diazinon (0.02 mg/kg to 0.13 mg/kg) and propoxur (0.03 mg/kg) in some of the farmers' localities and that the concentration of the insecticides exceeded the acceptable daily intake (ADI) of drinking water set by the World Health Organization (WHO).

Afful *et al.* (2013) investigated levels of synthetic pyrethroids in the Weija Lake water in Ghana. The mean concentration reported in ng/L for lake water were allethrin (0.69), bifenthrin (< limit of detection (LOD)), fenpropathrin (2.88), lambda-cyhalothrin (<LOD), permethrin (0.33), cyfluthrin (1.02), cypermethrin (0.25), fenvalerate (0.86) and deltamethrin (0.40). The study concluded that the concentrations of the detected pyrethroids in the Weija water were far below the maximum residue limits set by European Union (EU) and the Japanese Government.

Another study by Okoya *et al.* (2013b) investigated levels of organochlorine pesticide (OCP) residues in water samples from nearby cocoa plantations in Ondo State, Nigeria. The commonly occurring pesticide residues in water were (range µg/g) cis-chlordane (0.03-6.99), α-endosulfan (0.03-6.99), p,p´-DDE (0.08-19.04) and dieldrin

(not detected-1.51 µg/L). Similarly, Idowu *et al.* (2013) examined the concentration of organochlorine pesticide residue in river water from cocoa producing areas in Ondo central senatorial district, Nigeria. The ranges of OCPs concentration in the water reported in mg/L were dieldrin (ND-0.002), lindane (ND-0.04), α-endosulfan (0.38-6.49), and β-endosulfan (0.001-0.03). The results from the study revealed that the concentration of lindane and dieldrin were above the stated WHO guideline limit values of 0.002 mg/L and 3.00 x 10^{-5} mg/L in drinking water.

Olayinka (2013) investigated the levels of organochlorine pesticides (OCPs) residue in soil, water and cocoa beans obtained from selected cocoa farms in Ilawe-Ekiti, south western part of Nigeria. From the samples collected, the mean OCPs in soil ranged from (0.05-7.34 µg/kg), water (0.003-0.07 µg/L) and cocoa beans (0.02-0.55 µg/kg). The mean concentration in µg/kg of some of the residues quantified in the soil were lindane (0.07), aldrin (0.09), DDT (6.99), that of water in µg/L were aldrin (0.01), lindane (0.05), heptachlor (0.01), DDT (0.03) and that of cocoa beans in µg/kg were lindane (0.07), aldrin (0.08), DDT (0.30). The results of the study concluded that the mean levels of OCPs in all the samples were below the recommended maximum residue levels (MRLS) set by the European Union (EU) Commission.

It can be concluded from the various studies that the most problematic class of pesticide in cocoa growing fields in Ghana has been organochlorine. The detection of organochlorine residues suggests the continuous use of the chemicals in Ghana although their agricultural use has been banned or severely restricted. However, this situation is only true and holds, since, most of the very few available studies to determine pesticide contaminations in the cocoa industry in Ghana have focused much more on the analysis of organochlorine pesticides, with little information on the

residual levels of organophosphorus and synthetic pyrethroids which are approved for agricultural purposes in Ghana (Environmental Protection Agency (EPA), 2009). To fill this knowledge gap, this study seeks to assess the contamination levels of organophosphorus and synthetic pyrethroids, in addition to the already well-known organochlorine pesticide residues in drinking water sources in and around cocoa farms, cocoa growing soils and cocoa beans from the Dormaa West District of Ghana. This information will assist in a scientific assessment of the impacts of pesticides on public health, agriculture and the environment.

2.8 Studies on farmers' pesticide use practices, operational habits and health related issues of pesticide usage

Lawal *et al.* (2005) examined the operational habits and health hazards associated with pesticide usage by cocoa farmers in Nigeria. Prominent operational habits revealed in the study included scooping or stirring pesticides with bare hand, chewing kolanut or something else, drinking, smoking, eating and talking when spraying. The farmers also indicated that they normally experienced redness of eyes, body pains, headache, excessive sweating, sneezing, and breathing difficulty when they apply pesticides. The results also showed that 99.8% of the farmers did not dispose the pesticide containers after use, but rather they kept them for storing palm oil or kerosene or for any other household use. The study further revealed a positive and significant relationship between the number of operational habits of the cocoa farmers and age (r=0.26) and period of farming (r=0.24), while the level of education has a negative, but significant relationship (r=-0.37). There was no significant relationship between the number of operational habits of the cocoa farmers and the number of health hazards experienced. It was however concluded that the training on pesticides

usage must be integrated into extension practice and such training must be based on farmers' age, farming experience and level of education.

In another study, Tijani (2006) investigated pesticides commonly used in cocoa agriculture and dangers associated with their use in Idanre local government area of Ondo state, Nigeria. The results revealed that most of the pesticides commonly used by cocoa farmers were classified as 'highly' or 'moderately' hazardous by the World Health Organization and have been banned or restricted in many economically advanced countries. However, analysis from the study showed that farmers were not taking the necessary precautions to prevent hazards associated with their use. Farmers and farm workers suffered from discomforts ranging from headaches, tiredness, vomiting and nausea to skin problems such as skin burn and itching after using these pesticides.

Sosan and Akingbohungbe (2009) also assessed the occupational insecticide exposure and perception of safety measures among cocoa farmers in South-western Nigeria. It was revealed that farmers used lindane, diazinon, endosulfan, and propoxur for cocoa mirid control. Factors identified to be promoting exposure of farmers to pesticides included, eating and drinking during spraying operations, failure to use protective clothing, improper storage and disposal of insecticides. Varying proportions of the farmers experienced common symptoms associated with exposure hazards. These symptoms were frequent fever, strained breathing, sleeplessness, loss of memory, etc.

Similarly, Ogunjimi and Farinde (2012a) investigated farmers' knowledge level of precautionary measures and operational habits with the associated health problems among farmers in cocoa growing communities of Osun and Edo States, Nigeria. The results showed high risk exposure of cocoa farmers to toxicity and hazards of

agrochemicals used on their cocoa farms. More than 50% of the cocoa farmers in the two states were in the habits of eating, drinking and smoking during spraying. About 65% of cocoa farmers in Osun had no extension contact and training on safe handling of chemicals compared to 97.0% of the farmers in Edo state. Also, majority (60%) of the farmers in the two states claimed that they have health problems with the following symptoms: body itching, cough and difficulty in breathing, which often occurred during and after usage of chemicals.

Owombo *et al.* (2014) investigated the safety options cocoa farmers were aware of as well as the factors influencing their adherence to the safety precautions in Nigeria. The study found out that cocoa farmers were aware of the use of eye glasses, nose mask, mouth cover, protective clothing, protective boot, hand glove as well as washing/bathing after application and disposing off chemical container, but adopted only the protective boot, protective clothing and washing/bathing after application. Farmers' adherence to safety practices in the area was influenced by age, number of extension contact, cocoa income, livestock income as well as level of education.

A study by Yeboah *et al.* (2004) and Mensah *et al.* (2004), revealed that about 82% of farmers in Ghana are illiterates and do not always use any form of standard protective clothing. The results showed that most of the farmers were not aware of long term chemical and physiological effect associated with improper agrochemical handling. About 41.5% of farmers claim they change their cloths before and after pesticide use, however, less than 5% washed these clothing before using them again. It was also revealed that some of the farmers were involved in unhealthy practices (drink from water bodies near their farms and eat without washing their hand with any detergent.) that put them at high risk of being affected by the pesticides.

In a study to assess how much farmers know about the safe handling and use of pesticides and what they perceive to be the hazards around their use in the cocoa belts of the Ashanti and Western regions of Ghana, Zhu (2015) revealed that only 15.6% of the respondents fully protect themselves during spraying operations; others either wore partial protective clothing (38%) or did not wear any protective clothing at all (46.4%), thereby coming into direct contact with pesticides. The study further indicated that over 80% of the respondents re-entered their farms within 3 days of pesticide application; harvest their produce within 7 days, without observing safe harvest interval protocols. It was also revealed that the farmers were aware of and had experienced pesticide hazards such as headache, dizziness, body weakness, itching, burning sensation, catarrh, stomach pain, unconsciousness, itching of eyes and body pains. The study finding showed that most farmers dispose of empty pesticide containers and wash water from sprayers by throwing or disposing them on their farms. It was concluded that farmers were misapplying pesticides by disregarding the potential harmful effects of pesticides on human health and the environment.

A study on farmer's perception and use of pesticides in Ghana by Ntow *et al.* (2006), revealed that various inappropriate practices in the handling and use of pesticides caused possible poisoning symptoms among those farmers who generally did not wear protective clothing. The study however showed that farmers did not necessarily associate hazardous pesticides with better pest control. A study by Antwi-Agyakwa *et al.* (2015) to investigated insecticide use practices in Cocoa production in four Regions (Ashanti, Eastern, Volta and Western) in Ghana showed that farmers used mostly imidacloprid and bifenthrin insecticides and the frequency of application was more than that recommended by Ghana cocoa board (COCOBOD). Among the three recommended insecticides, 43% each of the farmers across the three regions used

either confidor or atemaster whilst the remaining 14% used actara. The number of years' farmers had consistently used a particular insecticide ranged between 5 and 16 years. It was also revealed that whilst some cocoa farmers do not apply insecticides to their farms, others, however, do as many as 11 applications in a year. Most of the insecticides used by farmers in the study regions are classified as class II under WHO Hazard category, and the farmers used very minimal protective clothing during pesticides application. The results of the study indicated the need to intensify education on safe handling and use of pesticides to reduce pesticide abuse, especially by cocoa farmers, in order to sustain effective management of pests and protect farmers, consumers and the environment.

2.9 Programmes undertaken to educate and prevent poor use of pesticides in the Cocoa industry in Ghana

Over the decade, the Government of Ghana (GOG) through the Ghana COCOBOD has been implementing several programs to control and prevent the poor use of pesticides in the cocoa industry, and to reduce their impacts on human health and the environment. Specifically, the Government of Ghana through the Ghana COCOBOD in the year 2001/2002 cocoa season introduced the National Cocoa Diseases and Pests Control programme (CODAPEC), which involved mass spraying of cocoa farms using approved and recommended synthetic insecticides and fungicides against Capsid and Black pod, respectively. This become necessary after the Ghana COCOBOD had identified that most cocoa farmers felt reluctant to maintain their farms to the extent of abandoning them due the high cost of fungicides and insecticides, and that those who maintained their farms used unapproved and/or not recommended pesticides. Another objective of the programme was to train cocoa farmers and technical personnel on the cultural and chemical methods of pests and

diseases control, and also to educate and train local sprayers on safe pesticides usage (Adjinah and Opoku, 2010). According Osei-Boadu (2014), the programme also aimed at educating and training cocoa farmers on the dosage of the various pesticides, dangers of exposure to pesticides, importance of the use of protective clothing, observance of personal hygiene, environmental safety issues, first-aid and techniques of application and handling and disposal of empty containers.

Rutherford (2009), reported that promotional and training activities already underway across the region (including Ghana), include cocoa farmer rallies held in cocoa producing areas specifically to educate farmers on the use of approved and unapproved pesticides, proper handling and use of pesticides, associated residual effects, and environmental and health impacts. As a means of communication favoured by farmers the mass media is being used by Ghana COCOBOD, in particular radio and television broadcasts- including interviews, discussion panels, phone-ins, newspaper advertisements as well as farmer field schools organised by Ghana COCOBOD extension officers to educate famers of the approved pesticides and unapproved pesticides to use on cocoa farms, the environmental and health impacts of the these pesticides, the impacts of pesticides residues, the protective measures required in pesticides application, among others. Clearly communicating the products and active substances approved and recommended for use on cocoa, as well as those that are prohibited or should be avoided, is a fundamental requirement of all communication activities of Ghana COCOBOD. These are also being supported by the production and widespread distribution of illustrated advisory and technical leaflets, posters, manuals and other materials – suitable for direct consultation by farmers and other stakeholders and for use by advisory and training organisations from Ghana COCOBOD.

According to Rutherford (2009), a number of multi-stakeholder workshops, attended by farmers, cocoa traders, chemical retailers, scientists, NGOs and policy makers among others, have been held by Ghana COCOBOD with it partners to facilitate open discussions and the planning and initiation of national and local activities. These include: prohibiting or restricting the import, manufacture and marketing of particular chemical products; withdrawal and buy-back of product containing prohibited and problematic substances, some of which are in widespread circulation; amending and updating registers of approved and prohibited products and substances, and creating mechanisms for promoting this information more effectively; introducing and improving mechanisms for monitoring agrochemicals supply and use, by establishing and better empowering environmental protection agencies for example; implementing training programmes across a spectrum of stakeholder groups, including farmers, chemical retailers and cocoa quality control services; and establishing or improving capacity for analysing residue levels at various points prior to cocoa bean export and generally improving quality control monitoring throughout the cocoa supply chain.

CHAPTER THREE

3.0 MATERIALS AND METHODS

3.1 Study area

The study was carried out in the Dormaa West District located at the western part of the Brown Ahafo Region of Ghana (Figure 3.1). It shares boundaries in the north with the Dormaa Central Municipality, in the east by Asunafo North Municipality, in the west by La Cote D'Ivoire and in the south west by Bia East District. The District capital is Nkrankwanta, located about 125 km away from the regional Capital, Sunyani. The 2010 population and Housing Census put the district's population at 38,638 comprising of males 18,701 (48.4%) and 19,937 females (51.6%). The district is generally an agrarian economy which contributes immensely to the food basket of the country. Agriculture is the main source of employment (82%) in the district. The major economic activities in the district include the cultivation of food and cash crops (including cocoa), poultry and livestock farming, oil palm extraction, cassava processing and sand winning (Ghana Statistical Service, 2014).

Climate and Vegetation

The Dormaa West District is located within the wet semi-equatorial climate region with a bimodal rainfall regime. The mean annual rainfall is between 125 cm and 175 cm. The major rainy season starts in May and ends in June with the peak of the season occurring in June. The minor season starts in September and ends in October. The dry season is quite pronounced with the main season beginning around the latter part of November and ending in February. The highest mean temperature of the District is about 30 ^{o}C which occurs between March and April and the lowest about 26.1 ^{o}C in August. The climatic condition of the District is suitable for the cultivation of various

cash crops such as cocoa, coffee and food crops such as plantain, cocoyam and cassava. The major vegetation types are the open forest, partly broken forest and extensively cultivated forestland and forest reserve (Pamu-Mpameso Forest Reserve covering 197.67 square kilometres). The major types of flora found in these forests range from shrubs and climbers to giant silk cotton tress. The predominantly timber species are Wawa (*Triplochiton scleroxylon*), Odum (*Milicia excelsa/Chloiphora excelsa*), Sapele (*Entandrophragma cylindricum*) and Mahogany (*Khaya ivorensis; K., iootensis/anthotheca*). The availability of these timber species has contributed extensively to the growth of the carpentry industry in the District. The activities of timber firms within the District have contributed to the depletion of the forest cover with its adverse consequences on climate (Ghana Statistical Service, 2014).

Relief and Drainage

The District topography is generally undulating and arises between 180 metres and 375 metres above sea level. The highest point is a little over 235 meters above sea level. The medium range rises gradually between 240 metres and 300 metres above sea level. The area is well drained as evidenced by the network of rivers spread out within the District. The rivers are mostly perennial due to the double maxima rainfall, which is experienced in the area. Notable among them are the Bia, Nkasapim and Pamu Rivers. These rivers are mostly used as a source of water for the cultivation of vegetables such as tomatoes, pepper and okra during the dry season. There are however, traditional restrictions on the use of the rivers for fishing.

Geology and Soil

The rocks underlying the soils are of the Birimain formulation which covers more than three quarters of the closed forest zone. Soils in the District belong to the

Bekwai-Nzema compound Associations. The Nkrankwanta Association dominated the south-western section of the District. The Nzema series, which are made up of quartz gravels and ironstone are moderately well-drained. Currently, the soil types within the District tend to support cultivation of both commercial and domestic food crops, which include cocoa, coffee, oil palm, citrus, cola-nuts, plantain, cassava and maize.

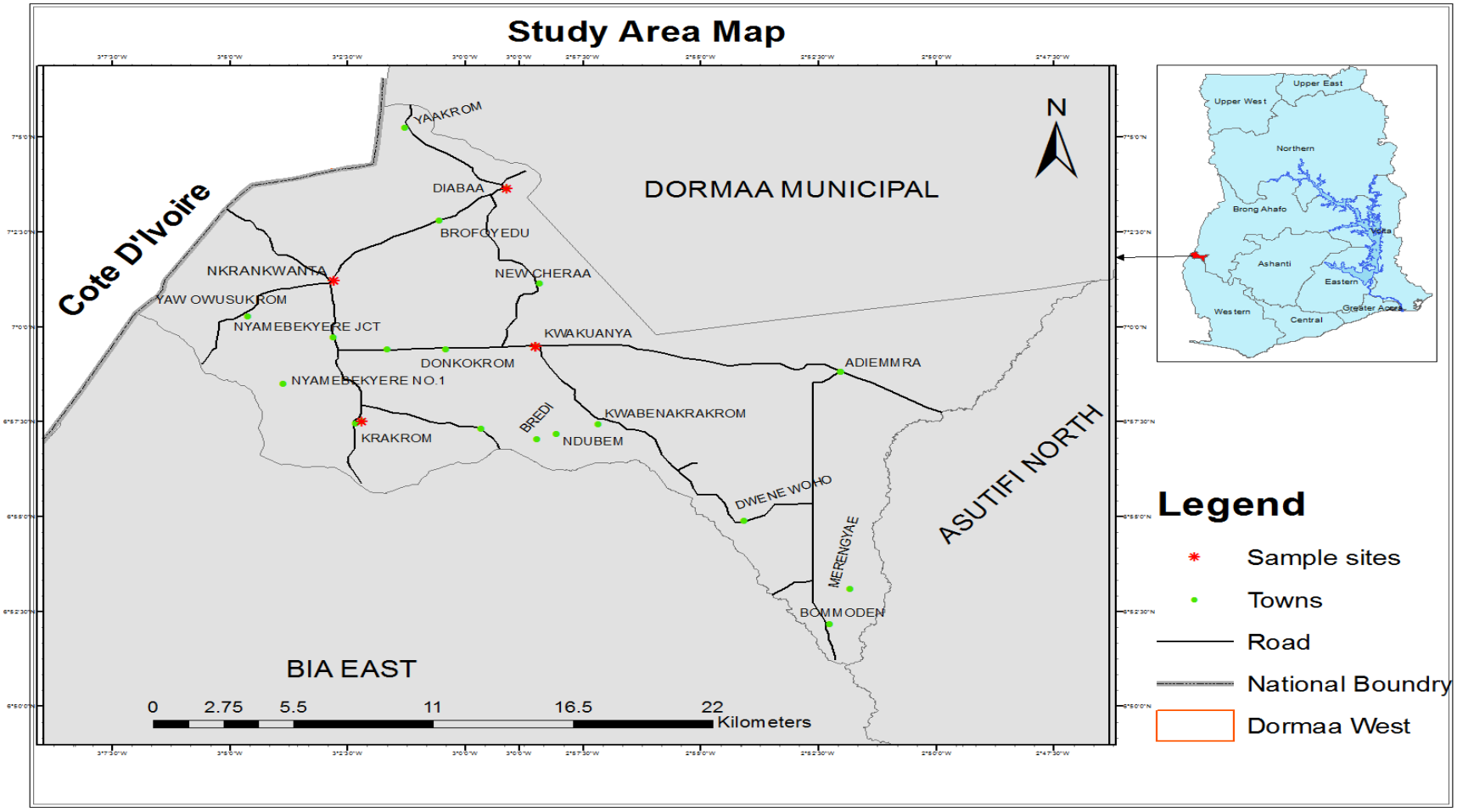

Figure 3.1: Map of Dormaa West District showing sampling Locations

3.2 Selection of sample sites

A reconnaissance visit was made to the study area in October, 2014. In order to select suitable communities for the study. The list of all major cocoa producing/growing communities in the district was obtained from the Quality Control Division of Ghana COCOBOD and the purchasing clerks of the various licensed cocoa buying companies in the district. Four cocoa growing communities were randomly selected. With this method, names of all the cocoa growing communities obtained were written on pieces of paper, folded and put in a small box. The communities selected were Nkrankwanta, Diabaa, Krakrom and Kwakuanya (Figure 3.1) and were coded as sites S1, S2, S3 and S4, respectively.

The sampling design for the research involved both purposive and random sampling. Sixteen (16) cocoa farms (Four (4) for each community) were identified purposively in the four cocoa growing communities randomly selected. The criteria for the selection was based on (i) Distance of farm to the nearest drinking water source (hand dug wells) and (ii) age of cocoa farm (farms not less than 8 years and not more than 20 years with a history of at least five years of pesticides application). A Global Positioning System (GPS) device (Model, GARMIN etrex 20) was used to take all the coordinates of the selected cocoa farms (Appendix A). Water, soil and cocoa bean samples were taken within a period of three months (December 2014-February 2015).

3.3 Physico-chemical analysis

3.3.1 Water

3.3.1.1 Sampling design and preparation of samples of water

Water samples were collected from hand dug wells located within and around the sixteen (16) selected cocoa farms in the study area. Wells were selected based on

distance to cocoa farms in the order; 0-15 m and 16-30 m whiles wells beyond 30 m were used as the control. These distances were chosen because the World Health Organization (WHO) and various studies recommends that hand dug wells should be at least 100ft (30 m) away from an agricultural field where chemicals (pesticides and fertilizers) are handled (Harris *et al.*, 1996; WHO, 2004). The distances of wells to sampling cocoa farms were determined using a tape meter (model, ZJF-100 m) and are presented in Appendix B. Water samples were collected from two hand dug wells from each of the distance categories (between 0-15 m and 16-30 m) within each selected community. Water samples were also taken from three (3) open wells at above 30 m distance to serve as control (S5). Three replicates were collected from each well making a total of fifty-seven (57) water samples. A water sampler was used to collect water samples into 1.5 L and 500 mL polyethylene sample bottles with stopper that had been pre-cleaned with tap water and rinsed with distilled water for pesticide residues and physico-chemical analysis, respectively. All the wells were shallow wells (<15 m) which represents unconfined aquifers. At each sampling point, the sampling bottles and caps were rinsed thoroughly with the water of the source. The bottles were then filled and sealed to prevent air from entering. Water temperature, pH, conductivity and total dissolve solids were measured in-situ using a Multi pH parameter probe (Model YSI 63). The samples were labelled and transported to the laboratory (Ecological Laboratory (ECOLAB), of University of Ghana, Legon) within 24 to 48 hrs on ice in clean ice chests and stored in the refrigerator at 4 ^{o}C until they were analyzed for physico-chemical parameters and pesticide residues. Water samples for pesticide residues analysis were sent to the Ghana Standards Authority Pesticide Residues Laboratory in Accra and were

extracted within 24 hrs of arrival at the laboratory. Before extraction, water samples were filtered using a Whatman No 42 filter, 9 cm and the filtrate used for analysis.

3.3.1.2 Parameters analyzed in water

The water physico-chemical parameters analysis were carried out at the University of Ghana Ecological Laboratory. Physico-chemical parameters measured were turbidity, total suspended solids, nitrate, ammonia, phosphate, sodium and potassium. All analyses were determined using appropriate certified and acceptable international procedures outlined in the standard methods for the examination of water and waste water (APHA, 1998).

pH, Conductivity, Temperature and Total dissolve solids

Physical parameters such as pH, conductivity, temperature, and total dissolved solids were measured in-situ using a Multi pH parameter probe (Model YSI 63) immediately after collecting the water sample. A pre-treated clean plastic bucket was filled with water samples. The tip of the probe to be used was first washed with distilled water and cleaned with the water sample before being dipped into it and readings taken directly from the meter. The electrodes were rinsed with distilled water after each sample measurement, wiped with a clean tissue paper and then cleaned with the next water sample before use. The test was duplicated for each sample and the means taken. Readings were recorded after stabilization. The stabilization state was determined when the signal became steady after 2 minutes.

Turbidity

Turbidity was measured using a turbidimeter (Model HACH 2100P) NTU. A clean dry cuvette was rinsed distilled water and three times with the sample to be treated. The cuvette was filled with 10 ml water sample to be analyzed. The outer surface of

the cuvette was wiped dry with a clean tissue paper. It was then pushed firmly into the chambers of a turbidimeter (Model HACH 2100P) NTU and the lid closed. The Nephelometric Turbidity Units (NTU) values were measured automatically by pressing the read button and the value was recorded after the display has stopped flashing.

Nitrate (NO_3^-)

The method used for the nitrate analysis was the Cadmium reduction method. The nitrate level in each sample was measured using Nitrate powdered pillows in a direct reading HACH spectrophotometer (Model DR. 2010). Ten (10) ml of the sample was measured into sample cell of the spectrophotometer. One Nitraver 5 nitrate reagent powder pillows was added to the sample. The mixture was then shaken vigorously for 1 minute. Five minutes was allowed for the solution to react to allow development of the colour. An orange colour of the mixture indicates the presence of nitrate. A blank was placed into the cell holder to calibrate it. The prepared sample was then placed into the cell holder to determine the nitrate-nitrogen concentration at 500 nm in mg/l.

Ammonia (NH_3)

The method used for the ammonia analysis was the salicylate and spectrophotometric methods. The ammonia level in each sample was measured using salicylate reagent powder pillows (reagent 1) and cyanurate reagent powder pillows (reagent 2) in a direct reading HACH spectrophotometer (Model DR. 2010). Ten (10) ml of the sample was measured into sample cell of the spectrophotometer. One salicylate reagent powder pillow was added to the sample. The mixture was then shaken vigorously and three minutes' reaction period was allowed for the solution to react. After the three minutes, one cyanurate reagent powder pillow was added to the sample

and shaken to dissolve and a 15-minute reaction period was allowed. A green colour of the mixture indicates the presence of ammonia. After the fifteen minutes, another cell was filled with 10 ml of only the sample (blank). The blank sample was placed in the spectrophotometer to calibrate it (to zero the spectrophotometer). The prepared sample was then placed into the cell holder to determine the ammonia concentration at 655 nm in mg/l.

Phosphate (PO_4^{3-})

A 25 ml of water (prepared sample) was placed in the sample cell. Phos Ver 3 phosphate reagent powder pillow was added to the sample content and swirled immediately to mix. A two-minute reaction period was allowed. A blue coloration of the mixture indicates the presence of phosphate. A blank was placed into the cell holder to calibrate it. After reaction period, the prepared sample was placed into the cell holder and the level of phosphate-phosphorus was determined at 890 nm. The spectrophotometer displayed the results in mg/l PO_4^{3-} .

Sodium and Potassium ions

Sodium (Na^+) and Potassium (K) ions were analyzed by the Flame emission photometric method using Gallenkamp digital flame analyser. Samples were digested and filtered into a 100 ml volumetric flask. The sample was aspirated and the valves read out from digital display. Samples whose concentrations were higher than that of the standard were diluted and results multiplied by the dilution factor. Trace amount of K were determined at wavelength of 768 µm and Na^+ was determined at a wavelength of 589 µm. The intensity of light at these wavelength is approximately proportional to the concentration of K and Na^+ respectively in the sample.

Total suspended solids analysis (TSS)

The photometric (non-filterable residue) method was used to determine the TSS of the water samples. A 500 ml of sample was blended at high speed for two minutes. This was poured into a 600 ml beaker, stirred and 25 ml immediately poured into a sample cell. The stored programme number for suspended solids, 630, was entered. The wavelength was set to 810 nm. A sample cell was filled with 25 ml de-mineralized water (blank). This was placed in the cell holder and standardized. Next, the sample was placed in the cell holder and the reading taken in mg/l suspended solids.

3.3.2 Soil

3.3.2.1 Sampling design and preparation of samples of soil

In each of the sixteen (16) cocoa farms, two quadrats of 80 x 80 metres were marked. In each quadrat, five (5) core soil samples were collected randomly and put together to form a composite sample. Soils were taken at depth 0-20 cm at each quadrat with a soil auger. This depth was taken because nutrient uptake by plant is reported to be usually within this horizon (Aiyesanmi and Idowu, 2012). Additionally, soil samples were taken from three (3) natural forests nearby to act as a control (S5) due to absence of organic cocoa farms. Two soil replicates were collected from each cocoa farm. These gave a total of 32 soil samples from the study area. The factors considered during soil sampling were slope, drainage and erosion of the farm. All soil samples were stored in well labelled plastic polythene containers and then transported to the Ecological laboratory of the University of Ghana, for sample preparation.

Soil samples were air-dried at room temperature for three days at the Ecological laboratory of the University of Ghana. All debris, plant residues, gravels and stones were removed. They were then disaggregated using porcelain pestle and mortar, and

sieved with a 2 mm nylon mesh sieve to give the fine earth fraction. Sub samples of about 1 kg each was taken into a pre-cleaned zip-locked plastic bag and sent to the pesticide residue laboratory of the Ghana Standard Authority Accra for pesticides residue analysis. The remaining fine earth fraction (< 2 mm) was used for the various soil physico-chemical analysis at the Ecological laboratory of the University of Ghana, Accra.

3.3.2.2 Parameters analyzed in soil

The soil physico-chemical parameters analysis was carried out at the University of Ghana Ecological Laboratory. Physico-chemical parameters measured were soil pH, conductivity, soil particle size, soil organic carbon/organic matter, total nitrogen, ammonium, nitrate, available phosphorus, available potassium and exchangeable potassium.

Soil pH and Electrical conductivity

These parameters of the fine earth fraction (< 2 mm) of each air-dried soil sample was determined in a 1:1 soil to distilled water ratio (McKeague, 1978; McLean, 1982) using microprocessor pH meter. A 10 g soil was weighed into a 50 ml polythene beaker and 10 ml of distilled water added. The soil-distilled water solution was stirred vigorously with a magnetic stirrer for 30 minutes and allowed to stand for one hour for the suspended soil particles to settle. After calibrating the pH meter with standard buffer solution of pH 4.0 and pH 7.0, the electrode was then inserted into the supernatant (the upper part) of the soil solution. Soil pH and conductivity values were then recorded. The test was duplicated for each sample and the means taken. Readings were recorded after stabilization. The stabilization state was determined when the

signal became steady after 2 minutes. The electrode was rinsed with distilled water after each sample measurement before being used for other measurements.

Soil particle size

The particle size analysis of the soil was determined using the Bouyoucos Hydrometer method modified by Day (1965). Forty (40) grams of the air-dried and sieved soil sample was weighed into a plastic bottle and 100 mL of 5% calgon (sodium hexametaphosphate) solution was added. The content of the bottle was then shaken on a mechanical shaker for 2 hours after which it was transferred into a 1.0 litre measuring cylinder and topped up to the mark with distilled water. The suspension was then agitated with a plunger and five minutes thereafter, the density of the suspension (silt and clay) was taken using a hydrometer. The hydrometer reading of the suspension was taken again after eight hours (clay). The temperatures of the suspensions, T_1 and T_2, were respectively recorded during the 5 minute and 8-hour hydrometer readings. The contents of the cylinder after the eight-hour reading were emptied onto a 47-µm sieve and effluent discarded. The sand retained on the sieve was then washed off into a moisture can and dried at 105 ºC for 24 hours, after which the dry weight of the sand, was recorded (Day, 1965; FAO, 1974). Blank sample hydrometer readings at five minutes and eight hours were also taken for the 5 % calgon solution topped up to 1.0 L. The particle size distribution was then determined using the formulae below. Temperature of the suspensions at T_1 and T_2 = 28 °C

$$\% \text{ Clay and Silt} = \frac{(5 \text{ minute reading} - \text{correction for temperature})}{\text{oven dry mass of soil sample}} \times 100\% \quad [3.1]$$

$$\% \text{ Clay} = \frac{(8 \text{ hour reading} - \text{correction for temperature})}{\text{oven dry mass of soil sample}} \times 100\% \quad [3.2]$$

$$\% \text{ Silt} = \% \text{ (Clay and Silt)} - \% \text{ Clay} \quad [3.3]$$

$$\% \text{ Sand} = \frac{(\text{oven dry weight of particles retained on the 47 µm sieve})}{\text{oven dry mass of soil sample}} \times 100\% \quad \text{..... [3.4]}$$

Temperature effect on density of the soil particles was accounted for using the relation provided by Day (1965): for every 1 °C increase in temperature, above 19.5°C, there is an increase of 0.3 in the density of the particles in suspension.

Hence, increase in weight = (T2 – T1) × 0.3 = (28 – 28) × 0.3 = 0.

Correction for temperature = blank hydrometer reading – increase in weight of particles.

Thus = blank hydrometer reading-0.

Hence, Correction for temperature = blank hydrometer reading.

With the percentages of sand, silt and clay, each soil sample was assigned a textural class using the United States Department of Agriculture textural triangle. Average proportions of the soil types in each soil core were determined and the corresponding average textural class was determined.

Soil organic carbon/ Organic matter

The organic carbon content of the soil was determined using the wet combustion method of (Walkley and Black, 1934). Ten millilitres of 0.167 M potassium dichromate ($K_2Cr_2O_7$) solution and 20 ml of concentrated sulphuric acid (H_2SO_4) were added to a 0.5 g soil which had been passed through a 2 mm sieve in a 250 Erlenmeyer flask. The flask was then swirled to ensure full contact of the soil with the solution after which the mixture was allowed to stand for 30 minutes. The unreduced $K_2Cr_2O_7$ remaining in solution after the oxidation of the oxidizable organic material in the soil sample was titrated with 0.2 M ferrous ammonium sulphate solution after adding 10 mL of orthophosphoric acid and 2 mL of barium diphenylamine sulphonate indicator from a dirty brown colour to a bright green end point. A standardization

titration of the $K_2Cr_2O_7$ with the ferrous ammonium sulphate was done and the amount of oxidizable organic carbon calculated by subtracting the moles of unreduced $K_2Cr_2O_7$ from that of $K_2Cr_2O_7$ present in the standardized titration. The titre value was used to calculate the percent carbon (% C) as:

$$\% \text{ OC} = \frac{[0.3x\ (10 - XN)]}{w} \times 1.33 \quad \text{..... [3.5]}$$

X = Titre value of the ferrous ammonium sulphate

N = Molarity of the ferrous ammonium sulphate (0.2M)

W = Weight of the soil sample

Additionally, % Organic C is converted to organic matter using the following equation: % Organic Matter (OM) = % Organic carbon x 1.724.

Total nitrogen

The Kjeldahl (1883) method was used in the determination of total nitrogen. Two (2) grams of soil was weighed into 300 ml Kjedahl flask and a tablet of a digestion accelerator (selenium catalyst) was added. This was followed by addition of 5 ml of concentrated H_2SO4. The mixture was digested until the digest became clear. The flask was then cooled and its content transferred into a 100 ml volumetric flask. The content was made to the 100 ml mark with distilled water. An aliquot of 5 ml of the digest was taken into a Markham distillation apparatus and 10 ml of 40 % NaOH was added and the mixture distilled. The distillate (liberated ammonia) was collected in 5 ml of 2 % boric acid (H_3BO_3). Three drops of a mixed indicator containing methylene blue and methyl red were added to the solution and then back titrated with 0.01 M HCl from green to reddish end point. The percent N was calculated as follows:

$$\%N = \frac{0.01 \times \text{titre volume} \times 0.014 \times \text{volume of extract} \times 100}{\text{Soil Sample weight (g)} \times \text{volume of aliquot (mL)}} \quad \text{..... [3.6]}$$

Where; 0.01 = Molarity of HCl, and 0.014 = Milliequivalent of Nitrogen

Ammonium (NH_4^+) and Nitrate (NO_3^-)

Five grams of the soil sample was weighed into a 100 mL centrifuge bottle and 50 mL of 2 MKCl extracting solution added. The contents were shaken for 30 minutes on a mechanical shaker after which the sample was filtered through a Whatman No.42 paper. Five millilitres of the filtrate were pipetted into a 100 mL micro Kjeldahl flask and 0.2 g of Magnesium oxide (MgO) was added. The flask was connected to a distillation apparatus and about 30 mL of the distillate was collected in 5 mL of 2 % boric acid to which three drops of methyl red-methylene blue indicator mixture had been added. The distillate was then back titrated against 0.01 M HCl to a purplish end point for Ammonium-N determination. Five millilitre of sulphamic acid and 0.2 g Devarda's alloy were then added to the contents of the flask and the distillate collected in a new conical flask containing 5 mL of 2 % boric acid and three drops of the mixed methyl red and methylene blue indicator. The distillate was then back titrated against 0.01 M HCl from a green to a purplish end point to account for the level of nitrate in the soil. The respective concentrations of NH_4^+ and NO_3^- in the soil were then determined from the number of moles of HCl consumed in the two back titration reaction. Calculation of NH_4-N and NO_3-N,

$$NH_4^+ \text{ (mg/kg)} = \frac{0.01 \text{ x titre value x } 18 \text{ x } 10^{-3} \text{ x V x } 10^6}{\text{al x w}} \quad \text{.....[3.7]}$$

$$NO_3^- \text{ (mg/kg)} = \frac{0.01 \text{ x titre value x } 18 \text{ x } 10^{-3} \text{ x V x } 10^6}{\text{al x w}} \quad \text{..... [3.8]}$$

Where; V = Volume of sample prepared = 100 ml.

al = aliquot of soil taken = 5 ml.

w = dry weight of the sample in grams

Available potassium (K)

Available potassium was determined using the ammonium acetate method. One mol of ammonium ethanoate and 57.5 ml of acetic acid was diluted with distilled water and then neutralized with concentrated NH_4OH to the pH of 7. A buffer solution was prepared by dissolving 60 g of ammonium chloride in 200 ml of distilled water; 570 ml of concentrated ammonium hydroxide was added and diluted to1 litre volume. Potassium cyanide at 50 g / 500 ml and potassium hydroxide 100 g / 1 litre was then taken to prepare an aliquot. The potassium in the aliquot extract was sprayed into a flame photometer and reading taken.

Available phosphorus

The available phosphorus in soil samples was determined using 1 M ammonium fluoride (NH_4F) standard solution, potassium hydroxide, sulphuric acid and hydrochloric acid (Bray and Kurtz, 1945). A 0.1 g of soil sample was weighed and put into a centrifuge bottle and 50 ml of Bray 1 solution (0.03N NH_4F + 0.025N HCL) was added. The mechanical shaker was used to mix the suspension by shaking for 5 mins and left to settle overnight for the suspension. The suspension was then filtered into a 100 ml volumetric flask and made up to the volume. The available phosphorus in the filtrate was determined using molybdate-ascorbic acid method. Five ml of the aliquot was taken into a 50 ml volumetric flask and the pH was adjusted by adding P-nitrophenol indicator and drops of 4M NH_4OH until the colour changed to yellow. Then 40 ml of distilled water was added to dilute the solution. A solution which was made from a mixture of 12 g ammonium, 0.29 g potassium antimony tartrate, 140 ml of concentrated H_2SO_4 and 1.056 g of ascorbic acid (reagent B) was prepared. Eight ml of the reagent B was added to the solution and mixed thoroughly by shaking and allowing to settle for 15 min until the colour changed to different shades of blue

depending on the P content in the samples. A blank of was prepared using distilled water and 8 ml of reagent B. A Philips PU 8620 spectrophotometer was used to measure the intensity of the P content at a wavelength of 712 nm. The P content was then calculated as

$$P\ (mg\ kg^{-1}) = \frac{(\text{Spectrophotometer reading-blank reading}) \times \text{volume of extract}}{\text{Volume of aliquot X sample weight (g)}} \quad \ldots [3.9]$$

Exchangeable potassium (K)

Ten grams (10 g) of soil was weighed into an extraction bottle and 100 ml of 1 M ammonium acetate (NH_4OAc) was added and shaken for 30 minutes. The suspension was allowed to settle, after which it was decanted and filtered. The filtered solutions (aliquots) were used for the determination of K. The concentrations of potassium (K) were determined using the flame photometer (Chapman, 1965). The flame photometer was standardized such that 10 mg/kg of K gave 100 full scale deflections. The flame photometer after standardization was used to determine the concentration of potassium in 10 ml aliquot. The result was used in the calculation of the amount of potassium present in the soil as shown in the formula below.

$$\text{Exchangeable K (cmol/kg soil)} = \frac{R \times V \times 100}{\text{Weight of soil} \times 39.1} \quad \ldots\ldots [3.10]$$

Where R = Flame Photometer reading for K (ppm), 39.1= Molecular weight of Potassium, V= Volume of extract (100 ml)

3.4 Cocoa bean

3.4.1 Sampling design and preparation of samples of cocoa bean

In each of the sixteen (16) cocoa farms, two quadrats of 80 x 80 metres were marked. For each quadrat, five (5) cocoa trees were randomly selected. Five (5) fresh, mature and riped cocoa pods were randomly taken and kept in labelled bags. The pods were

broken and the cocoa beans fermented for seven days and sun-dried for 21 days. The dried cocoa beans from each quadrat were then bulked together to form a composite sample and 1 kg sub-samples were taken into a clean labelled polythene bag and transported to the Ghana Standards Authority Pesticide Residue Laboratory in Accra, for analysis of pesticides residue. There was no control for the cocoa beans because of absence of organic cocoa farms within the district. Two cocoa bean replicates were collected from each cocoa farm. These gave a total of 32 cocoa beans samples from the study area.

Foreign objects found in each sample were removed by hand picking. Using the hammer mill at the Ghana Standards Authority Pesticide Residue Laboratory, Accra, each of the labelled fermented dried cocoa bean samples of each farm were ground into fine powder and collected into a new sample plastic bag and re-labelled accordingly to form each individual analytical sample for each farm, weighing 1 kg. After each sample was ground, the mill was thoroughly cleaned with a brush. To avoid cross contamination, a few grams of the next sample to be prepared were ground and discarded before the analytical sample was collected into a new labelled sample plastic bag.

3.5 Pesticide residues in water, soil and cocoa beans

3.5.1 Laboratory requirements

The individual certified reference standards; lindane, beta- HCH, delta-HCH, aldrin, heptachlor, gamma-chlordane, alpha-endosulfan, dieldrin, endrin, beta-endosulfan, p,p´- DDT, p,p´-DDD, p,p´-DDE, endosulfan sulfate, methoxychlor, methamidophos, phorate, fonofos, diazinon, dimethoate, pirimiphos-methyl, chlorpyrifos, malathion, fenitrothion, parathion, chlorfenvinphos, profenofos, allethrin, bifenthrin,

fenpropathrin, lambda-cyhalothrin, permethrin, cyfluthrin, cypermethrin, fenvalerate, deltamethrin, used for the identification and quantification were obtained from Dr. Ehrenstorfer GmbH (Augsburg, Germany) and stored in the freezer to minimize degradation.

Information pertaining to the identity (name), grade and source of reagents used in this research work are summarised in Table 3.1 below.

Table 3.1 Reagents and materials used for analysis

Reagent	**Grade**	**Source**
Acetonitrile	Pesticide	BDH, England
Acetone	Pesticide	BDH, England
Ethyl Acetate	Pesticide	BDH, England
Toluene	Pesticide	BDH, England
Dichloromethane	Pesticide	BDH, England
Sodium sulfate (anhydrous)	Analytical	BDH, England
Sodium chloride (anhydrous)	Analytical	BDH, England
Dipotassium hydrogen phosphate	Analytical	BDH, England
Potassium dihydrogen phosphate	Analytical	BDH, England
Magnesium sulphate (anhydrous)	Analytical	BDH, England
Envi-Carb/LC-NH_2 500 mg / 500 mg / 6 mL	-	Supelco, USA
Strata C18-E 55 um, 70 A, 1000 mg / 6 ml	-	Phenomenex, USA
Bond elute C18 SPE cartridge, 1 g / 6 ml	-	Phenomenex, USA
Silica gel (1000 mg/ 6 ml)	-	Phenomenex, USA
Filter paper No. 4	-	Whatman Int. Ltd, England
Distilled water	-	-

Information pertaining to the identity of instruments, apparatus and types used in this research work are summarised in Table 3.2. below.

Table 3.2 Details of equipment used

Equipment	Type
Gas Chromatography (GC)	Varian CP-3800 with a CombiPAL Autosampler, Electron Capture Detector and Pulse Flame Photometric Detector
Analytical column	30 m + 10 m EZ guard column x 0.25 mm internal diameter fused silica capillary coated with VF-5 ms (0.25 µm film thickness) from Varian Inc. or equivalent 30 m x 0.25 mm internal diameter fused silica capillary coated with VF-1701 ms (0.25 µm film thickness) from Varian Inc. or equivalent
Centrifuge	Jouan CR3i multifunction
Vacuum manifold	Phenomenex and Varian
Macerator	IKA Ultra Turrax homogenizer
General laboratory glassware	Separating funnels/flasks, round bottom flasks, pear shape flasks, volumetric flasks, centrifuge tubes, measuring cylinder, 10 ml bulb pipettes
Water bath	Bibby, RE 200B and Buchi, B-491
Extraction jars	250 mL capacity, Nalgene
Glass vials	2 mL
Preparation equipment	Wearing Laboratory Blender, Hobart
Recirculating chiller	Buchi B-740
Rotary film evaporator (RFE)	Bibby RE 200 and Buchi Ratovapor R-210
Horizontal shaker	Ika-Werke HS 501 Digital
Ultrasonic baths	Clifton SW 3H and Grant XUB 18 UK
Vortex mixer	Thermolyne (Mai Max-Plus)

3.5.2 Pesticides concentration in water

Extraction

The extraction technique employed in this work was the US EPA Method 3510 for aqueous matrix for the analysis of semi-volatile and non-volatile organics. After filtration, 1000 ml portion of the water sample was transferred into a 2 L capacity glass-separating funnel. Then 30 ml of saturated sodium chloride (NaCl) was added to produce a salt out effect. It was thoroughly mixed by inverting the flask three to four times. 100 ml of dichloromethane as extraction solvent was added and this was vigorously shaken manually for 2-3 minutes and releasing the pressure intermittently. The phases were then allowed to separate for 5 minutes and the dichloromethane extract (organic layer) was separated or collected from the aqueous layer. The extraction was repeated two another times with 100 ml of dichloromethane and the organic layers were put together and dried over anhydrous magnesium sulphate. The extracts from water samples were then concentrated on rotary vacuum evaporator to about 2 ml and subjected to clean up.

Clean-up of extract (purification using silica SPE cartridge)

One gram of silica gel that previously had been activated at 130 ºC for 10 hours was carefully packed into 10 mL polypropylene cartridge column and 6 mL dichloromethane was used to condition the cartridge. The concentrated extract was then loaded onto the column and 50 mL pear shape flask was placed under the column to collect the elute. A 10 mL dichloromethane was used to elute the column afterwards, and the total filtrate collected concentrated to just dryness using the rotary evaporator set at 38 ºC. The residue was re-dissolved in 1 mL ethyl acetate and transferred into a 2 mL standard vial prior to quantitation by Gas Chromatography (GC).

3.5.3 Pesticides concentration in soil

Extraction

Ten grams of soil sample was weighed and quantitatively transferred into a 250 mL separating funnel. A 10 mL of acetonitrile was added to the soil sample in the funnel and ultra-sonicated for 2 minutes. An additional 10 mL acetonitrile was added, and the separating funnel closed tightly and placed on a horizontal shaker. It was then set to shake continuously for 30 minutes at 300 mot/min and finally allowed to stand for 5minutes to sufficiently separate the phases. A 10 mL of the supernatant was carefully taken and dried over 2 g anhydrous magnesium sulphate through filter paper into 50 mL round bottom flask. This was then concentrated to about 1mL using the rotary evaporator, and made ready for silica clean up step.

Clean up (Extraction purification using silica)

One gram of silica gel that previously had been activated at 130 ºC for 10 hours was carefully packed into 10 mL polypropylene cartridge column and 6 mL acetonitrile was used to condition the cartridge. The concentrated extract was then loaded onto the column and 50 mL pear shape flask was placed under the column to collect the eluate. A 10 mL acetonitrile was used to elute the column afterwards, and the total filtrate collected concentrated to just dryness using the rotary evaporator set at 38ºC. The residue was re-dissolved in 1 mL ethyl acetate and transferred into a 2 mL standard vial prior to quantitation by Gas Chromatography.

3.5.4 Pesticides concentration in cocoa beans

Extraction

Sample preparation, extraction, clean-up and analysis were carried out according to the procedure described in multi-residue method for agricultural chemicals with slight modifications (Syoku-An, 2006). Approximately, 10 g of the sample was weighed

into a 250 ml Nalgene jar and labelled accordingly. A 20 ml of distilled water was then added and stirred to form a homogeneous mixture and allowed to stand for 15 minutes to dissolve water soluble pesticides if any. A 50 ml acetonitrile was added and homogenized using the ultra Turrax for 2 minute to dissolve non-water soluble pesticides in the samples. It was then centrifuged at a speed of 3000 rpm for 3 minutes and decanted through filter paper into labelled 100 ml volumetric flasks. A 20 ml acetonitrile was added to the residue and further homogenized for 2 minutes, and 5 ml acetonitrile was used to rinse the dispersing element into the jar. Then centrifuged at 3000 rpm for 3 minutes and filtered again into each corresponding labelled 100 ml volumetric flask. A further 15 ml acetonitrile was used to rinse the jar and residue, filtered and all filtrates adjusted to the 100 ml mark with acetonitrile. An aliquot of 20 ml was pipetted into labelled 250 ml separating funnel, and 10 g of NaCl and 20 ml of 0.5 mol/L phosphate buffer (pH 7.0) were added. The separating funnel was corked and shaken for 10 minutes using the horizontal shaker and allowed to stand for another 10 minutes. The NaCl and lower aqueous layers in each separating funnel were carefully removed and the organic layers transferred into labelled 50 ml beakers for further clean-up.

First clean up using bond elute C-18 cartridge

Bond elutes C-18 (1000 mg / 6 ml) cartridges were conditioned using 10 ml each of acetonitrile. Labelled 30 ml flasks were placed under the columns to collect elutes. Sample extracts from the extraction stage were loaded onto each corresponding column, and 2 ml acetonitrile was used to elute each column. Anhydrous Na_2SO_4, 5 g were placed on filter paper in funnels and the extracts dried over them. The receiving flask was rinsed with acetonitrile and passed over the Na_2SO_4. Each filtrate was collected into labelled 50 ml round bottom flask and was concentrated below 40 ºC to

dryness using the rotary evaporator. The residue was re-dissolved in 2 ml of a mixture of toluene/acetonitrile in a ratio of 1:3 prior to the second clean-up step.

Second clean up using Envi-Carb/LC-NH_2 cartridge

ENVI-Carb/LC-NH_2 (500 mg / 500 mg / 6 ml) cartridges were conditioned using 10 ml of 1:3 toluenes: acetonitrile mixture. Labelled 50 ml pear shape flasks were placed under the columns, and the extracts from the previous clean-up step loaded onto the corresponding cartridges. The extracts were allowed to filter and the cartridges eluted each with 20 ml of the toluene / acetonitrile mixture in four portions with intermittent vacuum use. All filtrates were concentrated below 40 ºC to approximately 1 ml on the rotary evaporator, and 10 ml of acetone added to each flask and further concentrated just to dryness. The extracts were re-dissolved in 1 ml ethyl acetate and transferred into labelled 15 ml screw capped tube, closed and placed in freezer for about 20 minutes. They were removed and immediately centrifuged at 3000 rpm for 5 minutes, and the top layer carefully transferred into labelled 2 ml GC standard opening vial prior to quantification by Gas Chromatography (GC).

3.5.5 Gas chromatographic (GC) conditions for analysis of pesticide residues

The organochlorine and synthetic pyrethroids pesticide residues were analyzed by Gas Chromatograph-Varian CP-3800 (Varian Association Inc. USA) equipped with combiPAL Autosampler and ^{63}Ni electron capture detector (ECD) that allowed the detection of contaminants even at trace level concentrations (in the lower µg/g and µg/kg range) from the matrix to which other detectors do not respond. The GC conditions and the detector response were adjusted so as to match the relative retention times and response as spelt out by Japanese analytical methods for agricultural chemicals (Syoku-An, 2006). The GC conditions used for the analysis

were capillary column coated with VF-5 ms (30 m + 10 m EZ guard column x 0.25 mm internal diameter, 0.25 µm film thickness). The injector and detector temperature were set at 270 ºC and 300 ºC respectively. The oven temperature was programmed as follows: 70 ºC held for 2 min, ramp at 25 ºC min^{-1} to 180 ºC, held for 1 min, and finally ramp at 5 ºC min^{-1} to 300 ºC. Nitrogen was used as carrier gas at a flow rate of 1.0 mL min^{-1} and detector make-up gas of 29 mL min^{-1}. The injection volume of the GC was 1.0 µL. The total run time for a sample was 31.4 min.

The organophosphorus pesticide residues were analyzed by Gas Chromatograph-Varian CP-3800 (Varian Association Inc. USA) equipped with combiPAL Autosampler and pulse flame photometric detector (PFPD) that allowed the detection of contaminants even at trace level concentrations (in the lower µg/g and µg/kg range) from the matrix to which other detectors do not respond. The GC conditions and the detector response were adjusted so as to match the relative retention times and response as spelt out by Japanese analytical methods for agricultural chemicals. The GC conditions used for the analysis were capillary column coated with VF-1701 ms (30 m x 0.25 mm internal diameter, 0.25 µm film thickness). The injector and detector temperature were set at 270 ºC and 280 ºC respectively. The oven temperature was programmed as follows: 70 ºC held for 2 min, ramp at 25 ºC min^{-1} to 200º C, held for 1 min, and finally ramp at 20 ºC min^{-1} to 250 ºC maintained for 3.3 min. Nitrogen was used as carrier gas at a flow rate of 2.0 mL min^{-1} and detector make-up gases (17.0, 14.0 and 10.0 mL min^{-1}) for air-1 hydrogen and air-2, respectively. The injection volume of the GC was 2.0 µL. The total run time for a sample was 14 min.

3.5.6 Quantification and limit of detection of pesticides

The residue levels of pesticides were quantitatively determined by the external standard method using peak area. Measurement was carried out within the linear range of the detector. The peak areas whose retention times coincided with the standards were extrapolated on their corresponding calibration curves to obtain the concentration. The limit of detection of the pesticides determined was based on the extract of the fortified samples that were serially diluted by factor of two to give different concentrations. One out of each concentration that gave a response three times the standard deviation of the least fortified sample was noted. This was used to estimate the statistical significance of differences between low level analyte responses and the combined uncertainties in both the analyte and the background measurement (Frimpong *et al.*, 2012d).

3.6 Quality control and quality assurance

Proper quality assurance procedures and precautions were taken to ensure the reliability of the results. The samples were carefully handled to avoid any external influences that could interfere with the integrity of the sample and hence contaminate it. Glasswares were properly cleaned, and reagents were of analytical grades. All the glassware used for Pesticides residue analysis (extraction and cleaning) were rigorously washed with detergent and tap water. They were then rinsed with distilled water and thoroughly rinsed with analytical grade acetone and dried overnight in an oven at 150ºC. The glass wares were then removed from the oven and allowed to cool down and stored in dust free cabinets. Deionized water was used throughout the study. For the spectrophotometric analysis, reagent blank determinations were used to correct the instrument readings. For validation of the analytical procedure, repeated analysis of the samples against internationally certified/standard reference material

(SRM-1570) of National Institute of Standard and Technology were used. With the exception of temperature, multi probe meters were calibrated together using the same standard and procedures. Electrical conductivity was calibrated against 0.005, 0.05 and 0.5 M standard potassium chloride solution; pH was calibrated with standard buffer at pH of 4 and 9.2. Temperature was checked against standard mercury thermometer for consistency.

Additionally, the quality of pesticides residues was assured through the analysis of solvent blanks, procedural matrix blanks and duplicate samples. All reagents used during the analysis were exposed to same extraction procedures and subsequently run to check for interfering substances. In the blank for each extraction procedure, no pesticide was detected. Sample of each series was analyzed in duplicates. All extracts were kept frozen until quantification was achieved. Recalibration curves were run with each batch of samples to check that the correlation coefficient was kept around r^2=0.99. The method used was an international method, optimized and validated using various agricultural products (Frimpong *et al.,* 2012d). The method was optimized and validated by fortifying and spiking with standard mixture before analysis to evaluate the recovery of compounds. The recoveries of internal standards ranged between 70% and 119% for most of the pesticides analyzed.

Recovery (%) =

$$\frac{\text{Concentration of Pesticide recovered from fortified sample}}{\text{Concentration of organochlorine pesticide added to sample}} \times 100 \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad [3.11]$$

3.7 Farmers' survey

3.7.1 Research design

To obtain a cross sectional data of typical pesticide use pattern in the selected communities, a quantitative and qualitative analysis was employed.

3.7.2 Sampling technique and size

The respondents were cocoa farmers within the Dormaa West District of the Brong Ahafo Region of Ghana who apply pesticides on their cocoa farms. A random sampling technique was used to sample 60 cocoa farmers from each of the four selected cocoa growing communities. A total of 240 cocoa farmers were selected for the study.

3.7.3 Instrumentation for data collection

A pre-tested structured questionnaire (Appendix C) was developed as an instrument for the study. The structure of questions in the data collection instrument was a combination of close-ended, open-ended and partially close-ended questions. The questionnaire was designed to consist of four (4) main parts. Part one (1) considered the demographic and farm-related characteristics namely sex, age, marital status, educational level, farm ownership, years of experience, household size, age of cocoa farm, size of farm, number of farms and yields of respondents. Part two (2) consisted of information on farmer's field including access to extension offices, information received from them and source of farm inputs and planting materials. Part three (3) involved information on pesticide use patterns, pest and disease of cocoa, types of pesticides used, source of pesticides, frequency of pesticides application, methods of pesticides application, source of information on pesticides, handling of personal pesticides application, health related issues from pesticides usage, operational habits during pesticide usage, safety practices or precautions (protective cloth) adhered to and pesticide use history of farmers. Part four (4) involved access of cocoa farmers to water sources on their farms, the type and the age of the source of water, the number of people in the household and families that depend on the water source, the location

and the distance of source of water to their cocoa farm. The survey was conducted from December, 2014 to March, 2015. There was a 100% response rate.

3.8 Data analysis

Statistical Package for Social Sciences (SPSS) software version 20.0 was used to generate the minimum, maximum and means for the physico-chemical parameters of water and soil as well as the pesticide residues in water, soil and cocoa beans. One-way Analysis of variance (ANOVA) was used to test for the significant differences and similarities between the water and soil physico-chemical properties as well as the pesticide residues in water, soil and cocoa beans from the various sampled sites. Significant means obtained were separated by least significant difference (LSD) method at 5% significance level. A Pearson correlation analysis was also carried out to establish the degree of relationship between the physico-chemical parameters of water and soil and the various pesticides residues detected in water and soil samples.

Descriptive statistics such as percentages and frequencies were calculated for the results from the farmers' survey using the Statistical Package for Social Science (SPSS) version 20.0 and Microsoft Excel. The probit model was used to examine the factors influencing cocoa farmers' choice of pesticide source, factors influencing cocoa farmers' knowledge on pesticide application rate and the use of protective clothes. An ordinary least square regression model was used to examine the explanatory variables that were capable of influencing the frequency of pesticide application by cocoa farmers.

CHAPTER FOUR

4.0 RESULTS

4.1 Physico-chemical properties of water samples

The results of physico-chemical parameters of water samples for the various distance categories to cocoa farms are presented in Table 4.1.

Temperature

Analysis of variance (ANOVA) revealed that there was no significant difference ($p > 0.05$) in temperature in relation to distances of water sources to cocoa farms within the study period (Appendix D). The mean temperature recorded at distances 16-30m was relatively higher compared to the mean temperatures at distances 0-15m and the control (above 30m) (Table 4.1). The temperature of water source at distances 0-15m varied from 25.3℃ at S4 to 26.4℃ at S1 with a mean value of 25.9±0.41℃ while the temperature of water at distances 16-30m varied from 25.9℃ at S2 to 32.3℃ at S1 with a mean value of 27.9±2.31℃ (Table 4.1).

pH

The mean pH of water sampled within the various distances were in the decreasing order of ranking; 0-15m >16-30m> control (>30m) (Table 4.1). The pH of water recorded at distances 0-15m ranged from 5.05 at S3 to 6.93 at S4 with a mean value of 5.82±0.62 (Table 4.1) whereas the pH recorded at distances 16-30m ranged from 5.34 at S4 to 5.86 at S1 with a mean value of 5.54±0.17 (Table 4.1). Statistical analysis revealed no significant difference ($p > 0.05$) in pH with respect to distances of water sources to cocoa farms (Appendix D).

Table 4.1 Summary of water physico-chemical properties at Dormaa West District of Brong Ahafo region

Distance (m)	0 – 15m						Distance (m) 16– 30m						Above 30m (S5) (Control)	
Sites Parameters	S1	S2	S3	S4	Mean	SD	S1	S2	S3	S4	Mean	SD	(Mean)	SD
Temp (◦C)	26.4	25.6	26.3	25.3	25.9	0.41	32.3	25.9	26.6	26.6	27.9	2.31	27.2	1.16
pH	5.51	5.78	5.05	6.93	5.82	0.62	5.86	5.47	5.48	5.35	5.54	0.17	5.18	0.33
EC (µS/cm)	135.0	98.0	73.0	233.0	134.0	54.4	142.0	103.0	74.0	198.0	129.0	41.5	93.0	47.5
TDS (mg/L)	67.0	49.0	36.0	110.0	65.5	25.0	71.0	51.0	37.0	98.0	64.3	20.5	46.3	23.3
Turbidity (NTU)	12.8	3.87	32.6	205.0	63.6	23.3	121.0	29.5	12.6	1.77	41.2	6.21	2.29	0.91
TSS (mg/L)	16.0	6.00	34.0	227.0	70.0	26.8	126.0	14.0	19.0	3.00	40.0	5.45	4.00	2.08
NO_3^- (mg/L)	4.70	1.00	12.8	5.40	5.90	3.80	6.50	2.90	3.10	3.50	4.00	1.30	2.20	0.87
NH_3 (mg/L)	0.45	0.17	0.49	3.88	1.25	0.56	1.38	0.48	0.32	0.44	0.66	0.37	0.18	0.04
PO_4^{3-}	0.66	0.49	0.62	1.22	0.75	0.25	1.22	0.57	0.80	0.48	0.77	0.26	0.67	0.36
Sodium (mg/L)	7.10	10.2	12.3	17.5	11.8	3.38	20.0	17.9	10.4	26.2	18.6	5.05	17.1	7.86
Potassium(mg/L)	4.20	5.00	1.90	6.70	4.45	1.54	1.10	6.10	3.10	2.80	3.30	1.61	2.90	0.67

S1=Nkrankwanta, S2=Diabaa, S3=Krakrom, S4=Kwakuanya, S5=Control, SD=Standard deviation, Temp=Temperature, EC=Electrical conductivity, TDS=Total dissolved solids, TSS=Total suspended solids, PO_4^{3-}= Phosphate, NO_3^-=Nitrate, NH_3=Ammonium.

Electrical conductivity (EC)

The mean conductivity recorded at distances 0-15m was comparatively higher compared to the mean values at distances 16-30m and above 30m (control) (Table 4.1). The conductivity of water sampled at distances 0-15m ranged from a minimum of 73.0 µS/cm at S3 to a maximum of 233.0 µS/cm at S4 (Table 4.1) whereas the values at distance 16-30m ranged from a minimum of 74.0 µS/cm at S3 to a maximum of 198.0 µS/cm at s S4 (Table 4.1). The conductivity of water recorded during the sampling period did not show any statistically significant difference among the sampling distances from cocoa farms ($p > 0.05$) (Appendix D).

Total dissolved solids (TDS)

The mean values of total dissolved solids of water sampled from the various distance categories were in the decreasing order of ranking; 0-15m >16-30m> control (>30m) (Table 4.1). The TDS of water sampled at distance 0-15m ranged from 36.0 mg/L at S3 to 110.0 mg/L at S4 with a mean value of 65.5±25mg/L whereas the TDS of water at distances 16-30m ranged from 37.0 mg/L at S3 to 98.0 mg/L at S4 with a mean value of 64.3±20.5mg/L (Table 4.1). There was no significant difference ($p > 0.05$) in mean values of TDS among the various distances of water sources to cocoa farms (Appendix D).

Turbidity

The mean turbidity values of water samples recorded at the various distances was generally high at distances 0-15m and low at distances above 30m (control) (Table 4.1). The turbidity of sampled water at distances 0-15m ranged from a minimum of 3.87 NTU (Nephlometic turbidity units) at S2 to a maximum of 205.0 NTU at S4 with a mean of 63.6±23.3 NTU whilst the turbidity values recorded at 16-30m ranged from

a minimum of 1.77 NTU at S4 to a maximum of 121.0 NTU at S1 with a mean of 41.2±6.21 NTU (Table 4.1). Analysis of variance (ANOVA) showed no significant difference ($p > 0.05$) in turbidity in relation to distances of water sources to cocoa farms within the study period (Appendix D).

Total suspended solids (TSS)

Analysis of variance (ANOVA) revealed no significant difference ($p > 0.05$) in TSS in relation to distances of water sources to cocoa farms within the study period (Appendix D). The mean TSS of water sampled within the various distance categories followed the decreasing order of ranking; 0-15m> 16-30m> control (>30m) (Table 4.1). The TSS of water sampled analyzed at distances 0-15m ranged from a minimum of 6.00 mg/L at S2 to a maximum of 277.0 mg/L at S4 with a mean value of 70±26.8 mg/L (Table 4.1) whereas the TSS values recorded at distances 16-30m ranged from a minimum of 3.00 mg/L at S4 to a maximum of 126.0 mg/L at S1 with a mean value of 40±5.45 mg/L (Table 4.1).

Nitrate (NO_3^-)

The mean nitrate value of water recorded at distances 0-15m was relatively higher compared to the mean values recorded at distances 16-30m and the control (Table 4.1). The nitrate of the water sampled at distances 0-15 ranged from 1.0 mg/L at S2 to 12.80 mg/L at S3 with a mean value of 5.90±3.8 mg/L whilst the nitrate values recorded at distances 16-30m ranged from 2.90 mg/L at S2 to 6.5 mg/L at S1 with a mean value of 4.00±1.30 mg/L (Table 4.1). There was however no significant difference ($p > 0.05$) in nitrate values recorded in relation to distances of water sources to cocoa farms within the study period (Appendix D).

Ammonia (NH_3)

The mean ammonia levels of water sampled from the various distances were in the decreasing order of 0-15m >16-30m> 30m (Table 4.1). At distances 0-15m ammonia values of water ranged from a minimum of 0.17 mg/L at S2 to a maximum of 3.88 mg/L at S4 with a mean value of 1.25±0.56 mg/L whereas at 16-30m, values ranged from a minimum of 0.32 mg/L at S3 to a maximum of 1.38 mg/L at S1 with a mean value of 0.66±0.37 mg/L (Table 4.1). Analysis of variance (ANOVA) showed there were no significant difference ($p > 0.05$) in ammonia in relation to distances of water sources to cocoa farms within the study period (Appendix D).

Phosphate (PO_4^{3-})

Analysis of variance (ANOVA) revealed no significant difference ($p > 0.05$) in phosphate concentrations in relation to distances of water sources to cocoa farms within the study period (Appendix D). The average phosphate concentration of water sampled recorded at distances 16-30m was comparatively higher than the average values recorded at distances 0-15m and above 30m (control) (Table 4.1). The concentration of phosphate recorded at distances 0-15m varied from 0.49 mg/L at S2 to 1.22 mg/L at S4 (Table 4.1) whereas the concentration of phosphate recorded at distances 16-30m varied from 0.48 mg/L at S4 to 1.22 mg/L at S1. The mean values of phosphate at 0-15m, 16-30m and above 30m (control) were 0.75±0.25 mg/L, 0.77±0.26 mg/L and 0.67±0.36 mg/L respectively.

Sodium

The mean concentration of sodium recorded at 16-30m was higher than at distances 0-15m and the control (Table 4.1). The values of sodium concentrations at 0-15m ranged from 7.10 mg/L at S1 to 17.5 mg/L at S4 with a mean value of 11.8±3.38

mg/L whilst the values of sodium recorded at 16-30m ranged from 10.4 mg/L at S3 to 26.2 mg/L at S4 with a mean value of 18.6±5.05 mg/L (Table 4.1). There was no significant difference ($p > 0.05$) in sodium in relation to distances of water sources to cocoa farms within the study period (Appendix D).

Potassium

The mean concentrations of potassium in water sampled at the various distances followed the decreasing order of ranking; 0-15>16-30m>30m (control) (Table 4.1). The values of potassium recorded at 0-15m ranged from a minimum of 1.90 mg/L at S3 to a maximum of 6.70 mg/L at S4 with a mean of 4.45±1.54 mg/L. On the other hand, the concentration of potassium recorded at 16-30m ranged from a minimum of 1.10 mg/L at S1 to a maximum of 6.10 mg/L at S2 with a mean value of 3.30±1.61 mg/L (Table 4.1). ANOVA showed no significant difference ($p > 0.05$) in potassium among the various distances of water sources to cocoa farms within the study period (Appendix D).

4.2 Physico-chemical properties of soil samples

Table 4.2 presents summary of results of the physico-chemical properties of soil samples at the study sites

pH of soil

The mean soil pH ranged from a minimum of 7.35 at S5 (control) to a maximum of 8.49 at S3 (Table 4.2). Analysis of variance (ANOVA) showed there were significant difference ($p < 0.05$) in pH of soil among the various sampled sites (Table 4.2). When the Least significant difference (LSD) was used to compare the means, there was no difference in pH between S1 and S2; S4 and S3 but they were however significantly different from S5 (Appendix E).

Electrical conductivity

The mean conductivity of soil sampled within the study area ranged from a minimum of 203.0 µS/cm at S3 to a maximum of 251.0 µS/cm at S5 (control) (Table 4.2). There was however no significant difference ($p > 0.05$) in conductivity of soil among the various sampled sites (Table 4.2).

Percentage organic carbon

As shown in Table 4.2 the mean percentage organic carbon content of soil sampled ranged from a minimum of 1.38% at S1 to a maximum of 6.25% at S5 (control). Analysis of variance revealed significant difference ($p < 0.05$) in percent organic carbon among the sites (Table 4.2). When the Least significant difference (LSD) was used to compare the means, there was no difference in percent organic carbon among the following sampled sites; S2, S3, S4 and S5 but they were however significantly different from S1 (Appendix E).

Percentage organic matter

The mean percentage organic matter of soil samples ranged from a minimum of 2.38% at S1 to a maximum of 10.8% at S5 (control) (Table 4.2). Analysis of variance at 95% confidence interval revealed that the percent organic matter of the soil differed significantly ($p < 0.05$) among the various sampled sites (Table 4.2). When the Least significant difference (LSD) was used to compare the means, there was no difference in percent organic matter among the following sampled sites; S2, S3, S4 and S5 but they were however significantly different from site S1 (Appendix E).

Table 4.2 Summary of soil physico-chemical properties at Dormaa West District of Brong Ahafo region

Sites	S1				S2				S3				S4				S5 (Control)				p-val
	Mini	Maxi	Mean	SD	Mini	MaxI	Mean	SD	Mini	Maxi	Mean	SD	Mini	Maxi	Mean	SD	Mini	Maxi	Mean	SD	
pH	7.34	7.80	7.56	0.23	7.73	7.96	7.88	0.13	8.46	8.52	8.49	0.03	8.21	8.39	8.34	0.04	7.12	7.76	7.35	0.36	**
EC(µS/cm)	138.0	296.0	210	79.8	163.0	282	242	68.4	183	239	203	30.9	156	283	204	68.9	203	336	251	73.3	NS
%OC	0.89	1.95	1.38	0.53	5.67	5.99	5.83	0.16	5.78	6.14	5.94	0.18	5.78	6.46	6.16	0.35	6.14	6.38	6.25	0.12	**
%OM	1.54	3.36	2.38	0.92	9.78	10.3	10.0	0.28	9.96	10.6	10.3	0.31	9.96	11.1	10.6	0.60	10.59	11.0	10.8	0.21	**
Ava-K (ppm)	0.39	0.95	0.59	0.30	0.45	0.50	0.48	0.03	0.36	0.89	0.64	0.27	0.21	0.50	0.35	0.15	0.50	1.40	0.86	0.48	NS
%TN	1.61	2.63	2.10	0.51	1.74	2.46	2.13	0.36	1.57	2.10	1.87	0.27	1.51	1.79	1.64	0.14	1.79	2.16	1.98	0.26	NS
Ava-P(mg/kg)	0.55	0.70	0.64	0.08	0.50	0.91	0.71	0.21	0.55	0.69	0.63	0.07	2.40	2.50	2.47	0.06	0.58	0.92	0.72	0.18	**
NH_4^+(mg/L)	23.1	46.9	38.9	13.7	30.1	42.0	34.8	6.35	43.4	48.3	45.0	2.83	35.0	49.0	42.9	7.18	30.1	49.0	36.4	10.9	NS
NO_3^- (mg/L)	23.8	29.4	25.7	3.23	33.6	45.5	40.1	6.04	38.5	44.1	40.6	3.05	28.0	30.1	28.9	1.07	35.7	43.4	40.1	3.98	**
ExK(cmol/kg)	0.20	0.26	0.24	0.03	0.27	0.51	0.43	0.14	0.38	0.51	0.60	0.27	0.21	1.15	0.67	0.47	0.51	0.78	0.64	0.14	NS
%Sand	50.1	83.3	65.9	16.7	59.7	80.5	67.8	11.0	59.5	60.4	59.8	0.47	57.0	69.0	63.3	6.04	46.3	55.5	50.8	4.59	**
%Clay	12.5	35.0	24.2	11.3	7.50	15.0	11.7	3.81	12.5	17.5	15.8	2.89	12.5	12.5	12.5	0.00	25.0	25.0	25.0	0.00	NS
% Silt	4.20	14.9	9.96	5.41	12.0	25.3	20.5	7.35	22.1	28.0	24.3	3.25	18.5	30.5	24.2	6.04	19.50	28.7	24.2	4.59	**
Texture	SCL				SL				SL				SL				SCL				

S1=Nkrankwanta, S2=Diabaa, S3=Krakrom, S4=Kwakuanya, S5=Control, Mini=Minimum, Maxi=Maximum, SD=Standard deviation, p-val=p-value OC=Organic carbon, OM=Organic matter, %TN=Percentage nitrogen, Ava-P=available phosphorus, Ava-K= available potassium, EC=Electrical conductivity, ExK=Exchangeable potassium, NO_3^-=Nitrate, NH_4^+=Ammonium, SCL=Sandy-clay-loam, SL=Sandy-loam, **=Significant at 95% confidence level, NS= Not significant

Available potassium

The mean potassium concentration of soil sampled ranged from a minimum value of 0.35 ppm at S4 to a maximum value of 0.86 ppm at S5 (control). Analysis of variance at 95% confidence interval did not showed any statistically significant difference ($p > 0.05$) in potassium among the various sampled sites (Table 4.2).

Percentage nitrogen

The results of percent total nitrogen in soil samples analyzed are shown in Table 4.2. The mean total nitrogen concentrations ranged from a minimum of 1.64% at S4 to a maximum of 2.13% at S2. Analysis of variance (ANOVA) however showed no significant difference ($p > 0.05$) in percent nitrogen among the various samples sites (Table 4.2).

Available phosphorus

Table 4.2 shows the results of available phosphorus in soil samples analyzed. The minimum mean value of 0.63 mg/kg was recorded at S3 while the maximum mean value of 2.47 mg/kg was recorded at S4 (Table 4.2). Analysis of variance at 95% confidence revealed significant ($p < 0.05$) sites difference for available phosphorus (Table 4.2). When the Least significant difference (LSD) was used to compare the means, there was no difference in available phosphorus among S2, S3, S1 and S5 but they were however significantly different from S4 (Appendix E).

Ammonium (NH_4^+)

The mean ammonium concentration in soil samples as shown in Table 4.2 ranged from 34.8 mg/L to 45.0 mg/L. The lowest mean value was recorded at S2 while the highest mean value was recorded at S3. Analysis of variance did not show any

significant difference in ammonium concentration ($p > 0.05$) among the various sampled sites (Table 4.2).

Nitrate (NO_3^-)

Analysis of variance at 95% confidence interval revealed significant difference ($p < 0.05$) in soil nitrate among the various sites (Table 4.2). The nitrate in soil ranged from a minimum mean value of 25.7 mg/L at S1 to a maximum mean value of 40.6 mg/L at S3 (Table 4.2). When the Least significant difference (LSD) was used to compare the means, there was no difference in nitrate concentration among S2, S3 and S5. There was also no difference between S4 and S1 (Appendix E).

Exchangeable K

The values for exchangeable K for soil samples from the various sampling sites are shown in Table 4.2. The mean exchangeable K ranged from a minimum of 0.24cmol/kg at S1 to a maximum of 0.67cmol/kg at S4. Analysis of variance showed no significant differences in exchangeable potassium ($p > 0.05$) among the sites (Table 4.2).

Percentage sand, clay and silt

The mean percent sand of soil samples analyzed ranged from a minimum value of 50.8% at S5 (control) to a maximum value of 67.8 % at S2 (Table 4.2). There was no significant site difference ($p > 0.05$) for percent sand (Table 4.2).

The percent clay of soil ranged from a minimum value of 11.7% at S2 to a maximum value of 24.2% at S1 (Table 4.2). Analysis of variance revealed significant site difference ($p < 0.05$) in percent clay (Table 4.2). The comparison of the means,

showed significant difference in percent clay among S4, S1, S2 and S5, but were however not statistically different from S3 (Appendix E).

Table 4.2 shows the percentage silt values of soil. The mean percent silt ranged from a minimum of 9.96% at S1 to a maximum 24.3% at S3. Analysis of variance showed significant sites difference ($p < 0.05$) in percent silt (Table 4.2). When the Least significant difference (LSD) was used to compare the means, there were no significant difference in percent clay among S2 and S3, S4 and S5 but were statistically different from S1 **(**Appendix E).

4.3 Pesticide residue levels in water, soil and cocoa beans from selected cocoa growing communities in the Dormaa West District of Ghana

Samples of water, soils and cocoa beans from selected cocoa farms in the Dormaa West District of Ghana were analyzed for a total of 37 pesticides, comprising 13 organophosphorus pesticides (OPs) (methamidophos, ethoprophos, phorate, diazinon, fonofos, dimethoate, pirimiphos-methyl, chlorpyrifos, malathion, fenitrothion, parathion, chlorfenvinphos, profenofos), 15 organochlorine pesticides (OCs) (β-HCH, γ-HCH, δ-HCH, heptachlor, aldrin, γ-chlordane, p,p´-DDE, p,p´-DDT, p,p´-DDD, dieldrin, endrin, α-endosulfan, β-endosulfan, endosulfan-sulfate and methoxychlor), and 9 synthetic pyrethroid pesticides (allethrin, bifenthrin, fenpropathrin, λ-cyhalothrin, permethrin, cyfluthrin, cypermethrin, fenvalerate, deltamethrin). Analysis of the samples revealed varying concentrations of pesticide residues. Results revealed recovery ranges between 70-94% for organophosphorus pesticide residues, 70-119% for organochlorine pesticide residues and 73-100% for synthetic pyrethroids pesticide residues respectively for all the samples analyzed. The total percentage pesticide

residues found in cocoa bean, soil, and water samples were in the order of 40.5%, 35.1%, and 35.1%, respectively and are discussed accordingly.

4.3.1 Concentrations of organophosphate, organochlorine and synthetic pyrethroids pesticides in water samples

Thirteen pesticide compounds were detected in the water samples from the various sites with respect to distance from the nearest cocoa farms. These comprised of three (3) organophosphates (chlorpyrifos, diazinon and pirimiphos-methyl), six (6) organochlorines (lindane, alpha-endosulfan, dieldrin, p,p´-DDT, endosulfan-sulfate and heptachlor), and four synthetic pyrethroids (allethrin, deltamethrin, cypermethrin and fenvalerate) (Table 4.3). Detection rates of the organophosphate residues decreased in the following order: chlorpyrifos (42.1%) > diazinon (31.6%) > pirimiphos-methyl (27%). The high frequency of occurrence of the organochlorine residues was heptachlor (52.6%), followed by p,p´-DDT (31.6%), alpha-endosulfan (26.3%), lindane (15.5%), dieldrin (15%) and endosulfan-sulfate (13.5%). In addition, the order of percentage of the synthetic pyrethroids residues occurring in the samples was as follows: deltamethrin (26.6%) > allethrin, cypermethrin, fenvalerate (26.3%). The limit of detection (LOD) of organophosphate, organochlorine and synthetic pyrethroids residues were 0.05 µg/L, 0.01 µg/L and 0.05 µg/L, respectively.

The average chlorpyrifos concentration recorded at distances 16-30m was higher than the average concentration recorded at distances 0-15m (Table 4.3). The concentrations of chlorpyrifos recorded at distances 16-30m varied from a minimum of 0.02 µg/L at S3 to a maximum of 0.06 µg/L at S2 and S4 respectively (Table 4.3). However, S3 with a mean value of 0.03 µg/L was the only site that recorded chlorpyrifos concentration at distances between 0-15m. The mean concentration of chlorpyrifos at

0-15m and 16-30m were 0.03 µg/L and 0.05±0.02 µg/L, respectively (Table 4.3). Levels of chlorpyrifos was undetected at S5 (control) for distances above 30m (Table 4.5).

Water samples analyzed from distances 0-15m and 16-30m from the nearest cocoa farms recorded mean concentrations of 0.04±0.02 µg/L respectively (Table 4.3). At distances 0-15m, the mean concentrations of diazinon in the samples analyzed ranged from 0.03 µg/L at S3 to 0.06 µg/L at S4 whereas at 16-30m the mean concentration of diaznion ranged from 0.03 µg/L at S2 to 0.04 µg/L at S1 (Table 4.3). Water samples analyzed from site S5 at distance above 30m (control) had no detectable diazinon concentration (Table 4.3).

Samples analyzed from distances 0-15m and 16-30m recorded mean concentrations of 0.03 µg/L for pirimiphos-methyl respectively (Table 4.3). The mean concentrations of pirimipos-methyl recorded at distances 0-15m ranged from 0.02 µg/L at S3 to 0.04 µg/L at S1 whereas the mean concentrations recorded at 16-30m ranged from 0.01 µg/L at S4 to 0.05 µg/L at S2. No concentration of pirimiphos-methyl was recorded at S5 (control) at distance above 30m (Table 4.3).

None of the water samples analyzed from distances 0-15m and above 30m (control) had detectable lindane concentrations. However, water samples from S4 and S2 at distances 16-30m to the nearest cocoa farms recorded the minimum and maximum mean concentrations of 0.02 µg/L and 0.04 µg/L of lindane with a mean value of 0.03±0.01 µg/L respectively (Table 4.3).

Table 4.3 Mean and standard deviation of organophosphate, organochlorine and synthetic pyrethroids concentrations (µg/L) in water samples from the study area with respect to the various distance categories from the nearest cocoa farms

Distance (m)	0 – 15m						Distance (m) 16– 30m						Above 30m (Control) S5			
Sites	**S1**	**S2**	**S3**	**S4**	**Mean**	**SD**	**S1**	**S2**	**S3**	**S4**	**Mean**	**SD**	**Mini**	**Maxi**	**Mean**	**SD**
Chlorpyrifos [a]	ND	ND	0.03	ND	0.03	-	0.05	0.06	0.02	0.06	0.05	0.02	ND	ND	ND	-
Diazinon [a]	ND	ND	0.03	0.06	0.04	0.02	0.04	0.03	ND	ND	0.04	0.01	ND	ND	ND	-
Pirimiphos-methyl [a]	0.04	ND	0.02	ND	0.03	0.01	ND	0.05	ND	0.01	0.03	0.02	ND	ND	ND	-
Lindane [b]	ND	ND	ND	ND	ND	-	ND	0.04	ND	0.02	0.03	0.01	ND	ND	ND	-
Alpha-Endosulfan [b]	ND	0.03	ND	0.02	0.03	0.01	0.01	ND	ND	0.03	0.02	0.01	ND	ND	ND	-
Dieldrin [b]	<0.01	ND	ND	0.03	0.03	-	ND	ND	ND	ND	ND	-	ND	ND	ND	-
p,p´-DDT [b]	<0.01	ND	0.03	ND	0.03	-	0.05	0.03	ND	<0.01	0.04	0.01	ND	ND	ND	-
Endosulfan-sulfate [b]	0.02	0.04	ND	ND	0.03	0.01	ND	ND	ND	ND	ND	-	ND	ND	ND	-
Heptachlor [b]	ND	0.01	0.01	0.03	0.02	0.01	0.01	0.02	0.04	ND	0.02	0.01	<0.01	<0.01	<0.01	-
Allethrin [c]	ND	0.05	ND	0.04	0.05	0.01	<0.01	ND	0.04	ND	0.04	-	ND	ND	ND	-
Fenvalerate [c]	0.02	ND	0.04	ND	0.03	0.01	ND	0.02	ND	0.05	0.04	0.02	ND	ND	ND	-
Cypermethrin [c]	ND	ND	0.04	0.04	0.04	0.00	0.02	ND	ND	ND	0.02	-	ND	ND	ND	-
Deltamethrin [c]	ND	ND	0.03	0.07	0.05	0.02	0.04	ND	ND	ND	0.04	-	ND	ND	ND	-

[a-] Organophosphate, [b-]Organochlorine, [c-]Synthetic Pyrethroids, S1=Nkrankwanta, S2=Diabaa, S3=Krakrom, S4=Kwakuanya, S5=Control site, Mini=Minimum, Maxi=Maximum, SD=Standard deviation and ND=non-detected

The mean concentration of alpha-endosulfan in water samples analyzed at distances 0-15m was higher than the mean value recorded at distances 16-30m (Table 4.3). On the contrary, S5 at distance above 30m (control) recorded no detectable concentration of alpha-endosulfan (Table 4.3). The mean concentrations of alpha-endosulfan recorded at distances 0-15m ranged from 0.02 µg/L at S4 to 0.03 µg/L at S2 (Table 4.3) with a mean value of 0.03±0.01 µg/L whereas the concentrations recorded at distances 16-30m ranged from 0.01 µg/L at S1 to 0.03 µg/L at S4 (Table 4.3) with a mean value of 0.02±0.01 µg/L.

Eendosulfan-sulfate was only detected in waters samples analyzed from S1 and S2 at distances 0-15m from the nearest cocoa farms with mean concentrations of 0.02 µg/L and 0.04 µg/L respectively (Table 4.3). The mean value recorded for the two sites was 0.03±0.01 µg/L (Table 4.3).

None of the water samples analyzed from distances 16-30m and above 30m (control) had detectable dieldrin concentrations. However, water samples from S1 and S4 at distances 0-15m to the nearest cocoa farms recorded the minimum and maximum mean concentrations of <0.01 µg/L and 0.03 µg/L of dieldrin respectively with a mean value of 0.03 µg/L (Table 4.3).

The mean p,p´-DDT concentration recorded at distances 16-30m was comparatively higher than the mean value recorded at distances 0-15m (Table 4.3). The mean p,p´-DDT concentrations observed for sites at distances 0-15m ranged from a minimum of <0.01 µg/L at S1 to a maximum of 0.03µg/L at S3 whereas the mean concentrations recorded at distances 16-30m ranged from a minimum of <0.01 µg/L at S4 to a maximum of 0.05 µg/L at S1 (Table 4.3). The mean values of p,p´-DDT for distances

0-15 and 16-30m were 0.03 µg/L and 0.04±0.01 µg/L respectively (Table 4.3). No concentration of p,p´-DDT was recorded at S5 at distances above 30m (control) (Table 4.5).

The mean concentration of heptachlor recorded at distances above 30m (control) was generally low compared to the mean values recorded at distances 0-15m and 16-30m (Table 4.3). However, the concentrations of heptachlor recorded at distances 0-15m ranged from a minimum mean of 0.01 µg/L at S2 and S3 to a maximum mean of 0.03 µg/L at S4 with a mean value of 0.02±0.01 µg/L whereas the values recorded at distances 16-30m ranged from a minimum mean of 0.01 µg/L at S1 to a maximum mean of 0.04 µg/L at S3 with a mean value of 0.02±0.01 µg/L (Table 4.3).

The mean allethrin concentration value recorded at distances 0-15m was relatively higher than at distances 16-30m (Table 4.3). On the other hand, water samples analyzed at distances above 30m (control) had no detectable allethrin concentration (Table 4.3). The concentrations of allethrin recorded at distances 0-15m ranged from 0.04 µg/L at S4 to 0.05 µg/L at S1 with an average concentration of 0.05±0.01 µg/L whereas the values recorded at 16-30m ranged from <0.01 µg/L at S1 to 0.04 µg/L at S3 with a mean value of 0.04 µg/L (Table 4.3).

The fenvalerate average residue observed at distances 16-30m to the nearest cocoa farms was higher than the mean value recorded at distances 0-15m (Table 4.3). Values recorded for water samples at distances 16-30m ranged from 0.02 µg/L to 0.05 µg/L (Table 4.3) whereas values recorded at distances 0-15m ranged from 0.02 µg/L to 0.04 µg/L (Table 4.3). The mean values of fenvalerate at 16-30m and 0-15m were 0.04±0.02 µg/L and 0.03±0.01 µg/L respectively. The lowest value at distances 16-

30m was observed at S1 and the highest at S4, while S1 and S3 recorded the lowest and highest values of fenvalerate at distances 0-15m respectively. Samples from the control sites (S5) at distances above 30m recorded no concentration of fenvalerate (Table 4.3).

Cypermethrin average concentration recorded at distances 0-15m was higher than the average value recorded at 16-30m to the nearest cocoa farms (Table 4.3). At distances 0-15m, cypermethrin residues in the water samples ranged from 0.04 µg/L at S3 to 0.04 µg/L at S4 with a mean value of 0.04±0.00 µg/L (Table 4.3) whereas S1 at distance 16-30m with a mean concentration of 0.02 µg/L was the only site with detectable cypermethrin concentration in the samples analyzed from the distance category (Table 4.3). No concentration of cypermethrin was recorded at S5 (control) for distance above 30m (Table 4.5).

The mean concentration of deltamethrin recorded at distances 0-15m was higher than the mean concentration recorded at distances 16-30m. However, samples from distances above 30m (control) recorded no value for deltamethrin (Table 4.3). Deltamethrin concentrations observed at distances 0-15m ranged from 0.03 µg/L at S3 to 0.07 µg/L at S4 (Table 4.3) with a mean value of 0.05±0.02 µg/L. On the other hand, S1 with a mean value of 0.04 µg/L at 16-30m, was the only site that recorded delatmethrin residue for the distance category (Table 4.3).

Analysis of variance at 95% confidence level revealed that the mean concentrations of pesticide residues recorded in the water samples did not differ significantly ($p > 0.05$) among the sampling distances to the nearest cocoa farms (Appendix D) even though there were differences in residual concentrations of pesticides.

4.3.1.1 Correlation between physico-chemical properties and pesticides residue in water

To investigate the association, the direction and strength of the physico-chemical properties and pesticide residue concentrations measured in the water sample, Pearson's product moment correlation coefficient was used. As shown in Appendix F, considerable numbers of strong positive significant correlation were observed between the following physico-chemical variables in the water. pH was positively correlated with (TDS, NH_3 and EC at ($p < 0.05$) and with TSS at ($p < 0.01$)). Similarly, EC correlated positively with (TSS and NH_3 ($p < 0.05$) and with TDS ($p < 0.01$)). TDS on the other hand correlated positively ($p < 0.05$) with (TSS and NH_3). Temperature was also positively correlated with (Turbidity at ($p < 0.01$) and K^+ at ($p < 0.05$)). Similarly, TSS correlated positively ($p < 0.01$) with (NH_3). Finally, Turbidity was correlated positively ($p < 0.05$) with (K^+).

Additionally, Table 4.4 shows some observations made in terms of strong significant positive relationship between water physico-chemical parameters and pesticide residues in the water samples. Temperature was positively ($p < 0.05$) correlated with (p,p´-DDT and fenvalerate). Similarly, pH correlated positively ($p < 0.05$) with (diazinon, pirimiphos-methyl, p,p´-DDT and deltamethrin and with lindane and endosulfan-sulphate at ($p < 0.01$)). EC was positively ($p < 0.05$) correlated with (diazinon, chlorpyrifos and deltamethrin) and with p,p´-DDT at ($p < 0.01$). Furthermore, TDS correlated positively ($p < 0.05$) with (diazinon, chlorpyrifos and deltamethrin) and with p,p´-DDT at ($p < 0.01$). Similarly, Turbidity correlated positively with (lindane ($p < 0.01$) and with p,p´-DDT ($p < 0.05$)). Also, TSS was positively correlated with (diazinon and p,p´-DDT at ($p < 0.05$) and with lindane at (p

< 0.01)). Additionally, ammonia was positively correlated with (diazinon, lindane at (p < 0.01) and with p,p´-DDT at (p < 0.05)). Similarly, phosphate was positively correlated with (pirimiphos-methyl and p,p´-DDT at (p <0.05) and with lindane (p < 0.01)). Sodium also correlated positively with (chlorpyrifos at (p < 0.05) and with endosulfan-sulfate at (p < 0.01)). In addition, potassium was positively correlated with (pirimiphos-methyl, p,p´-DDT and allethrin at (p < 0.05) and with lindane and endosulfan-sulfate at (p < 0.01)). On the other hand, some strong negative significant correlations were also observed between water physico-chemical parameters and pesticide residues detected as shown in Table 4.4. Temperature correlated negatively with (pirimiphos-methyl, alpha-endosulfan and cypermethrin at (p < 0.05) and with lindane and endosulfan-sulfate at (p < 0.01)). Additionally, pH was negatively (p < 0.01) correlated with (fenvalerate). Similarly, EC correlated negatively with (lindane and endosulfan-sulfate at (p < 0.01). TDS correlated negatively with lindane and endosulfan-sulfate (p < 0.01)). Again, turbidity correlated negatively with (alpha-endosulfan and endosulfan-sulfate at (p < 0.01) and with allethrin at (p < 0.05)). Similarly, TSS significantly correlated negatively with (alpha-endosulfan at (p < 0.05) and with endosulfan-sulfate and deltamethrin at (p < 0.01)). Furthermore, nitrate levels in the water correlated negatively with (alpha-endosulfan, allethrin and deltamethrin at (p < 0.05) and with endosulfan-sulfate and lindane at (p < 0.01)). Ammonia was negatively (p < 0.01) correlated with (endosulfan-sulfate and deltamethrin). Similarly, phosphate was negatively correlated with (alpha-endosulfan, fenvalerate and allethrin, at (p < 0.05) and with endosulfan-sulfate at (p <0.01)). Sodium negatively correlated with (lindane at (p < 0.01), and with cypermethrin and fenvalerate at (p < 0.05)). Finally, potassium correlated negatively with (alpha-endosulfan and fenvalerate at (p < 0.05)).

Table 4.4 Pearson's product moment correlation coefficient between water physicochemical parameters and pesticide residues detected

	EC	pH	TDS	Temp	TSS	Turbidity	NO_3^-	NH_3	PO_4^{3-}	Na^+	K^+
Diazinon[a]	0.984*	0.977*	0.978*	-0.116	0.981*	-0.106	-0.274	0.997**	-0.031	0.303	0.064
Chlorpyrifos[a]	0.748*	0.286	0.745*	0.140	0.027	0.136	-0.368	0.271	-0.032	0.739*	0.474
PIRI[a]	-0.437	0.614*	-0.433	-0.806*	0.057	0.449	-0.368	0.307	0.820*	-0.382	0.935*
Lindane[b]	-0.999**	0.985**	-0.957**	-0.963**	0.981**	0.978**	-0.963**	0.999**	0.956**	-0.916**	0.975**
Cypermethrin[c]	-0.140	0.269	-0.202	-0.666*	0.378	-0.380	0.588	0.456	-0.495	-0.773*	-0.482
ALPHA[b]	-0.080	-0.368	-0.076	-0.801*	-0.672*	-0.933**	-0.881*	-0.461	-0.975*	0.060	-0.764*
Dieldrin[b]	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR
p,p´-DDT[b]	0.901**	0.855*	0.904**	0.998*	0.986*	0.981*	-0.156	0.984*	0.682*	0.500	0.855*
ENDOSUL[b]	-0.956**	0.976**	-0.965**	-0.974**	-0.961**	-0.983**	-0.995**	-0.953**	-0.976**	0.986**	0.965**
Heptachlor[b]	0.177	0.297	0.158	-0.342	0.177	-0.414	-0.330	0.277	0.394	0.337	-0.497
Allethrin[c]	-0.374	-0.321	-0.361	-0.297	-0.545	-0.880*	-0.853*	-0.531	-0.792*	-0.966*	0.829*
Fenvaerate[c]	0.431	-0.614**	0.427	0.679*	-0.117	-0.388	0.300	-0.233	-0.677*	0.535	-0.916*
Deltamethrin[c]	0.980*	0.980*	0.969*	-0.402	-0.968**	-0.382	-0.786*	-0.978**	0.074	0.551	0.034

*Correlation is significant at the 0.05 level (2-tailed) ** Correlation is significant at the 0.01 level (2-tailed) NR = No Established Relationship

[a-] Organophosphate, [b-]Organochlorine, [c-]Synthetic Pyrethroids, Temp=Temperature, EC=electrical conductivity, TDS=Total dissolved solids, TSS=Total suspended solids, PO_4^{3-}=Phosphate, NO_3^-=Nitrate, NH_3=ammonia, Na^+=Sodium, K^+=Potassium, ALPHA=alpha-endosulfan, ENDOSUL=endosulfan-sulfate, PIRI=pirimiphos-methyl

4.3.2 Concentrations of organophosphate, organochlorine and synthetic pyrethroids pesticides in soil samples

Soil samples analyzed showed the presence of thirteen different pesticide residues comprising three organophosphates, four organochlorines and six synthetic pyrethroids (Table 4.5). The order of percentage of the organophosphate residues occurring in the samples was as follows; chlorpyrifos (56.3%) > pirimiphos-methyl (43.8%) > profenefos (37.5%). The detection rates of the organochlorine residues decreased in the following order: dieldrin (62.5%) > p,p´-DDT (50%) > lindane (31.3%) > beta-HCH (26.6%). The percentage occurrence of synthetic pyrethroids pesticide residues was highest for lambda-cyhalothrin and cypermethrin (50%) respectively, followed by cyfluthrin (43.8%), deltamethrin (37.5%), bifenthrin (31.3%), with allethrin (25%) being the lowest. The limit of detection (LOD) of organophosphate, organochlorine and synthetic pyrethroids residues were 0.010 mg/kg, 0.005 mg/kg and 0.010 mg/kg, respectively.

The mean concentrations of chlorpyrifos in soil samples analyzed from the sampled sites ranged from 0.01 mg/kg to 0.04 mg/kg (Table 4.5). The lowest concentration was recorded at S3 while the highest concentration was recorded at S1. No concentration of chlorpyrifos was recorded in samples at S5 (control) (Table 4.5).

The lowest mean concentration of profenofos in the soil samples analyzed was observed at S1 and S4 with a concentration of 0.02 mg/kg respectively while the highest mean concentration was observed at S2 and S3 with concentrations of 0.04 mg/kg respectively (Table 4.5). S5 (control) recorded no profenofos residue concentration (Table 4.5).

Table 4.5 Minimum, maximum, mean and standard deviation of organophosphate, organochlorine and synthetic pyrethroids concentrations (mg/kg) in soil samples from the study area

Sites	S1				S2				S3				S4				S5 (Control)			
Pesticides	**Mini**	**Maxi**	**Mean**	**SD**	**Mini**	**Maxi**	**Mean**	**SD**	**Mini**	**Maxi**	**Mean**	**SD**	**Mini**	**Maxi**	**Mean**	**SD**	**Mini**	**Maxi**	**Mean**	**SD**
Chlorpyrifos [a]	0.03	0.06	0.04	0.02	ND	0.04	0.03	0.01	ND	0.01	0.01	-	ND	0.03	0.03	0.00	ND	ND	ND	-
Profenofos [a]	ND	0.02	0.02	-	ND	0.04	0.04	-	ND	0.04	0.04	-	ND	0.02	0.02	0.00	ND	ND	ND	-
Pirimiphos-methyl [a]	ND	0.05	0.04	0.01	ND	0.02	0.02	-	ND	0.02	0.02	-	ND	0.01	0.01	-	ND	ND	ND	-
Lindane [b]	ND	0.03	0.03	0.00	ND	ND	ND	-	ND	0.04	0.04	-	ND	0.05	0.05	-	ND	ND	ND	-
Dieldrin [b]	ND	ND	ND	-	0.02	0.03	0.02	0.00	ND	0.02	0.02	0.00	0.01	0.03	0.02	0.01	ND	<0.01	<0.01	-
Beta-HCH [b]	ND	<0.01	<0.01	-	ND	0.03	0.03	-	ND	0.05	0.05	-	ND	0.04	0.04	-	ND	ND	ND	-
p,p´-DDT [b]	ND	0.05	0.04	0.02	ND	0.02	0.02	-	ND	ND	ND	-	ND	0.03	0.03	0.00	ND	<0.01	<0.01	-
Lambda-cyhalothrin [c]	ND	0.02	0.02	0.00	ND	0.04	0.03	0.01	ND	0.03	0.03	-	ND	0.04	0.03	0.01	ND	ND	ND	-
Allethrin [c]	ND	ND	ND	-	ND	0.02	0.02	-	ND	0.03	0.02	0.01	ND	ND	ND	-	ND	ND	ND	-
Cyfluthrin [c]	ND	ND	ND	-	ND	0.06	0.04	0.02	ND	0.05	0.04	0.01	ND	0.05	0.03	0.01	ND	ND	ND	-
Cypermethrin [c]	ND	<0.01	<0.01	-	ND	0.04	0.04	0.00	ND	0.05	0.03	0.02	ND	0.06	0.04	0.02	ND	ND	ND	-
Deltamethrin [c]	ND	0.03	0.03	0.00	ND	0.03	0.03	-	ND	0.04	0.04	-	ND	0.06	0.06	-	ND	ND	ND	-
Bifenthrin [c]	ND	<0.01	<0.01	-	ND	0.02	0.02	-	ND	0.03	0.03	-	ND	0.03	0.03	-	ND	ND	ND	-

[a-] Organophosphate, [b-]Organochlorine, [c-]Synthetic Pyrethroids, Mini=Minimum, Maxi=Maximum, Mn=Mean, SD=Standard deviation, ND=non-detected, S1=Nkrankwanta, S2= Diabaa, S3=Krakrom, S4=Kwakuanya, S5=Control sites

The mean pirimiphos-methyl concentrations in the soil samples analyzed ranged from a minimum of 0.01 mg/kg at S4 to a maximum of 0.04 mg/kg at S1 (Table 4.5). Samples from S5 (control) had no detectable pirimiphos-methyl concentration (Table 4.5).

The mean concentration of lindane in soil samples analyzed from the study area ranged from a minimum of 0.03 mg/kg at S1 to a maximum of 0.05 mg/kg at S4. Soil samples from S2 and S5 recorded no lindane concentration (Table 4.5).

The mean dieldrin concentrations in the soil samples ranged from <0.01 mg/kg to 0.02 mg/kg (Table 4.5). The lowest mean concentration was recorded at S5 (control) whiles the highest mean concentrations was observed at S2, S3, and S4 respectively (Table 4.5). No dieldrin residue was however recorded at S1 (Table 4.5).

The mean beta-HCH concentrations in the soil samples analyzed ranged from a minimum concentration of <0.01 mg/kg at S1 to a maximum concentration of 0.05 mg/kg at S3 (Table 4.5). No concentration of beta-HCH was recorded at S5 (control) (Table 4.5).

The mean concentrations of p,p´-DDT in the soil samples analyzed ranged from <0.01 mg/kg at S5 (control) to 0.04 mg/kg at S1 (Table 4.5). Samples from S3 recorded no p,p´-DDT concentration (Table 4.5).

The mean lambda-cyhalothrin residue in the soil samples ranged from 0.02 mg/kg to 0.03 mg/kg (Table 4.5). The lowest mean concentration was recorded at S1 while the highest mean concentration was recorded at S2, S3 and S4 respectively (Table 4.5). However, no lambda-cyhalothrin residue was detected in soil samples from S5 (control) (Table 4.5).

Allethrin concentration in the soil samples analyzed was recorded only in soil samples at S2 and S3 with mean concentrations of 0.02 mg/kg respectively (Table 4.5).

The mean concentrations of cyfluthrin in the soil samples analyzed ranged from a minimum of 0.03 mg/kg at S4 to a maximum of 0.04 mg/kg at S2 and S3 respectively (Table 4.5). No cyfluthrin concentration was however observed in soil samples analyzed from S1 and S5 (control) (Table 4.5).

The mean cypermethrin concentrations in the soil samples ranged from <0.01 mg/kg to 0.04 mg/kg (Table 4.5). The minimum mean concentration was obtained at S1 while the maximum mean concentration of was recorded at S2 and S4 respectively. Samples of soil analyzed from S5 (control) recorded no cypermethrin concentration (Table 4.5).

The mean concentrations of deltamethrin in the soil samples analyzed ranged from 0.03 mg/kg to 0.06 mg/kg (Table 4.5). The lowest mean concentration was recorded at S1 and S2 respectively while the highest mean concentration was recorded at S4 (Table 4.5.). Sampled site S5 (control) on the other hand recorded no deltamethrin concentration (Table 4.5).

Bifenthrin concentration was detected in all sampled sites except S5 (control). Samples from S1 recorded the least mean bifenthrin concentration of <0.01 mg/kg while samples from S3 and S4 recorded the highest mean concentrations of 0.03 mg/kg respectively (Table 4.5).

The mean concentrations of the detected pesticides in the soils samples analyzed did not differ significantly among the various sampling sites ($p > 0.05$) (Appendix G).

4.3.2.1 Correlation between physico-chemical properties and pesticides residue in soil

To investigate the association, the direction and strength of the physico-chemical properties and pesticide residues concentrations measured in the soil samples, Pearson's product moment correlation coefficient was used.

Considerable numbers of significant strong positive and negative correlations were observed between the following physico-chemical variables in the soils (Appendix H).

pH was positively ($p < 0.05$) correlated with (NH_4^+). Additionally, % OC correlated positively with (nitrate and exchangeable potassium at ($p < 0.05$) and with % Silt and % OM at ($p < 0.01$)). Similarly, % OM correlated positively with (exchangeable K at ($p < 0.05$) and with % Silt and nitrate at ($p < 0.01$)). Also, nitrate was positively ($p < 0.05$) correlated with (% Silt). Similarly, exchangeable potassium correlated positively ($p < 0.05$) with (% Silt). Also, available K was positively ($p < 0.05$) correlated with (% Clay).

On the other hand, pH was negatively ($p < 0.05$) correlated with (EC, TN, pH and % clay). Additionally, EC correlated negatively ($p < 0.05$) with (NH_4^+). Similarly, exchangeable potassium correlated negatively ($p < 0.05$) with (% Sand). Again, %TN was negatively ($p < 0.05$) correlated with (NH_4^+, exchangeable K and available P). In addition, available K correlated negatively ($p < 0.05$) with (available P and % sand).

Additionally, Table 4.6 shows considerable numbers of significant strong positive and negative correlation observed between some soil physico-chemical parameters and pesticide residue recorded in the soils.

pH was positively ($p < 0.05$) correlated with (lindane, dieldrin, beta-HCH, lambda-cyhalothrin, cyfluthrin, cypermethrin, deltamethrin and befenthrin). Similarly, organic carbon correlated positively with (lindane, dieldrin, beta-HCH and cypermethrin, at ($p < 0.05$) and with lambda-cyhlothrin, cyfluthrin and bifenthrin at ($p < 0.01$)). Additionally, a strong positive correlation also existed between organic matter and (lindane, dieldrin, beta-HCH, cypermethrin, cyfluthrin and bifenthrin at ($p < 0.05$) and with lambda-cyhlothrin at ($p < 0.01$)). There was also a high positive ($p < 0.05$) correlation between available potassium and pirimiphos-methyl. Similarly, available phosphorus positively ($p < 0.05$) correlated with (lindane) and with deltamethrin at ($p < 0.01$). The ammonium levels in the soil also correlated positively with (lindane at ($p < 0.05$) and with deltamethrin at ($p < 0.01$)). There was also a strong positive ($p < 0.05$) correlation between nitrate and (profenofos, dieldrin, beta-HCH, lambda-cyhalothrin, allethrin and cyfluthrin). Similarly, exchangeable potassium correlated positively ($p < 0.05$) with (lindane, dieldrin, beta-HCH, lambda-cyhalothrin, cyfluthrin, cypermethrin, deltamethrin and bifenthrin). Similarly, percent sand was positively ($p < 0.05$) correlated with chlorpyrifos. Also, percent clay was positively ($p < 0.05$) correlated with (pirimiphos-methyl). Percent silt was also positively correlated with deltamethrin, lambda-cyhalothrin and cyfluthrin at ($p < 0.05$) and with beta-HCH, dieldrin and bifenthrin at ($p < 0.01$).

On the other hand, pH was negatively ($p < 0.05$) correlated with (chlorpyrifos, pirimiphos-methyl, and p,p´-DDT). EC correlated negatively ($p < 0.05$) with (lindane and bifenthrin). Similarly, organic carbon was negatively ($p < 0.05$) correlated with (chlorpyrifos, pirimiphos-methyl and p,p´-DDT). Additionally, a high negative ($p < 0.05$) correlation also existed between organic matter and (chlorpyrifos, pirimiphos-

methyl and p,p´-DDT). Available potassium was also negatively ($p < 0.05$) correlated with (lindane and deltamethrin). Similarly, available phosphorus was negatively ($p < 0.05$) correlated with (pirimiphos-methyl and cyfluthrin). The ammonium levels in the soil also correlated negatively ($p < 0.05$) with (chlorpyrifos). Also, nitrate was negatively ($p < 0.05$) correlated with (chlorpyrifos and p,p´-DDT). Furthermore, exchangeable potassium correlated positively ($p < 0.05$) with chlorpyrifos and with pirimiphos-methyl at ($p < 0.01$). Similarly, total nitrogen was negatively correlated with (pirimiphos-methyl, beta-HCH and bifenthrin at ($p < 0.05$) and with lindane and deltamethrin at ($p < 0.01$)). Percent sand also correlated negatively ($p < 0.05$) with (p,p´-DDT and beta-HCH). In addition, percent clay correlated negatively ($p < 0.05$) with (lindane, dieldrin, beta-HCH, lambda-cyhalothrin, cyfluthrin, cypermethrin and bifenthrin). Similarly, percent silt correlated negatively ($p < 0.05$) with (chlorpyrifos, lindane and pirimiphos-methyl) and with p,p´-DDT and cypermethrin at ($p < 0.01$)).

Table 4.6 Pearson's product moment correlation coefficient between soil physicochemical parameters and pesticide residues detected

	pH	EC	% OC	% OM	% TN	NH_4^+	NO_3^-	Ava. K	Ava. P	Ex-K	% Sand	% Clay	% Silt
CHL[a]	-0.863*	0.270	-0.653*	-0.661*	0.342	-0.628*	-0.751*	-0.360	0.144	-0.656*	0.803*	0.401	-0.741*
PROF[a]	0.352	0.486	0.530	0.533	0.329	-0.128	0.985*	0.404	-0.564	0.180	-0.133	-0.465	0.455
PIRI[a]	-0.784*	0.018	-0.947*	-0.945*	-0.725*	-0.323	-0.392	0.648*	-0.673*	-0.932**	0.329	0.920*	-0.942*
LIND[b]	0.753*	-0.792*	0.886*	0.882*	-0.997**	0.645*	0.204	-0.774*	0.864*	0.932*	-0.425	-0.970*	-0.863*
DIEL[b]	0.793*	0.172	0.998*	0.998*	-0.482	0.222	0.708*	-0.388	0.348	0.851*	-0.327	-0.951*	0.965**
HCH[b]	0.959*	-0.167	0.932*	0.936*	-0.622*	0.554	0.666*	-0.168	0.308	0.925*	-0.997*	-0.943*	0.980**
DDT[b]	-0.755*	0.034	-0.660*	-0.667*	0.141	-0.420	-0.886*	-0.402	0.297	-0.544	-0.637*	0.452	-0.700**
LAM[c]	0.793*	0.172	0.998**	0.998**	-0.482	0.222	0.708*	-0.388	0.348	0.851*	-0.327	-0.951*	0.965*
ALL[c]	0.352	0.486	0.530	0.533	0.329	-0.128	0.985*	0.404	-0.564	0.180	-0.133	-0.465	0.455
CYF[c]	0.736*	0.284	0.953**	0.953*	-0.281	0.137	0.862*	-0.185	-0.999*	0.729*	-0.300	-0.895*	0.903*
CYP[c]	0.656*	0.294	0.970*	0.967*	-0.459	0.055	0.592	-0.581	0.461	0.794*	-0.122	-0.997*	-0.901**
DEL[c]	0.654*	-0.563	0.523	0.524	-0.980**	0.632**	-0.247	-0.678*	0.934**	0.823*	-0.483	-0.449	0.626*
BIF[c]	0.941*	-0.998*	0.956**	0.959*	-0.712*	0.528	0.558	-0.348	0.474	0.970*	-0.592	-0.829*	0.997**

*Correlation is significant at the 0.05 level (2-tailed) ** Correlation is significant at the 0.01 level (2-tailed)

[a-] Organophosphate, [b-]Organochlorine, [c-]Synthetic Pyrethroids, OC=Organic carbon, OM=Organic matter, %TN=percentage nitrogen, Ava-P=available phosphorus, Ava-K=available potassium, EC=Electrical conductivity, Ex-K=Exchangeable potassium, NO_3^-=Nitrate, NH_4^+= Ammonium, CHL=chlorpyrifos, PROF=profenofos, PIRI=pirimiphos-methyl, LIND=lindane, DIEL=dieldrin, HCH=beta-HCH, DDT=p,p´-DDT, LAM=lambda-cyhalothrin, ALL=allethrin, CYF=cyfluthrin, CYP=cypermethrin, DEL=deltamethrin, BIF=bifenthrin

4.3.3 Concentrations of organophosphate, organochlorine and synthetic pyrethroids pesticides in cocoa beans samples

Cocoa beans samples analyzed showed the presence of fifteen different pesticide residues comprising three organophosphates, six organochlorines and six synthetic pyrethroids (Table 4.7). The different organophosphates residues detected were in the order: chlorpyrifos (75%) > pirimiphos-methyl (62.5%) > diazinon (56.3%), in terms of percentage of occurrence. The high frequency of occurrence of the organochlorine residues was p,p´-DDT (62.5%), followed by lindane (56.3%), beta-HCH (50%), aldrin (43.8%), dieldrin (37.5%) and methoxychlor (31.3%). The detection rates of the synthetic pyrethroids residues decreased in the following order: cypermethrin (87.5%) > deltamethrin (56.3%) > allethrin (50%) > lambda-cyhalothrin, permethrin and bifenthrin (31.1%), respectively. The limit of detection (LOD) of organophosphate, organochlorine and synthetic pyrethroids were 0.010 mg/kg, 0.005 mg/kg and 0.010 mg/kg respectively.

Diazinon concentrations were detected in cocoa beans samples analyzed from all the sampled sites. The mean concentration of diazinon in the samples ranged from a minimum of 0.02 mg/kg at S2, S3, and S4 respectively to a maximum of 0.04 mg/kg at S1 (Table 4.7).

The highest mean concentration of chlorpyrifos was 0.42 mg/kg and was recorded at S3 while the lowest mean concentration was 0.09 mg/kg and was observed at S1. Samples from S2 however, recorded no detectable chlorpyrifos residue (Table 4.7).

Table 4.7 Minimum, maximum, mean and standard deviation of organophosphate, organochlorine and synthetic pyrethroids concentrations (mg/kg) in cocoa beans samples analyzed from the study area

Sites	S1				S2				S3				S4			
Pesticides	**Mini**	**Maxi**	**Mean**	**SD**	**Mini**	**Maxi**	**Mean**	**SD**	**Mini**	**Maxi**	**Mean**	**SD**	**Mini**	**Maxi**	**Mean**	**SD**
Diazinon [a]	ND	0.04	0.04	-	ND	0.02	0.02	0.00	ND	0.02	0.02	-	ND	0.02	0.02	0.00
Chlorpyrifos [a]	0.04	0.16	0.09	0.06	ND	ND	ND	-	ND	0.74	0.42	0.09	0.06	0.15	0.10	0.05
Pirimphos-methyl [a]	ND	0.03	0.03	0.00	ND	0.03	0.03	-	ND	0.05	0.04	0.02	ND	ND	ND	-
Lindane [b]	ND	0.03	0.03	-	ND	0.04	0.04	0.00	ND	0.05	0.05	-	ND	0.04	0.03	0.01
Beta-HCH [b]	ND	<0.02	<0.02	-	ND	<0.02	<0.02	-	0.02	0.04	0.03	0.01	ND	ND	ND	-
Dieldrin [b]	ND	0.02	0.02	-	ND	0.05	0.05	-	ND	0.05	0.05	-	ND	0.03	0.03	-
Aldrin [b]	ND	<0.02	<0.02	-	ND	0.05	0.05	-	ND	ND	ND	-	ND	0.06	0.06	-
p,p´-DDT [b]	ND	0.05	0.04	-	ND	0.06	0.06	-	ND	0.04	0.04	-	ND	ND	ND	-
Methoxychlor [b]	ND	0.04	0.04	-	ND	<0.01	<0.01	-	ND	0.03	0.03	-	ND	ND	ND	-
Allethrin [c]	ND	<0.01	<0.01	-	ND	0.01	0.01	-	ND	<0.01	<0.01	-	ND	0.02	0.02	-
Lambda-cyhalothrin [c]	ND	0.02	0.02	-	ND	ND	ND	-	0.03	0.06	0.05	0.02	ND	ND	ND	-
Cypermethrin [c]	0.02	0.06	0.04	0.02	ND	0.02	0.02	0.00	ND	0.04	0.04	-	ND	0.06	0.05	0.01
Deltamethrin [c]	ND	<0.01	<0.01	-	ND	0.06	0.06	-	ND	0.06	0.06	-	ND	0.05	0.04	0.01
Permethrin [c]	ND	0.02	0.02	-	ND	0.02	0.02	-	ND	ND	ND	-	ND	0.03	0.03	-
Bifenthrin [c]	ND	<0.01	<0.01	-	ND	0.03	0.03	-	ND	ND	ND	-	ND	<0.01	<0.01	-

[a-] Organophosphates, [b-]Organochlorines, [c-]Synthetic Pyrethroids, ND=non-detected, Mini=Minimum, Maxi=Maximum, SD=standard deviation, S1=Nkrankwanta, S2=Diabaa, S3=Krakrom and S4=Kwakuanya

The mean concentrations of pirimiphos-methyl in the cocoa beans analyzed ranged from 0.03 mg/kg to 0.04 mg/kg (Table 4.7). The lowest mean concentration occurred at S1 and S2 respectively whiles the highest mean concentration occurred at S3. Cocoa beans from S4 recorded no pirimiphos-methyl concentration (Table 4.7).

Lindane concentration was recorded in cocoa beans analyzed from all the sampled sites and ranged from a mean of 0.03 mg/kg to 0.05 mg/kg. The lowest mean concentration was recorded at S1 and S4 whiles the highest mean concentration was recorded at S3 (Table 4.7).

The mean concentration of beta-HCH in cocoa beans samples ranged from <0.02 mg/kg to 0.03 mg/kg. The lowest mean concentration was recorded at S1 and S2 respectively whiles the highest mean concentration was recorded at S3 (Table 4.7). S4 recorded no concentration of beta-HCH (Table 4.7).

Concentrations of dieldrin were recorded at all the sampled sites. The mean dieldrin residues in the samples analyzed ranged from a minimum concentration of 0.02 mg/kg at S1 to a maximum concentration of 0.05 mg/kg at S2 and S3 respectively (Table 4.7).

Cocoa beans samples from S1 recorded the lowest mean concentration of <0.02 mg/kg of aldrin whiles S4 recorded the highest mean concentration of 0.06 mg/kg (Table 4.7). However, cocoa beans samples from S3 recorded no aldrin residue concentration (Table 4.7).

The mean p,p´-DDT concentrations in cocoa beans samples analyzed ranged from a minimum of 0.04 mg/kg at S1 and S3 respectively to a maximum of 0.06 mg/kg at S2 (Table 4.7). p,p´-DDT residue was however, not detected at S4 (Table 4.7).

The lowest mean concentration of methoxychlor in the cocoa beans analyzed was recorded at S2 with a mean value of <0.01 mg/kg whiles the highest mean concentration of methoxychlor was recorded at S1 with a mean value of 0.04 mg/kg. Methoxychlor was however, not detected at S4 (Table 4.7).

The mean concentrations of allethrin in cocoa beans samples analyzed ranged from <0.01 mg/kg to 0.02 mg/kg (Table 4.7). The minimum mean concentration was recorded at S1 and S3 respectively whiles the maximum mean concentration was recorded at S4 (Table 4.7).

Lambda-cyhalolthrin concentration was detected only in cocoa beans samples analyzed from S1 and S3 with mean concentrations of 0.02 mg/kg and 0.05 mg/kg respectively (Table 4.7).

The mean concentration of cypermethrin in cocoa beans samples analyzed ranged from 0.02 mg/kg to 0.05 mg/kg as shown in Table 4.7. The lowest mean concentration was recorded at S2 whiles the highest mean concentration was recorded at S4 (Table 4.7).

The lowest mean concentration of deltamethrin in cocoa beans was observed for samples analyzed from S1 with a mean value of <0.01 mg/kg whiles the highest mean concentration was observed for cocoa beans samples analyzed from S2 and S3 with a concentration of 0.06 mg/kg respectively (Table 4.7).

The mean permethrin concentrations recorded in the cocoa beans samples analyzed ranged from a minimum of 0.02 mg/kg at S1 and S2 respectively to a maximum value of 0.03 mg/kg at S4 (Table 4.7). Samples from S3 recorded no concentration of permethrin (Table 4.7).

Cocoa beans samples analyzed from S1 and S4 recorded the lowest mean concentration of <0.01 mg/kg for bifenthrin respectively whiles samples analyzed from S2 recorded the highest mean concentration of 0.03 mg/kg for bifenthrin (Table 4.7). However, S3 recorded no concentration of bifenthrin (Table 4.7).

Analysis of variance (ANOVA) revealed no significant differences ($p > 0.05$) in pesticide residues in cocoa beans among sampled sites even though there were differences in residual concentrations of pesticides (Appendix I).

4.4 Farmers' survey

A total of 240 cocoa farmers were interviewed during the field survey in Nkrankwanta, Diabaa, Krakrom and Kwakuanya cocoa growing communities in the Dormaa West District of the Brong Ahafo Region of Ghana.

4.4.1 Demographic characteristics of farmers

The demographic characteristics of farmers are shown in Table 4.8. A total of 87.5% of respondents were males while 12.5% were females. Majority (63.8%) of the respondents were aged between 40-59 years while 25.8% were above 60 years. Only 10.4% of the farmers were between the ages of 20-39 years. The mean age of the cocoa farmers was 52 years and the maximum age was about 83 years. About 81.2% of the respondents had formal education, mostly middle/senior high school (43.3%), while 34.6% had primary/junior high school education and tertiary education (3.3%), with 18.8% of the farmers with no formal education. As shown in Table 4.8 about 94.2% of the farmers had 11 or more years of farming experience in cocoa production. The average number of years farmers have been in cocoa farming in the study area was 21.8.

Table 4.8 Demographic characteristics of respondents

Variable	Description	Percentage (%)
Sex of farmers	Male	87.5
	Female	12.5
Age of farmers	20-29	2.1
	30-39	8.3
	40-49	32.5
	50-59	31.3
	Above 60	25.8
Educational level	No Education	18.8
	Primary/JHS	34.6
	Middle/SHS	43.3
	Tertiary	3.3
Farmers years of experience in cocoa cultivation	5-10	5.8
	11-15	15.7
	16-20	17.8
	Above 20	60.7

Source: Field work, 2015

4.5 The types, sources and methods of pesticide application of cocoa farmers

4.5.1 Farmers' benefiting from cocoa mass spraying programme by Government of Ghana

The free mass cocoa spraying exercise introduced in the 2001/2002 farming season by the Government of Ghana was evaluated. Majority of the farmers (60.4%) benefited from the spraying exercise in the year under review (2014/2015). Some farmers (39.6%) however do not benefit from the exercise due to the location of their farms, particularly those situated between two communities which sometimes led to demarcation problems. In addition, the distance to some farms, and the age of the cocoa farms (cocoa plantations that were more than 30 years) also deterred mass sprayers. The breakdown of spraying machine and lack of adequate amount of chemicals as well as poor productivity of some cocoa plantations among others were some reason given for not benefiting from the exercise. The study however showed that majority of farmers (51.7%) that benefited from the programme in the year under

review had their farms sprayed only once while only 6.9% of farmers had their farms sprayed four times (Appendix J).

4.5.2 Knowledge of the COCOBOD approved pesticides and frequency of application

The insecticides approved by COCOBOD for use by cocoa farmers are Confidor (Imidacloprid), Akatemaster (Bifenthrin), Cocostar (Bifenthrin + Pirimiphos-methyl), Carbamult (Promecarb) and Actara (Thiamethoxam). The approved fungicides for use by cocoa farmers are Ridomil (Metalaxyl cuprous oxide), Nordox (Cuprous oxide), Funguran (Cuprous Hydroxide), Champion (Cuprous Hydroxide), Kocide (Cupric Hyroxide), Fungikill (Cupric Hydroxide + Metalaxyl) and Metalm (cuprous Oxide + Metalaxyl) (Adjinah and Opoku, 2010). All the respondents in the study area know about the approved insecticides and fungicides for cocoa pest and disease control when interviewed. The Cocoa Research Institute of Ghana (CRIG) recommends that cocoa farms should be sprayed between July and November when insect and fungus infestation is high (Abankwah *et al.*, 2010). It was clear that majority of the farmers (72.9%) do not know about this recommendation.

4.5.3 Types of chemicals used by cocoa farmers in controlling insect pests and diseases

All the respondents indicated they depend on chemicals to control pest and diseases. Among the COCOBOD recommended pesticides, Confidor, Akatemaster, Nordox, Kocide, Champion, Funguran, Metalm and Ridomil are the mostly used. However, 75% of farmers indicated the use of other pesticides that are not approved by COCOBOD for cocoa production, i.e. Akatesuro, Argine, Buffalo-Super, Lamtox,

Sunpyrifos, Sumitox, DDT, Dursban, Pyrethroids-Decis, Kombat, and Controller-super, among others (details as shown in Appendix K).

4.5.4 Farmers' sources of pesticides and knowledge on application rates

Majority (87.9%) of farmers purchase their pesticides from agro-chemical shops whereas the remaining (12.1%) obtain their pesticides from other cocoa farmers. However, majority of farmers (42.1%) indicated that the selection of pesticides is based on its effectiveness in pest and disease control, while 27.1% indicated that pesticides selection is based on the availability in the market. In addition, 16.3% indicated that their choice is based on affordability whiles the remaining (14.5%) indicated recommendations by fellow farmers and extension agents as the basis for selection. In response to question of knowledge on pesticides application rates, majority of cocoa farmers (85%) indicated that they have knowledge on pesticides application rates. When asked about the source of this knowledge, majority of the respondents (50%) indicated they depend on chemical sellers for the application rates of pesticides, whereas 10% seek help from extension officers. Only 15% of the respondents indicated they read instructions on the pesticides label themselves while the remaining 25% of the farmers obtain information on pesticides application rate from fellow cocoa farmers and farm based organizations.

4.5.4.1 Factors influencing farmers' choice of source of pesticides

Table 4.9 presents the results of probit regression for the factors influencing the choice of source of pesticides.

Table 4.9 Probit results on factors influencing farmers' choice of source of pesticides

Variable	Coefficient	P values	Marginal effect
Gender	2.765	0.000**	0.811
Education level	1.758	0.002**	0.228
Farming experience	-0.015	0.281	-0.004
Cocoa income	0.000	0.007**	0.000
Extension services	0.612	0.073	0.158
Chemical shop	0.459	0.101	0.115
FBO	0.184	0.580	0.043
Age	-0.029	0.048*	-0.007
Farm size	0.016	0.345	-0.004
Constant	-1.662	0.028*	
Regression Diagnostics			
Log likelihood	-65.633		
Pseudo R2	0.5249		
LR chi2 (9)	145.05		
Prob > chi2	0.0000		

*, ** indicate 5% and 1% significance levels

Source: Author's computation (2015)

Results show that, farming experience, access to extension services, presence or nearness to agrochemical shop, membership of farm based organization (FBO) and farm size did not influence the source of choice of pesticide. However, gender, educational level and income from cocoa significantly ($p < 0.01$) influenced the choice of source of purchased of pesticide with age influencing at probability $p < 0.05$.

4.5.4.2 Factors influencing farmers' knowledge on pesticides application rate

Table 4.10 presents the results of the probit regression for the factors influencing the choice of a source of pesticides.

Table 4.10 Probit results on factors influencing farmers' knowledge on application rates

Variable	Coefficient	P values	Marginal effect
Education level	0.448*	0.019	0.177
Farming experience	0.012	0.060	0.005
Extension services	0.660**	0.001	0.255
Chemical shop	0.431*	0.020	0.171
FBO	0.399*	0.028	0.158
Age	-0.025**	0.000	-0.010
Constant	-1.247**	0.008	
Regression Diagnostics			
Log likelihood	-141.236		
Pseudo R2	0.1495		
LR chi2 (6)	49.64		
Prob > chi2	0.0000		

*, ** 5% and 1% significance levels

Source: Author's computation (2015)

From the Table, knowledge of pesticides application rate is significantly influenced by educational level of famer, access to extension services, presence of agro chemical shop, membership of farm base organisation (FBO) and age of farmer. Farming experience did not however influence knowledge of pesticides application rate.

4.5.5 Frequency of pesticides applications in the year under review

Majority of farmers (51.2%) indicated more than three times pesticides spray in the year under review whilst 24.6%, 14.2% and 10% applied pesticides thrice, twice and once respectively (Appendix L) in addition to what some farmers (60.4%) received from the Government of Ghana cocoa mass spraying exercise. Farmers' decision to apply pesticide was informed by various sources. About 50.8% of the farmers interviewed mainly look out for the presence of pest and disease on cocoa to inform them on when to apply pesticides while 16.7% did routine (calendar) spraying of pesticides to control insect pests and diseases on their cocoa. On the other hand,

15.8% received recommendation from agrochemical dealers in order to decide on when to apply pesticides. Only 21 farmers (8.8%) consulted extension officers to advise them on when to apply pesticides while 7.9% of farmers receive recommendation from fellow farmers. When farmers were asked whether they consider the direction of wind before spraying, majority (67.5%) of the farmers indicated they do not consider the direction of the wind while 32.5% answered in the affirmative.

4.5.5.1 Factors influencing frequency of pesticides application

Table 4.11 presents the results of regression analysis of factors influencing frequency of pesticides application.

Table 4.11 Regression estimate of the factors influencing farmers' frequency of pesticide application

Variable	Coefficient	Standard	t	P values
Gender	0.429	0.233	1.84	0.066
Farming experience	0.004	0.005	0.70	0.484
Age	0.047	0.007	6.85	0.000**
Extension service	-0.509	0..155	-3.29	0.001**
Chemical shop	-0.384	0.192	-1.99	0.047*
FBO	-1.378	0.211	-6.53	0.000**
Farm size	0.003	0.066	0.44	0.658
Knowledge of COCOBOD recommendation	0.977	0.256	3.82	0.000**
Cocoa income	0.000	0.000	2.39	0.018*
Educational level	0.447	0.165	2.71	0.007**
Cons	2.718	0.4880	5.57	0.000**
R-squared	0.8658			
Adj R-squared	0.8599			
Prob > F	0.0000			

*, ** indicate 5%, and 1% significance levels

Source: Author's computation (2015)

From Table 4.11, results indicate that gender, farming experience, and farm size did not influence the frequency of pesticides application. However, age, access to extension service, availability of chemical shop, membership of farm base organisation (FBO), knowledge of COCOBOD recommendation of pesticides application, income from cocoa and level of education significantly influenced the frequency of pesticides application. Except for income and presence of agro-chemical shop which was significant at $p < 0.05$, the rest were significant at $p < 0.01$.

4.5.6 Pesticides combination (Cocktails) used by farmers

Thirty-five percent (35%) of the farmers indicated that they mix different pesticides together when spraying while 65% responded otherwise. Majority of the farmers (82.1%) who mix pesticides indicated they mixed two different pesticide types when controlling pests and diseases, while 17.9% indicated that they mixed three pesticides It was obvious that out of the 35% farmers who mixed different pesticides, most of them (63.1%) did so because they perceived it was the most effective way to control pests and diseases, while 25% said they mix to saved time and labour. Only 11.9% said it produced healthy and disease free products. It was observed that majority of the farmers who mixed pesticides use a combination of confidor and akatemaster or other pesticides from the open market.

4.5.7 Spraying methods of cocoa farms by farmers'

The survey revealed that 72.9% of the farmers used blanket-spraying methods to spray their cocoa farms, while the remaining 27.1% used the spot spraying methods.

4.6 Operational habits and common health related issues associated with the usage of pesticides by farmers

4.6.1 Dress code during pesticides application

Less than half of the respondents (35%) in the study area put on full protective clothing during spraying. About 20% apply pesticides with no protective clothing while majority of the farmers (45%) put on partial protective clothes. The full protective clothing includes a cap/hat, respirator, goggles, rubber gloves, overall and Wellington boots (rubber boots). Partial protective cloth/costume is any of these and no protective clothe is when farmers use their farming gear without any of the items mentioned above. Reasons assigned by farmers (20%) who do not use any protective cloths during pesticide application was further examined. It was revealed from the survey that 33.3% of the respondents did not have the protective cloths to wear, 20.8% of the farmers were not comfortable wearing protective cloths while 20.8% said they were too costly to buy. Another 12.5% of the farmers indicated that protective cloths were not necessary, 6.3% said they were not available on the markets whereas 6.3% said costumes were not good protectors and that parts of the body are exposed during spraying.

4.6.1.1 Factors influencing farmers' decision to wear protective clothing

Table 4.12 presents the result of the probit regression to estimate the factors influencing farmers' decision to put on protective cloths when applying pesticides.

Table 4.12 Probit results on factors influencing farmers' decision to put on protective clothes

Variable	Coefficient	Standard Error	Z	P values
Gender	1.679	1.858	0.90	0.366
Experience	0.017	0.319	0.52	0.603
Age	-0.054	0.032	-1.05	0.295
Extension visit	2.824	0.805	3.51	0.009**
Chemical shop	-0.689	1.158	-0.59	0.552
Farm size	0.197	0.048	4.06	0.000**
Cocoa income	0.000	0.000	0.56	0.575
Educational level	2.025	0.799	2.53	0.011*
FBO	3.331	0.808	4.12	0.000**
Cons	0.990	1.739	0.57	0.569
Log likelihood	-54.225			
Pseudo R2	0.6322			
LR chi2 (9)	186.44			
Pro >chi2	0.0000			

*, ** 5% and 1% significance levels

Source: Author's Computation

The results show that gender, farming experience, age, presence of chemical shop and income from cocoa did not influence farmers' decision to put on protective clothing. However, extension service, farm size and membership of FBO significantly ($p < 0.01$) influenced decision to put on protective clothes. On the other hand, educational level significantly ($p < 0.05$) influenced farmers' decision to put on protective clothes.

4.6.2 Attitudes of cocoa farmers during and after pesticides application

Appendix M shows personal attitudes of cocoa farmers during application of pesticides on their farms. About 67.5% of the farmers' scoop or stir pesticides with bare hand, 37% chew gum, kola nut or chewing stick when spraying, 67% sing, 76% receive visitors, 89% talk, 35.6% remove blockages in sprayer nozzles with their mouth, 45% eat, 37% drink, and 22% smoke when spraying. In terms of washing of hands after pesticides application, a higher proportion (72.1%) of the farmers in the

study area washed their hands with water and soap, 20.8% used only water whilst 7.1% used water and other substances such as leaves of plants, sand among others to wash their hands. Although, all the farmers interviewed indicated they bathed after spraying event, the interval between spraying event and bathing varied from farmer to farmer. Generally, in the study area, more than half (52.1%) of the farmers took their bath between 31-60 minutes after a spraying event, 24.2% bathed between 15-30 minutes, 12.9% in less than 15 minutes whilst 10.8% bathed at least one hour after spraying. Those farmers who bathed few minutes after application bathed along the banks of water bodies around cocoa farms whilst those who took their bath between 15-60 minutes after application bathed in their homes on farms.

4.6.3 Health related issues experienced by farmers as a result of pesticides application

All the respondents agreed that pesticides application has an effect on their health. When cocoa farmers were asked the health related issues they experienced during and after the application of pesticides, 82.5% of the farmers indicated that they experience watery eyes after spraying while 74.2% said they experience headache. Fifty-five (55%) of the respondents indicated that they feel dizzy after spraying. Chest pain, nausea, skin irritations, itchy eyes, cough, burning eyes, weakness, fever and excessive sweating are experienced by 41.6%, 22.1%, 30%, 25%, 31.7%, 21.7%, 15.4%, 5.4% and 17.1% of respondents, respectively (Appendix N).

4.6.4 Disposal of chemical container and waste water from sprayer

Appendix O shows how farmers in the study area disposed of their empty pesticides containers. Most farmers (65%) leave the empty chemical containers on the farm after pesticide application. A few others (1.7%) dig holes in the farms and bury the

containers, whilst others (9.6%) burn them. Some farmers (7.5%) carry the containers away and throw on the ground elsewhere while a few others (10.4%) dispose of the containers at refuse dumps. About 5.8% of the farmers however, used empty pesticide containers to keep water and other food items such as salt, palm oil, etc. Disposal of left over spraying solution and water used for washing spraying machine after spraying varies. About 55% and 65% of respondents dispose of left over spray solution and water used for cleaning sprayer after spraying on the field, respectively, while 45% and 25% of the farmer's dispose of left over spray solution and water used for cleaning the sprayer after spraying at a designated area.

4.6.5 Factors influencing the operational habits of cocoa farmers during spraying

Using Pearson's correlation co-efficient (r), relationship between farmers' operational habits, health hazards experienced and some selected characteristics were also assessed. There was a significant and positive correlation between number of operational habits put up by cocoa farmers when they are using pesticides on their cocoa farm and their age ($p < 0.05$, r=0.359) and experience of farming ($p < 0.05$, r=0.287). There was also a significant and negative relationship between the number of operational habits and the level of education ($p < 0.05$, r=-0.449), membership of farm base organisation (FBO) ($p < 0.05$, r= -0.322) and extension service ($p < 0.05$, r= -0.423). However, results of the study indicated that farm size, income and gender were not statistically significant. There was no significant relationship between the number of operational habits of the farmers and the number of health hazards experienced.

CHAPTER FIVE

5.0 DISCUSSION

5.1 Physico-chemical properties of water samples in and around cocoa farms

Temperature and pH

There was no significant difference in water temperature in relation to the distances of source to farm. Temperature is an important biologically significant factor, which plays an important role in the metabolic activities of organisms as well as the physical and chemical characteristic of water (Murhekar, 2011; Sirajudeen and Mubashir, 2013; Sanjay, 2014). The permissible limit of temperature by WHO is between 22℃ and 29℃ for drinking water (WHO, 1998; Addo *et al.*, 2011). With the exception of water sampled from S1 at a distance 16-30m which recorded a mean temperature value of 32.3 ºC, all the other sites at distances 0-15m, 16-30m and >30m (control) recorded values that were within the WHO permissible limit. The variations in the temperature of water could be attributed to the weather that prevailed during the period of investigation and groundwater influx. Additionally, this could possibly be due to the different depth of wells with which the samples were taken as well as the time of the day.

With the exception of water sampled from S4 at a distance 0-15m which recorded a mean pH value of 6.93, all the water sampled from the various study sites recorded mean pH values below the WHO acceptable range of 6.5-8.5 stipulated for drinking water and domestic purposes (WHO, 2004). This indicates an acidic condition of water for the entire study period. The low pH values recorded could be due to the amount of acidic cations present in the soil or the presence of high level of organic

matter within the soil zones whose oxidation releases carbon dioxide that reacts with water to produce a weak carbonic acid (Langmuir, 1997; Kortatsi, 2007). According to Ansa-Asare *et al.* (2009), the nature of the geology in an area could also account for low pH values. Nkansah *et al.* (2010) reported that pH values lower than 6.5 are considered acidic for human consumption and can cause significant health problems such as acidosis and adverse effects on digestive and lymphatic system. Additionally, acidity increases the capacity of the water to attack geological materials and leach toxic trace metals into the water making it potentially harmful for human consumption as reported by Kortatsi (2007). Furthermore, it was observed by Kortatsi (2007) that acidity gives sour taste. Thus, the acidity of the groundwater samples suggests that the water samples are susceptible to trace metal pollution if these metals are present in the rock matrix through which the water percolates. The range of pH recorded in this study was similar to the range of 3.69-8.88 reported by Rossiter *et al.* (2010) in water samples from Ghana.

Electrical conductivity (EC), Total dissolved solids (TDS), Total suspended solids (TSS) and Turbidity

Electrical conductivity (EC) is an indication of the concentration of total dissolved solids and major ions in a given water body as well as the temperature at which the measurement is taken (Dahiya and Kaur, 1999; Amoako *et al.*, 2011; Gyamfi *et al.*, 2012). The conductivity values recorded for all the sites during the study period were within the WHO (2004) permissible limit of 1000 µS/cm for drinking water. The maximum conductivity value observed in this study was lower than reported by Rossiter *et al.* (2010) in water samples from Ghana. However, the high mean conductivity values recorded at S4 (233.0 µS/cm) and S1 (135.0 µS/cm) at distances

0-15m and S1 (142.0 µS/cm) and S4 (198.0 µS/cm) at distances 16-30m may be due to the presence of high amounts of dissolved inorganic substances in ionized form in the water sampled (Murhekar, 2011; Sanjay, 2014). Moreover, the low conductivity in majority of the water samples analyzed indicates that the water is unable to react with the rock matrix to equilibrium which indicates short resident times as observed by Kortatsi (2007). This may also be due to the fact that the well waters have low concentration of dissolved ions.

Total dissolved solids (TDS) are a measure of the total organic and inorganic substances dissolved in water. Murhekar (2011) and Sirajudeen and Mubashir (2013) reported that total dissolved solids indicate the salinity behavior of groundwater. According to Tay (2007), total dissolved solids can be used as a common indicator for polluted waters. The total dissolved solids measured in the water samples were all below the WHO (2004) guideline limit of 1000 mg/L for drinking water, indicating that the groundwater is generally of accepting quality. In a similar study, Rossiter *et al.* (2010) recorded TDS values of 4.963 mg/L to 1454 mg/L in water samples from Ghana which were higher compared to those recorded in this study. An elevated concentration of TDS above 1000 mg/L is an indication of high mineral content. This gives water an unpalatable taste, bad odour, displeasing colour and may contribute to induced physiological reaction in the consumer (Spellman and Drinan, 2000).

Total suspended solids (TSS) relatively measure the visual observation of water sample and consist of material originating from the surface and re-suspended from the bed of a water source (Chapman, 1996). Although, TSS in drinking water does not have a WHO health based guideline limit, it is recommended that it should not exceed 500 mg/l for it to be considered safe (Ewusi *et al.,* 2013). The values of TSS recorded

for the entire study period were (3-227 mg/L) which are far below the recommended limit/guideline. The results are similar to the findings of Amoako *et al.* (2011) who reported TSS range of 10 mg/L to 45 mg/L. The low values recorded in this study may be as a result of the filtering capacity of the soil and earth materials. Total suspended solids (TSS) correlated positively with diazinon, lindane and p,p´-DDT and negatively with alpha-endosulfan, endosulfan-sulfate and deltamethrin for the water samples. This suggests that an increase in water TSS resulted in a corresponding increase in the concentrations of diazinon, lindane and p,p´-DDT while an increase in water TSS resulted in a corresponding decrease in the levels of alpha-endosulfan, endosulfan-sulfate and deltamethrin or vice versa.

Turbidity in water is the reduction of transparency due to the presence of particulate matter such as clay or silt, finely divided organic matter, plankton or other microscopic organism (Murhekar, 2011; Gyamfi *et al.,* 2012). With the exception of water samples from S2 at a distance 0-15m, S4 at a distance 16-30m and S5 at a distance above 30m (control) which recorded mean turbidity values of 3.87 NTU, 1.77 NTU and 2.29 NTU respectively, all the other sites at the various distances recorded turbidity values that far exceeded the WHO permissible limit of 5 NTU. The water was thus not conducive for drinking. The results of this study were lower compared to the findings of Rossiter *et al.* (2010) who reported Turbidity range of 0 NTU to 629.7 NTU in water samples from Ghana. The high turbidity values may be due to erosion and run-off from cocoa farms that carried soil particles and deposited them in the well as most of the wells were not protected. This could also be due to the shallow nature of the well causing disturbance and re-suspension during water withdrawal from the well. Elevated turbidities are often associated with the possibility

of microbiological contamination, as turbidity makes it difficult to disinfect water properly (Fatoki *et al.,* 2001). Gyamfi *et al.* (2012) noted that water samples with high turbidity presents colloidal materials which provides adsorption sites for chemicals and organisms that may be harmful or cause undesirable tastes and odors in water. The strong positive correlation between turbidity and (lindane and p,p´-DDT) indicates that turbidity of water could have enhanced the adsorption of these pesticide compounds. Thus, increase in turbidity resulted in a corresponding increase in concentrations of lindane and p,p´-DDT. On the other hand, the negative correlation between turbidity and (alpha-endosulfan, endosulfan-sulfate and allethrin) indicates that alpha-endosulfan, endosulfan-sulfate and allethrin residue levels in water decrease with increase in water turbidity and vice versa.

Phosphate

Phosphate may occur naturally in water and often in high amounts during periods of low biological productivity (Gyamfi *et al.,* 2012). However, the presence of phosphate in water is also a significant indicator of anthropogenic pollution (Addo *et al.,* 2011). Phosphate concentration generally decreased with distance away from cocoa farms. However, the variation of phosphate with distance was not statistically significant. The mean phosphate ion concentrations of the water samples analyzed in this study was generally lower at S5 (distance above 30m) compared to sites at distances 0-15m and 16-30m. Phosphate concentration in the water samples ranged from 0.48 mg/L to 1.22 mg/L. Although there is no WHO guideline value, phosphate may not be toxic to humans unless they are present in very high levels where digestive problems could occur. The phosphate concentrations recorded in this study were lower than the values of 0.33-9.30 mg/L reported by Nkansah *et al.* (2010) in

hand-dug wells in the Kumasi metropolis of Ghana, but were similar to the range of <0.100-1.214 reported by Rossiter *et al.* (2010) in water samples from Ghana. The low phosphate levels recorded in this study may possibly be due to its adsorption by soils as well as P deficiency in Ghanaian soils hence, applied phosphate might have been used up by cocoa plants as observed by Ewusi *et al.* (2013). Possible sources of phosphates in the water samples analyzed are organophosphorus pesticides and fertilizers used by farmers in the study area.

Nitrate and Ammonia

Nitrate and ammonia are considered to be non-cumulative toxins in water (Dalas and Day, 1993). Following pesticides nitrate is listed as the second greatest chemical threat to surface and groundwater in the world (Akoto and Adiyiah, 2008). With the exception of S3 at a distance 0-15m from cocoa farm which recorded a mean nitrate value of 12.8 mg/L, water sampled from all the other sites recorded mean nitrate values that were below the WHO permissible concentration level of 10 mg/L for drinking water. This suggests that water sampled from these sites is not contaminated with nitrate and hence good for domestic water needs as reported by Addo *et al.* (2011). A study by Rossiter *et al.* (2010) in Ghana reported nitrate range as up to 507.7, which was higher than were recorded in this study. Nitrates are conservative in groundwater, hence, the high concentration in S3 may probably be due to leaching and run-off of nitrogen based mineral fertilizers from cocoa farms which were close to the water source. The presence of nitrate may also result from weathering of rocks containing nitrates as a result of geology of the area as observed by Ansa-Asare *et al.* (2009) and Amoako *et al.* (2011). Baird (1999) reports that high levels of nitrate in water are directly associated with methemoglobaenemia or infant cyanosis, an acute

condition which is most frequently found among bottle-fed infants less than three months of age. Other ailments associated with high nitrate concentrations are diarrhea, respiratory diseases and stomach cancer when it reacts with protein compounds in the body to form nitrosamines, a well-documented, cancer causing agent (Tricker and Preussmann, 1991; Spellman and Drinan, 2000).

Ammonia can occur naturally in surface water and groundwater and can be produced by the deamination of organic nitrogen containing compounds and by the hydrolysis of urea (Karikari *et al.,* 2007; Tay, 2007). From the results, with the exceptions of S4 at a distance 0-15m and S1 at a distance of 16-30m which recorded high ammonia mean values of 3.88 mg/L and 1.38 mg/L respectively, all the other sites at the various distances recorded mean ammonia values that were within the WHO guideline value of 0.5 mg/L for drinking water as reported by Tay (2007). The high levels recorded at S4 and S1 may be as a result of leaching applied fertilizers and or run-off at those sites as these wells were in close proximity to cocoa farms. Ammonia has a toxic effect on healthy humans only if the intake becomes higher than the capacity to detoxify.

Sodium and Potassium

Sodium (Na^+) and potassium (K^+) are generally essential for human health and metabolism (Safe Drinking Water Comm., 1980). Although these substances are not necessarily harmful to health, they may give rise to complaints from consumers because of the aesthetic effects they produce (Kortatsi, 2007). The mean sodium values recorded for all the sites during the entire study period fell within the WHO (1998) permissible limit of 200 mg/l for drinking water. The major source of potassium in fresh water is weathering of rocks, but the quantities increase in polluted

water due to disposal of wastewater in the water body (Sirajudeen and Mubashir, 2013). All the water samples studied from the various distances recorded potassium concentrations below the WHO (2004) permissible limit of 30 mg/L for drinking water. The Na^+ and K^+ concentrations recorded in this study pose neither physiological nor aesthetic problems to water usage for drinking or domestic purposes within the study area.

5.2 Physico-chemical properties of soil samples

Soil pH and Electrical conductivity (EC)

Soil pH is an indication of the acidity or alkalinity of soil. pH is one of the factors which influences the bio-availability and transport of pesticides in the soil (Aiyesanmi *et al.,* 2008). The measured mean pH (in H_2O) of the study soils ranged from 7.35 at S5 to 8.49 at S3. Thus, the mean pH values recorded ranged from slightly alkaline to very alkaline. The mean pH of soils from the sampled cocoa farms; S1 (7.46), S2 (7.88), S3 (8.49) and S4 (8.34), were alkaline and above the optimum value of 6.5 recommended to be the ideal hydrogen concentration for cocoa production as reported by Ogunlade *et al.* (2006), as compared to S5 (control) which was slightly alkaline. This may be as a result of high concentration of sodium and calcium in the soils of selected cocoa farms as observed by Aikpokpodion (2010). Additionally, this could be as a result of variability in the use of fertilizers and poultry manure in cocoa farms as reported by Ololade *et al.* (2010). The high positive correlation between soil pH and (lindane, dieldrin, beta-HCH, lambda-cyhalothrin, cyfluthrin, cypermethrin, deltamethrin and befenthrin) suggests that an increase in soil pH resulted in a corresponding increase in the concentrations of lindane, dieldrin, beta-HCH, lambda-cyhalothrin, cyfluthrin, cypermethrin, deltamethrin and befenthrin. Also the high

negative correlation between soil pH and (chlorpyrifos, pirimiphos-methyl and p,p´-DDT) suggests that an increase in soil pH resulted in a corresponding decrease in chlorpyrifos, pirimiphos-methyl and p,p´-DDT residues, respectively, and vice versa. This finding is similar to Bentum *et al.* (2006), who reported significant negative correlations between extracted lindane and propoxur residues with soil pH, but contrary to a study by Aiyesanmi and Idowu (2012) which reported no significant ($p > 0.05$) correlations between soil pH and total organochlorine pesticides (mg/kg) measured in soil samples from selected cocoa farms in Ondo State Central District in Nigeria.

Similarly, the mean EC values of the soil at all the sampled sites were below the critical level of 4 dS/m for plants growth. The soils were likely to contain very little levels of soluble salts and were very conducive for cocoa production.

Organic carbon/Organic matter

Despite the high rate of decomposition/depletion of organic matter often found in tropic soils as reported by Dankyi *et al.* (2014), soils from the study sites were characterized by high organic carbon (OC) and organic matter (OM) content perhaps due to the high influx of litter and microbial activities. Percentage organic carbon ranged from 1.38% at S1 to 6.25% at S5 (control). A similar observation was made by Dankyi *et al.* (2014) who reported 1.28-7.43% organic carbon in cocoa growing soils across cocoa-growing regions in Ghana. Additionally, the soil samples from the various sites had relatively high organic matter content (OM) with reference to the CSIR classification of soil organic matter (CSIR, 1994) (Appendix P). However, the organic matter content recorded at S1 (2.38%), S2 (10.10%), S3 (10.3%) and S4 (6.16%) were below the organic matter content of 25% recommended to be ideal for

optimum cocoa production as reported by Ogunlade *et al.* (2006). Soil organic carbon and organic matter are known to influence the dynamics and behaviour of both inorganic and organic pollutants in soils (Gale *et al.*, 2004; Aiyesanmi *et al.*, 2008). The organic carbon and organic matter contents of the sampled sites indicates the tendency of such soils to adsorb pesticides. In addition, persistence of pesticides in these soils would also be higher as observed by Bentum *et al.* (2006). The binding of pesticides to organic carbon or organic matter decreases its potential for downward movement through the soil (Ahumada *et al.*, 2013). A very high positive correlation existed between organic carbon and (lindane, dieldrin, beta-HCH, lambda-cyhlothrin, cypermethrin, bifenthrin and cyfluthrin) suggesting that the pesticide residue levels in the soils possibly increased with increase organic carbon content of soils. There was also a high negative correlation between organic carbon content of soils and (chlorpyrifos, pirimiphos-methyl and p,p´-DDT) suggesting that an increase in soil organic carbon content of the soil resulted in a corresponding decrease in the concentrations of chlorpyrifos, pirimiphos-methyl and p,p´-DDT and vice versa. This confirming that soil organic carbon enhances adsorption and deposition of pesticides compounds in soils. The findings are in line with a study by Bentum *et al.* (2006) who reported that both extracted lindane and propoxur residues of cocoa growing soils correlated negatively with organic carbon. Additionally, soil organic matter correlated positively with (lindane, dieldrin, beta-HCH, lambda-cyhlothrin, cypermethrin bifenthrin and cyfluthrin), indicating that an increased in soil organic matter resulted in a corresponding increase in the concentrations of lindane, dieldrin, beta-HCH, lambda-cyhlothrin, cypermethrin bifenthrin and cyfluthrin. Also, the negative correlation of organic matter with chlorpyrifos, pirimiphos-methyl and p,p´-DDT indicates that increase in soil organic matter resulted in a corresponding decrease in

concentrations of chlorpyrifos, pirimiphos-methyl and p,p´-DDT and vice versa. This suggests that the pesticides residue levels in the soil are possibly associated with organic matter content of the soil and could be attributed to pesticide molecules having high tendency of binding to organic matter in soil, similar to fats or lipids of plants and animals as reported by Swackhamer and Hites (1988) and Bentzen *et al.* (2008). This finding is similar to a study by Aiyesanmi and Idowu (2012), which reported a significant ($p < 0.05$) correlations between organic matter and total organochlorine pesticides (mg/kg) measured in the soil samples from selected cocoa farms in Ondo State Central District in Nigeria.

Particle size analysis

In general, the content of sand was greater than 50% at all the sampled sites and varied widely, whiles clay content was lower than 20% in more than half of the analyzed samples. The content of clay did not vary much across the sites in the study area. Clay content may play an important role in determining the fate of pesticides in the soil (Gale *et al.*, 2004; Aiyesanmi *et al.*, 2008). Additionally, silt content of the samples analyzed were greater than 20% at almost all the sampled sites except S1 which recorded a mean value of 9.96%. The high proportions of sand in the soils may be attributed to the type of parent material from which the soil was formed. Thus the soil type is sandy loam according to the United States Department of Agriculture (USDA) classification system (USDA, 1987). Similar observations were made by Aiyesanmi and Idowu (2012) and Dankyi *et al.* (2014) in soils of cocoa farms in Ondo State Central District, Nigeria and soils across cocoa-growing regions in Ghana respectively.

Percent sand had a positive correlation with chlorpyrifos and a negative correlation with p, p'-DDT and beta-HCH in soils. This indicates influence of sand on the extractable pesticide residues in soils. In a similar study, Bentum *et al.* (2006) and Aiyesanmi and Idowu (2012) reported no significant ($p > 0.05$) correlations between percentage of sand and extractable lindane, propoxur residues and total organochlorine pesticides (mg/kg) measured in the soil samples from selected cocoa farms, respectively. Percentage clay correlated positively with pirimiphos-methyl and negatively with lindane, dieldrin, beta-HCH, lambda-cyhalothrin, cyfluthrin, cypermethrin and bifenthrin in soils. This suggests that percent clay has significant influence on the distribution of pesticides in soils. This finding is however contrary to a study done by Aiyesanmi and Idowu (2012), which reported no significant ($p > 0.05$) correlations between percentage clay and total organochlorine pesticides (mg/kg) measured in the soil samples from selected cocoa farms in Ondo State Central District in Nigeria. There was a positive correlation between silt and (dieldrin, beta-HCH, bifenthrin deltamethrin, lambda-cyhalothrin and cyfluthrin), indicating that an increased in silt resulted in a corresponding increase in the concentrations of dieldrin, beta-HCH, bifenthrin, deltamethrin, lambda-cyhalothrin and cyfluthrin. On the other hand, there was a negative correlation between silt and (chlorpyrifos, lindane, pirimiphos-methyl, p,p´-DDT and cypermethrin) in the soil, suggesting that an increase in silt resulted in a corresponding decrease in concentrations of chlorpyrifos, lindane, pirimiphos-methyl, p,p´-DDT and cypermethrin residues and vice versa. However, this finding is in disagreement with a study by Aiyesanmi and Idowu (2012), which reported no significant ($p > 0.05$) correlations between percentage silt and total organochlorine pesticides (mg/kg) measured in soil samples from selected cocoa farms in Nigeria.

Percentage nitrogen, Available potassium and Phosphorus

The mean percentage nitrogen content of the soils analyzed ranged from 1.64 at S4 to 2.13 at S2. The percentage nitrogen content of the soils at S1 (2.10%), S2 (2.13%), S3 (1.87%) and S4 (1.64%) is adequate for cocoa production, since all the values were higher than the critical level of 0.09% required for cocoa cultivation as reported by Aikpokpodion (2010). This may be attributed to high content of nitrogen in the annual litter fall which is about 20% to 45% of the total N in the vegetation and 2% to 3% of the total N in the soil as observed by Aikpokpodion (2010). The potassium concentrations of the sampled cocoa farms were generally below the critical level of 100 ppm of potassium required for cocoa cultivation. Additionally, the phosphorous contents of the selected cocoa farms soil were appreciably below the required maximum concentration of 35 ppm required for optimum cocoa cultivation as reported by Ogunlade *et al.* (2006) and Aikpokpodion (2010).

5.3 Levels of pesticide residues in water samples from the various distance categories

Form the results of this study, the most problematic class of pesticide residues occurring in the water samples analyzed was organochlorine (6), followed by synthetic pyrethroids (4) and organophosphates (3) (Table 4.3). The high frequency of occurrence among the organochlorine residues was heptachlor (52.6%) while the high frequency of occurrence among the synthetic pyrethroids residues was deltamethrin (26.6%). On the other hand, the most occurring residue among the organophosphate pesticides was chlorpyrifos (42.1%). The trends of all the pesticide residues detected in the water samples analyzed from the various distances to cocoa farms decreased

with an increase of water source (distance) to cocoa farm (ranking; 0–15 > 16–30 > above 30 m).

With the exception of water samples from S1, S2 and S4 at distance, 16-30m (Table 4.3), all the other sites with detectable chlorpyrifos concentrations within the various distances recorded mean values below the WHO MRL value of 0.05 µg/L for drinking water. The sites S1, S2 and S4 recorded mean chlorpyrifos concentrations of 0.05 µg/L, 0.06 µg/L and 0.06 µg/L which were comparable to and above the WHO MRL value of 0.05 µg/L for drinking water respectively. The presence and occurrence of chlorpyrifos in the water samples confirmed the use of the pesticide in cocoa production in the study area as corroborated by farmers from the field survey.

The mean concentrations of diazinon recorded in water samples within the various distances were found to be below the WHO MRL of 0.05 µg/L for drinking water except S4 at a distance 0-15m, which recorded a mean concentration (0.06 µg/L) above the WHO MRL. The detection of diazinon confirms the findings from the field survey, which revealed that diazinon, is an active ingredient of a pesticide with a trade name Akatesuro, which is extensively used by cocoa farmers in the study area. Diazinon is in WHO category II insecticides (i.e. moderately hazardous with acute oral LD ≥50≤500) and is capable of causing acute as well as chronic intoxication (Sosan *et al.,* 2008). However, the mean diazinon values recorded in this study, were lower than the mean value of 16.65 µg/L reported by Sosan *et al.* (2008) in domestic water sources from cocoa farmers' localities in selected villages of South-western Nigeria.

Additionally, the mean concentrations of pirimiphos-methyl recorded at sampled sites with detectable residues, were found to be below the WHO permissible residue Limit of 6.00 µg/L for drinking water. The detection of pirimiphos-methyl in the water samples suggests the use of pesticides with this compound as its active ingredient in the control of cocoa pests and diseases by farmers in the study area, even though it's use was not established from the field survey.

The mean concentrations of lindane recorded at sampled sites with detectable residues were below the WHO permissible limit of 2.00 µg/L for drinking water. The presence of lindane in the water samples suggests the illegal or previous use of the pesticide in the study area; as lindane had been banned in several countries including Ghana for agricultural purposes as reported by Afful *et al.* (2010). Although, the level of lindane in the water samples did not exceed the WHO limit, exposure to large amount of lindane have been reported to have negative effects on the nervous system with symptoms from headaches and dizziness to convulsions and more rarely, death (Leena *et al*, 2012). The mean lindane values, recorded in this study were lower than the mean values of 37.0 µg/L and 0.0578 µg/L reported by Idowu *et al.* (2013) and Olayinka (2013) respectively in river water sources selected from cocoa producing areas of Ondo State central senatorial district, Nigeria and Ilawe-Ekiti, Ekiti State, Nigeria.

In addition, alpha-endosulfan, an isomer of the parent chemical endosulfan, was detected in water samples analyzed at distances 0-15m and 16-30m to cocoa farms. With the exception of water samples from S1 at a distance 16-30m which recorded a mean concentration of 0.01 µg/L, all the other sites with detectable alpha-endosulfan concentrations recorded mean values above the WHO MRL of 0.01 µg/L for drinking

water. The mean residue concentrations of alpha-endosulfan in this study were however lower than, the mean values of 3200 µg/L and 0.597 µg/L reported by Idowu *et al.* (2013) and Okoya *et al.* (2013b) in river water samples analyzed from cocoa producing areas in Ondo State, Nigeria respectively.

Additionally, endosulfan-sulfate, a metabolite of parent compound endosulfan, (Frimpong *et al.*, 2012d) was detected only in water samples analyzed from S1 (0.02 µg/L) and S2 (0.04 µg/L) at distances 0-15m from the nearest cocoa farm. However, the mean values recorded at the two sites (S1 and S2) were above the WHO MRL of 0.01 µg/L for endosulfan-sulfate in drinking water.

The continual use of endosulfan for agricultural purposes over time and the possible leaching or run-off with surface water, might have accounted for the detection of endosulfan compounds in the water samples. Though endosulfan was considered for restriction in December 2008 from the registered pesticides in Ghana (Afful *et al.*, 2010; Tutu *et al.*, 2011), it was found to be used by some cocoa farmers in the study area with a trade name thiodan. In addition, the relatively lower detection and levels of endosulfan-sulfate compared to alpha-endosulfan may suggest that previous input of endosulfan has not metabolized to endosulfan-sulphate or there is minimal inputs of endosulfan at present. Endosulfan is known to be easily absorbed by the stomach, the lungs and the skin as noted by Sosan *et al.* (2008). Long-term exposure to low doses of endosulfan has been shown to cause endocrine disruptions, reproductive and developmental damage in animals and humans (Sosan *et al.*, 2008; Leena *et al.*, 2012). It can therefore, be concluded that pollution from this pesticide may pose a threat to consumers of the water samples.

Aldrin degrades to dieldrin (Miles *et al.*, 2009). Dieldrin was only detected in water samples analyzed from S1 and S3 at distances 0-15m with mean concentrations of <0.01 µg/L and 0.03 µg/L, which were below and comparable to the WHO MRL of 0.03 µg/L for drinking water respectively. The presence of dieldrin may suggest a possible degradation of aldrin to dieldrin in the environment as aldrin, marketed as Argine, was found to be used by cocoa farmers in the study area. However, current or direct application and bioaccumulation of dieldrin as an insecticide cannot be ignored entirely. The mean values recorded for dieldrin in this study were lower, as compared to the mean values of 2 µg/L and 0.94 µg/L reported by Idowu *et al.* (2013) and Okoya *et al.* (2013b) respectively in river water samples analyzed from selected cocoa producing areas in Ondo State, Nigeria.

Leena *et al.* (2012) asserted that DDT is an organochlorine insecticide nearly insoluble in water with a half-life of 2-15 years. An isomer of DDT (p,p´-DDT), was detected in water sampled within distances 0-15m and 16-30m. The mean concentrations recorded were however below the WHO MRL value of 2.00 µg/L set for drinking water. The presence of p,p´-DDT in the water samples was surprising since DDT has been banned in Ghana as reported Afful *et al.* (2010). Their presence could be as a result of current application of the pesticide, since some farmers still use products which contain functional DDT with different trade names. The detection of p,p´-DDT also suggest previous contamination, as they degrade slowly and persist in the environment for a long time. Long-term exposure to low doses of DDT has been shown to affect the endocrine, reproductive systems, immune system and cause cancers as reported by Afful *et al.* (2010) and Okoya *et al.* (2013b). The mean concentrations of p,p´-DDT recorded at the various sites in this study were similar to

the mean value of 0.0298 µg/L reported by Olayinka (2013) in river water samples analyzed from cocoa farms in Ilawe-Ekiti, Ekiti State, Nigeria. On the contrary, the values recorded in this study were higher than the mean value of 0.02 µg/L reported by Okoya *et al.* (2013b) in river water samples from cocoa producing areas in Ondo State, Nigeria.

Heptachlor is the only pesticide detected in water samples analyzed from the control (distances greater than 30m from the nearest cocoa farms). With the exception of S4 at a distance 0-15m and S3 at a distance 16-30m which recorded mean concentrations of 0.03 µg/L and 0.04 µg/L which were comparable to and above the WHO MRL for portable water respectively, the rest were below the WHO guideline value of 0.03 µg/L for drinking water. The high occurrence of heptachlor in samples suggests the continual usage of the illegal pesticide by cocoa farmers in the study area. Also, the levels may be attributed to previous contamination as well as environmental persistence from past usage of the chemical. Heptachlor is known to have implications in a broad range of adverse human health effects including endocrine disrupting properties, reproductive failures and birth defects, immune system malfunction, Parkinson's disease and cancers as reported by Afful *et al.* (2010) and Okoya *et al.* (2013b), hence their presence is of serious concern. However, the results of this study were higher than the mean value of 0.0067 µg/L for heptachlor in river water samples from selected cocoa farms in Ilawe-Ekiti, Ekiti State, Nigeria, as reported by Olayinka (2013).

The concentrations of allethrin in water samples from all sites with detectable residue were found to be below the WHO guideline value of 0.05 µg/L for drinking water except S2 at distance 0-15m which recorded a mean concentration of 0.05 µg/L which

was comparable to the WHO guideline value. The presence of allethrin suggests the use of the pesticides by cocoa farmers in the study area as they are registered for use in Ghana for either agricultural or household purposes (EPA Ghana, 2009). On the other hand, the mean concentrations of allethrin recorded at the various sampled sites in this study were higher than the mean value of 0.00069 µg/L in water samples from the Weija Lake in Ghana as reported by Afful *et al.* (2013).

The mean concentrations of fenvalerate, observed at all sites with detectable residue, were below the WHO MRL of 0.05 µg/L set for portable water except water sampled from S4 at distance 16-30m which recorded a mean concentration of 0.05 µg/L which was comparable to the WHO MRL for drinking water. The detection of fenvalerate in water samples confirms the use of the pesticides in cocoa farms by farmers, as revealed from the field survey. Fenvalerate, with a trade name Sumitox, was found to be used by cocoa farmers in the study area. The presence of the pesticide in the water samples analyzed could be as a result of improper application and handling of the pesticide by farmers. However, the mean values of fenvalerate recorded in this study were higher than the mean value of 0.0086 µg/L reported in a similar study by Afful *et al*. (2013) in water samples analyzed from the Weija Lake in Ghana.

Cypermethrin is a very popular synthetic pyrethroids in Ghana, and has been registered for cocoa production (EPA Ghana, 2009). The mean cypermethrin concentrations observed at the various sampled sites with detectable residues were found to be below the World Health Organisation (WHO) Maximum Residue Limit of 0.05 µg/L for portable water. The presence of cypermethrin suggests its use in the study area. The mean values of cypermethrin recorded in this study were higher than

the mean concentration of 0.00025 µg/L reported by Afful *et al.* (2013) in water samples analyzed from the Weija Lake in Ghana.

Additionally, the mean concentrations of deltamethrin recorded at sampled sites with detectable residue were found to be below the WHO MRL of 0.05 µg/L for drinking water except S4 at distance 0-15m which recorded a mean deltamethrin concentration of 0.07 µg/L which was above the WHO MRL for drinking water. The occurrence of deltamethrin confirms the use of the pesticide in cocoa production in the study area as indicated by farmers during the field survey. The mean values of deltamethrin recorded in this study were however, higher than the mean value of 0.0004 µg/L reported by Afful *et al.* (2013) in water samples analyzed from the Weija Lake in Ghana.

5.4 Levels of pesticide residues in sampled soil from the study area

The most problematic class of pesticide residues occurring in the soil samples analyzed was synthetic pyrethroids (6), followed by organochlorine (4) and organophosphates (3) (Table 4.5). The percentage occurrence of the synthetic pyrethroids residues was highest for lambda-cyhalothrin and cypermethrin (50%) respectively, that of the organochlorine residues was dieldrin (62.5%), while that of the organophosphate was chlorpyrifos (56.3%).

The mean concentrations of chlorpyrifos recorded in soils sampled from S3 (0.01 mg/kg), S2 and S4 (0.03 mg/kg respectively) were below and comparable to the US MRL of 0.03 mg/kg for agricultural soils. On the contrary, soil samples analyzed from S1 recorded a mean concentration of 0.04 mg/kg above the US MRL for agricultural

soils. The detection of chlorpyrifos in the soils samples confirmed its use in the study area.

The mean concentrations of profenofos, recorded at all the sampled sites with detectable residues, were found to be below the United States (US) MRL of 0.05 mg/kg for agricultural soils. The occurrence of profenofos in the soil samples indicated a current use of the pesticide in cocoa production in the study area, even though its usage was not confirmed from the field survey.

Again, the mean concentrations of pirimiphos-methyl recorded at the various sampled sites with detectable residues were found to be within the United States (US) MRL of 0.03 mg/kg for agricultural soil except S1 which recorded a mean pirimiphos-methyl concentration of 0.04 mg/kg which was above the US MRL for agricultural soils. The detection of pirimiphos-methyl in the soil confirmed the assertion made earlier that cocoa farmers in the study area may be using pesticides with prirmiphos-methyl as its active ingredient.

The mean concentration of lindane recorded at S1 (0.03 mg/kg) and S3 (0.04 mg/kg) were below and comparable to US MRL of 0.04 mg/kg for agricultural soils respectively. However, soil samples analyzed from S4 recorded a mean lindane concentration (0.05 mg/kg) above the US MRL for agricultural soils. The concentrations of lindane were generally higher in soil than in water. This may be due to its higher binding capacity to soil particles than water molecules as most organic compounds binds to organic matter in soil as reported by Tarus *et al.* (2007). The presence of lindane in the soil samples suggests the current or previous use of the pesticide by cocoa farmers in the study area. Agyen (2011) and Olayinka (2013)

reported lindane values (0.002 mg/kg and 0.00007 mg/kg) from soil samples from cocoa farms in Kade in the Eastern Region of Ghana and Ilawe-Ekiti, Ekiti State, Nigeria respectively which were lower than those recorded in this study. In addition, Bentum *et al.* (2006) and Aiyesanmi and Idowu (2012) reported lindane mean values of 8.6 mg/kg and 0.257 mg/kg from soils of selected cocoa farms in the central region of Ghana and Ondo State, Nigeria respectively which were higher than those reported in this study.

The isomer of benzene hexaachloride (BHC) or hexa-chlorocyclohexane (HCH): beta-HCH was detected in few soil samples from the study area. The mean beta-HCH concentrations observed at S3 (0.05 mg/kg) and S4 (0.04 mg/kg) were found to be above the US MRL of 0.03 mg/kg for agricultural soils while soils from S2 and S1 recorded mean values of 0.03 mg/kg and <0.01 mg/kg which were comparable to and below the US MRL for agricultural soils respectively. The measured concentrations of beta-HCH in the studied soils can be attributed to the current or previous use of the Ɣ-isomer (lindane) which is the only BHC or HCH isomer with powerful insecticidal action as reported by Aiyesanmi and Idowu (2012). This is because all the studied sites with detectable levels of lindane gave quantifiable levels of beta HCH. The mean residues of beta-HCH recorded in this study were higher than the mean value of 0.001 mg/kg reported by Agyen (2011) in soil samples of selected cocoa farms in Kade in the Eastern Region of Ghana. On the contrary, Aiyesanmi and Idowu (2012) reported 0.617 mg/kg mean value from soils of selected cocoa farms in Ondo State, Nigeria which is higher than the values recorded in this study.

The mean concentrations of dieldrin recorded at all sampled sites with detectable residue were comparable to the US MRL of 0.02 mg/kg for agricultural soils except

S5 (control) which recorded a mean concentration of <0.01 mg/kg which was below the US MRL for agricultural soils. The detection of dieldrin in soil samples suggests a higher rate of conversion or decomposition of aldrin to dieldrin in the environment, as aldrin was not detected in the soil samples but was found to be used by cocoa farmers in the study area. Additionally, the presence of dieldrin may be attributed to the current or previous use of dieldrin as an insecticide, even though it usage was not confirmed from the field survey. On the other hand, the detection of dieldrin at S5 (control) may be as a result of previous usage or atmospheric deposition of the pesticides, as no farming activities was found to be going on in the area. However, the mean values of dieldrin recorded in this study were relatively lower than the mean value of 0.197 mg/kg reported by Aiyesanmi and Idowu (2012) in a similar study in soils of selected cocoa farms in Ondo State Central District, Nigeria. On the contrary, the measured concentrations of dieldrin in this study were higher than the mean value of 0.0032 mg/kg reported by Agyen (2011) in soils of selected cocoa farms in Kade in the Eastern Region of Ghana.

The mean concentrations of p,p´-DDT registered at all sampled sites with detectable residues were found to be below the US MRL of 0.05 mg/kg for agricultural soils. The presence of p,p´-DDT in the soil samples analyzed confirms their illegal or previous usage in the study area as it was also detected in water samples. The mean concentrations of p,p´-DDT reported in this study were above the mean values of 0.003 mg/kg and 0.007 mg/kg reported by Agyen (2011) and Olayinka (2013) in soil samples analyzed from selected cocoa farms in Kade in the Eastern Region of Ghana and Ilawe-Ekiti, Ekiti State, Nigeria respectively.

With the exception of soil samples analyzed from S1 which recorded a mean lambda-cyhalothrin concentration of 0.02 mg/kg which was comparable to the US MRL of 0.02 mg/kg for agricultural soils, all the other sites with detectable lambda-cyhalothrin residue recorded values above the US MRL for agricultural soils. This high concentrations of lambda-cyhalothrin in the soil samples may be attributed to its high affinity for soil as reported by Tarus *et al.* (2007). The occurrence of lambda-cyhalothrin in the samples confirms the extensive use of the pesticide in cocoa production in the study area as indicated by farmers from the field survey.

Additionally, the mean concentrations of allethrin, recorded at all sampled sites with detectable residues, were found to be above the US MRL of 0.01 mg/kg for agricultural soil. The high occurrence of allethrin suggests the current use of the pesticide in cocoa production in the study area as it also occurred in the water samples analyzed. The usage of this pesticides however, could be attributed to the fact that allethrin are registered for use in Ghana for either agricultural or household purposes (EPA Ghana, 2009).

Also, the mean concentrations of cyfluthrin recorded in soil samples at the various sampled sites with detectable residues were found to be far below the US Maximum Residue Limit of 0.15 mg/kg for agricultural soils. The detection of cyfluthrin in the soil samples analyzed may suggest its current usage in cocoa production in the study area, possibly as an active ingredient in one of the pesticides used by farmers as its use was not confirmed from the field survey.

Furthermore, the mean concentrations of cypermethrin observed at all sampled sites with detectable residues were found to be below the US MRL of 0.05 mg/kg for

agricultural soil. The use of cypermethrin in the control of cocoa pest and diseases by farmers in the study area, might have accounted for the detection levels in the soil samples analyzed as it was also recorded in the water samples analyzed.

In addition, the mean concentrations of deltamethrin in soil samples at all sites with detectable residues were found to be within the US MRL of 0.05 mg/kg for agricultural soils except S4 (0.06 mg/kg) which was above the US MRL for agricultural soils. The detection of deltamethrin in the soils confirms the use of the pesticide by cocoa farmers in the study area as deltamethrin was also detected in the water samples analyzed.

Bifenthrin was detected at all the sampled sites except S5 (control). However, the mean concentrations of bifenthrin recorded were found to be below the US MRL of 0.04 mg/kg for agricultural soils. The detection of bifenthrin suggests the current use of a pesticide with bifenthrin as its active ingredient by cocoa farmers in the study area.

5.5 Levels of pesticide residues in samples of cocoa bean from the study area

The most problematic class of pesticide residues occurring in the cocoa bean samples analyzed was synthetic pyrethroids and organochlorine (6) followed by and organophosphates (3) (Table 4.7). The percentage occurrence of the synthetic pyrethroids residues was highest for cypermethrin (87.5%), that of the organochlorine residues was p,p´-DDT (62.5%), while that of the organophosphate was chlorpyrifos (75%) .

The mean concentrations of diazinon recorded in cocoa beans from all sampled sites with detectable residues were comparable to the European Union (EU) Maximum

Residue Limits (MRL) of 0.02 mg/kg for cocoa beans except S1 (0.04 mg/kg) which recorded a mean value above the EU MRL. The detection of diazinon in the cocoa samples confirmed the use of diazinon as a pesticide in the control of pests and diseases by farmers in the study area. The mean values of diazinon recorded in this study were relatively lower compared to the mean value of 0.12 mg/kg reported by Aikpokpodion *et al.* (2012a) in cocoa beans samples analyzed from three ecological zones in Nigeria. On the other hand, the values recorded in this study was comparatively higher than the mean value of 0.005 mg/kg reported by Frimpong *et al.* (2012b) in cocoa beans samples ready for export in Ghana.

The mean chlorpyrifos concentrations recorded at S1 (0.09 mg/kg) and S4 (0.10 mg/kg) were within and comparable to the EU MRL of 0.10 mg/kg for cocoa beans respectively. However, the mean concentration of chlorpyrifos recorded at S3 (0.42 mg/kg) was above the EU MRL set for cocoa beans. Among the organophosphates pesticides, chlorpyrifos recorded the widest spread concentrations among the sampled sites with detectable residue (0.09 mg/kg to 0.42 mg/kg). The occurrence of chlorpyrifos in cocoa beans samples confirmed the extensive use of the pesticide in cocoa production by farmers in the study area as chlorpyrifos was also detected in water and soil samples analyzed. The mean concentrations of chlorpyrifos recorded at the various sampled sites were higher than the mean values of 0.05 mg/kg and 0.02 mg/kg reported by Frimpong *et al.* (2012b) and Daanu (2011) in cocoa beans samples ready for export and from Asukese and its environs in the Tano North district of Ghana respectively. On the contrary, the mean values of chlorpyrifos recorded in this study were lower compared to the mean value of 10.55 mg/kg recorded in a similar

study by Boakye (2012) in cocoa beans samples analyzed from the Brong Ahafo and Ashanti Regions of Ghana.

Pirimiphos-methyl, one of the three organophosphates pesticides screened routinely for shipment to Japan and Europe (GSA, 2011) was detected in the cocoa beans samples analyzed from the study area. The concentrations of pirimiphos-methyl recorded at study sites with detectable residues were below the European Union (EU) MRL of 0.05 mg/kg for cocoa beans. These findings were in line with the mean value of 0.03 mg/kg reported by Frimpong *et al.* (2012b) in cocoa beans ready for export in Ghana. The detection of this pesticide in cocoa beans samples suggest that pirimiphos-methyl was used by cocoa farmers as it was also detected in water and soil samples from the study area.

The mean concentrations of lindane recorded at sampled sites with detectable residues were below the European Union (EU) MRL of 1.00 mg/kg for cocoa beans. However, the mean values recorded in this study (0.03-0.05 mg/kg) were below the values reported by Lynés (1978) (0.001 to 0.600 mg/kg) and Apau and Dodoo (2011) from (0.055 to 0.897 mg/kg), but relatively higher than what was reported by Frimpong *et al.* (2012d) and Olayinka (2013) from non-detected to 0.02 mg/kg and from 0.001 to 0.0001 mg/kg, respectively. Additionally, the mean lindane concentrations obtained at the various sites were higher than mean values of 0.01 mg/kg, 0.01 mg/kg, 0.01 mg/kg and 0.0001 mg/kg obtained in cocoa beans samples as reported by Botchway (2000), Frimpong *et al.* (2012d), Frimpong *et al.*, (2012c) and Olayinka (2013). However, the mean lindane concentrations in this study were lower than the mean value of 0.411 mg/kg obtained by Apau and Dodoo (2011) in cocoa bean from Central Region of Ghana. This finding is however contrary to, the results of Owusu-

Ansah *et al.* (2010) who recorded no lindane residue in cocoa beans from the Twifo Praso district of Ghana. The presence of lindane in cocoa beans analyzed could be attributed to the current or previous use of the pesticide as it was also detected in water and soil samples analyzed. Lindane was marketed in Ghana as Gammalin 20 and was widely used on cocoa plantations until 2007 when it was banned (Agbeve *et al.*, 2014).

Even though gamma-HCH (lindane) is the only isomer of HCH that possesses insecticidal activity, beta-HCH was also detected in cocoa beans sampled from the study sites. This suggests the use of technical HCH in cocoa production, either currently or in previous times. The mean concentrations of beta-HCH recorded at the various sites were below the EU MRL of 0.02 mg/kg set for cocoa beans except S3 (0.03 mg/kg) which was above the EU MRL. However, the mean values of beta-HCH recorded in this study were higher than the mean value of 0.01 mg/kg reported by Frimpong *et al.* (2012d) in cocoa beans ready for export in Ghana. On the other hand, the mean values of beta-HCH recorded in this study were similar to the mean values reported by Boakye (2012) and Frimpong *et al.* (2012c) in cocoa beans analyzed from the Ashanti and Brong Ahafo Region and cocoa beans ready for export in Ghana, respectively.

The mean concentrations of aldrin recorded in samples from S2 (0.05 mg/kg) and S4 (0.06 mg/kg) were found to be comparable and above the EU MRLs of 0.05 mg/kg set for aldrin in cocoa beans respectively. The presence of aldrin in the cocoa beans samples confirms the illegal use of the pesticide by cocoa farmers as revealed in the field survey, although its usage has been banned in Ghana. The mean values in this study were higher than the mean values of 0.01 mg/kg and 0.01 mg/kg reported by

Frimpong *et al.* (2012d) and Frimpong *et al.* (2012c) in cocoa beans ready for export in Ghana. Similarly, the mean concentrations of dieldrin recorded in cocoa beans sampled were below the EU MRL of 0.50 mg/kg for cocoa beans. This suggests degradation of aldrin to dieldrin in the environment. In addition, the presence of aldrin and dieldrin might have originated from previous use of the chemicals. In a similar study Boakye (2012) reported no concentration of aldrin but high concentrations of dieldrin in cocoa beans samples from the Brong Ahafo and Ashanti regions of Ghana which was attributed to the degradation of aldrin to dieldrin.

The mean concentrations of p,p´-DDT recorded at the various sampled sites were below the European Union (EU) Maximum Residue Limit (MRL) of 0.50 mg/kg for cocoa beans. However, the mean p,p´-DDT residues recorded in this study were higher than the mean p,p´-DDT residues of 0.01 mg/kg, 0.03 mg/kg, 0.003 mg/kg and 0.0003 mg/kg reported by Daanu (2011), Frimpong *et al.* (2012d), Frimpong *et al.* (2012c) and Olayinka (2013), but lower than the mean p,p´-DDT value of 0.06 mg/kg reported by Aikpokpodion *et al.* (2012b) in cocoa beans samples analyzed from Ghana and Nigeria respectively. The occurrence of p,p´-DDT is an indication of current use of the pesticides as confirmed from the field survey, in addition to persistence from previous contamination as reported by Bempah and Donkor (2010). Due to the chemical and physical nature of DDT, they accumulate in the food chain and cause health threats in humans.

Methoxychlor, one of the banned pesticides in Ghana (EPA Ghana, 2009), was detected in cocoa beans sampled from the study area. Methoxychlor concentrations at the detected sites were within the EU MRL of 0.10 mg/kg for cocoa beans. However, the mean values recorded were higher than the mean value of 0.002 mg/kg recorded

by Frimpong *et al.* (2012d) in cocoa beans ready for export in Ghana. On the other hand, the mean values reported for methoxychlor in this study were contrary to the findings of Frimpong *et al.* (2012c) who reported no methoxychlor residue in cocoa beans ready for export in Ghana. The presence of the pesticide in the study area proves that methoxychlor had either been used on cocoa in the past or their presence in the environment had not diminished. Additionally, the presence may be either as a result of historical use of DDT which technically contains about 88% methoxychlor of the p,p´-isomer or recent DDT input into the environment as reported by WHO (1996).

The mean concentrations of allethrin recorded at S4 (0.02 mg/kg) and S2 (0.01 mg/kg) were found to be above and comparable to the EU Maximum Residue Limit of 0.01 mg/kg for cocoa beans whiles the rest were within the EU MRL. The mean residues of allethrin recorded in this study were similar to the mean value of 0.01 mg/kg reported by Frimpong *et al.* (2012a) in cocoa beans ready for export in Ghana. The detection of allethrin in cocoa beans samples confirms the use of the pesticide in the study area as it was also detected in water and soil samples analyzed.

Cypermethrin, a very popular synthetic pyrethroids in Ghana and also registered for cocoa production (EPA Ghana, 2009) was detected in the cocoa beans samples. The mean cypermethrin concentrations recorded in cocoa beans from all sampled sites were below the European Union (EU) Maximum Residue Limit of 0.10 mg/kg for cocoa beans and the findings of Boakye (2012). However, the mean cypermethrin concentrations recorded in this study were higher than mean values of 0.02 mg/kg and 0.03 mg/kg reported by Daanu (2011) and Frimpong *et al.* (2012a) in cocoa beans sampled from Ghana, respectively.

Additionally, the concentrations of lambda-cyhalothrin recorded at the various sampled sites were below the EU MRL of 0.05 mg/kg for cocoa beans except S3 which recorded a mean value of 0.05 mg/kg comparable to the EU MRL. The results of this study were higher than the mean value of 0.01 mg/kg of lambda-cyhalothrin reported by Frimpong *et al.* (2012a) in cocoa beans ready for export in Ghana The detections of lambda-cyhalothrin in cocoa beans samples confirms the current use of the pesticide in the study area. Lambda-cyhalothrin was also detected in the soil samples analyzed.

With the exception of the mean concentrations of deltamethrin recorded at S2 and S3 (0.06 mg/kg respectively) which were above the EU MRL of 0.05 mg/kg for cocoa beans, all the other sites with detectable residues recorded values below the EU MRL. The mean residue concentrations of deltamethrin recorded in this study were found to be higher than the mean value of 0.0003 mg/kg and 0.04 mg/kg reported by Daanu (2011) and Frimpong *et al.* (2012a) in cocoa beans samples analyzed from Ghana respectively.

Permethrin mean concentrations recorded at all sampled sites with detectable residue were below the European Union (EU) Maximum Residue Limit (MRL) of 0.10 mg/kg for cocoa beans. The detection of permethrin suggests the use of the pesticides in the study area, even though it use was not established from the field survey. The mean values of permethrin recorded in this study were lower compared to the mean value of 0.04 mg/kg recorded by Frimpong *et al.* (2012a) and Boakye (2012) but higher than the mean value of 0.01 mg/kg recorded by Daanu (2011) in cocoa beans samples analyzed from Ghana, respectively.

Mean concentrations of bifenthrin in cocoa beans were found to be within the EU MRL of 0.10 mg/kg. The occurrence of bifenthrin in the cocoa beans samples confirms the current use of the pesticide in the study area as it was also detected in the soil samples. This finding is in line with the mean value (0.01 mg/kg) reported by Frimpong *et al.* (2012a) in cocoa beans samples ready for export in Ghana but lower than the values reported by Boakye (2012) in cocoa beans from the Brong Ahafo and Ashanti Regions of Ghana.

Generally, there were no statistically significant variations in pesticide residues detected in water samples in relation to distances to cocoa farms, soil and cocoa bean samples from the various study sites. However, it was observed that there were differences in the concentrations or levels of pesticide residues in water, soils and cocoa beans samples analyzed from the different sites. The difference may be attributed to a number of reasons. The first has to do with the different agricultural practices adopted by individual farmers and also accessibility of the pesticides. This could also be due to persistence pest and disease attack and the frequency of pesticides application by individual farmers. Another reason may be due to farmers mixing cocktails of various pesticides to increase their efficacy or potency. This practice may also alter both the type and the concentration of pesticides residue in the water, soils and cocoa beans. In addition, within the same field, cocoa trees, soil and nearby water bodies may have received varying amount of pesticides due to wind drift, leaching, run-off and also due to non-uniform spraying. The properties (e.g. solubility, adsorption etc.) and the half-life of the chemical used by farmers could further explain the variation in the distribution of the various pesticides in the samples analyzed. Although the variations in the levels of pesticides may be due to the amount

of pesticides and frequency of application, interactions in soil often determined by the physical and chemical properties of both the pesticide and soil may play a significant role in determining fate of pesticides. Processes such as sorption, leaching and degradation may be significant in this regard (Dankyi *et al.*, 2014). The age of the farm receiving the application is another factor. New cocoa farms would have received fewer pesticides applications relative to older farms. The last but not the least is the fact that cocoa trees may exhibit different abilities to take up pesticides residues upon exposure. This is because different plants have different biochemical mechanism of dealing with foreign chemicals.

5.6 Farmers' survey

5.6.1 Demographic characteristics of respondents

It was evident from the results that males dominated cocoa farming in the study area. This could be attributed to the fact that men are household heads and traditionally control assets such as land and tree crops as reported by Anang *et al.* (2013). Male cocoa farmers provided more effective labour on their farms in addition to other sources of labour than their female counterparts. The male to female ratio is in line with the findings of Bosompem and Mensah (2012), Anang *et al.* (2013) and Boateng *et al.* (2014).

The result of the study generally shows that cocoa farmers in the study area were old and ageing. The health of an individual normally decline with old age, hence, the finding has implications for future cocoa production in the study area. This finding also has a negative impact on new technology adoption as older farmers are more likely to stick to their old ways of doing things compared to younger ones. The result of this study was in line with those reported by Bosompem and Mensah (2012),

Anang *et al.* (2013) and Boateng *et al.* (2014) in cocoa growing Districts like Birim-South, Wassa-Amenfi West and Atiwa Districts of Ghana, respectively.

Byrness and Byrness (1978) reported that education enhances one's ability to receive, decode and understand information. In view of this, it is assumed that a farmer's level of education to some extent, determines the type of tasks he/she can undertake in any programme as well as the type and level of participation. Since majority (81.2%) of the farmers had some form of formal education, it was possible to understand the components of pesticides usage to some extent. However, since their level of education was generally low, it probably affected their ability to perform some critical tasks (e.g. calibration of sprayers, measurement and mixing of pesticides) that required a little bit of higher education. This may have adverse effect on farmers' operational habits and health related hazards in relation to chemical usage. The results are in line with studies done by Bosompem and Mensah (2012), Anang *et al.* (2013) and Boateng *et al.* (2014) on cocoa farmers in Ghana. The results suggested that the literacy rate has improved over the years among cocoa farmers since Dankwa (2002) and Kumi (2003) reported that about 50-55% of cocoa farmers in Ashanti and Eastern Region of Ghana had no formal education about a decade ago.

Considerable amount of experience may facilitate the adoption of cocoa technologies. The result of the study showed that majority of the respondents had 11 years and above experience and very few had less than 10 years experience. This clearly portrayed that most cocoa farmers in the study area have adequate experience in cocoa production. It is therefore likely that their adoption levels of cocoa technologies such as pesticide use would be high. The results of the study is similar to those

reported by Bosompem and Mensah (2012) and Anang *et al.* (2013) in the Birim-South and Wassa-Amenfi West Districts of Ghana, respectively.

5.7 The types, sources and methods of pesticide application of cocoa farmers

5.7.1 Knowledge of COCOBOD approved pesticides and application recommendations

Lack of knowledge of the COCOBOD recommended pesticides and frequency of application can result in farmers' usage of chemicals that are inferior and banned. This can increase the level of chemical residue in harvested cocoa beans, the environment as well as pesticides resistance and pest resurgence. It was evident from the study that most of the farmers have in-depth knowledge on the COCOBOD approved pesticides to use than the recommended frequency of pesticide application. This confirmed the findings by Antwi-Agyakwa (2013) which stated that cocoa farmers in some cocoa producing regions in Ghana have adequate knowledge on the COCOBOD pesticides to use on their cocoa than the frequency of pesticide application. Farmers who were members of farm based-organizations in the study area indicated that they were aware of the approved pesticides through their organizations and the proportion of the respondents who adopted/used the approved pesticides in the year under review depicted a high level of awareness among the respondents. This result is in agreement with Tijani (2010) who reported that membership to a cooperate organization by cocoa farmers in Ondo State, Nigeria increased their adoption to a particular pesticides.

5.7.2 Farmers' benefiting from cocoa mass spraying Programme by Government of Ghana

Cocoa farms in the district are to be sprayed four times a year between July and November (personal communication) when insect and fungus infestation is high as recommended by the Cocoa Research Institute of Ghana (CRIG) under the Cocoa Diseases and Pests Control (CODAPEC) or mass cocoa spraying programme with COCOBOD approved pesticides (Abankwah *et al.,* 2010). Even though the study revealed that more than half of the farmers benefited from the mass cocoa spraying exercise in the year under review, majority had their farms sprayed only once. The result is in line with a study by Anang *et al.* (2013) which reported that majority of cocoa farmers in the Wassa Amenfi West District of Ghana had their farms sprayed only once under the cocoa mass spraying programme. Moreover, this supported claims that spraying frequency of the 'mass spraying exercise' was not adequate and cocoa farmers were expected to do additional spraying (Aneani *et al.*, 2012; Danso-Abbeam *et al.*, 2014). The finding was also in line with Abankwah *et al.* (2010) and Anang *et al.* (2013), who reported that the government spraying program to control pest and disease in Ghanaian cocoa farms has not reached its full potential because it has not been able to fulfil its mandate of ensuring that cocoa farms were sprayed four times a year between July and November.

5.7.3 Cocoa farmers' sources and types of pesticides used

Although some of the farmers who benefited from the cocoa mass spraying exercise indicated that they were given some amount of pesticides to be used on their farms by spraying agents, they claimed the amounts given were not sufficient as per their farm lands. This leaves cocoa farmers in the study area (both farmers who benefitted and

those who did not benefit from the mass spraying programme in the year under review) with no choice but to purchase pesticides from chemical sellers within their communities or nearby communities, with very few purchasing from fellow cocoa farmers. This is an indication that chemicals were readily available on the open market so farmers could purchase. This confirms findings by Adeogun and Agbongiarhuoyi (2009) in Ondo State, Nigeria, where majority of cocoa farmers purchased their chemicals from open market with few obtaining it from cocoa buyers and the Ministry of Agriculture.

Result indicates that all kinds of pesticides (whether registered or not by Ghana EPA and approved by COCOBOD for cocoa production) were being used by cocoa farmers in the study area. Usually, pesticides that were not approved for cocoa cultivation were cheaper, hence, most farmers could easily afford. Among the recommended pesticides, Confidor, Akatemaster, Nordox, Kocide, Champion, Funguran, Metalm and Ridomil are mostly used. However, majority of the framers used pesticides which were not approved by COCOBOD for cocoa production. These pesticides include Akatesuro, DDT, Buffalo super, Controller super, Consider, Sumitox, Sunpyrifos, Condifor, Lambda, Lamtox, Okumakate, Argrine, Fast-track, Clement powder, among others. The reasons given by farmers for using these unapproved pesticides were that those approved by COCOBOD were not for sale at chemical shops so farmers could purchase. Additionally, farmers also indicated that they used these pesticides due to their effectiveness in the control of pest and diseases and their affordability. This practice contributes to indiscriminate use of pesticides which might have led to the high pesticides residues in the environment as laboratory analysis of samples from the study area revealed. The continuous use of these unapproved pesticides by farmers

needs to be discouraged because of the hazardous effect on farmers' health, non-harmful pest and its residual effect in soils, water source and cocoa beans as well as the implications for cocoa beans export. Hence the need to sensitize farmers on the dangerous effects of the use of these chemicals among cocoa farmers is necessary. When all the pesticides used by farmers were grouped into their various classes, the results showed that apart from growth regulators, the use of organophosphates was on the rise, followed by synthetic pyrethroids and the organochlorines.

5.7.3.1 Factors influencing farmers' choice of source of pesticides

Gender of respondents had a significant positive relationship with the choice of source of pesticide. The empirical result implies that the probability of a male sourcing pesticide from formal source (chemical shop) is higher than their female counterparts by 0.81%. The empirical result can be explained that female cocoa farmers prefer to source pesticides from other farmers rather than buying from a chemical shop. This is due to the fact that they mostly have less knowledge about the pesticides to use compared to their male counterparts.

The educational level of respondents also has a positive significant influence on source of pesticides. This implies that farmers with higher level of education are more likely to source pesticides from chemical shop than those with less or no formal education. It also implies that farmers with higher level of education are able to understand the health and environmental implication of purchasing pesticides outside a chemical shop.

Income from cocoa positively influenced the choice of source of pesticides. The result implies that the probability of sourcing pesticides from a chemical shop increases with

the income from cocoa farm. This means that the farmers who gain more income from cocoa sale are more likely to purchase pesticides from a chemical shop which is expensive yet more productive other than sourcing from other farmers.

Age had a negative significant effect with choice of source of pesticides. This implies that the probability of sourcing pesticides from a formal source (chemical shop) decreases with age. This means that an increase in farmers' age reduces the likelihood of the farmer sourcing pesticide from chemical shops.

5.7.4 Farmers' knowledge on pesticides application rates

Majority of respondents had knowledge on pesticides application rates. However, the main source of information on pesticides application rates were mainly from chemical sellers or shop attendants with some farmers relying on follow farmers and farmer based organizations. Although majority of the farmers had some form of formal education only few could read the instructions on pesticides labels themselves. This could be attributed to the fact that the instructions on the chemicals are technical and some farmers get confused trying to follow the instructions. Extension officers were not readily available to farmers and hence very few respondents approached them for help regarding instructions and application rates of pesticides. There is likelihood of distortion of knowledge received from chemical sellers and other farmers as indicated from the study. These observations are contrary to the report by Tijani (2006) where 46% of cocoa farmers and 44% farm workers using pesticides obtained knowledge of pesticide application rates from extension agents.

5.7.4.1 Factors influencing farmers' knowledge on pesticide application rate

Educational level significantly ($p < 0.05$) influenced knowledge on pesticide application rate. This means the higher the educational level of the farmer, the more likely the farmer will have knowledge on pesticide application rate. The empirical result indicates that 1% increase in the educational level of the respondents leads to 0.177% increase in the knowledge on application rate of the pesticides.

Extension service significantly ($p < 0.01$) influenced knowledge on pesticide application rate with marginal effect of 0.255. This implies that 1% increase in the number of extension service received by farmers will lead to 0.255% increase in the knowledge acquisition on pesticides application rate. This is because extension officers educate farmers on best farming practices to increase productivity.

Availability of chemical shop also influenced knowledge on pesticide application rate significantly ($p < 0.05$) with a marginal effect of 0.171. This implies that 1% increase in the availability of chemical shop in a farming community leads 0.171% increase in the knowledge acquisition on the pesticides application rate. The result can be explained on the basis that chemical sellers mostly educate farmers on the application rate, so their availability in a farming community will help farmers gain more knowledge on it.

FBO was statistically significant at 0.05% with a marginal effect of 0.158. The FBO had a positive relationship with knowledge on pesticide application rates. Intuitively, the probability of a cocoa farmer to gain knowledge on pesticide application rate increases with membership of FBO. This is due to the fact that members of FBOs are

educated on a new method and proper ways of farming as revealed from the field survey.

Age was statistically significant ($p < 0.01$) with a marginal effect of 0.010. It had a negative relationship with knowledge on pesticides application rate. This implies that 1% increase in the age of a cocoa farmer will lead to 0.010% decrease in the knowledge on pesticides application rate. The result can be explained on the bases that aged farmers do not easily adopt or accept new knowledge due to the fact that they have long farming experience and hence feel they know it all.

5.7.5 Mixing of pesticides by cocoa farmers

Most of the farmers mixed two or more different pesticide together to combat insect pest and disease regardless of their side effects. Thus, mixing of pesticides was as a result of farmers desiring to have a rapid and effective pest and disease controlled. This idea is questionable (Medina, 1987), at least as practised, because the combinations used are indiscriminate. Majority of the farmers who mixed pesticides use a combination of confidor and akatemaster or other pesticides on the open market. However, it was a common practice for farmers to mix pesticides with the same active ingredients but different trade names. Typical example was lambda-cyhalothrin groups and this was a clear misuse of pesticides which would affect the health of farmers and the environment. The practice defies some of the basic principles of insecticides management (Ntow *et al.,* 2006). Metcalf (1980), in his recommendation of strategies for pesticide management, stated that the use of mixtures of insecticides must be avoided. This is because, mixture of insecticides generally result in simultaneous development of resistance. This however, contradict the report by

Georghiou (1980) who indicated that such practice helps to manage pesticides resistance.

5.7.6 Pesticides application frequency of cocoa farmers

The number of sprays per season, however, varied widely from locations and the farmers interviewed in the survey. The fact that farmers usually under apply or exceed the application frequency of the pesticides even though some were aware of the recommended pesticides and the rates to apply, indicates that farmers are not guided by the peak of pest and disease population as indicated by COCOBOD, rather, they control pest and disease just when they deem it appropriate. Some farmers indicated that they prepare to spray just when they notice pests and diseases in the farm. This confirms the report by Padi *et al.* (2000) which states that field surveys done by COCOBOD in 1997/98 and 1998/99 revealed that out of 1,750 farmers interviewed, only 3.5% of the farmers used the recommended pesticides Unden 20 and Gamma BHC at the recommended dosage, time and frequency. However, the findings of this work are in variance with Adeogun and Agbongiarhuoyi (2009) who reported that all cocoa farmers interviewed in Ondo State, Nigeria sprayed based on recommendations. Although it is undeniable that cocoa needs large quantities of pesticides for the control of their pest and diseases, it remains doubtful whether all the sprays are really necessary. The spraying regime of farmers also varied between climatic seasons. Farmers sprayed more during the wet season when pests and diseases proliferated. Besides, increased wash-off by rainfall necessitated further application of pesticides (Ntow *et al.*, 2006) .

5.7.6.1 Factors influencing farmers' frequency of pesticides application

Age of a farmer has a positive significant ($p < 0.01$) effect on the frequency of pesticide application. The result indicates that as the age of a farmer increase by one year, the frequency of pesticide application increases by 0.047. This is in contravention with the findings of Adejumo *et al.* (2014) which states that as the age of a farmer increases, pesticide usage decreases.

Extension visit has a negative significant ($p < 0.01$) effect on the frequency of pesticide application. The result indicates that as the extension visit increase by one, the frequency of pesticide application decreases by 0.509. This could be attributed to the fact that farmers get information on the effect of indiscriminate application of pesticide and the recommended frequency of pesticide application.

Availability of chemical shop has a negative significant ($p < 0.05$) effect on the frequency of pesticide application. The result indicates that the more the farmer purchase pesticide from chemical shop the less the frequency of pesticide application.

Membership of farm base organization (FBO) has a negative significant ($p < 0.01$) effect on the frequency of pesticide application. The result indicates that as a farmer joins an FBO, the frequency of pesticide application decreases by 1.378. This could be due to the fact that a farmer obtains information on the recommended application rate from fellow farmers in an FBO.

Knowledge of COCOBOD recommendation on pesticide application rates has a positive significant ($p < 0.01$) effect on the frequency of pesticide application. The result indicates that as farmer gains knowledge of COCOBOD recommendation for pesticide application, the frequency of pesticide application increases by 0.977. This

result could be due to the fact that farmers do not follow the COCOBOD recommendation because of high rate of insect infestation and climate change incidence.

Cocoa income has a positive significant ($p < 0.05$) effect on the frequency of pesticide application. The result indicates that as the cocoa income of a farmer increase by Ghana 1 cedi, the frequency of pesticide application remains the same. The result could be due to the fact that a farmer would channel his/her increase in cocoa income into other farm and non-farm activities.

Educational level has a positive ($p < 0.01$) significant effect on the frequency of pesticide application. The result indicates that as the education of a farmer increase by one level, the frequency of pesticide application increase by 0.447. This could be due to the fact that though the farmer is formally educated, he/she might not have knowledge on the COCOBOD recommendation of pesticide application rate.

5.7.7 Spraying methods of cocoa farmers in the study area

On farmers ways of spraying cocoa, results revealed that majority use blanket-spraying methods (whole farm is sprayed) to spray their cocoa farms with very few using the spot spraying method. The results of this study is in line with a study by Adeogun and Agbongiarhuoyi (2009) who reported that majority of cocoa farmers in Ondo State, Nigeria used the blanket-spraying method to spray their farm, with few using the spot method. This implies that farmers waste more chemicals during application as some of the pesticides fall on untargeted areas. Bateman (2004) reported that massive amount of pesticides are washed by run-off from cocoa onto the soil, thereby, contaminating the environment (ground and surface water, air etc.)

when blanket-spraying is used. The possible detection of pesticide residue in cocoa farm soils and drinking water sources as revealed from the laboratory analysis may be due to the method of spraying. Additionally, majority of the farmers revealed spraying pods until they are soaked with the chemical. This definitely leads to chemical wastage as pods require only the fume of the chemical for the control of pest and diseases. This might have led to pesticide residues in cocoa beans samples analyzed as pesticides can be adsorbed by cocoa beans through the cocoa pod.

5.8 Operational habits during pesticides application and common health related issues during and after pesticides application

5.8.1 Wearing of protective clothing by farmers

With regards to farmers' protection during spraying event, some farmers did spraying without wearing protective clothing (no costume). These farmers used their casual farm clothing to spray. Others wore protective clothing but without respirator or goggles (partial costume) which exposes a greater part of their body to pesticides. Few of the farmers however, wear all that is recommended for personal protection during spraying. This report is in line with Sosan *et al.* (2008), Sosan and Akingbohungbe (2009), Ogunjimi and Farinde (2012a) and Antwi-Agyakwa (2013) which reported that only a small percentage of cocoa farmers interviewed actually wore protective clothing when spraying whiles majority did not see the use of protective clothing as a necessity. However, the personal protective clothing the farmers used during the field survey were woefully inadequate and not up to standard. This agrees with the statement that most farmers are aware of the kind of equipment that should be used to offer protection but in practice only few farmers use the recommended gears (Helen, 2002). It was observed that most of these farmers are

financially handicapped, therefore cannot afford all the necessary equipment and attire (boots, hand gloves, goggles, trousers, rubber coat, nose mask and cap/hat) to offer adequate protection. This confirms findings by Ntow *et al.* (2006) which states that the use of personal protective equipment by Ghanaian farmers during mixing, loading and application of pesticides is low mainly because of financial difficulties. Other cocoa farmers interviewed stated that they feel uncomfortable in these wears and as such it hinders effective work.

5.8.1.1 Factors influencing farmer's decision to wear protective clothing when applying pesticides

The extension visit had a positive significant relationship between wearing of protective cloth when applying pesticides. This implies that farmers that get access to extension service mostly wear protective cloth when spraying. This is due to the fact that extension officers as part of their activities educate farmers on the negative effect of spraying without protective clothing.

Farm size had a positive significant effect on decision to wear protective cloth during pesticides application. The result can be explained on the basis that a farmer with large farm size normally takes more time to apply the pesticides. Due to this, it is believed that the effect of spraying without wearing protective cloth is high, so they mostly wear protective cloth to reduce the harmful effect of the chemicals.

The educational level of a farmer had a positive significant effect on the decision to wear protective cloth during pesticide application. The result implies that the probability of a farmer wearing protective clothing during pesticide application increases with educational level. This is due to the fact that an educated person is

believed to be knowledgeable about the harmful effect of pesticide which will motivate him/her to wear a protective cloth when spraying.

Farmer Based Organization (FBO) had a positive significant effect on wearing of protective clothing. The result implies that the probability of a farmer wearing protective clothing increases with a membership of FBO. This is due to the fact that members of FBOs are mostly educated on the health risk associated with spraying without wearing protective clothing. In a similar study Antwi-Agyakwa (2013) reports a positive correlation between cocoa farmer membership of farm-based organisations and the costume farmers wear..

5.8.2 Attitudes put up by farmers during and after pesticides application

Some farmers exhibited habits such as smoking, eating, drinking water, using sticks and their bare hands to mix pesticides in a container and removal of blockages with mouth during pesticides application without recourse to proper hygiene. This readily predisposes them to exposure contamination through oral route. The result of this study is in line with Sosan *et al.* (2008), Sosan and Akingbohungbe (2009), Ogunjimi and Farinde (2012a) and Ogunjimi and Farinde, (2012b) which stated that majority of cocoa farmers in South-western and Osun and Edo states, Nigeria, were in the habit of drinking, eating, smoking, mixing chemicals with bare hands and removing blockage with mouth during spraying of agro-chemicals which usually exposed them to health related problems. However, a similar study by Tijani (2006) on cocoa farmers and farm workers in Ondo state, Nigeria, revealed that 78% of the farmers do not eat or drink while spraying. Farmers who eat and drink whiles spraying do so to regain energy.

The situation that about half of the farmers washed their hands with water and soap after spraying may explain why most of the farmers are aware of the harmful effects of pesticides on humans. However, the revelation that more than half of the farmers wait for about 31-60 minutes after spraying before taking their bath is frightening as this practice may allow their bodies to absorb the chemical which comes in contact during spraying and expose them to harmful effects of pesticides. This finding is however, in variance with a similar study by Ogunjimi and Farinde (2012b) which reports that majority of cocoa farmers in Osun and Endo State, Nigeria claimed taking their bath immediately after spraying of chemical. Also the fact that those farmers who bath immediately after spraying bath near water bodies presents another potential threat to aquatic life and humans as the pesticides will contaminate the water bodies. Additionally, majority of the farmers claimed not washing their contaminated cloths after spraying of chemicals. This may constitute health problems to the farmers because of the fact that contaminated protective clothing is in direct contact with their body hence can cause body irritation. This confirms the report by Ogunjimi and Farinde (2012a) which states that majority of cocoa farmers in Osun and Edo State, Nigeria do not wash their contaminated cloths after spraying of chemicals. However, the result of the study contradicts a study by Tijani (2006) who reports that 68% of cocoa farmers in Ondo state, Nigeria, washed their cloths after spraying.

5.8.3 Spraying directions by cocoa farmers during spraying

The findings of the study revealed that farmer's opinions on the direction of spraying varied. Whereas very few farmers considered the wind direction during spraying and therefore sprayed with the wind direction, majority did not. The latter category of farmers sprayed back and forth and even against the wind or perpendicular to the

wind direction. Where this occurs, the wind blows the chemical onto the body, including the face of the farmer. According to Ntow *et al.* (2006), this poor spraying practice presents great potential for exposure of the farmers to chemicals from both skin contact and inhalation. This may also possibly present a pollution problem to the environment as it can lead to the contamination of soils and nearby water bodies as chemical carried in air as spray drift can travel long distance from treated fields. A similar observation was made by Tijani (2006) which reported that low proportions of cocoa farmers (44%) followed the direction of wind when spraying.

5.8.4 Health related issues reported by farmer during and after pesticides usage

All the farmers surveyed had become ill from pesticides exposure and were aware that chemicals are dangerous to health. In view of this, farmers were expected to be careful on how to handle pesticides but in reality they do not. A similar observation was made by Adeogun and Agbongiarhuoyi (2009) on cocoa farmers in Ondo State, Nigeria. Most of the farmers pointed out that watery eyes, headache, dizziness, chest pain, skin irritation and cough were the major symptoms encountered during and after spraying. The use of inadequate protective clothing during spraying and the chemical composition of pesticides could have accounted for these symptoms. Also, this might be due to exposure of the body during spraying (as most of the farmers sprayed against directions of the wind), the high rate of eating, drinking, smoking, using mouth to remove blockage and using bare hands to mix chemicals as revealed from the field survey. It could also be attributed to long term effects and improper handlings of pesticides by farmers in the study area. In a similar study, Tijani (2006) reported that about 80% of both cocoa farmers and farm workers in Ondo state Nigeria, experienced discomfort such as headaches, tiredness, vomiting, nausea, and

skin problems (itching and skin burns) after spraying. The findings are also in line with Ogunjimi and Farinde (2012a) and Ogunjimi and Farinde (2012b) who reported similar health related issues of cocoa farmers in Osun and Edo states in Nigeria. According to Sosan *et al.* (2008), acute intoxication of pesticides is generally what is of immediate concern but there are also equally worrisome long-term effects that could result from their chronic accumulation.

5.8.5 Disposal methods of pesticides container, left over spray solution and sprayer wash water

Farmers in the study area mostly dispose of empty chemical containers, left over chemical solutions and sprayer wash water on the field. This could result in contamination of farm soils and surrounding water bodies. The results of this study confirms the findings of Tijani (2006) and Antwi-Agyakwa (2013) which stated that throwing of containers on the field is the commonest method cocoa farmers adopt in the disposing of empty chemical containers in their various studies. As one walks at the edges of cocoa farms, one could clearly see pesticides containers lying on the ground. According to Ntow *et al.* (2006), where farms are close to waterways (which is the case in many farming communities) the disposal of unwanted pesticide solutions and empty containers in the field presents a pollution problem for aquatic systems which are sources of livelihood for human communities and support varied animal and plant life. The Environmental Health Manual (2010) as cited in Antwi-Agyakwa (2013), identifies the community rubbish damp as the best place to discard empty pesticides containers after the containers have been triple washed with the appropriate solvent. The manual again warned against the burning of pesticides containers because they can give off poisonous gases. It is unfortunate that most

cocoa farmers in Ghana do not attach much importance to the handling and disposal of chemical containers.

5.8.6 Factors influencing the operational habits of cocoa farmers during pesticides application

The results revealed that there was a positive significant relationship between the number of operational habits put up by cocoa farmers when spraying and famers' age and experience in cocoa farming. This implies that as a farmer ages and also his/her experience increase, the more the number of the operational habit he/she puts up when applying pesticides on his farm. The finding on experience was surprising because, as a person gains experience in a particular activity, his/her working habits change. Furthermore, as the farmer ages, he/she might not be critical about the hazards involved in using pesticide, even when they are much aware of the operational habits. There was a negative significant relationship between level of education and the number of operational habits put up by cocoa farmers. This implies that the higher the level of education of a farmer, the less the number of operational habits he/she may report. There was also a negative significant relationship between membership of FBO and extension visit and the number of operational habits put up by cocoa farmers. This is due to the fact that farmers acquire knowledge on the best practices required in pesticide application resulting in less number of operational habits put up by the cocoa farmers. There was however, no relationship between the number operational habits exhibited by cocoa framers' and the number of health hazard reported. This shows that the number of health hazards experienced had nothing to do with the number of operational habits put up.

CHAPTER SIX

6.0 CONCLUSION AND RECOMMENDATIONS

6.1 Conclusions

Pesticide residue levels and physico-chemical properties of water and soil were assessed in some selected water sources, soils, and cocoa beans samples in the Dormaa West District of Ghana. In addition, pesticides use practices and operational habits exhibited by cocoa farmers' during and after pesticides applications in the district were accessed.

The study revealed that the physico-chemical parameters of water in the study area were of good quality. Apart from pH, turbidity, nitrate and ammonia concentrations of water whose mean values exceeded the World Health Organization (WHO) guideline limits for drinking water at some sampled sites, the remaining physico-chemical parameters (temperature, conductivity, TDS and potassium and sodium concentrations) analyzed in the water samples from the various distances were within the WHO permissible limits for drinking water. The low pH, turbidity and ammonia of water could be attributed to the geology of the study area, as well as leaching and run-off from cocoa farms which were in close proximity to water sources.

The soils samples from the study area showed similar properties probably because they exist in the same agro-ecological zone of similar parent materials. However, some soil physical and chemical properties such as organic matter, available potassium and phosphorous were observed to be below the minimum required value for cocoa cultivation. On the contrary, soil properties such as total nitrogen and pH were found to be above the recommended limit required for cocoa production. The

differences in soil physical and chemical properties could be attributed to differences in farming practices such as fertilizers application and the use of pesticides.

The results of this study revealed that water sources, soils and cocoa beans from the study area were contaminated with different types of pesticides of which organochlorines and synthetic pyrethroids were the most common, followed by organophosphates. Nine organochlorine pesticides namely; aldrin, dieldrin, lindane, p,p´-DDT, endosulfan-sulfate, alpha-endosulfan, beta-HCH, methoxychlor, and heptachlor were detected in the samples analyzed and were among the banned pesticides of the Environmental Protection Agency (EPA) of Ghana. The occurrence of organochlorine pesticide residues in the samples analyzed could be due to its illegal use by farmers as revealed from the farmers' survey or due to historic use since these chemicals are prohibited from agricultural use. Heptachlor and dieldrin were the most common organochlorine pesticide while cocoa beans and drinking water sources were the most frequently contaminated samples with organochlorines.

Eight synthetic pyrethroids namely, fenvalerate, deltamethrin, cypermethrin, bifenthrin, permethrin, lambda-cyhalothrin, allethrin, cyfluthrin and four organophosphate pesticides namely, diazinon, chlorpyrifos, pirimiphos-methyl, profenofos were detected in samples analyzed form the study area. Cypermethrin and chlorpyrifos were the most frequent pesticides among the synthetic pyrethroids and organophosphates respectively. This indicates a higher preference for synthetic pyrethroids and organophosphates pesticides among cocoa farmers in the study area and could be attributed to the fact that most of these pesticides are registered for use in Ghana for either agricultural or household purposes as reported by EPA Ghana (2009).

The trends of pesticide residues distribution in water samples from the various distances to the nearest cocoa farms indicated frequent occurrence and higher residue concentrations in water samples at distances 0-15m and 16-30m than in water samples at distance above 30m (Control). The presence of pesticides in the water samples could be traced to direct overspray, atmospheric transport of volatilized pesticides or wind drift, direct spillage, pesticide misuse by farmers, leaching and run-off from application fields and surrounding areas during and after pesticide applications. Although most of the pesticide residues recorded in water were below the WHO MRLs for drinking water, some pesticides such as chlorpyrifos, diazinon, alpha-endosulfan, endosulfan-sulfate, heptachlor and deltamethrin exceeded the WHO MRLs at some sampled sites. The results therefore suggests that pesticides residue concentrations in some of the wells from which samples were obtained for this study may pose health hazard to farmers household and their entire community who utilize water from these same sources.

Additionally, the concentrations of pesticide residues in the soil samples analyzed were generally low and below the US MRLs for agricultural soils. However, some sampled sites recorded mean concentrations of pesticide such as chlorpyrifos, pirimiphos-methyl, lindane, beta-HCH, lambda-cyhalothrin, allethrin and deltamethrin above the US EPA MRLs for agricultural soils. Pesticides may have found their way into the soils via spray drift during cocoa tree treatment, wash-off from treated cocoa tree and wrong disposal of left over spray solution, sprayer wash water and pesticide containers as observed from the famers' survey. Apart from the potential danger pesticides in soil may pose to the soil organisms, their possible translocation into edible parts of crops (cocoa beans) and emission into surrounding

water bodies have elicited a great deal of interest. The concentrations of pesticide residues in the soil samples of the control site were either generally lower or not detected compared to those from cocoa plantations in the study area. This difference is understood as the direct effect of pesticides usage on cocoa farms.

Pesticide residues detected in the cocoa bean samples analyzed form the study sites were below the EU MRL set for cocoa beans, with the exception of diazinon, chlorpyrifos, beta-HCH, aldrin, allethrin and deltamethrin which recorded mean concentrations that were above the EU Maximum Residue Limits at some sampled sites. However, considering levels of pesticides residues in fermented dried cocoa beans against the European (EU) commission regulations on pesticide residues, cocoa beans analyzed in the study area will not pose any significant threat to the cocoa industry as far as shipment to Europe is concern. Contamination of cocoa beans could have occurred directly by treating the crop with pesticides before harvest, where pesticide residues are adsorbed by the cocoa beans through the cocoa pod. Also the possibility of translocation of these residues from the treated soil into the cocoa fruits through the root system cannot be over looked. This could have occurred indirectly by uptake from the soil of residual pesticides by the subsequent cocoa farming.

Results from farmers' survey revealed that the major pesticides used by farmers in the study area in combating the pests and diseases on their cocoa farms included: diazinon, chlorpyrifos-ethyl, acetamiprid/chlorfenvinphos, imidacloprid, permethrin, chlorpyrifos, lambda-cyhalothrin, lambda-cyhalothrin, thiamethoxam, fenvalerate, DDT, endosulfan, bifenthrin cuprous oxide, cupric hydroxide, cuprous hydroxide, cuprous hydroxide, cuprous oxide + metalaxyl, metalaxyl cuprous oxide, among others, some of which are banned and not approved for cocoa production. Farmers

obtained the pesticides that they used from agrochemicals shops, fellow farmers and the Government of Ghana via the free cocoa mass spraying programme. Majority of cocoa farmers in the study area sprayed their farms using the blanket spraying method compared to the spot spraying method. Additionally, these cocoa farmers were predominantly indulged in the habits of eating, drinking, smoking, talking, spraying towards the direction of air and not wearing protective clothing when using these pesticides on their farms. In this regard, farmers suffered from discomforts ranging from watery eyes, headaches, dizziness, skin irritation, cough, chest pain and burning eyes during and after using these pesticides.

The study therefore accept the alternative hypothesis (H_1); that drinking water sources, soils and cocoa beans from selected cocoa farms in the Dormaa West District showed relatively elevated levels of some pesticides as a result of their usage by farmers.

6.2 Recommendations

Based on the findings of the study, the following effective measures are recommended.

- Proper site selection for the location of domestic water wells (above 30m) in relation to distances from the nearest cocoa farms and proper well construction to reduce potential pesticides contamination of drinking water sources, as most of the water samples analyzed within distances 0-30m were found to be contaminated with pesticides residues.
- The Ministry of Agriculture and the Environmental Protection Agency need to check and enforce regulations on the use of banned pesticides in Ghana as these pesticides were found to be used by cocoa farmers in the study area.

- CODAPEC must institute a monitoring mechanism to make sure that farmers who privately spray their farms do so with approved cocoa pesticides. This is because majority of farmers in the study area who sprayed their farms privately did so with unapproved pesticides.
- The Crop Research Division of Council for Scientific and Industrial Research (CSIR) in collaboration with Cocoa Research Institute of Ghana (CRIG) should research into Integrated Pest Management for cocoa to solve the problem of pesticide residues bedeviling the cocoa sector in Ghana.
- Farmer education on safe pesticide use should be intensified to limit the levels of pesticides residues in drinking water sources, soils and cocoa beans as poor practices were observed from the study area.
- Cocoa farmers' must be educated on repercussion of the health hazards associated with the various operational habits they perpetuate when applying pesticides on their farms.
- Cocoa farmers must be encourage to use the spot spraying method which are more economical, time and energy saving and does not contaminate the environment compared to the blanket spraying method which was the case in the study area.
- Future monitoring programs are recommended to acquire adequate information regarding the pesticide use patterns and levels of pesticides especially synthetic pyrethroids and organophosphates in drinking water sources, soil and cocoa beans in cocoa growing communities in Ghana.

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APPENDICES

Appendix A

Location of sampling cocoa farms (GPS readings)

Code/ID	Sampling sites	Global Positioning System Points
NKT1	Nkrankwanta 1	(06.97467º N, 003.10004º W)
NKT2	Nkrankwanta 2	(06.96551º N, 003.10228º W)
NKT3	Nkrankwanta 3	(06.97062º N, 003.10749º W)
NKT4	Nkrankwanta 4	(06.96906º N, 003.10082º W)
DIA1	Diabaa 1	(07.04022º N, 002.98075º W)
DIA2	Diabaa 2	(07.03976º N, 002.96963º W)
DIA3	Diabaa 3	(07.04497º N, 002.96963º W)
DIA4	Diabaa 4	(07.03976º N, 002.97807º W)
KRA1	Krakrom 1	(06.95722º N, 003.06171º W)
KRA2	Krakrom 2	(06.96395º N, 003.05923º W)
KRA3	Krakrom 3	(06.96245º N, 003.05312º W)
KRA4	Krakrom 4	(06.95724º N, 003.06123º W)
KWA1	Kwakuanya 1	(06.96953º N, 002.96760º W)
KWA2	Kwakuanya 2	(06.97728º N, 002.96554º W)
KWA3	Kwakuanya 3	(06.98652º N, 002.96350º W)
KWA4	Kwakuanya4	(06.97043º N, 002.96760º W)

Appendix B

Sampled hand dug wells codes and the nearest cocoa farm distance

Sampling point	Code/ID	Distance (m)
NKT1	Nkrankwanta 1	12
NKT2	Nkrankwanta 2	15
NKT3	Nkrankwanta 3	19
NKT4	Nkrankwata	22
DIA1	Diabaa 1	23
DIA2	Diabaa 2	17
DIA3	Diabaa 3	13
DIA4	Diabaa4	11
KRA1	Krakrom 1	12
KRA2	Krakrom 2	11
KRA3	Krakrom 3	18
KRA4	Krakrom 4	23
KWA1	Kwakuanya 1	12
KWA2	Kwakuanya 2	22
KWA3	Kwakuanya 3	11
KWA4	Kwakuanya 4	26
CONT1	Control 2	41
CONT2	Control 1	36
CONT3	Control 3	40

Appendix C

QUESTIONAIRE

UNIVERSITY OF GHANA

INSTITUTE FOR ENVIRONMENT AND SANITATION STUDIES

QUESTIONNAIRE ON FARMERS' KNOWLEDGE AND PERCEPTION OF PESTICIDE USE AND APPLICATION

CONFIDENTIALITY: THIS QUESTIONNAIRE IS BEING USED FOR AN ACADEMIC PURPOSE THEREFORE; INFORMATION PROVIDED SHALL BE KEPT CONFIDENTIAL. THANKS FOR YOUR ASSISTANCE

Date: ……

Location of farm..... Town/Community/Village: .....

PART ONE: PERSONAL INFORMATION

1. Farmer's Name: .....

2. Sex: a. Male ( ) b. Female ( )

3. Farm ownership: a. Farm Owner ( ) b. Labourer (farm worker) ( )

4. Age: a. 20 - 29 ( ) b. 30 - 39 ( ) c. 40 - 49 ( ) d. 50 – 59 ( ) c. above 60 ( )

5. Marital Status: a. Single ( ) b. Married ( ) c. Divorced ( ) d. Widow/Widower ( )

6. Are you the family head? a. YES ( ) b. NO ( )

6.1. Household size: a. 1- 4 ( ) b. 5 - 9 ( ) c. 10- 14 ( ) d. 15 -19 ( ) e. >20 ( )

7. Source of labour? a. family labour ( ) b. hired labour ( ) c. self ( ) d. others ( )

8. Educational level: a. No Education ( ) b. Primary/JHS ( ) c. Middle/SHS ( ) d. Tertiary ( )

9. Are you engaged in other economic activities? a. YES ( ) b. NO ( )

9.1. If Yes, please specify……

10. How many years have you been in cocoa farming? a. less than 4 years ( ) b. 5- 10 years ( ) c. 11- 15 years ( ) d. 16- 20 years ( ) e. 21- 25 years ( ) f. 26– 30 years ( ) g. 31-35 years ( ) h. 36-40 years ( ) i. 41-45 years ( ) j. 46 -50

11. What is the age of the cocoa farm? a.5 – 15 years ( ) b. 16 – 30 years ( ) c. 31-40 ( ) d. above 40 years ( )

12. Where did you get the planting material from? …….

13. How many cocoa farms do you have?

Plot/farm number	Farm size (acres)	Output per acre (bags)

PART 2: INFORMATION ON FARMERS' FIELD

14. Do you have agricultural extension officers in your community? a. YES ( ) b .NO ( ) c. doesn't know ( )

14.1. If Yes, Does the extension officer visit your farm? a. YES ( ) b. NO ( )

15. If Yes, how many times did he/she visit in the last cropping season?

a. only once ( ) b. two times ( ) c. three times ( ) d. four times ( ) e. five times ( ) f. Six times ( ) g. Seven times ( ) h. Eight times ( ) i. others (specify)……..

16. Does he/she talk about cocoa pest and diseases: a. YES ( ) b. NO ( )

16.1. If Yes, What kind of cocoa pest and disease information do you receive from the extension officer? a. Control ( ) b. Management ( ) c. Others.....

17. Do you obtain information about pesticides and usage from extension officers?

a. YES ( ) b. NO ( )

17.1. What kind of pesticides information do you receive? a. the recommended pesticides to use on cocoa farms ( ) b. the frequency of spraying in year ( ) c. the dosage of chemicals to use ( ) d. spraying directions ( ) e. the type of equipment to use for spraying ( ) f. how to store pesticides ( ) g. the types and how to use protective clothing during spraying ( ) h. how to spray ( ) j. how to adjust the spray nozzle ( ) k. how to mix pesticides ( ) l. none ( ) m. others…….

18. Are cocoa input shops available in your town /community: a. YES ( ) b. NO ( )

18.1. If No, where do you buy your cocoa inputs? .....

19. Are you member of a farmer's organisation: a. YES ( ) b. NO ( )

19.1. If yes, please specify .....…….....…….

20. Where do you get education or technical information on cocoa farming from?

a. own experience ( ) b. extension service ( ) c. farm organization ( ) d. cocoa rally ( ) e. experience advice from friends ( ) f. radio ( ) g. combination of sources ( ) h. NGO ( ) i. don't know ( ) j. others (specify)…….

PART 3: COCOA PEST AND DISEASE CONTROL (PESTICIDE USE)

21. What are your major cocoa production constraints: a. Insect's pest ( ) b. Diseases ( ) c. low Soil fertility ( ) d. Lack of farm implements (fertilizer, improve seeds, pesticides etc) ( ) e. Unpredictable rainfall ( ) f. Lack credit facilities ( ) g. High price of farm implements ( ) h. Shortage of labourer ( ) i. Inadequate farm lands () j. High temperature ( ) k. None ( ) l. others (please specify).....

22. Which insect pests and diseases do you consider as key? a. Mirids '*akate*' or capsid ( ) b. black pod disease or pod rot ( ) c. cocoa swollen shoot virus '*cocoa sasabro*' ( ) d. cocoa stem borers ( ) e. cocoa pod borer ( ) f. Termites ( ) g. grasshopper ( ) h. doesn't know ( ) i. shield bug ( ) j. others specify.....

23. Do you know about the Government Cocoa Mass spraying Exercise? a. YES ( ) b.NO ( )

23.1. If yes, is the programme going on in your cocoa farming community? a. YES ( ) b. NO ( )

24. Do you benefit from the Government Cocoa Mass spraying? a. YES ( ) b. NO ( )

24.1. If No, why.....

25. If YES, How many times did they spray your farm this season? a. One time ( ) b. two times ( ) c. three times ( ) d. four times ( ) e. five times ( ) f. six times ( ) g. seven times ( ) h. Others (specify) .....

26. Do you know about the COCOBOD approved pesticides? a. YES ( ) b. NO ( )

26.1. If Yes, tick a. I don't know the entire products ( ) b. akatemaster ( ) c. cocofeed ( ) d. confidor ( ) e. actara ( ) f. cocostar ( ) g.carbamult ( ) h. matalm ( ) i. fungikill ( ) j. kocide ( ) k. champion ( ) l. funguran ( ) m. nordox ( ) n. ridomil ( ) o. fungicide ( ) p. fungukill ( ) q. metacide ( ) r. cocobre ( ) s. sidalco ( ) t. don't know ( ) u. others specify ……

26.2. If No, Why ……..

27. Do you know about the COCOBOD timing of application? a. YES ( ) b. NO ( )

27.1. If Yes, state: .....

28. Do you control cocoa pest and disease on your own? a. YES ( ) b. NO ( )

29. If YES, What methods do you use to control the pest and diseases?

a. Cultural methods ( ) b. Biological method ( ) c. Chemical methods ( )

30. If your answer includes option C, please name of chemicals (pesticides) used:

a. I don't know the entire Products ( ) b. akatemaster ( ) c. cocofeed ( ) d. confidor ( ) e. actara ( ) f. cocostar ( ) g. carbamult ( ) h. matalm ( ) i. fungikill ( ) j. kocide ( ) k. champion ( ) l. funguran ( ) m. nordox ( ) n. ridomil ( ) o. fungicide ( ) p. fungukill ( ) q. metacide ( ) r. cocobre ( ) s. sidalco ( ) t. don't know ( ) u. DDT ( ) v. consider ( ) w. controller super ( ) x. others specify ……

31. Source of these chemicals: a. chemical sellers' ( ) b. other farmers ( ) c. Extension Agents ( ) d. Mass cocoa Spraying Agents ( ) e. others (specify) ……

32.1. What do you consider before buying a pesticide? a. Price ( ) b. Availability ( ) c. Toxicity ( ) d. Recommended by someone ( ) e. efficacy ( ) f. persistency ( ) g. safely ( ) h. others specify …….

33. What dosage of chemical was used? .....

34. How many times did you spray the chemical last year? a. One time ( ) b. two times ( ) c. three times ( ) d. four times ( ) e. five times ( ) f. six times ( ) g. seven times ( ) h. Eight times ( ) i. others specify.....

35. For how long have you used this chemical? a. 1 year ( ) b. 2 years ( ) c. 3 years ( ) d. 4 years ( ) e. 5 years ( ) f. 6 years ( ) g. 7 years ( ) h. 8 years ( ) i. 9 years ( ) j. 10 years ( ) k. 11 years ( ) l. 12 years ( ) m. 13 years ( ) n. 14 years ( ) o. 15 years ( ) p. Others specify ……

36. How many acres did you apply the chemical on?)? a. < 1 acre ( ) b. 1– 5 acres ( ) c. 6 – 10 acres ( ) d. 11-15 acres ( ) e. 16-20 acres ( ) f. 21-30 acres ( )

37. Do you normally mix two or more pesticides for spraying? a. YES ( ) b. NO ( )

37.1. If Yes, What chemicals do you mix? .....

37.2. Why do you mix? ……

38. Do you have knowledge about pesticide application rate? a. YES ( ) b. NO ( )

39. If Yes, Where do you get your Knowledge on pesticide application rates from?

a. Reading of pesticides Label ( ) b. Extension officer ( ) c. Fellow farmer ( ) d. Chemical sellers/ dealer/ retailer ( ) e. adverts (radio, TV, newspaper) ( ) f. don't know ( ) f. others specify ……..

40. Do you know about pesticide label? a. YES ( ) b NO ( )

40.1. If Yes, Are you able to read and understand the instructions on pesticides labels? a. YES ( ) b. NO ( )

40.2. If yes, what does the label tell you? ……

41. If No, who provides you with the information? a. Other farmers ( ) b. Chemical Sellers ( ) c. Friends ( ) d. Extension officers ( ) e. others.……

42. Do you follow the label? a. YES ( ) b. NO ( ) c. partially follow ( )

43. Do you have knowledge about direction of spraying? a. YES (.) b. NO ( )

43.1 If yes, do you follow wind direction during spraying? a. YES ( ) b. NO ( )

44. Do you put on protective clothing when spraying? a. YES ( ) b. NO ( ) c. don't matter ( )

44.1. If Yes, Please indicate the protective clothing you employ when applying pesticides: a. Boots/shoes ( ) b. Gloves ( ) c. Nose mask/respirator ( ) d. eye Goggles/face mask ( ) e. overcoat or Overalls ( ) f. handkerchiefs ( ) g. long-sleeves shirt ( ) h. trousers ( ) i. helmet/cap ( ) j. others ……

44.2. If No, Why? a. too expensive ( ) b. not available ( ) c. uncomfortable ( )

d. Sweating ( ) e. others specify ……

45. Have you experienced any health problems after spraying? a. YES ( ) b. NO ( ) c. No idea ( )

45.1. If Yes please tick: a. Chest pain ( ) b. Watery eyes ( ) c. Nausea ( ) d. Dizziness ( ) e. Fever ( ) f. Skin Irritation ( ) g. Itchy eyes ( ) h. Headache ( ) i. Weakness ( ) j. Burning eyes ( ) k. vomiting ( ) l. stomach pain ( ) m. excessive sweating ( ) n. Cough ( ) o. convulsion ( ) p. sneezing ( ) q. staggering ( ) r. blurred vision ( ) s. excessive salivation ( ) t. No symptoms ( ) q. other (Specify)……..

45.2. Which types of pesticides gives you such unfavourable reactions? ……....

46. Knowledge of ways pesticides enter the body? If you have had any unfavourable reaction after pesticides use, which part of your body do you think was the route of exposure? a. Eyes ( ) b. Skin ( ) c. Inhalation (nostrils) ( ) d. mouth (Swallowing) ( ) e. Others specify …….....

47. How is empty pesticide containers disposed of or discard? a. Burn ( ) b. Bury ( ) c. Cut and leave on farm ( ) d. reuse ( ) e. throw on the ground ( ) f. throw into water bodies ( ) g. others specify …….

48. Why do you choose that method of disposal? .....

49. If you have any spray liquid left, how do you dispose of the left-over? a. on Filed ( ) nearby stream ( ) c. on crops and weeds ( ) d. other specify……

50. How is water disposed of after washing sprayer? a. Field ( ) b. nearby stream ( ) c. others specify ……

51. Do you wash your hands after pesticides application? a. Yes ( ) b No ( )

51.1. If yes, what do you wash your hands with? a. Only water ( ) b. Water and soap ( ) c. Others specify ……

51.2. How often do you wash your hands after pesticides use? a often ( ) b. not often ( )

52. Do you take your bath after pesticides application? a. Yes ( ) b. No ( ).

52.1. If yes, after what period do you take your bath? a. < 15mins ( ) b. 15 – 30mins ( ) c. 31 – 60mins ( ) d. > 60mins ( )

PART FOUR: PERCEPTION OF RESPONDENTS ON DRINKNG WATERS SOURCES

53. Do you have a water facility in your farm? a. Yes ( ) b. No ( )

53.1 If yes what type of water facility? a. Borehole ( ) b. hand dug well ( ) c. River/Stream ( )

54. Where is the water facility located? a. within farm ( ) b. outside farm ( ) c. on the edge of the farm d. others, specify…….

55. How far is your cocoa farm from the water source? a. 0-30m ( ) b. 31-60m ( ) c. 60-70m ( ) d. 71-90m ( ) e. >100m ( )

56. How old is the water sources? a. <1 year ( ) b. 1-10 years ( ) c. 11-15 years ( )

57. What do you use the water for? Tick as many as applied to you. a Washing ( ) b. Cooking ( ) c. Drinking ( ) d. Bathing ( )

58 How many people depend on the water source? a 1-5 ( ) b. 6-10 ( ) c. 11-15 ( ) d. 16-20 ( ) e. 21-25 ( ) f. 26-30 ( )

59. What human activities do you observe around the water source?

Appendix D

ANOVA FOR WATER PARAMETERS AND PESTICIDE RESIDUES

Parameter	F-value	P-value
pH	0.742	0.497
Temperature	1.056	0.378
Conductivity	0.468	0.637
Total Dissolved Solids	0.470	0.636
Total Suspended Solids	0.924	0.424
Turbidity	0.731	0.502
Nitrate	0.752	0.493
Ammonia	1.139	0.352
Sodium	1.545	0.253
Potassium	0.420	0.666
Phosphate	0.247	0.785
Chlorpyrifos [a]	0.684	0.469
Diazinon [a]	0.106	0.766
Pirimiphos-methyl [a]	0.000	1.000
Lindane [b]	-	-
Alpha-Endosulfan [b]	0.200	0.698
Dieldrin [b]	-	-
p,p´-DDT [b]	0.360	0.591
Endosulfan-sulfate [b]	-	-
Heptachlor [b]	0.364	0.579
Allethrin [c]	1.600	0.333
Fenvalerate [c]	0.077	0.808
Cypermethrin [c]	0.333	0.667
Deltamethrin [c]	0.188	0.707

[a]- Organophosphate, [b]-Organochlorine, [c]-Synthetic Pyrethroids

Appendix E

Multiple comparism of the mean difference in soils from the various sampling sites using the Least Significant difference (LSD).

Multiple Comparisons								
Dependent Variable		(I) DISTANCE	(J) DISTANCE	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
							Lower Bound	Upper Bound
pH	LSD	Nkrankwanta site	Diabaa site	-.32333	.16318	.076	-.6869	.0402
			Krakrom site	-.93000*	.16318	.000	-1.2936	-.5664
			Kwakuanya	-.78667*	.16318	.001	-1.1502	-.4231
			control site	.20667	.16318	.234	-.1569	.5702
		Diabaa site	Nkrankwanta site	.32333	.16318	.076	-.0402	.6869
			Krakrom site	-.60667*	.16318	.004	-.9702	-.2431
			Kwakuanya	-.46333*	.16318	.018	-.8269	-.0998
			control site	.53000*	.16318	.009	.1664	.8936
		Krakrom site	Nkrankwanta site	.93000*	.16318	.000	.5664	1.2936
			Diabaa site	.60667*	.16318	.004	.2431	.9702
			Kwakuanya	.14333	.16318	.400	-.2202	.5069
			control site	1.13667*	.16318	.000	.7731	1.5002
		Kwakuanya	Nkrankwanta site	.78667*	.16318	.001	.4231	1.1502
			Diabaa site	.46333*	.16318	.018	.0998	.8269
			Krakrom site	-.14333	.16318	.400	-.5069	.2202
			control site	.99333*	.16318	.000	.6298	1.3569
		control site	Nkrankwanta site	-.20667	.16318	.234	-.5702	.1569
			Diabaa site	-.53000*	.16318	.009	-.8936	-.1664
			Krakrom site	-1.13667*	.16318	.000	-1.5002	-.7731
			Kwakuanya	-.99333*	.16318	.000	-1.3569	-.6298
% Organic-carbon	LSD	Nkrankwanta site	Diabaa site	-4.45333*	.25298	.000	-5.0170	-3.8897
			Krakrom site	-4.57000*	.25298	.000	-5.1337	-4.0063
			Kwakuanya	-4.78333*	.25298	.000	-5.3470	-4.2197

			control site	-4.87667*	.25298	.000	-5.4403	-4.3130
		Diabaa site	Nkrankwanta site	4.45333*	.25298	.000	3.8897	5.0170
			Krakrom site	-.11667	.25298	.655	-.6803	.4470
			Kwakuanya	-.33000	.25298	.221	-.8937	.2337
			control site	-.42333	.25298	.125	-.9870	.1403
		Krakrom site	Nkrankwanta site	4.57000*	.25298	.000	4.0063	5.1337
			Diabaa site	.11667	.25298	.655	-.4470	.6803
			Kwakuanya	-.21333	.25298	.419	-.7770	.3503
			control site	-.30667	.25298	.253	-.8703	.2570
		Kwakuanya	Nkrankwanta site	4.78333*	.25298	.000	4.2197	5.3470
			Diabaa site	.33000	.25298	.221	-.2337	.8937
			Krakrom site	.21333	.25298	.419	-.3503	.7770
			control site	-.09333	.25298	.720	-.6570	.4703
		control site	Nkrankwanta site	4.87667*	.25298	.000	4.3130	5.4403
			Diabaa site	.42333	.25298	.125	-.1403	.9870
			Krakrom site	.30667	.25298	.253	-.2570	.8703
			Kwakuanya	.09333	.25298	.720	-.4703	.6570
% Organic-matter	LSD	Nkrankwanta site	Diabaa site	-7.67667*	.43600	.000	-8.6481	-6.7052
			Krakrom site	-7.87667*	.43600	.000	-8.8481	-6.9052
			Kwakuanya	-8.24333*	.43600	.000	-9.2148	-7.2719
			control site	-8.40667*	.43600	.000	-9.3781	-7.4352
		Diabaa site	Nkrankwanta site	7.67667*	.43600	.000	6.7052	8.6481
			Krakrom site	-.20000	.43600	.656	-1.1715	.7715
			Kwakuanya	-.56667	.43600	.223	-1.5381	.4048
			control site	-.73000	.43600	.125	-1.7015	.2415
		Krakrom site	Nkrankwanta site	7.87667*	.43600	.000	6.9052	8.8481
			Diabaa site	.20000	.43600	.656	-.7715	1.1715
			Kwakuanya	-.36667	.43600	.420	-1.3381	.6048
			control site	-.53000	.43600	.252	-1.5015	.4415
		Kwakuanya	Nkrankwanta site	8.24333*	.43600	.000	7.2719	9.2148

			Diabaa site	.56667	.43600	.223	-.4048	1.5381
			Krakrom site	.36667	.43600	.420	-.6048	1.3381
			control site	-.16333	.43600	.716	-1.1348	.8081
		control site	Nkrankwanta site	8.40667*	.43600	.000	7.4352	9.3781
			Diabaa site	.73000	.43600	.125	-.2415	1.7015
			Krakrom site	.53000	.43600	.252	-.4415	1.5015
			Kwakuanya	.16333	.43600	.716	-.8081	1.1348
Available P	LSD	Nkrankwanta site	Diabaa site	-.07333	.10805	.513	-.3141	.1674
			Krakrom site	.00667	.10805	.952	-.2341	.2474
			Kwakuanya	-1.83000*	.10805	.000	-2.0708	-1.5892
			control site	-.08333	.10805	.458	-.3241	.1574
		Diabaa site	Nkrankwanta site	.07333	.10805	.513	-.1674	.3141
			Krakrom site	.08000	.10805	.476	-.1608	.3208
			Kwakuanya	-1.75667*	.10805	.000	-1.9974	-1.5159
			control site	-.01000	.10805	.928	-.2508	.2308
		Krakrom site	Nkrankwanta site	-.00667	.10805	.952	-.2474	.2341
			Diabaa site	-.08000	.10805	.476	-.3208	.1608
			Kwakuanya	-1.83667*	.10805	.000	-2.0774	-1.5959
			control site	-.09000	.10805	.424	-.3308	.1508
		Kwakuanya	Nkrankwanta site	1.83000*	.10805	.000	1.5892	2.0708
			Diabaa site	1.75667*	.10805	.000	1.5159	1.9974
			Krakrom site	1.83667*	.10805	.000	1.5959	2.0774
			control site	1.74667*	.10805	.000	1.5059	1.9874
		control site	Nkrankwanta site	.08333	.10805	.458	-.1574	.3241
			Diabaa site	.01000	.10805	.928	-.2308	.2508
			Krakrom site	.09000	.10805	.424	-.1508	.3308
			Kwakuanya	-1.74667*	.10805	.000	-1.9874	-1.5059
Nitrate	LSD	Nkrankwanta site	Diabaa site	-14.46667*	3.12353	.001	-21.4263	-7.5070
			Krakrom site	-14.93333*	3.12353	.001	-21.8930	-7.9737
			Kwakuanya	-3.26667	3.12353	.320	-10.2263	3.6930

			control site	-14.46667*	3.12353	.001	-21.4263	-7.5070
		Diabaa site	Nkrankwanta site	14.46667*	3.12353	.001	7.5070	21.4263
			Krakrom site	-.46667	3.12353	.884	-7.4263	6.4930
			Kwakuanya	11.20000*	3.12353	.005	4.2403	18.1597
			control site	.00000	3.12353	1.000	-6.9597	6.9597
		Krakrom site	Nkrankwanta site	14.93333*	3.12353	.001	7.9737	21.8930
			Diabaa site	.46667	3.12353	.884	-6.4930	7.4263
			Kwakuanya	11.66667*	3.12353	.004	4.7070	18.6263
			control site	.46667	3.12353	.884	-6.4930	7.4263
		Kwakuanya	Nkrankwanta site	3.26667	3.12353	.320	-3.6930	10.2263
			Diabaa site	-11.20000*	3.12353	.005	-18.1597	-4.2403
			Krakrom site	-11.66667*	3.12353	.004	-18.6263	-4.7070
			control site	-11.20000*	3.12353	.005	-18.1597	-4.2403
		control site	Nkrankwanta site	14.46667*	3.12353	.001	7.5070	21.4263
			Diabaa site	.00000	3.12353	1.000	-6.9597	6.9597
			Krakrom site	-.46667	3.12353	.884	-7.4263	6.4930
			Kwakuanya	11.20000*	3.12353	.005	4.2403	18.1597
% Clay	LSD	Nkrankwanta site	Diabaa site	12.50000*	4.47214	.019	2.5355	22.4645
			Krakrom site	8.33333	4.47214	.092	-1.6312	18.2979
			Kwakuanya	11.66667*	4.47214	.026	1.7021	21.6312
			control site	-.83333	4.47214	.856	-10.7979	9.1312
		Diabaa site	Nkrankwanta site	-12.50000*	4.47214	.019	-22.4645	-2.5355
			Krakrom site	-4.16667	4.47214	.373	-14.1312	5.7979
			Kwakuanya	-.83333	4.47214	.856	-10.7979	9.1312
			control site	-13.33333*	4.47214	.014	-23.2979	-3.3688
		Krakrom site	Nkrankwanta site	-8.33333	4.47214	.092	-18.2979	1.6312
			Diabaa site	4.16667	4.47214	.373	-5.7979	14.1312
			Kwakuanya	3.33333	4.47214	.473	-6.6312	13.2979
			control site	-9.16667	4.47214	.068	-19.1312	.7979
		Kwakuanya	Nkrankwanta site	-11.66667*	4.47214	.026	-21.6312	-1.7021

			Diabaa site	.83333	4.47214	.856	-9.1312	10.7979
			Krakrom site	-3.33333	4.47214	.473	-13.2979	6.6312
			control site	-12.50000*	4.47214	.019	-22.4645	-2.5355
		control site	Nkrankwanta site	.83333	4.47214	.856	-9.1312	10.7979
			Diabaa site	13.33333*	4.47214	.014	3.3688	23.2979
			Krakrom site	9.16667	4.47214	.068	-.7979	19.1312
			Kwakuanya	12.50000*	4.47214	.019	2.5355	22.4645
% Silt	LSD	Nkrankwanta site	Diabaa site	-10.55667*	4.49467	.041	-20.5714	-.5419
			Krakrom site	-14.31333*	4.49467	.010	-24.3281	-4.2986
			Kwakuanya	-14.25667*	4.49467	.010	-24.2714	-4.2419
			control site	-14.26333*	4.49467	.010	-24.2781	-4.2486
		Diabaa site	Nkrankwanta site	10.55667*	4.49467	.041	.5419	20.5714
			Krakrom site	-3.75667	4.49467	.423	-13.7714	6.2581
			Kwakuanya	-3.70000	4.49467	.430	-13.7148	6.3148
			control site	-3.70667	4.49467	.429	-13.7214	6.3081
		Krakrom site	Nkrankwanta site	14.31333*	4.49467	.010	4.2986	24.3281
			Diabaa site	3.75667	4.49467	.423	-6.2581	13.7714
			Kwakuanya	.05667	4.49467	.990	-9.9581	10.0714
			control site	.05000	4.49467	.991	-9.9648	10.0648
		Kwakuanya	Nkrankwanta site	14.25667*	4.49467	.010	4.2419	24.2714
			Diabaa site	3.70000	4.49467	.430	-6.3148	13.7148
			Krakrom site	-.05667	4.49467	.990	-10.0714	9.9581
			control site	-.00667	4.49467	.999	-10.0214	10.0081
		control site	Nkrankwanta site	14.26333*	4.49467	.010	4.2486	24.2781
			Diabaa site	3.70667	4.49467	.429	-6.3081	13.7214
			Krakrom site	-.05000	4.49467	.991	-10.0648	9.9648
			Kwakuanya	.00667	4.49467	.999	-10.0081	10.0214

*. The mean difference is significant at the 0.05 level.

Appendix F

Pearson's product moment correlation coefficient between physicochemical parameters of water

	EC	pH	TDS	Temp	TSS	Turbidity	NO_3^-	NH_4^+	PO_4^{3-}	Na^+	K^+
EC	1.000										
pH	0.708*	1.000									
TDS	0.999**	0.684*	1.000								
Temp	-0.015	-0.051	0.011	1.000							
TSS	0.658*	0.881**	0.632*	0.199	1.000						
Turbidity	0.044	0.170	0.055	0.885**	0.441	1.000					
NO_3^-	-0.065	-0.126	-0.078	0.179	0.272	0.392	1.000				
NH_3	0.748*	0.910*	0.719*	-0.012	0.970**	0.236	0.193	1.000			
PO_4^{3-}	-0.152	0.083	-0.149	0.587	0.183	0.549	-0.222	0.066	1.000		
Na^+	0.460	0.034	0.478	0.224	0.058	0.053	-0.326	0.101	0.304	1.000	
K^+	0.103	0.311	0.119	0.654*	0.284	0.701*	-0.206	0.145	0.432	-0.014	1.000

*Correlation is significant at the 0.05 level (2-tailed) ** Correlation is significant at the 0.01 level (2-tailed)

Temp=Temperature, EC=electrical conductivity, TDS=Total dissolved solids, TSS=Total suspended solids, PO_4^{3-}=Phosphate, NO_3^- =Nitrate and NH_3=ammonia

Appendix G

ANOVA FOR SOIL PARAMETERS AND PESTICIDES RESIDUES

Parameter	F-value	P-value
pH	18.004	0.000
EC	0.354	0.836
%OC	137.233	0.000
%OM	137.263	0.000
Available K	1.320	0.328
Available P	110.367	0.000
NH_4^+	0.686	0.618
NO_3-	10.656	0.001
%Exchangeable K	1.473	0.282
%TN	1.024	0.445
%Sand	1.469	0.283
%Clay	4.049	0.033
%Silt	3.785	0.040
Chlorpyrifos [a]	1.767	0.292
Profenofos [a]	-	-
Pirimiphos-methyl [a]	1.200	0.571
Lindane [b]	-	-
Dieldrin [b]	0.195	0.829
Beta-HCH [b]	-	-
p,p´-DDT [b]	0.333	0.750
Lambda-cyhalothrin [c]	0.357	0.790
Allethrin [c]	0.000	1.000
Cyfluthrin [c]	0.111	0.898
Cypermethrin [c]	0.125	0.887
Deltamethrin [c]	-	-
Bifenthrin [c]	-	-

[a]- Organophosphate, [b]-Organochlorine, [c]-Synthetic Pyrethroids

Appendix H

Pearson's product moment correlation coefficient between physicochemical parameters of soil

	pH	EC	% OC	%OM	% TN	NH_4^+	NO_3-	Ava. K	Ava. P	Ex-K	% Sand	% Clay	% Silt
pH	1.000												
EC	-0.701*	1.000											
% OC	0.382	0.302	1.000										
OM	0.383	0.299	0.998**	1.000									
% TN	-0.632*	0.540	-0.473	-0.475	1.000								
NH_4^+	0.799*	-0.876*	0.096	0.103	-0.738*	1.000							
NO_3-	0.080	0.557	0.704*	0.707*	0.196	-0.196	1.000						
Ava. K	-0.580	0.520	0.011	0.019	0.387	-0.262	0.468	1.000					
Ava. P	0.420	-0.397	0.305	0.301	-0.844*	0.390	-0.459	-0.676*	1.000				
Ex-K	0.400	0.050	0.889*	0.892*	-0.751*	0.378	0.442	0.074	0.492	1.000			
% Sand	0.309	-0.389	-0.421	-0.428	0.197	-0.020	-0.435	-0.803*	0.133	-0.611*	1.000		
% Clay	-0.761*	0.248	-0.512	-0.506	0.372	-0.243	-0.179	0.782*	-0.469	-0.291	-0.548	1.000	
% Silt	0.442	0.169	0.977**	0.979**	-0.593	0.266	0.650*	0.065	0.341	0.956*	-0.518	-0.432	1.000

*Correlation is significant at the 0.05 level (2-tailed) ** Correlation is significant at the 0.01 level (2-tailed)

OC=Organic carbon, OM=Organic matter, %TN=percentage nitrogen, Ava-P=available phosphorus, Ava-K=available potassium, EC=Electrical conductivity, Ex-K=Exchangeable potassium, NO_3^-=Nitrate and NH_4^+= Ammonium

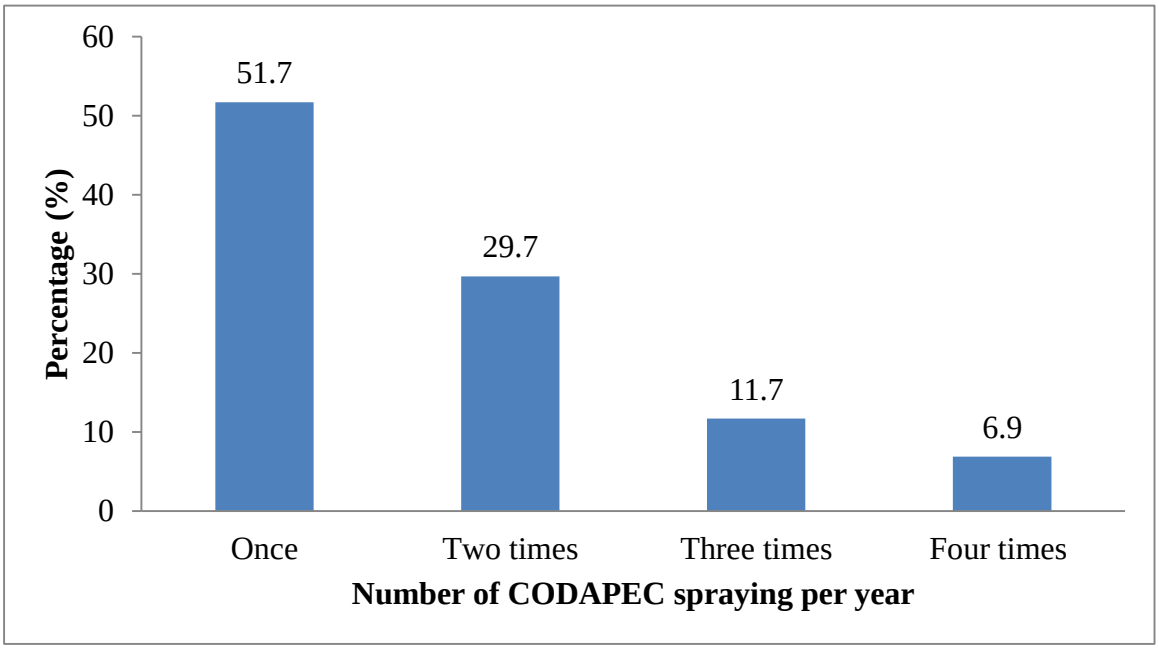
Appendix I

ANOVA FOR PESTICIDES IN COCOA BEANS SAMPLES

Parameter	F-value	P-value
Diazinon [a]	-	-
Chlorpyrifos [a]	1.722	0.270
Pirimphos-methyl [a]	0.067	0.937
Lindane [b]	1.111	0.506
Beta-HCH [b]	0.600	0.625
Dieldrin [b]	-	-
Aldrin [b]	-	-
p,p´-DDT [b]	0.472	0.717
Methoxychlor [b]	-	-
Allethrin [c]	-	-
Lambda-cyhalothrin [c]	2.286	0.270
Cypermethrin [c]	1.276	0.396
Deltamethrin [c]	1.000	0.577
Permethrin [c]	-	-
Bifenthrin [c]	-	-

[a]- Organophosphate, [b]-Organochlorine, [c]-Synthetic Pyrethroids

Appendix J



Percentage distribution of number of CODAPEC spraying in 2014/2015

Source: Field Work, 2015.

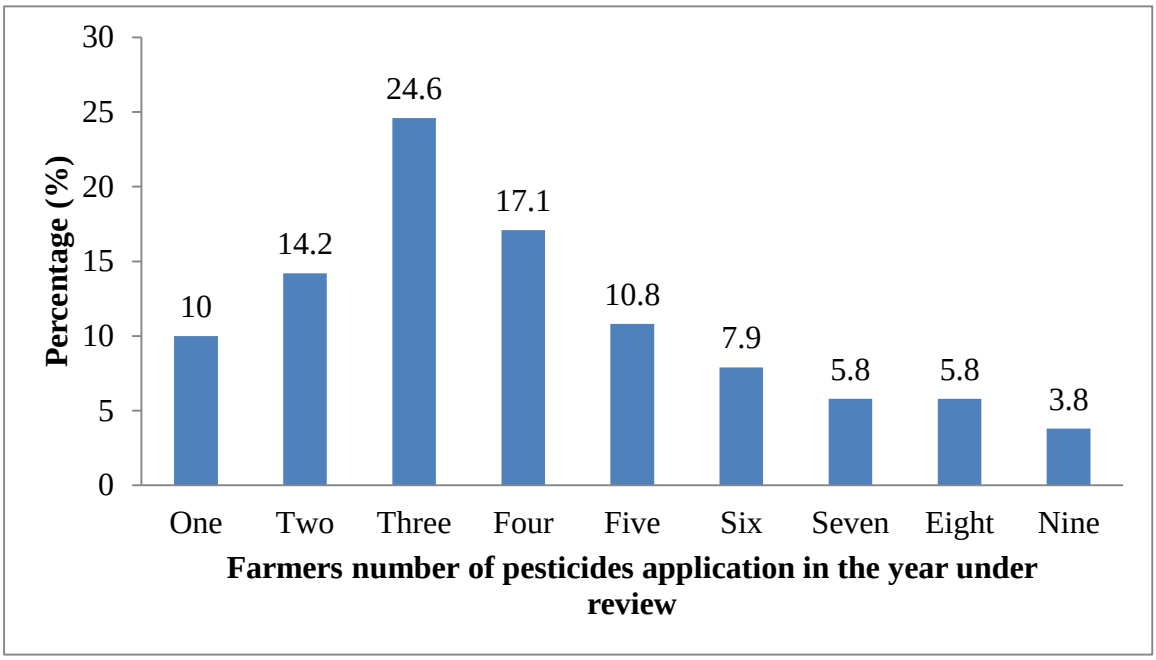
Appendix K

Commonly used unapproved pesticides for cocoa production in the study area

Trade name	Active ingredient
Akatesuro	Diazinon
Argine	Aldrin
Buffalo-Super	Acetamiprid/Chlorfenvinphos
Consider	Lmidacloprid
Controller-super	Lambda-Cyhalothrin
Sunpyrifos	Chlorpyrifos-Ethyl
Lamtox	Lambda-Cyhalothrin
Dursban	Chlorpyrifos
Okumakete	Thiamothoxam
Pyrethroids-Decis	Deltamethrin
Thiodan	Endosulfan
Sumitox	Fenvalerate
Lambda-M	Lambda-Cyhalothrin
Condifor	Imidacloprid
Kombat	Lambda-Cyhalothrin
Aceta-star	Methylthiophanate
Topsin-M	Methylthiophanate
Actala	
Polythrine	Cypermethrin
DDT	DDT
Clement powder	
Sumico 200 EC	Fenvalerate
Confidence	Chlopyrifos/Lambda-cyhalothrin
Super-gro	Permthrin

Some: Field Work, 2015

Appendix L



Percentage distribution of number of pesticide applications by cocoa farmers

Source: field work, 2015.

Appendix M

Attitudes put up by farmers' during pesticides application and after spraying

Variables	**Percentage (%)**
Talking	89
Receiving visitors	76
Singing	67
Chewing	37
Scooping/stirring with bare hands or sticks	67.5
Drinking	37
Whistling	26
Smoking	22
Eating	45
Snuffing	7.5
Remove blockage with their mouth	35.6

Multiple responses were recorded

Source: Field survey 2015

Appendix N

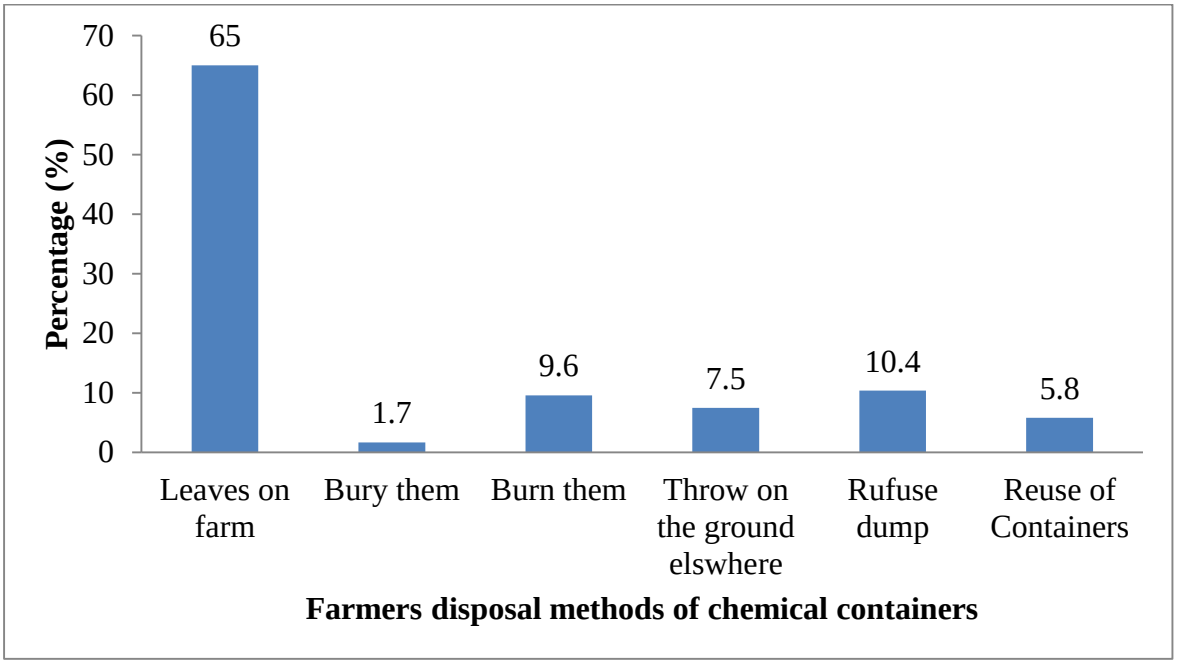
Health related issues experienced by farmers during and after pesticides use

Health related issues	**Percentage (%)**
Watery eyes	83
Headache	74
Dizziness	55
Chest pain	42
Cough	31.7
Skin irritation	30
Itchy eyes	25
Nausea	22
Burning eyes	21.7
Excessive sweating	17.1
Weakness	15.4
Fever	5.4

Multiple responses were recorded

Source: Field work, 2015

Appendix O



Percentage distribution of disposal of empty chemical containers by farmers

Source: Field work, 2015.

Appendix P

CSIR Soil Organic Matter classifications

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

Source: CSIR (1994)