LEVELS OF PESTICIDE RESIDUES IN SOIL AND WATER SAMPLES FROM WAANPU DAM IN THE BIMBILLA DISTRICT, GHANA

BY

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DECLARATION

This thesis is presented as partial requirement for MPhil Chemistry Degree, awarded by University of Ghana. I hereby declare that this submission is my own work and to the best of my knowledge, it contains no material previously published by another person nor material which has been accepted for the award of any other degree of the University of Ghana or any other university, except where due acknowledgement has been made in the text.

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DEDICATION

I dedicate this thesis to my parents, Mr. and Mrs. Yakubu, my wife Akonsi Kadijah, my son Fusheini Basit and to all my friends for their support and encouragement.

ABSTRACT

Nine pesticide residues were detected in soil and water samples from the Waanpu Dam in the Bimbilla District of Ghana at varying mean concentrations using Gas Chromatography. The pesticide residues detected in the soil and water samples were chlorpyrifos, beta-endosulfan, cypermethrin, aldrin, heptachlor, beta-BHC, heptachlor-epoxide, dieldrin, and methoxychlor. The concentration of beta-endosulfan was the highest among all the pesticides detected. It ranged from 0.001 – 0.070 µg/g for soil samples and 0.001 – 0.036 µg/g for water samples. The mean concentrations of pesticide residues in the soil samples analysed from the study sites were generally below WHO 2017 maximum residue levels, MRLs, for agricultural soils except for beta-endosulfan in all soil samples and chlorpyrifos at AS1, AS2, AS3, BS1, BS2, and BS3. The mean concentrations of beta-endosulfan and chlorpyrifos at the above mentioned sites were found to be above the respective WHO 2017 MRLs for agricultural soils. All pesticide residues recorded in the water samples from the various zones were below the respective WHO 2017 MRLs for potable water except for beta-endosulfan at W1, W2, W3, E1, E2, and E3 which exceeded the WHO 2017 MRLs of 0.03 µg/g. Pesticide residues of beta-BHC, Dieldrin, Heptachlor, Heptachlor-epoxide, Methoxychlor, cypermethrin, chlorpyrifos, and beta-endosulfan showed significant differences at $p<0.05$.

The presence of pesticide residues in the samples analysed was an indication of the use of the pesticides by farmers in the study area to control pests and diseases.

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LIST OF ABBREVIATIONS

ACh	Acetylcholine
ADI	Acceptable Daily Intake
ATSDR	Agency for Toxic Substances and Disease Registry
ANOVA	Analysis of Variance
BHC	Benzene Hexachloride
CCPR	Codex Committee on Pesticide Residue
CDC	Centre for Disease Control and Prevention
CEC	Cation Exchange Capacity
CFS	Centre for Food Safety
ChE	Cholinesterase Enzyme
CSIR	Council for Scientific and Industrial and Research
ECD	Electron Capture Detector
DDD	Dichlorodiphenyldichloroethane
DDT	DichloroDiphenyl Trichloroethane
DHHS	Department of Health and Human Services
EDSP	Endocrine Disruptor Screening Program
EH	Environmental Health
EPA	Environmental Protection Agency
EU	European Union
FAO	Food and Agricultural Organization of the United Nations
FDA	Food and Drugs Authority
GAP	Good Agricultural Practice
GC	Gas Chromatograph
GC-ECD	Gas Chromatograph with Electron Capture Detector
GC-MS	Gas Chromatograph with Mass Spectrometer
GUP	General Use Pesticide
HCH	Hexachlorocyclohexane

IHPA	International HCH and pesticide Association
JMPR	Joint FAO/WHO Meeting on Pesticide Residue
LLE	Liquid–liquid extraction
LOD	Limit of Determination or Detection
MAF	Ministry of Agriculture and Forestry
MCL	Maximum Contaminant Level
MOFA	Ministry of Food and Agriculture
MRL	Maximum Residue Level
ND	Not Detected
NOAEL	No Observed Adverse Effect
NTE	Neuropathy Target Ssterase
OCP	Organochlorine Pesticides
OP	Organophosphate pesticides
POP	Persistent Organic Pollutant
POPRC	Persistent Organic Pollutant Review Committee
PRDC	Pesticide Residues Problems in Developing Countries
RED	Reregistration Eligibility Decision
SARI	Savanna Agricultural Research Institute
SPE	Solid Phase Extraction
SPS	Sanitary and Phytosanitary Standard
SPSS	Statistical Package for the Social Sciences
TDI	Tolerable Daily Intake
UF	Uncertainty Factor
UNEP	United Nations Environment Programme
USA	United States of America
USDA ARS	United States Food and Drugs Association-Agricultural Research Service
WHO	World Health Organizations

CHAPTER ONE

INTRODUCTION

1.1 Background to the study

Pesticide is an adaptable substance used by road contractors, gardeners and farmers, to simply, and effectively, control unwanted pathogens. Its introduction after World War II to serve as warfare for example, the organophosphate insecticides were developed as nerve gases. Pesticides have become the most frequently used chemical in agriculture. This widespread use by farmers is as a result of its capability to control a wide spectrum of weeds and other pests. However, there are concerns about the increasing evidences of some potential toxic chemicals that are lingering in our bodies. It is becoming more common for people to get tested for dangerous farm chemicals such as glyphosphate, endosulfan, DDT, atrazine, lindane, aldrin, heptachlor, and more (EH 2005). In view of this, the environmental protection agency (EPA) is currently undertaking pesticides registration review in Ghana.

There are instances where insects, fungi, virus, bacteria, weeds, molluscs, and other pathogens, are doing well to stop us from being able to produce the high quality of affordable food that is need and farmers must do everything possible to control the devastating effects of these pests and diseases. The use of these compounds is justifiable since it helps to increase agricultural productivity tremendously. For example, Clarke *et al*., (1997) reported crop losses of the order of 40 – 75 % in tropical countries like Ghana as a result of pest infestation. These chemicals used in agriculture have been pivotal in reducing crop losses before and after harvest. Similarly, according to Gerken *et al*., (2001), pesticides use is in the ascendancy in Ghana and mostly common in cash crops and vegetables production. Also according to Clarke *et al*., (1997), for the past years in Ghana, pesticides have been deployed in the public health sector to mitigate disease and in agriculture to repel and destroy pathogens completely. However, frequent application of these potential toxic chemicals, together with the use and inappropriate handling of these pesticides by farmers can create unpleasant environmental and health effects. Invariably, these potential toxic chemicals can be dangerous to human health and to the environment when the magnitude of the exposure levels exceeds the safety limits. Meanwhile this exposure can be direct, such as the exposure of farm workers applying pesticides to various crops, and indirect by consumers consuming unwholesome products or even bystanders near application areas. It is palpable that, exposure to pesticides is responsible for death and various long-term and short-term defects (Wilson and Tisdell 2001).

The dangers of these pesticides in toxicological and agricultural sense of views may decrease if they are used with Good Agricultural Practices such as frequent monitoring procedures. In 1962 Rachel Carson first published a book raising political and public concerns of the threats of pesticides to wildlife, humans, and the ecosystem, and this was clearly written in the scientific literature by Pimentel *et al*., (1992) and by Pimentel and Greiner (1997). Pesticides identified as persistent organic pollutants (POPs) under the Stockholm Convention are still being used in agriculture and industry and these create negative health and environmental consequences (Ashburner and Friedrich, 2001). According to Briggs *et al* (1989) pesticides are highly toxic and have associated human health and environmental damages.

Poor farmers in developing countries are paying exorbitant money to purchase chemicals that do not meet internationally accepted quality standards. These chemicals purchased by these poor farmers do have some deleterious effects and have either been banned or restricted. In fact, poor formulation, poor production and inadequate selection of chemicals are the causes of low quality of pesticides (Williamson, 2001). Also it is quite glaring that privatization of the sale of these pesticides seems to be responsible for the low quality of pesticides and their effectiveness at the retail level (Williamson, 2001).

According to Miller (2004), millions of workers in developing countries who indulged in agriculture as a means of livelihood are inflected with severe poisoning, which subsequently lead to thousands of deaths as a result of agrochemical application. Most farmers tend to misapply some of these poisonous pesticides like organophosphates which are placed in the World Health Organization hazards categories I and II. However highly hazardous chemicals may pose acute or chronic effects to humans. For example, according to Jeyaratnam (1990), as many as 25 million workers in developing countries such as Ghana may suffer mild pesticide poisoning annually.

Furthermore, DDT, lindane, heptachlor, endosulfan, and other organochlorine pesticides are broadly used by farmers due to their efficacies in mitigating a wide range of pests and diseases (Darko and Acquah, 2007). However, these organochlorine pesticides are very resistant to microbial degradation and therefore accumulate in the environment and eventually in human body fats thereby causing serious health problems. Through their persistence and lipophilicity, the pesticides and their residues may concentrate in the adipose tissues and in blood serum of animals leading to environmental persistence and through the food chain (Darko and Acquah, 2007). Although the organochlorines are banned from importation, sale, and use in Ghana, there is evidence of their continued use and presence in the ecosystem (Darko and Acquah, 2007). Also the use of such pesticides on the farms can culminate in the deterioration of part of the soil, flora and fauna through physical and chemical destruction (Cowell and Clift, 1997). These pesticides therefore have the ability to perturb the ecosystems. For instance volatile pesticides can move off-site through air-drift and surface runoff to contaminate remote areas (including water bodies) where they have not been used. Also as a result of their lipophilicity and persistence, pesticides bioaccumulate along the food chain causing health threats to human beings.

Pesticides such as Atrazine, lindane, and other organochlorine pesticides (endrin, heptachlor, endosulfan, dieldrin, p‘‘p-DDE, p‘‘p-DDT, p‘‘p-DDD, gamma-Chlordane, methoxychlor, delta-HCH, β-HCH, endosulfan sulphate, and aldrin) have been used extensively in crop production. Though lindane use was banned in Ghana in 2009 (EPA, 2013) and atrazine (banned in EU) for their toxicity, they continue to be traded on local markets.

The bans and restrictions on pesticides are not working properly because of illicit trade often across national borders, which make these chemicals available for purchase (Williamson, 2001).

In spite of pesticides use in controlling weeds, insects, fungi, virus and other pathogens, it has been found by Cox (2001) to have neurological effects in humans and farm animals. Research has shown that, the level of pesticides in food, sediments and water, and in human fluids in many developing countries, including Ghana, is increasing tremendously (Ntow, 2001). The high application of pesticides has resulted in food contaminations (Wilson *et al*., 2007); ingestion of which has been linked with health conditions. Contaminated foods are a major source of morbidity, mortality, and increased risk of skin cancer, destruction of neurological cellular functions, chronic neurotoxicity, bladder and lung cancer, even at very low concentrations (Mensah *et al*., 2004; Sun *et al*., 2006). It is obvious that, the regular application and indiscriminate use of pesticides may pollute the environment (soils and drinking water sources) and affect human health. In fact most of the adverse human health effects by pesticides has been related to agricultural uses. The high use of the Waanpu Dam as a source of drinking water and other recreational activities by the people has thus guaranteed the need to investigate the levels of pesticide residues.

1.2 Problem Statement

Increasing population in the country, has led to increase demand for food and other agricultural products to satisfy human needs, therefore, larger acres of land are now put under agricultural production. According to Amoah *et al*., (2006), the increase of personnel in the cities and high use of agricultural products has led to the increased use of chemical pesticides for food production in Ghana. However, most of these pesticides can persist in our surroundings for longer time without losing their toxicity after their use, a notable example is organochlorines which are fat-soluble, meaning they can accumulate in humans, animals, plants and fatty tissues (William *et al*., 2008).

Exposure to pesticides through food and drinking water have lingering effect on our nervous system, thyroid function, low sperm count in males, birth defects, increased in testicular cancer, reproductive and immune malfunction, which are the results of endocrine disruptions, cancers, immune-toxicity, neurobehavioral and developmental disorders (Mesnage *et al*., 2010; Tanner *et al*., 2011; Cocco *et al*., 2013; Gill and Garg, 2014). Unfortunately most farms in Ghana are close to drinking water sources therefore exposing such water sources to pesticides pollution as a result of farming activities and agrochemical applications. However, increased accumulation of these chemicals in the food chain may pose serious health hazards if they are metabolized by the body and accumulate in the soft tissues (Akan *et al*., 2013; Agbeve *et al*., 2014). However, soil organisms such as earthworms and microbes which act as decomposers can be destroyed after spraying of pesticides and this decreases soil microbial biomass by directly destroying activities such as, reproduction, behavior and metabolism of organism which may permanently impair and alter the closely interactive ecosystem (Aktar *et al*., 2009; Gill and Garg, 2014).

Consumption of food and drinking water from areas where farmers solely rely on pesticides as a means to combat weeds, and other pathogens on their farms could pose serious health risk to consumers as well as reduce nutritional values of these agricultural produce and hence the need to address this problem.

1.3 Objectives

The overall aim of this work was to investigate levels of pesticide residues in the Waanpu dam and soils of some selected farms within the Bimbilla and its environs.

The specific objectives are:

1. To determine levels of pesticide residues in soils of some selected farms in the Bimbilla and its environs.

2. To determine levels of pesticide residues in the Waanpu dam.

3. To compare the level of pesticide residues in the Waanpu dam and soils of some selected farms in the Bimbilla area with National and WHO values.

1.4 Justification

The Bimbilla vicinity is predominantly agrarian (Ghana Statistical Service, 2014) and therefore majority of the indigens are mostly farmers who entirely rely on pesticides to combat pest and diseases which impact on the quality of drinking water and soils in the area. Even though, with the high use of pesticides in the area, little is known about the levels of their residues in water and soils in the District.

In view of the public health significance of pesticides residues and the uncertainty that exist regarding the long term effects of low dose exposure to these pesticides to human and the environment, it is relevant to investigate their levels in the environment to provide the necessary data that could be used by health professionals to protect people in the area. It is against this background that this study sought to address this concern and provide data on the levels of residues in water, and soils from some selected farms near the Waanpu Dam in the Bimbilla District.

1.5 Research questions

(a) What are the levels of pesticide residues in water from the Waanpu Dam and soils in its vicinity?

(b) What are the types and modes of application of pesticides used to combat pest and disease by farmers around the Waanpu Dam?

(c) What are the common health related issues of the use of pesticides by farmers?

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 Definition of Pesticide

Pesticide is defined under the Part II of the EPA Act, 1994 (Act 490), as any substance or mixtures of substances intended for preventing, destroying, mitigating, repelling or reducing the destructive effects of any pest. Or it is defined as mixture of substances intended for use as a plant regulator, defoliant, desiccant or wood preservative. However, pests can be insects, mice, unwanted plants (weeds), fungi or microorganism such as bacteria and viruses. The term pesticides can also refer to insecticides, fumigants, fungicides, herbicides, rodenticides and various other substances used to control pests. Crop production is under severe threat from pathogens (i.e. fungal, bacterial and viral or nematodes infestations) and these can damage plants above or below the ground. For example, in the 1980s, Ghana's crop production reduced drastically due to pest and diseases invasion (PAN, 2008). Climate change, trade and globalization as well as reduced resilience in cropping systems due to decade of agricultural intensification all lead to the spread of transboundary plant pest and diseases.

In Ghana, there has been a rapid rise in the quantity of pesticides used in agriculture over the past ten years (Hogson, 2003). In fact, the chemical classification of pesticides can be based on the functional groups with regards to their molecular structures or their specific biological activity on target species (Van-der and Van-Zoonen, 1999). Pesticides are often associated with the type of pest it controls. Another way to describe pesticides is to consider those that are chemical pesticides or are derived from a common source or production method. Other categories include bio-pesticides, antimicrobials, and pest control devices.

2.2 Advantages and disadvantages of pesticides

Pesticides are used to enhance agricultural productivity in Ghana, save human lives threatened by insect-borne diseases, such as malaria (mosquitoes) and sleeping sickness (tsetse flies) hence help to protect public health and wood preservation in industries. Pesticides therefore play a crucial role in the sustainable development in the country by simply helping farmers to save money and time, and thus increase their profitability. However, the use of these potential toxic chemicals with low technical know-how can pose serious health risks to human health and the environment. According to Barlas (2002), the successes of pesticides have been marred by side-effects resulting from the action of pesticides on non-target species, even though pesticides have contributed greatly to the increase of food production in agriculture and improved both human and animal health. The ecological effects of pesticide are often inter-related, varied and depend on two principal mechanisms. The adverse effects of pesticides on human health and the environment may come from both acute and chronic exposures and could lead to some debilitating effects. Such as most of the pesticides including chlorinated pesticides are broad-spectrum, therefore they affect more than the intended target organisms hence posing threat to non-target plants and animals. Also, some pesticides are mobile or are biomagnified in natural ecosystems and can persist in the environment for long period without losing their toxicity. Ecological effects of pesticides extend beyond individual organisms and can continue to ecosystems. Work indicates that application of pesticides is thought to be one of the most significant factors affecting biodiversity. Jonsson *et al*. (1990) reported that the continued decline of the Swedish partridge population is linked to changes in land use and the use of chemical weed control. Chemical used to combat weeds has the effect of reducing habitat, decreasing the number of weed species, and of shifting the balance of species in the plant community (as cited in WWF, 1992). The impact of pesticides on soil fertility, including inhibition of nitrification with concomitant, reduces uptake of nitrogen by plants (Torstensson 1990). For the above reasons, it is important to ensure that pesticide products used in the country are of acceptable quality, such that it does not present threat to the ecosystem, highly efficacious for the intended purpose and relatively safe to the user.

In 1996, the Pesticides Control and Management Act, Act 528 of Ghana was created. The enforcement of this Act coupled with the existence of Environmental Protection Agency of Ghana and other regulatory bodies such as the Ghana Standards Authority, the Food and Drugs Authority of Ghana and Council for Scientific and Industrial Research can help to achieve this noble objective.

2.3 Factors that affect crop yield

Good cultivation of crops requires a perfect climate that is found within areas where there are fertile lands.

Daily, seasonal, or annual variations in the values of the climatic elements are paramount in knowing the efficiency of crop growth (Ayoade, 2004). There are a number of factors that have serious impact on the growth of crops in Ghana. These factors are rainfall, temperature, sunlight and humidity and other factors such as, pest and diseases as well as soil nutrient status (Ojo and Sadiq, 2010).

Crops are highly sensitive to climatic changes, especially to areas where evapotranspiration is common due to the presence of high temperatures. In fact, it is clear that the higher the temperature the higher the yield of crops, while the lower the relative humidity, the better the yield of crops. Crops are known to produce well with minimal but sustained water availability throughout the year. However, differences in the yield of crops are perturbed more by rainfall than any other climatic factors.

2.3.1. Crop pests and diseases in Ghana

Farmers in the Country have recognized the good role of food production and non-food crops in improving their livelihoods and maintaining their better health. However, we have got to a stage now, where there are many cases of insects, molluscs, fungi, viruses, bacteria and rodents that are doing well to stop us from being able to produce the high quality of affordable food that we need. In fact, the problem of pests and diseases continues to pose a serious challenge and is among one of the biggest problems in increasing crop yields. Obviously, the only medium- and long-term solution is therefore to increase productivity per hectare and to reduce post-harvest losses using pesticides. Depending on the level of losses and the costs involved, an improvement in plant protection is likely to be an important strategy to increase food sources in the country. For instance, it is estimated that more than fifty percent of global agricultural production is lost before or following harvest because of the combined effects of disease, pest attacks and weeds. The causes of these high losses are mostly from phytophagous insects that are so devastating, rodents, nematodes, molluscs, fungus, virus and bacteria, and not forgetting weeds. Methods for crop protection and ways of controlling crop pests are paramount in order to maintain high levels of crop production.

Table 2.1: Some important pests of crops

CROPS	PESTS
Cassava	Mealy bugs, green mites, white scale
Cashew nuts	Mealy bug, stem borers, Helopeltis bugs
Cereals (maize, etc)	Stem borers, armyworm, leafhoppers (virus disease carriers)
Rice	Stem borers, leafhoppers, rice weevil, black weevil
Vegetable crops	Aphids, whitefly, leafhoppers, thrips, caterpillars that eat leaves and fruit, nematodes, mites
Citrus fruit	Caterpillars, aphids, leaf miner, whitefly, psyllids
Banana	Nematodes, banana weevil
Ornamental plants	Aphids, whitefly, mealy bugs, mites

Table 2.2: Some important diseases of crops

CROPS	DISEASES
Cotton	Bacterial blight, Fusarium wilt, Alternarial leafspot,
Cashew nuts	Powdery mildew, Anthracnose, and Die back
Cereals (maize, etc)	Leaf rusts, Leafblights, Maize streak, smuts
Rice	Blast (pyricularia), Brown spot, Blights,
Vegetable crops	Seed rot, rust, fruit and leaf rot, grey mold, powdery mildew and downy mildew, blights
Potato	Early and late blight, Bacterial wilt
banana	Fusarium, Sigatoka leaf spot
Groundnuts	Seed and Seedling rot, Cercospora leafspots, Rosette virus

2.4 Environmental fate of pesticides

Pesticides are mostly found in soils, sediments, oceans, air, surface waters, and groundwater during their use and disposal of products and as a by-product of other processes. Pesticides after application are widely distributed in environmental compartments, contaminating the air, soil and water (Verstraeten *et al*., 2002; Pucarević *et al*., 2003; Pucarevic and Sekulić, 2004; Pucarević *et al*., 2010). The use of these chemicals over the years has led to the contamination of various environmental compartments such as soil, ground and surface water and air as well as numerous agricultural food products (Fianko *et al*, 2011). Pesticides can accumulate up through the food chain and have been detected in breast milk.

Most pesticides are very slow to break down in air and can be subjected to long-range transport in the atmosphere. Pesticides in surface water may go into aquatic organisms, and by sedimentation into other organisms that remain in the sediment. In water it is adsorbed onto particles and sediment, with a half-life, under mid-European conditions, estimated to be between 2 and 820 years depending on photolysis and depth of water. It is strongly adsorbed onto soil particles and tend to remain for a long time in an inactive state, although it can also desorb again and become biologically active. Half-life in soil can be up to 20 years; the persistence of the pesticide depends on its physical and chemical properties (partition coefficients, degradation rates, deposition rates) and the characteristics of the environment. Climate characteristics also play a role in persistence. Pesticides have been detected in groundwater, drinking water, surface water, in soil and sediment samples both in agricultural areas where it was formerly used and in urban soils near production and waste disposal sites. Most organochlorine pesticides are very slow to break down in water and tend to adsorb to suspended particles and sediment in the water column and highly bioaccumulated by aquatic organisms like fish. Pesticides have low mobility in soil and may evaporate from soil surfaces. These chemicals are very persistent and take many years to break down and therefore are slowly degraded by soil microorganisms.

2.5 Route of Exposure of Pesticides

The main exposure of pesticides to the general public is through ingestion of food, such as consumption of fish caught in contaminated waters, and the ingestion of contaminated breast milk for infants. Fenik *et al*., (2011) argued that the widespread use of pesticides, their stability and tendency of bio-accumulation, make it particularly dangerous for man, hence, exposure through consumed food must be pointed out as a special health risk. Ingestion can occur through breastfeeding, accidental ingestion, residues in food and mouthing. Earlier studies in Ghana has shown the presence of pesticide residues in meat, water, sediment, vegetables, fruits, fish and soil at locations unknown for pesticide use (Osafo and Frempong, 1998; Aboagye, 2002; Mensah *et al*., 2004; Amoah *et al*., 2006; Adu-kumi *et al*, 2010).

The primary route of exposure to pesticides for the general population is through food. The high application of pesticides has resulted in food contaminations (Wilson *et al*., 2007), ingestion of which has been linked to health conditions. People may be exposed to very low levels of pesticides through ingestion of contaminated foods, such as fatty fish. Contaminated foods are a major source of morbidity, mortality and increased risk of skin cancer, destruction of neurological cellular functions, chronic neurotoxicity, bladder and lung cancer even at very low concentrations (Mensah *et al*., 2004; Sun *et al*., 2006). Young children may be exposed to pesticides by playing in contaminated soil.

Another way humans can be exposed to pesticides is through inhalation. However, inhalation can result from indoor and outdoor spraying and also through occupational exposure. In fact, children who play in and on contaminated soil may have a higher potential for exposure through the skin and through inhalation of contaminated dust. And when it gets in contact with the skin the chemical can cross the epithelium of the skin and mucous membranes that exchange gases (alveoli) or nutrients (gastrointestinal mucosa). However, the rate of absorption depends on chemical properties such as, amount of the chemical, length of exposure and the physical state of the molecule. There are other factors that may contribute to increased absorption for example Skin absorption is higher when there is vasodilatation especially during playing and running.

Children who eat on contaminated soil may ingest pesticides. Pesticides can also accumulate in breast milk. Breastfed babies may be exposed to pesticides through their mother's breast milk. Other sources of exposure may include contact with water or air contaminated with pesticides. Pesticides have been found in ambient water samples at concentrations of less than 0.1 parts per trillion (ppt) and ambient air samples at concentration ranges of 0.1 pg/m^3 to 1.5 ng/m^3. Workers involved in the production of organosulphate, chlorinated hydrocarbons in the factories, may also be exposed through their by-products. Also in some areas, there is a potential for release into the environment during formulation of pesticides in these factories. Exposure to pesticides may cause either acute and or chronic health effects (US EPA, 2007).

2.6 Health effects of pesticides

Studies have shown that pesticide can cause death, systemic (e.g., liver, skin, bone, and thyroid), neurological, developmental, endocrine, and immunological toxicity in humans and animals. Pesticides are extensively distributed in the environment due to their persistence and resistance to degradation. It bio-accumulates in human tissues and this eventually poses serious health risks to humans and animals (Ejobi *et al*., 1996).

Inhalation of pesticides through occupation can have associated effects with the liver both by increased porphyrins and weakly with hepatocellular carcinoma, immunological effects (decreased neutrophil activity, increased immunoglobulins, and susceptibility to infection), and renal effects (microproteinuria). Most inhalation of pesticides in humans and residents of a nearby town can result from factories that produce these chemicals. Exposure to these chemicals primarily through air pollution has been linked with elevated blood levels of pesticide and hepatic effects such as increased porphyrins and hepatic enzymes, thyroid effects (decreased thyroxine levels; weakly with hypothyroidism, goiter, and thyroid cancer), and impaired development of locomotor skills in infants. Other negative outcomes from pesticide exposure include neurological effects, birth defects, foetal death (Sarborn *et al*., 2007) and neuro-developmental disorder (Jurewicz and Hanke, 2008). Many more are believed to die of cancer caused by pesticides exposure. (Mckinney and Schoch, 2003). For example, epidemiological evidence was found in studies of a population orally exposed to pesticides in southeast Anatolia, Turkey. In the 1950s, widespread ingestion of bread made from grain that had been treated with pesticide caused an epidemic in this region. An extremely high rate of mortality occurred in infants under 2 years of age who had been breast fed by mothers who had ingested the contaminated bread. it was reported by the Daily Graphic newspaper that, the death of eight family members after eating a meal of beans at Shaibuipe in Northern Region of Ghana was attributed to acute poisoning of a pesticide (Daily Graphic, 24/11/12). A research conducted by Clarke, in 1997 revealed that about 36% of the farmers had experienced negative side effects such as headache, dizziness, fever, blurred vision, vomiting and nausea after applying pesticides.

2.7 Toxicity levels of pesticides

Table 2.3: Classification of pesticides based on hazards by the WHO in 2010

Toxicity	Route of exposure	Class	Effects
Acute toxicity	Inhalation	Class Ia and class Ib	Extremely hazardous and Highly hazardous
Acute toxicity	Oral intake	Class II	Moderately hazardous
Systemic toxicity	Dermal absorption	Class III	Slightly hazardous
Acute toxicity	Eye irritation	Class II	Moderate to severe
Unlikely to present acute toxicity	Skin irritation	Class IV	Minimal

2.8 Pesticide Formulations

It is unusual to spray or use pesticides in their pure form. Normally they are processed into a usable form for application. The main reason is that, the active ingredients in a pesticide product are the chemicals that control the target pest. Even though a pesticide product also has other ingredients called " inert" (or inactive) ingredients, these are added to dilute the pesticide or render it safer, more efficient, easier to measure, mix and apply, and more convenient to handle. The technique of preparing mixtures of active ingredients with these other materials is known as formulation. Normally the formulated products are kept in spray tanks and mixed with water for use. The following types of formulations are commonly in use:

- Dry formulations such as dusts, granules and baits
- Liquid formulation such as wettable powders, emulsifiable concentrates and flowables
- Gaseous formulations such as aerosols

2.9 Types and Classification of Pesticides by target pest

The classification of pesticide depends on the ability to mitigate the target pest, mode of action, chemical nature and its use. According to Draggan and Miller (2012), pesticides are classified based on the target pest are shown in table below:

Table 2.4: Classification of pesticides by target pest

PESTICIDES	DEFINITION	EXAMPLE
Herbicide	Capable of destroying weeds and other plants that are found where they are not needed.	Glyphosate, Gramoxone, Atrazine
Insecticide	Capable of combating or mitigating insects and other arthropods.	Lindane, Karate, Cymbush, Comfidor
Nematicide	Capable of combating nematodes.	Methyl-bromide or Diethyl- Dibromide
Bactericide	Capable of combating bacteria.	Streptomycin
Acaricide	Capable of mitigating or Killing mites that feed on plants and animals.	Dimethoate
Repellent	Capable of repelling pest such as mosquitoes.	N,N-Diethyl-meta-toluamide (DEET)
Larvicide	Capable of destroying larvae	Aquabac, Teknar, Vectobac, and LarvX
Growth regulators	Capable of changing plant growth normal processes	Butralin
Predacides	Ability to combat vertebrate pests	sodium fluoroacetate (1080)
Algaecides	Used to mitigate algae in water and other sites.	N,N-dimethylalkylamine
Piscicide	Used to mitigate fish	rotenone, saponins, TFM, niclosamide
Molluscicide	Kill snails and slugs.	Phorate
Termiticide	Capable of combating termites	Chlorpyrifos
Adulticide	Capable of combating adult insects	malathion, naled, chlorpyrifos, permethrin, resmethrin, sumithrin
Ovicide	Kill eggs of insects and mites.	Isoxathion
Arboricide / silvicide	Capable of combating trees, shrubs and herbs	bipyridylium zwitterion, paraquat
Fungicide	Mitigate fungi.	Dithane M-45, Kocide
Rodenticide	Control mice and other rodents.	Klerat
Miticide	Capable of destroying mites	Dimethoate

2.9.1 Classification by Mode of Action

Pesticides are classified based on their mode of action or how they work and are shown in the table below.

Table 2.5: Classification by mode of action

PESTICIDES	MODE OF ACTION
Fumigants	These are gases, which kill when they are inhaled or otherwise, absorbed by pests.
Chemosterilant	They cause sexual sterility in either female or male insect or animal.
Systemic	Taken into the blood of an animal or sap of plants. They kill insects without harming host. For instance, systemic pesticides applied to leaves, stems, or roots of plants move through the plant to other parts of the plant. An insect pest acquires translocated pesticides during feeding
Pheromones	Affects pests by changing their behavior
Sterilants	Makes pests unable to reproduce
Protectant	Applied to plants, animals and structures to prevent entry or damage by pests.
Synergist	Enhances the effectiveness of an active agent
Stomach poisons	Kills pests when swallowed. With insects pest, these enter insects body during feeding
Desiccant Dusts	They cause loss of body fluids and death by dehydration. Common desiccants include boric acid
Semiochemical	Pheromones, allomones and kairomones; substances emitted by plants or animals, which stimulate or inhibit certain behavioral activities of insects
Antifeedant	Inhibits feeding while insects remain on the treated plant; the insects eventually starve to death
Attractant Feeding Stimulants	These types of substances lure pests to treated locations, e.g. sex causes insects to feed more vigorously
Anti-transpirant	Capable of reducing or inhibiting transpiration
Contact	Kills pests on contact

2.9.2 Classification by Use

Pesticides can also be classified based on their use, for instance how it affects the target plants or by selectivity and soil or foliage when applied as illustrated in Table 2.6.

Table 2.6: Classification of pesticides by use

PESTICIDES	USES
Soil-applied selective	These type of chemicals are applied to the ground especially during pre-planting, and are recommended for pre-emergence and post-emergence treatments.
Selective pesticides	These chemicals are used to control weeds without causing destructive effects to desirable plants. For instance, narrow-leave weeds can be preferentially controlled. However care should be taken to ensure that selectivity is only relative, and misuse can result in negative consequences to desirable plants.
Non-selective	These types of chemicals are normally used to ensure complete removal of vegetation. These chemicals kill a lot of plants when applied.
Foliage-applied	These chemicals are applied on leaves and other parts of plant which are above the ground. Contact killing usually occurs here, since parts of the plant are sprayed.

2.9.3.1 Inorganic pesticides

According to Koehler and Belmont (1998), Pesticides can be classified into two main chemical groups and these are inorganic and organic.

These compounds are not fat soluble but act only as stomach poisons. They are generally crystalline and salt-like in appearance, and soluble in water, a typical example is Copper hydroxide, $Cu(OH)_2$. It was widely used to control insect pests before the discovery of synthetic organic compounds such as dichlorodiphenyltrichloroethane (DDT).

2.9.3.2 Organic pesticides

Organic pesticides are made from compounds containing carbon in addition to hydrogen. They can also contain oxygen, sulphur, phosphorus, chlorine and nitrogen in the molecule. Organic compounds constitute the majority of all modern pesticides. Most are insoluble in water. Organic pesticides can be divided into two groups: Synthetic organics & natural organics (Koehler and Belmont, 1998)

SYNTHETIC ORGANICS

These are products designed to combat certain organisms. However, they can be organic (natural origin) and man-made or synthetic. The synthetic organics can further be subdivided into several major groups, including the following:

- ORGANOCHLORINES (also known as chlorinated hydrocarbons): These are organic compounds containing one or more chlorine atoms as hydrogen substitutes in their molecule. It inhibits nerve membrane ion transport and block nerve signal transmission. It is known to be persistent organic pollutants and therefore persist in the environment for longer periods without losing their toxicity. It is very stable therefore its persistence and bioaccumulation is very strong (Rathore, 2012). However some of these pesticides have been banned or restricted throughout the world, but some continue to be actively used. The banned pesticides include DDT, Chlordane, Aldrin, Heptachlor, Dieldrin, Endrin, Methoxychlor etc
- ORGANOPHOSPHATES: These are synthetic hydrocarbon containing phosphorus complexes. It inhibits cholinesterase, an enzyme that regulates the peripheral nervous system; extremely toxic to mammals, birds, and fish (generally 10-100 times more poisonous than most chlorinated hydrocarbons) (Cunningham *et al*., 2003). It degrades easily, so its bioaccumulation is rare. Examples are parathion, malathion, dichlorvos, dimethyldichlorovinylphosphate (DDVP) and tetraethylpyrophosphate (TEPP).

- CARBAMATES: They are derived from carbamic acid and act as stomach poisons and have low bioaccumulation rates. Examples are carbaryl, aldicarb, aminocarb, and carbofuran.

NATURAL ORGANIC PESTICIDES

These pesticides are plant and animal extracts containing carbon in addition to hydrogen. Typical examples are nicotine and nicotinoid alkaloids from tobacco, rotenone from the roots of derris and cube plants and pyrethrum, extracted from Chrysanthemum cinerariaefolium.

2.9.4. Selected pesticides

2.9.4.1 Aldrin

Table 2.7: Physical and chemical properties of Aldrin

Chemical name	Aldrex, ISODRIN
Class number	309-00-2
Molecular weight	64.896 g/mol
Empirical formula	$C_{12}H_8Cl_6$
IUPAC Name	1,2,3,4,10,10-Hexachloro-1,4,4a,5,8,8a-hexahydro-1,4:5,8-dimethanonaphthalene
Melting Point	104 °C
Boiling Point	145 °C
Water solubility	0.014 mg/L at 25 ^{0}C
Trade name	Aldrec, Aldrex, Aldrex 30, Aldrite, Aldrosol
Use	Insecticide
Class name	Organochlorine
Classification by WHO	Class IB
Effects	*Acute Health Effects, Chronic Health Effects, Cancer Hazard and Reproductive Hazard.*

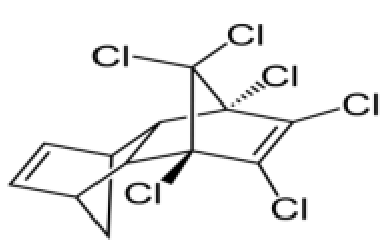

Figure 2.1: Struture of Aldrin

2.9.4.2 Beta-BHC

Table 2.8: Physical and chemical properties of beta-BHC

Chemical name	*Beta-BCH*
Class number	319-85-7
Molecular weight	290.83 g/mol
Empirical formula	$C_6H_6Cl_6$
IUPAC Name	1,2,3,4,5,6-hexachlorocyclohexane
Melting point	≥300 °C
Boiling Point	323 °C
Water solubility	Slightly soluble in water
Trade name	Lindane
Use	Insecticide
Class name	Organochlorine
Classification by WHO	Class II
Effects	*Highly toxic carcinogen. May cause irritation on contact. Hazardous decomposition products.*

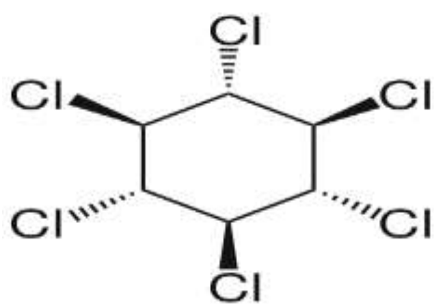

Figure 2.2: Structure of β-BHC

2.9.4.3 Heptachlor

Table 2.9: Physical and chemical properties of heptachlor

Chemical name	Heptachlorane; Heptamul; 3-Chlorochlordene; 76-44-8; Rhodiachlor
Class number	76-44-8
Molecular weight	373.32 g/mol
Empirical formula	$C_{10}H_5Cl_7$
IUPAC Name	1,4,5,6,7,8,8-Heptachloro-3a,4,7,7a-tetrahydro-4,7-methano-1H-indene.
Melting point	95 to 96 °C
Boiling Point	310 °C
Water solubility	> 0.1 mg/mL at 64° F
Trade name	Drinox, Heptagran, H-34 Heptamul, Heptox, Goldcrest
Use	Insecticide
Class name	Organochlorine
Classification by WHO	Class IB
Effects	*Acute inhalation may result in nervous system* effects*, gastrointestinal* effects*,* effects *on the liver and central nervous system from oral expos*ure.

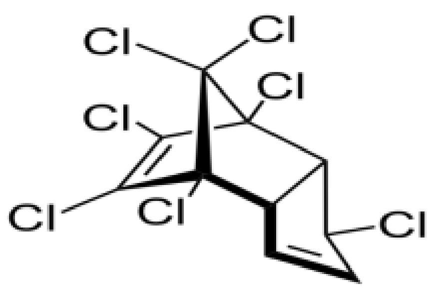

Figure 2.3: Structure of Heptachlor

2.9.4.4 Methoxychlor

Table 2.10: Physical and chemical properties of Methoxychlor

Chemical name	Methoxychlor; P,p'-Methoxychlor; 72-43-5; DMDT; Dimethoxy-DDT; Methoxy-DDT
Class number	72-43-5.
Molecular weight	345.644 g/mol
Empirical formula	$C_{16}H_{15}Cl_3O_2$
IUPAC Name	1,1,1-Trichloro-2,2-bis(4-methoxyphenyl)ethane
Melting point	87 °C
Boiling Point	Decomposes
Water solubility	0.00001% (20°C)
Trade name	Chemform, Dimethoxy-DT, DMDT, ENT 1716, Higalmetox, Methoxychlore, Marlate
Use	Insecticide
Class name	Organochlorine
Classification by WHO	Class II
Effects	*anxiety, dizziness, headache, confusion, reproductive* effects, *such as abortions, reduced fertility, reduced litter size, and skeletal* effects

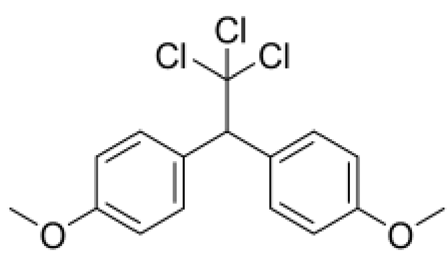

Figure 2.4: Structure of Methoxychlor

2.9.4.5 Dieldrin

Table 2.11: Physical and chemical properties of Dieldrin

Chemical name	*Dieldrin*
Class number	60-57-1.
Molecular weight	380.91 g/mol
Empirical formula	$C_{12}H_8Cl_6O$
IUPAC Name	1,2,3,4,10,10-Hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-1,4,5,8-dimethanonaphthalene
Melting point	176-177°C
Boiling Point	385 °C
Water solubility	0.1 mg/l
Trade name	Dieldrite, Dieldrex, Octalox,
Use	Insecticide
Class name	Organochlorine
Classification by WHO	Class IB
Effects	*Headaches, dizziness, uncontrollable muscle movements irritability, and vomiting. Exposure to high levels can cause convulsions and kidney damage*

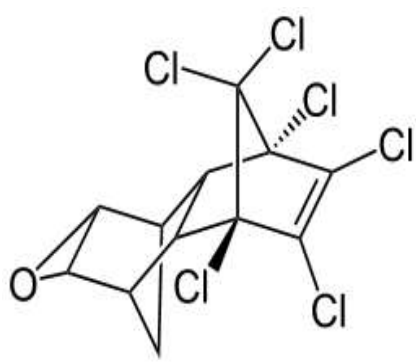

Figure 2.5 Structure of Dieldrin

2.9.4.6 Beta-endosulfan

Table 2.12: Physical and chemical properties of Beta-Endosulfan

Chemical name	*Endosulfan* I; *BETA-ENDOSULFAN*
Class number	3321-65-9
Molecular weight	406.904 g/mol
Empirical formula	$C_9H_6Cl_6O_3S$
IUPAC Name	6,7,8,9,10,10-hexachloro-1,5,5a,6,9,9a-hexahydro-, 3-oxide, (3α,5aα,6β,9β,9aα)-6,9-*M*ethano-2,4,3-benzodioxathiepin
Melting point	208-210°C
Boiling Point	-
Water solubility	0.32 mg/L
Trade name	Afidan
Use	Insecticide
Class name	Organochlorine
Classification by WHO	Class II
Effects	*Reproductive effects, Mutagenic effects, Chronic toxicity, Acute toxicity*

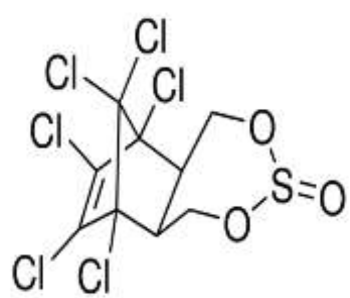

Figure 2.6: Structure of Beta-endosulfan

2.9.4.7 Chlorpyrifos

Table 2.13: Physical and chemical properties of Chlorpyrifos

Chemical name	Chloroprifos
Class number	2921-88-2
Molecular weight	350.62
Empirical formula	$C_9H_{11}Cl_3NO_3PS$
IUPAC Name	0, 0-diethy 0-3, 5, 6- trichloro-2pyridyl phosphorus thioate
Melting point	42 °C
Boiling Point	160 °C
Water solubility	2 mg/L
Trade name	Dursban, Lorsban
Use	Insecticide
Class name	Organophosphorus
Classification by WHO	Class II and considered moderately hazardous
Effects	*Neurological effects, persistent development disorders and auto-immune disorders*

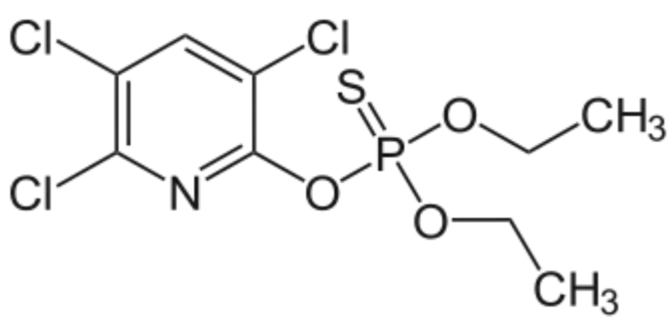

Figure 2.7: Structure of Chlorpyrifos

2.10 Maximum Residue Limits (MRL)

A maximum residue limit (MRL) is the highest acceptable level of a residue in food. It is interesting to note that MRL is set to ensure Good Agricultural Practice (GAP) so that the best methods of primary production are practiced to keep residues in soils and drinking water safe for human use as low as possible. However, violating a MRL do not mean that agricultural products are unsafe but is to alert the Ministry of Agricultural and Forestry (MAF) on crops safety or the possibility that the crops could have been better produced.

Zahedeh *et al*., (2010) noted that the detection and permanence of pesticides in water depends on parameters such as, the pesticide half-life and solubility in water, the spread and the amount of pesticides applications, and the soil type to leach insecticides into ground waters. In setting a maximum residue limit with holding period of farm produce, it is crucial to know the half-life and number of days the pesticides are effective against a pest. For example, if a pesticide is applied to a fruit in two weeks' days, it means the fruit should not be harvested until two weeks days after the last application of the pesticides. From this, if a residue in the crop, for example, has less than 0.2mg/kg after two weeks, then a MRL of 0.2 mg/kg is likely to be set. Any violation of this MRL would be from inappropriate use, or applying the insecticide at a rate above that specified on the label.

Table 2.14: WHO Guidelines

Source: WHO April 2017

PESTICIDES	WHO GUIDELINES (µg/g) IN SOIL AND WATER SAMPLE
Alpha BHC	2.000
Beta BHC	2.000
Gamma BHC	2.000
Delta BHC	2.000
Heptachlor	0.100
Aldrin	0.030
Heptachlor Epoxide	0.030
Alpha-Endosulfan	0.030
4,4-DDE	1.000
Deldrin	0.030
Endrin	0.600
Beta-Endosulfan	0.030
4,4-DDD	1.000
Endosulfan sulphate	0.030
4,4-d-DDT	1.000
Endrin ketone	-
Chlorpyrifos	0.050
Methoxychlor	20.000

2.11 Analytical methods for the determination of pesticides

There are so many environmental analytical methods employed to investigate the level of persistent organic pollutants (POPs). A notable example is the capillary gas chromatography (GC) equipment with either electron capture detector, nitrogen-phosphorus detector, or low-resolution mass spectrometry (MS) to separate and quantify the pesticides. Interestingly analytical procedures used for pesticide residues include: sample preparation, the extraction of the pesticide, clean-up of the sample extract and the analysis of the pesticide residues using the appropriate instrument. Meanwhile, screening of samples, especially in areas where OCPs use are abundant could be accomplished with bioanalytical methods such as specific commercially available enzyme-linked immuno absorbent assays (Muir and Sverko, 2006). Also new analytical techniques such as two-dimensional GC (2D-GC) and ―fast GC" using GC–ECD may be favourable for broader use in routine pesticide analysis in the near future because of its low costs, ability to provide high-resolution separations of pesticide, high versatility, sensitivity and selectivity. It is crystal clear that registered pesticides and their metabolites can be analyzed by using gas chromatography. Also GC ECD is the most widely used technique particularly for the determination of pesticides in different matrices (Santos and Galceran, 2004; Bruner, 1993). However, for the isolation of target compounds from matrices, extraction and clean-up procedures have been employed. For example, Soxhlet extraction is considered to be the best technique used for the extraction of OCPs from soils. However, soxhlet and shaking flask extractions are time consuming and require large volume of organic solvents (Bøwadt *et al*., 1995; Hartonen *et al*., 1997; Schantz *et al*., 1998). Therefore, in order to reduce the extraction time and the amount of solvent required, as well as sample amount, new extraction procedures, i.e., supercritical fluid extraction (SFE) (Bøwadt and Hawthorne, 1995), microwave assisted extraction (MAE) (Eskilsson and Björklund, 2000) and accelerated solvent extraction (ASE) (Björklund *et al*., 2000) etc., have been developed as alternative techniques.

Trace analysis of pesticides in environmental samples is usually performed by GC combined with a previous extraction or a pre-concentration step including traditional liquid–liquid extraction (LLE) (Barcelo , 1993, Fatoki and wofolu, 2003; Tahboub *et al*., 2005), solid phase extraction (SPE) (Aguilar *et al*., 1996; 1997), solid phase micro-extraction (SPME) (Page and Lacroix, 1997; Aguilar *et al*., 1999; Tomkins and Barnard, 2002; Li *et al*., 2003; Dong *et al*., 2005) and the more recently developed liquid phase micro-extraction under different names i.e., dispersive liquid–liquid micro-extraction (DLLME) (Cortada et al., 2009a; Leong and Huang, 2009; Tsai and Huang, 2009), liquid-phase micro-extraction (LPME) (Huang and Huang, 2007; Farahani *et al*., 2008), single-drop micro-extraction (SDME) (Cortada *et al*., 2009b), polymer-coated hollow fiber micro-extraction (PC-HFME) (Basheer *et al*., 2004), stir bar sorptive extraction (SBSE) (Leo n *et al*., 2003; Pe rez-Carrera *et al*., 2007), ultrasound assisted emulsification-micro-extraction (USAEME) (Ozcan *et al*., 2009a), vortex assisted liquid-liquid micro-extraction (VALLME) (Ozcan, 2010). Anastassiades *et al.,* 2003 developed a dispersive SPE method which involves the use of bulk SPE material as opposed to packed tubes to facilitate sample cleanup of the liquid extract prior to GC-MS analysis (Lehotay 2004, Anastassiades *et al.,* 2003). LLE is probably the most widely used method for the extraction of OCPs (Barcelo, 1993, Fatoki and wofolu, 2003; 34 Tahboub *et al.,* 2005). In the SPE method, analytes may be adsorbed, and complex matrices can cause settling in cartridges (Leong and Huang, 2009; Ozcan *et al*., 2009a; Quayle *et al*., 1997).

CHAPTER THREE

MATERIALS AND METHODS

3.1 Study Area

Bimbilla is the capital of the Nanumba North district and it lies in the South eastern part of the Northern Region and lies between latitudes 8.5º N and 9.25º N and longitudes 0.57º E and 0.5ºE.

According to the 2010 Population and Housing Census, the population of Nanumba North District is 141,584 representing 5.7 percent of the region's population of 2,479,461. Males constitute 49.4 percent and females represent 50.6 percent in the District. The District has a total land area of 2260.8 sq. Km. The predominant occupation is farming with about 97.7% of the district's economically active population (15 years and older) involved in farming staple food crops and cash crops. Less than fifty percent (50%) of the population in the district has access to safe drinking water namely treated water, boreholes and hand dug wells (www.ghanadistrics.com 2011).

The area receives an annual rainfall averaging approximately 600mm, enough for a single farming season. The annual rainfall pattern is erratic at the beginning of the raining season, starting in April, intensifying as the season advances raising the average from 600mm to 1000mm.Temperatures are usually high, averaging 34°C. The maximum temperature could rise as high as 41°C and the minimum as low as 16°C. The low temperatures are experienced from December to late February, during which the hot and dry North-East Trade winds (harmattan) greatly influence the weather in the district. The generally high temperatures as well as the low humidity favour high rates of evapotranspiration, leading to net water deficiencies.

The District is in the interior (Guinea) Savanna woodland which can sustain large scale livestock farming, as well as the cultivation of staple foods like rice, groundnuts, yams, cassava, maize, cowpea and sorghum. The trees found in the area tend to be drought resistant and hardly shed their leaves completely during the long dry season. Most of these are of economic value and serve as important means of livelihood especially for women. Notable among these are Shea trees, (the nuts which are used for making Shea butter) and dawadawa (Parkia biglobosa) that provide seeds used for condimental purpose. The sparsely populated north of the district has denser vegetation mostly with secondary forest. The populous south on the other hand, is depleted by human activities such as farming, bush burning and tree felling among others.

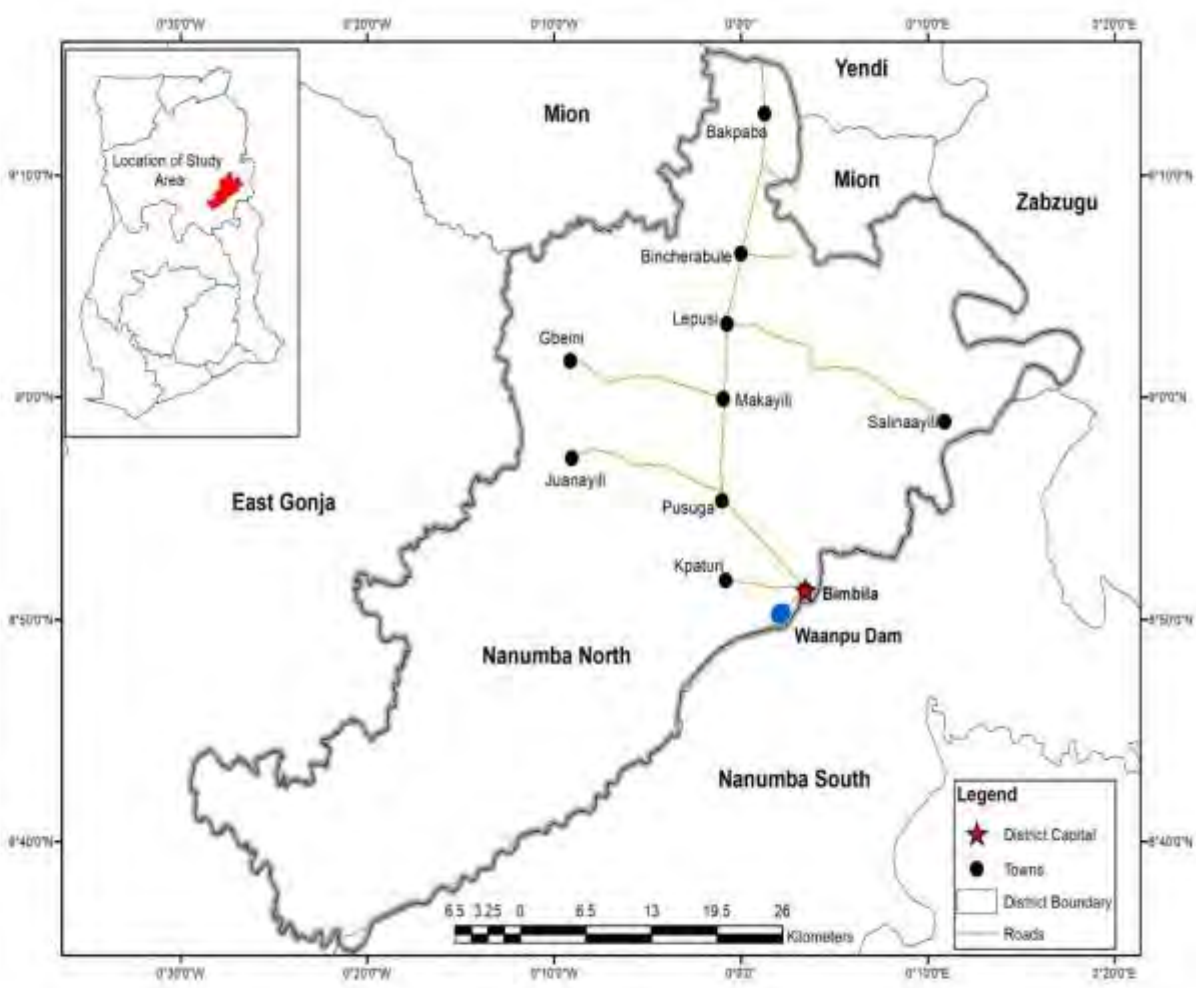

Figure 3.1: A map showing Nanumba North district in Northern Region of Ghana

3.2 Source of Data

The study collected primary and secondary data from farmers and from relevant institutions such as Savanna Agricultural Research Institute (SARI). The primary data was generated by administering both structured and semi-structured questionnaires to selected farmers in the catchment area. Whiles the secondary data was collected from institutional websites, data bases and journal publications and published reports. Water samples were also collected from Waanpu Dam three times for laboratory analysis.

3.3 Sample Size

In all, one hundred and twenty (120) farmers were interviewed from Bimbilla environs that is within the catchment area. The area was divided into three (3) clusters namely; the Northern cluster (AS), western cluster (BS), and the southern cluster (CS). 40 farmers were selected from each cluster and were interviewed using simple random sampling method.

3.4 Reagents and Materials

Table 3.1: REAGENTS AND MATERIALS USED

REAGENTS	GRADE	SOURCE
Acetone	Pesticides grades	Labort Fine PVT Ltd, India.
Hexane	Pesticides grades	BDH Laboratory Supplies, England
Acetonitrile	Pesticides grades	Sigma Aldrich, USA.
Toluene	Pesticides grades	SMM Chemicals Pty Ltd
Sodium sulphate	AnalaR	Labort Fine PVT Ltd, India.
Sodium hydroxide	AnalaR	BDH Laboratory Supplies, England
Sodium chloride	AnalaR	Avondale Laboratory, England.
Potassium dihydrogen phosphate	AnalaR	BDH Laboratory Supplies, England.
Dipotassium hydrogen phosphate	AnalaR	PX PARK Scientific Ltd, UK.
Ethyl acetate	AnalaR	SMM chemicals Pty Ltd
Bond elute C18 SPE cartridges	-	Supelco analytical USA
ENVI-Car LC-NH2 500mg.500mg.6ml		Supelco analytical USA
Filter paper		Whatman International Ltd, England.

INSTRUMENTATION AND APPARATUS

Table 3.2: DETAILS OF EQUIPMENT USED

EQUIPMENT	TYPE
Gas chromatograph	Shimadzu GC – 2010 with AOC 20 Autoinjector and AOC 20S Autosampler and Electron Capture Detector
Analytical column	30m x 0.25mm internal diameter fused silica capillary column coated with VF-5ms (0.25µm film).
Centrifuge	Sanyo (MSE) Harrier 18 / 80
Glass vials	2 mL
Vacuum manifold	209 x 200 – Aldrich TM round bottom flask
Horizontal shaker	Ika-Werke HS 501 Digital
Macerator	IKA Ultra Turrrax Homogenizer
General laboratory glassware	Round bottomed flasks, volumetric flasks, centrifuge tubes, separating funnels, funnels, measuring cylinders
Rotary film evaporator	Buchi Rotary evaporator (India)
Ultrasonic bath	Clifton SW 3H and Grant XUB 18 UK
Vortex mixer	Thermolyne (Mai Max-Plus)
Recirculating chiller	Buchi, B-740

3.5 ANALYSIS

The residues were analysed using Shimadzu gas chromatograph, GC-2010 equipped with ^{63}Ni, electron capture detector that allows the detection of contaminants even at trace level concentrations. The GC conditions and the detector response were adjusted to match the relative retention time and response. The conditions for analysis were capillary column coated with ZB-5(30mx0.25mm, 0.25µm film thickness). Sample preparation, extraction, cleanup and analysis were carried out according to the procedure described in multi-residue method for agricultural chemicals (Syoku-An, 2006).

3.5.1 Experimental Procedures

Before the samples were subjected for analysis, all glass-wares involved were washed with acetone and thoroughly cleaned with distilled water and dried in oven at 150^0C for about five hours.

3.5.2 Preparation of standard solutions

All the pesticides standard stock solutions were prepared in ethyl acetate with the aid of an ultrasonic bath, by dissolving a weight of the pesticides which when corrected for purity will be equivalent to 1000 µg/mL (e.g. 10mg in 10mL). This was labelled as a Parent Standard Reference for each Pesticides standard e.g Heptachlor, HEPT 1. These Parent Standard References were diluted for use as fortification standards in the procedural recovery process, and used in the calibration standards in instrument calibration. Working solutions of standards for fortification standards in the procedural recovery process, and as calibration standards in the instrument calibration were freshly prepared through dilution of an appropriate aliquot of the stock solutions with ethyl acetate. Distilled water was used to prepare all aqueous solutions. All solutions prepared for Gas Chromatography (GC) were filtered through a whatman filter paper. For validation of the analytical procedure, repeated analysis of the samples against internationally certified/standard reference material was done. Additionally, the quality of pesticide 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 analysed in duplicates. All extracts were kept frozen until quantification was achieved.

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 95% for most of the pesticides analysed.

$$\textbf{Recovery (\%)} = \frac{\text{Conc.of Pesticide residue recovered from fortified sample}}{\text{Concentration of pesticide added to sample}} \text{x}100$$

3.5.3. Preparation of 0.5 mol/l phosphate buffer (pH 7.0)

Using chemical balance an amount of 52.7 g of dipotassium hydrogen phosphate and 30.2 g of potassium dihydrogen phosphate were weighed accurately into a 250 mL beaker. The pH was adjusted to 7 with 1 mol/L NaOH and 1 mol/L HCl solution and transferred into a 1.0 L volumetric flask with the use of distilled water for dissolution.

3.6 Sampling methods

A preliminary field survey was conducted to have a general view of the variations in the study area. The preliminary field survey was conducted over a two months during the main farming season (June-July, 2017) with additional data collected towards the end of the season (August - September, 2017). However, a water sampler was used to collect water samples into 500 mL pre-cleaned Teflon sample bottles with caps for pesticide residues analysis at depth 0–20 cm. Twelve (12) water samples were collected from four zones in the Waanpu Dam labelled as, Northern zone N, Southern zone S, Eastern zone E, and Western Zone W. While a well beyond 30 m was used as the control (D1). This distance was chosen because the World Health Organization (WHO) and various studies recommends that hand dug well 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). Meanwhile water sample was collected into a Teflon bottle from the selected well making a total of thirteen samples.

The Teflon sampling bottles were rinsed with the dam water before taking the water samples. The samples were labelled and transported to the laboratory within 24–48 hours on ice in clean ice chests and stored in the refrigerator at 4 °C until they were analysed for pesticide residues. The samples for pesticide residues analysis were extracted within 24 hours of arrival at the laboratory of CSIR in Accra.

3.6.2 Soil sampling

Each of the selected farms, were grouped into three clusters that is, Northern cluster AS, Western cluster BS and Southern cluster CS also a quadrat of 50 × 50 m was marked in each cluster. In each quadrat, three (3) soil samples were collected randomly at depth 0–20 cm 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, one soil sample was taken from a nearby natural forest to act as a control (X1) where there were no farming activities. These gave a total of ten soil samples from the study area. All soil samples were kept in well-labelled plastic polythene containers and transported to the laboratory for analysis. At the laboratory of CSIR in Accra, the soil samples were oven–dried at 105 °C to constant weight and sieved using 2 mm nylon mesh. Sub-samples of the sieved soils were then taken for pesticide residues analysis.

3.6.3. Extraction of pesticides from water and soil samples

3.6.3.1 Extraction of soil samples

Ten grams (10 g) of soil samples were weighed and quantitatively transferred into 250 mL separating flasks. 10 mL of hexane was added to each of the soil samples in the flasks and ultra-sonicated for 5 min. An additional 10 mL of hexane was added, and the flasks closed tightly. The samples were placed on a horizontal mechanical shaker and set to shake continuous for 30 min at 300 mot/ min. The contents were then allowed to stand for 10 min to sufficiently separate the phases or layers. A 10 mL of the supernatants were carefully taken by pipette and dried over 2 g anhydrous magnesium sulphate through filter paper into 50 mL round bottom flasks. The concentrates were then adjusted to about 2 mL using the rotary film evaporator at 35 °C, and made ready for silica clean up.

3.6.4. Clean-up of soil extract

In order to remove the matrix compounds that could interfere in the GC analysis, there was the need for clean-up. Extracts clean up were done, using polypropylene cartridge columns, packed with one-gram silica gel previously activated for 10 h in an oven at 130 °C, which have one centimeter thickness layer of anhydrous $MgSO_4$ on top and conditioned with 6 mL acetonitrile. The concentrated extracts were then loaded onto the columns/ cartridges, and 50 mL flat bottom flasks placed under the columns to collect the eluates. A 10 mL hexane was used to elute the columns afterwards. The total filtrates collected were concentrated to dryness at 40 °C using the rotary evaporator. The residues were redissolved in 1 mL ethyl acetate by pipetting and transferred into 2 mL standard opening by gas chromatography (GC). All extracts were kept frozen until analysis was required.

3.6.5 Extraction of water samples

The water samples were filtered using the whatman filter paper to remove debris and suspended material, 1000 mL portions of the filtered water samples were transferred into two litre capacity separating flasks. A 30 mL of saturated solution of (NaCl) was added to each to produce a salt out effect in order to adjust the pH to 7. A 50 mL volume of hexane was introduced into a 2 liter separating funnel containing 1 liter of filtered water and were shaked manually for 5 minute and allowed to settle. After complete separation, the organic phase was drained into a 250 mL conical flask, while the aqueous phase was re-extracted twice with 50 mL of hexane. The extracted organic phases were combined and dried by passing through a glass funnel containing anhydrous sodium sulfate. The organic fraction was concentrated using rotary evaporator and subjected to silica clean up.

3.6.5.1 Clean-up of water Extract

Extracts clean up were done, using polypropylene cartridge columns, packed with one-gram silica gel previously activated for 10 h in an oven at 130 °C, which have 2 g layer of anhydrous sodium sulphate on top and conditioned with 6 mL hexane. The concentrated extracts were then loaded onto the cartridges, and 100 mL round bottom flasks were placed under the columns to collect the eluates. A 20 mL hexane was then used to elute the columns/cartridges after- wards, and the total eluents collected were concentrated just to dryness using the rotary evaporator set at 40 °C. It was then re – dissolved in 2 ml ethyl acetate, prior to analysis by gas chromatography (GC) equipped with electron capture detector. All extracts were kept frozen until quantification was achieved.

3.7 Data analysis

The completed questionnaires were individually checked to ensure that they had been filled correctly. The questionnaires retrieved from the field were counted to ensure that they were up to 120. The closed-ended questions were then coded. All the responses given to the coded closed-ended questions were typed onto the Statistical Package for Social Sciences (SPSS) worksheet. Socio-economic and pesticide data were analyzed using Statistical Package for Social Sciences (SPSS (Version 20). The SPSS was then used in analyzing the coded closed-ended responses to generate frequency tables, percentages, bar charts and pie charts to characterize farmers biodata, types of pesticides used. Statistical package for social sciences (SPSS) software version 20.0 was also used to generate the means, standard deviation and standard error for pesticide residues in soil and water. One-way analysis of variance (ANOVA) was performed to analyse significant differences in the concentrations of pesticide residues recorded from the four (4) different zones of the water samples and three different clusters of the soil samples.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1. Types of Pesticides available and in use by the farmers in the District

Types of pesticides available and in use by farmers in the district were obtained from farmers using a questionnaire. All pesticides were grouped appropriately. The active ingredient, the target organism, and the trade name of each pesticide used were recorded. An album of common pesticides used by the farmers in the Northern region was compiled to facilitate the identification process. In all 100 % of the farmers used eight pesticides, however, endo-sulfan was the most commonly used pesticide.

Table 4.1: Types of pesticides available and in use by farmers in the Bimbilla district

Pesticides Identified	**Type**	**Number of Users**	**Percentage (%)**	**Angle(^{o})**
Endo-sulfan	Insecticide	50	41.7	150
Heptachlor	Insecticide	27	22.5	81
Methoxychlor	Insecticide	15	12.5	45
Aldrin	Insecticide	8	6.7	24
Sarosate	Herbicide	7	5.8	21
Lindane	Insecticide	6	5.0	18
Pyrethroid	Insecticide	4	3.3	12
Atrazine	Herbicide	3	2.5	9
Total		**120**	**100**	**360**

Source: Field Survey Data, January, 2018

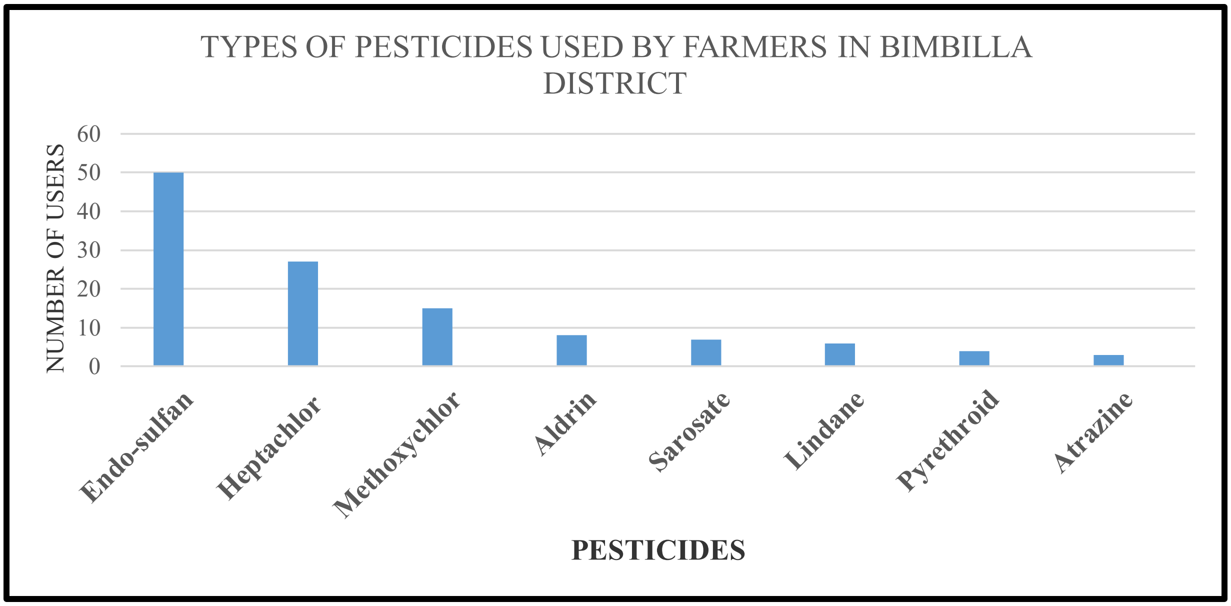

Figure 4.1: Types of pesticides available and in use by farmers in Bimbilla district

4.2 Socio-economic Background of Respondents

In all a total of 120 respondents were selected and analysed. However, the questionnaires were individually checked to ensure that they had been filled correctly.

Gender dynamics of farmers

One hundred and twenty (120) farmers were interviewed in the Bimbilla district. Majority of the respondents were males (114) and rest were females (6). Most of them (80%) were household heads and 20% were dependents of households. Farming was the main occupation (82%) of the people and 18% were engaged as drivers, traders, or public servants.

Table 4.2: Gender dynamics of farmers.

Gender	No. of respondents	Percentage (%)	Angle (^{o})
Male	114	95	342
Female	6	5	18
Total	120	100	360

The study revealed that women participation in crop production in the Bimbilla district is very low as five percent of the farmers interviewed were female and ninety-five percent (95%) of the farmers interviewed were males. Clearly this could be attributed to the fact that women do not own land in the study area and are sparingly involved in making production decisions, which can be explained by cultural factors such as household leadership in such patriarchy society.

When women do not own land, they cannot therefore make decisions on what the land should be used for. This correlates very well with the findings of the International Trade Center (2011) which stated that the percentage of women who owned land and participate in decision making in crop production in Africa is usually low, with a maximum variation of 10%.

However, the study found that women are mostly involved in field and support services in crop production in the district such as sowing of seeds, harvesting of food on the farms, taking care of the household and other farm-related chores. Field and support services are the only areas in crop production in Africa where women are mostly involved in decision making (25% in the field and 30% in support services, especially catering for cotton workers and farmers) (International Trade Centre (2011).

Most (78%) of the farmers interviewed were household heads and as such major stakeholders in providing basic needs for their households, the remaining 22% percent were dependents of households. Crop production in the district was a major source of income for household heads in supporting their families' basic needs. Some farmers also go into crop production with the aim of getting agro inputs for their farm animals.

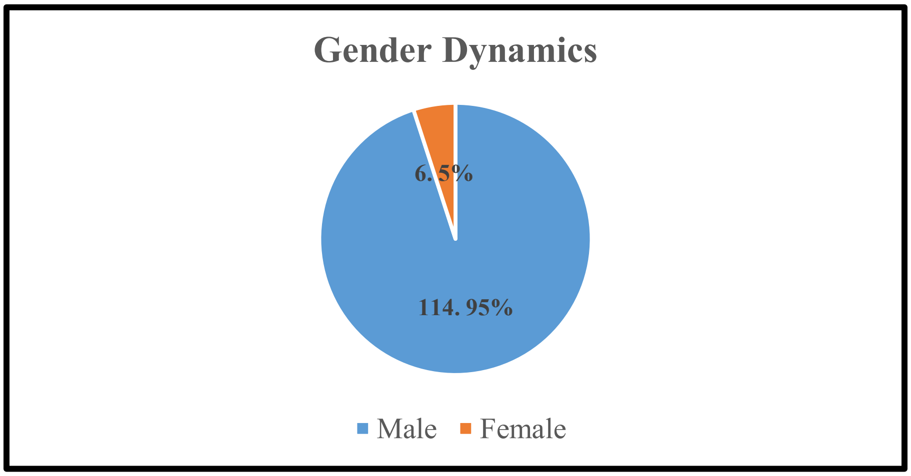

Figure 4.2: Gender dynamics of farmers.

4.2.2 Age Distribution of Respondents

Majority (70%) of farmers in the district were between the ages of 19- 60 with 25% above 60 years. And also, 5% were children below 18 years. The average age of farmers in the district was 35years (Table 4.3).

Table 4.3: Age distribution of respondents

Age	Frequency	Percentage (%)	Angle (^{o})
0-18	6	5	18^o
19-60	84	70	252^o
60+	30	25	90^o
Total	120	100	360^o

Source: Field Survey Data, January, 2017

Majority (70%) of the respondents were within the working class (19-60 years) and therefore there was an active labour force to ensure all year round crop production and other agricultural produce for subsistence in the Bimbilla district. Crop production by the farmers guaranteed constant cash flow from the sale of food crops to traders. Most of the aged (60+) who constitute 25% of the respondents were often more interested in animal production but participated in crop production activities to access agro inputs.

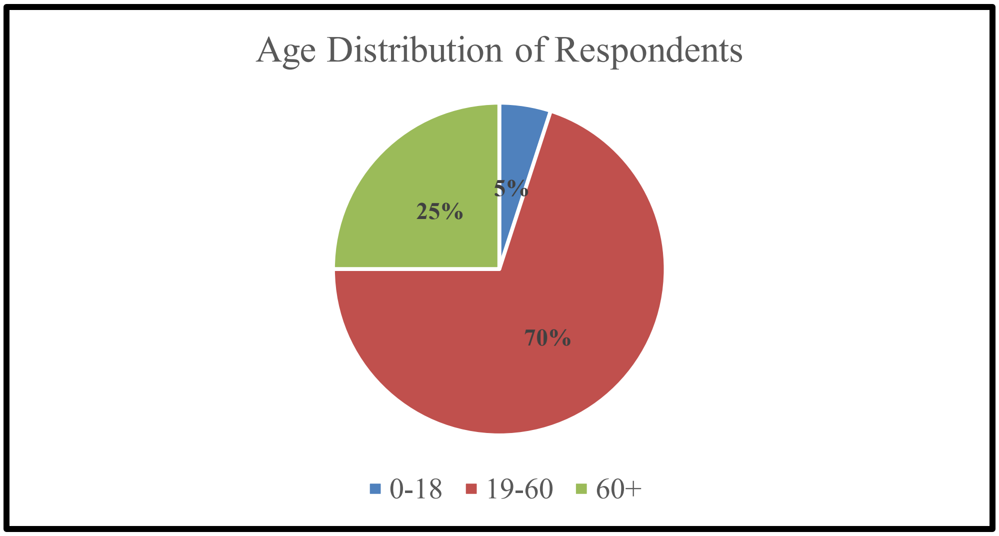

Figure 4.1: Age distribution of respondents

4.2.2 Level of Education

Sixty-five percent (65%) comprising the majority of farmers in the Nanumba North district had no formal education. Thirty-five percent (35%) had obtained basic, secondary and tertiary education (Table 4.4).

Table 4.4: Educational level of respondents

Educational level	Number	Percentage (%)	Angle (^{o})
No education	78	65	134
Basic education	30	25	90
Secondary education	6	5	18
Tertiary education	6	5	18
Total	120	100	360

Source: Field Survey Data, January, 2017

Illiteracy rate among farmers in the district was quite high as (65%) of respondents have never received any form of formal education. This may explain farmers' inability to read, understand and follow label instructions of various pesticides they use. Consequently, farmers were engaged in unhealthy practices such as spraying of pesticides without adequate protective clothing, drinking from water bodies close to sprayed farms and eating without washing hands with any detergent immediately after spraying. This exposes farmers to pesticide poisoning (Fianko *et al*., 2011; Yeboah *et al*., 2004; Mensah *et al*., 2004; Abudulai *et al*., 2006).

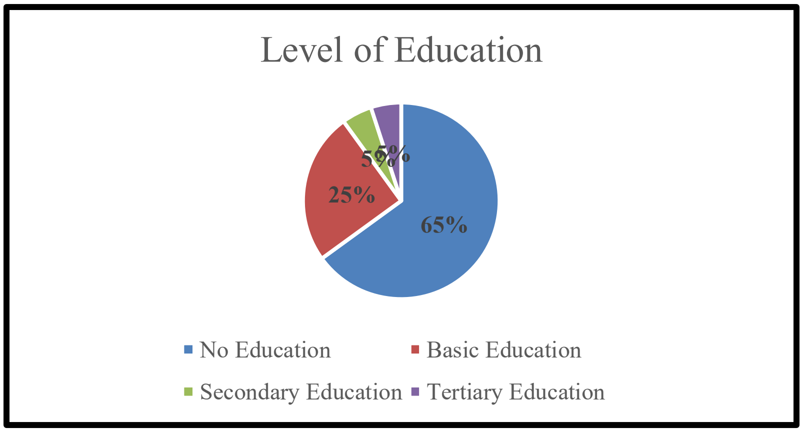

Figure 4.4: Educational level of respondents

Similarly, Sanfilippo and Perschau (2008) also attributed low level of safety awareness and precautions such as use of protective clothing, strict adherence to insecticides labels, unsafe storage and misuse of used containers in low income cotton growing communities to high illiteracy rate among farmers and chronic poverty.

4.3 Pesticide residues in soil and water

Pesticide residues were determined in soil and water samples from the Bimbilla district of the Northern Region of Ghana using Gas Chromatography with electron capture detector in the laboratory of CSIR in Greater Accra.

Accuracy or validation of the method was achieved using recovery method at fortification levels of 2.0 µg/mL, 1.5µg/mL, and 1.0µg/mL, depending on parameters such as, the sample processing procedure and analyte concentration. According to Bennett *et al*, 1997 and Salas *et al*, 2003, normally it is not usual to obtain satisfactory results for all of the compounds in multiresidue methods because of the diverse physical and chemical properties of the different classes of agricultural chemicals.

A total of nine pesticide residues were detected in soils of the selected farms and water samples from the Bimbilla district. These pesticide residues in the soil and water samples were Chlorpyrifos, Dieldrin, beta-endosulfan, Beta BHC, methoxychlor, aldrin, cypermethrin, heptachlor, and heptachlor-epoxide.

Also the individual retention times which were used to identify the detected pesticides in the soil and water samples are presented in Table 4.5

Table 4.5: SUMMARY OF RETENTION TIMES FOR PESTICIDES

Pesticides	**Retention Time (min)**
Beta BHC	13.74
Heptachlor-Epoxide	18.57
Aldrin	17.56
Dieldrin	20.79
Heptachlor	25.29
Endosulfan	19.62
Methoxychlor	13.80
Chlorpyrifos	16.92

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

Soil samples analyzed showed the presence of nine different potential toxic pesticide residues comprising seven organochlorines, one organophosphate, and one synthetic pyrethroid (Table 4.6). The order of percentage of the pesticide residues occurring in the soil samples was as follows: Beta-endosulfan (30%) > Chlorpyrifos (28%) > Methoxychlor (18%) > Beta-BHC (8%)

> Heptachlor (6%) > Dieldrin (4%) > Heptachlor-epoxide (3%) > cypermethrin (2%) > Aldrin (1%).

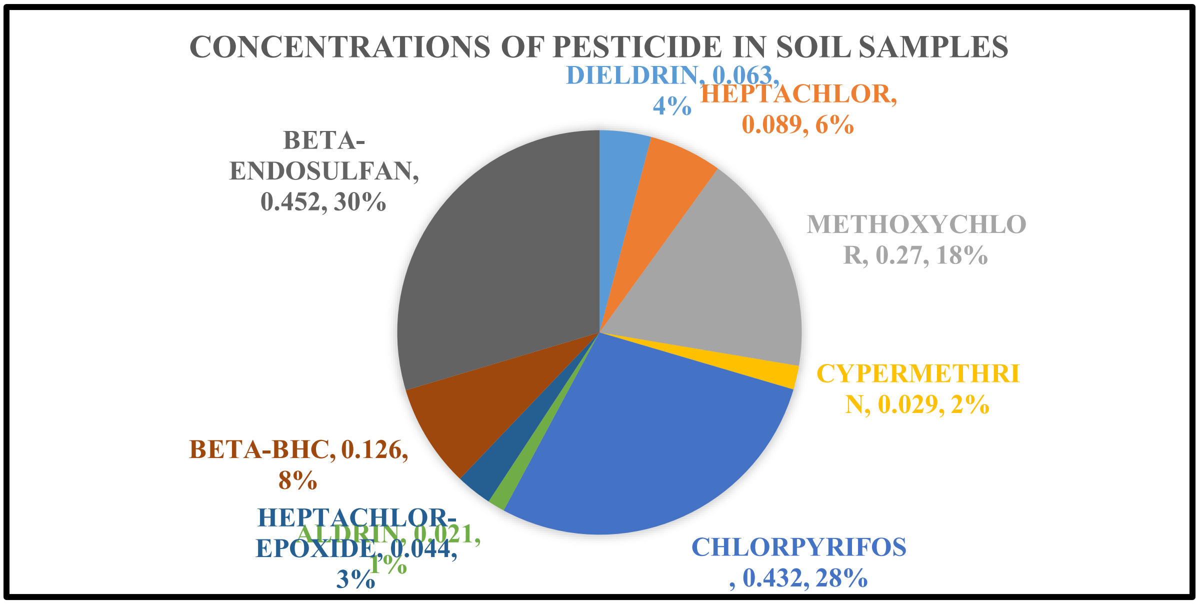

Figure 4.5: Total percentage concentrations of pesticide residues in soil from Bimbilla District

Beta-endosulfan occurs in 30 % of the soil samples analysed, however the lowest mean concentration of Beta-endosulfan in the soil samples analysed was observed at X1 with a concentration of 0.001 µg/g while the highest mean concentration was observed at BS3 with concentration of 0.070 µg/g (Table 4.6). Statistically, the concentrations of beta-endosulfan recorded in the soil samples were significantly (p = 8.67E-16) different among the various clusters. However, the mean concentrations of beta-endosulfan recorded in soils sampled from AS1(0.033 µg/g) AS2(0.031 µg/g) AS3(0.038 µg/g) BS1(0.047 µg/g) BS2(0.058 µg/g) BS3(0.070 µg/g) CS1 (0.062 µg/g), CS2 (0.059 µg/g) and CS3 (0.053 µg/g), respectively, were all above the WHO MRL of 0.030 µg/L for agricultural soils except the soil samples from the control which had mean concentration below the WHO MRL. Furthermore, Beta-endosulfan is an organochlorine and considered moderately hazardous (WHO II) under WHO Classification.

In spite of the adverse side effect of these chemicals, organochlorine pesticides (OCPs) form an essential aspect of modern Agriculture. The use of the chemicals is justifiable in terms of increase supply of food and other agricultural products, but problems arise when substantial amount of the chemicals are left on the field as residue which tend to affect the environment such as non-target organisms and water bodies. These results of the present study are in correlation with the study carried out by (Afful *et al*., 2010) which indicate significant level of in the same dam or study area? However, levels of these pesticide residues were also reported in the Lagos lagoon (Adeyemi *et al*., 2008) which were totally low compared to the level recorded in this work. The concentrations of Beta-endosulfan in all the soil samples were much higher than the WHO and FAO (Codex, 2009) set maximum residue limit (MRL) 0.1 mg/kg and the Acceptable Daily Intake value (ADI) of 0.006 mg/kg.

Chlorpyrifos occurs in 28 % of the soil samples analysed. The mean concentrations of chlorpyrifos in soil samples analyzed from the three clusters from the Bimbilla district ranged from 0.024 µg/g to 0.064 µg/g (Table 4.6). Statistically, the concentrations of chlorpyrifos recorded in the soil samples were significantly (p = 8.67E-16) different among the various clusters. However, the lowest concentration was recorded at CS3 while the highest concentration was recorded at BS2. No concentration of chlorpyrifos was recorded in samples at X1 (control) (Table 4.6). The mean concentrations of chlorpyrifos recorded in soils sampled from CS1 (0.031 µg/g), CS2 (0.028 µg/g) and CS3 (0.024 µg/g) respectively were found to be below the WHO MRL of 0.050 µg/g for agricultural soils. On the contrary, soil samples analyzed from AS1 (0.060 µg/g), AS2 (0.062 µg/g), AS3 (0.052 µg/g), BS1 (0.060 µg/g), BS2 (0.064 µg/g), and BS3 (0.051 µg/g), recorded a mean concentration above the WHO MRL of 0.050 µg/g for agricultural soils. It is quite palpable that, the detection of chlorpyrifos levels above WHO MRLs in samples has several health implications. Chlorpyrifos is moderately toxic to humans (Howard, 1992; Wauchope *et al*, 1995) and is reported to damage the developing nervous system, specifically targeting the immature brain (Pope, 1999; Barone *et al*, 2000). The results in this work partly agree with a study conducted by Amoah *et al.,* (2006), which revealed forty-seven lettuce samples with detectable chlorpyrifos contamination exceeding the recommended residue level of 0.05 mg kg–1 in Ghana. Also chlorpyrifos residue violations were again observed on 10 samples of tomatoes grown in the Upper East Region of Ghana (Binney, 2001) and on seven samples of cabbage grown in the Greater Accra Region of Ghana (Odhiambo, 2005). The detection of chlorpyrifos in a higher mean concentration could be attributed to the fact that it is widely used as agricultural insecticide and also has many uses in households for pest control (Essumang *et al*., 2007). Indeed, the occurrence of chlorpyrifos in the soil samples indicated a current use of the chemical in food production by farmers in the study area, even though its use was not confirmed from the field survey

Methoxychlor occurs in 18 % of the soil samples analysed. The mean methoxychlor concentrations in the soil samples analysed ranged from a minimum of 0.001 µg/g at BS2 to a maximum of 0.068 µg/g at BS1 (Table 4.6). Samples from X1 (control) had no detectable methoxychlor concentration (Table 4.6). Analysis of variance revealed significant difference (p = 8.67E-16) in methoxychlor among the clusters. However, the mean concentrations of methoxychlor, recorded at all the three clusters of soils from the selected farms in the Bimbilla district were found to be below the World Health Organization (WHO 2017) MRL of 20.00 µg/g for agricultural soils. From literature it is known that methoxychlor was intended to replace for DDT, but has since been banned due to its acute toxicity, and endocrine disruption activity and bioaccumulation. Amazingly the amount of methoxychlor in the environment changes as a result of farming activities, and it does not dissolve readily in water, so it is sometimes mixed with a petroleum-based fluid by these farmers and sprayed, or used as a dust. The sprayed chemical settles on the ground or in aquatic ecosystems, where it is normally deposited in soils, and this potentially dangerous chemical may take several months to degrade. Methoxychlor is ingested and absorbed by living organisms, and it accumulates in the food chain. Some metabolites may have unwanted side effects. Indeed, the occurrence of methoxychlor in the soil samples indicated a current use of the chemical in crop protection by farmers in the study area as was corroborated by farmers from the field survey.

Table 4.6: Pesticide residues in soil samples of the various clusters.

CLUSTERS	PESTICIDES (µg/g)							
	Dieldrin	Heptachlor	Methoxychlor	Cypermethrin	Chlorpyrifos	Aldrin	Heptachlor epoxide	Beta-BHC	Beta-Endosulfan
AS1	0.003	ND	0.043	0.002	0.060	0.002	0.003	0.001	0.033
AS2	0.004	ND	0.010	0.003	0.062	0.002	0.005	0.045	0.031
AS3	0.003	ND	0.035	0.004	0.052	0.001	0.008	0.040	0.038
BS1	0.011	0.002	0.068	0.004	0.060	0.001	0.004	0.020	0.047
BS2	0.004	0.003	0.001	0.004	0.064	0.001	0.005	ND	0.058
BS3	0.024	0.004	0.030	0.004	0.051	0.003	0.005	ND	0.070
CS1	0.003	0.020	0.031	0.001	0.031	0.003	0.005	ND	0.062
CS2	0.005	0.046	0.019	0.002	0.028	0.004	0.006	ND	0.059
CS3	0.006	0.014	0.033	0.005	0.024	0.004	0.003	0.020	0.053
X1	ND	ND	ND	ND	ND	ND	ND	ND	0.001
WHO 2017	0.030	0.100	20.000	0.050	0.050	0.030	0.030	2.000	0.030

AS1: soil sample from northern cluster one; AS2: soil sample from northern cluster two; AS3: soil sample from northern cluster three; BS1: soil sample from western cluster one; BS2: soil sample from western cluster two; BS3: soil sample from western cluster three; CS1: soil sample from southern cluster one; CS2: soil sample from southern cluster two; CS3: soil sample from southern cluster three; Control X1; ND: Non detectable.

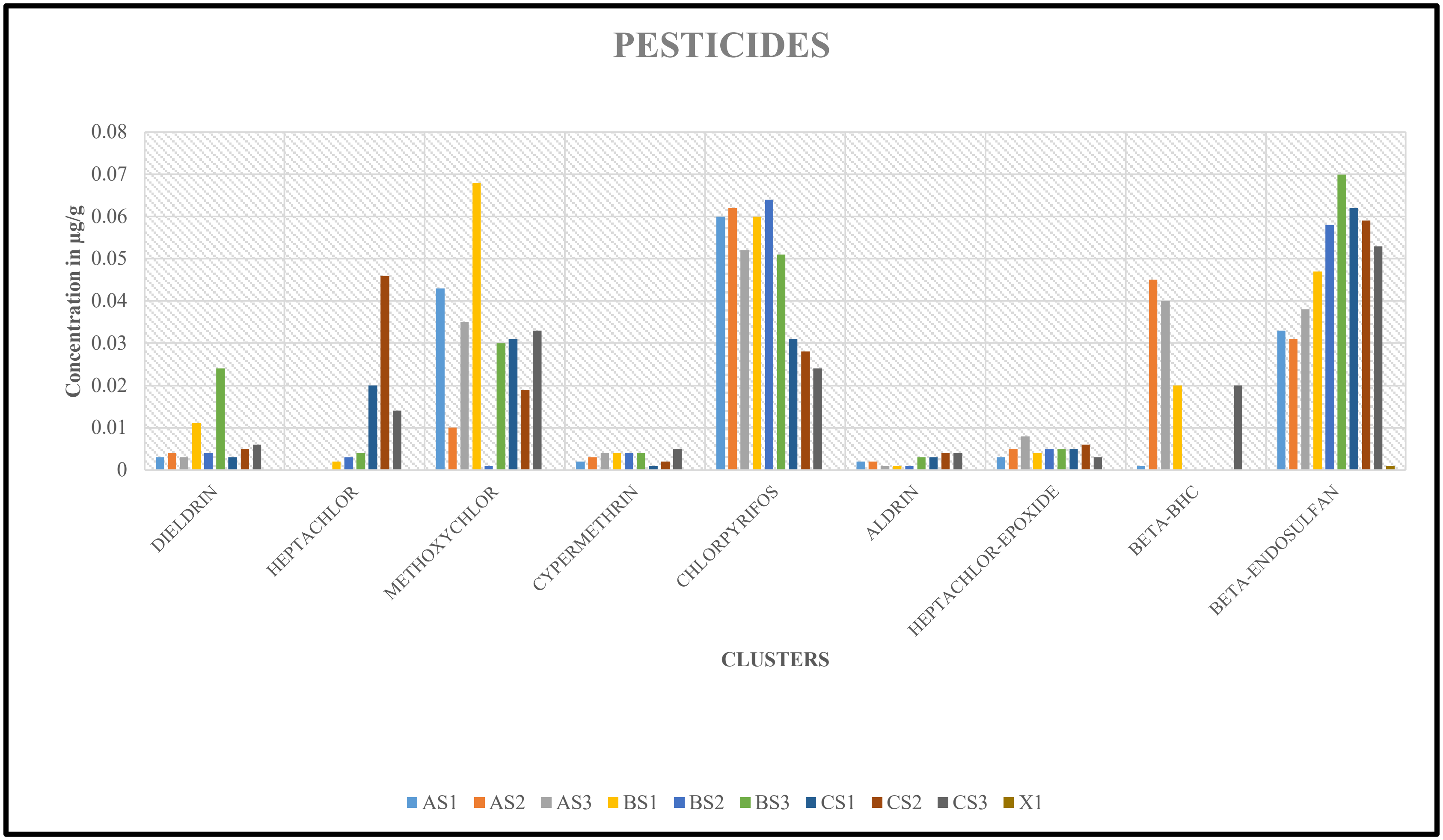

Figure 4.6: Mean concentrations of pesticide residues in soils from the Bimbilla District

Also the isomer of benzene hexachloride (BHC) or hexa-chlorocyclohexane (BHC): beta-BHC was detected in few soil samples from the study area and occurs in 8 % of the soil samples analysed. The mean beta-BHC concentrations in the soil samples analysed ranged from a minimum concentration of 0.001 µg/g at AS1 to a maximum concentration of 0.045 µg/g at AS3 (Table 4.6). No concentration of beta-BHC was recorded at X1 (control) (Table 4.6). Analysis of variance revealed significant difference (p = 8.67E-16) in beta-BHC among the clusters. The mean beta-HCH concentrations observed at AS1 (0.001 µg/g), AS2(0.045 µg/g), AS3 (0.04 µg/g), BS1 (0.02 µg/g) and CS3(0.02 µg/g) were found to be below the WHO MRL of 2.00 µg/g for agricultural soils while soils from BS1, BS2, BS3, CS1 and CS2 recorded no detectable limits. The measured low concentrations of beta-BHC in the studied soils can be attributed to the low use of the Y-isomer (lindane) which is the only BHC or HCH isomer with powerful insecticidal action as reported by Aiyesanmi and Idowu (2012). However, 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.

Dieldrin occurs in 4 % of the soil samples analysed, however the mean dieldrin concentrations in the soil samples ranged from 0.0105 µg/g to 0.024 µg/g (Table 4.6). The lowest mean concentration was recorded at BS1 whiles the highest mean concentration was observed at BS3 (Table 4.6). No dieldrin residue was however recorded at X1 (control) (Table 4.6). Whereas aldrin occurs in 1 % of the soil samples analysed, however the mean concentrations of aldrin in the soil samples analysed ranged from 0.001 µg/g to 0.004 µg/g (Table 4.6). The lowest mean concentration was recorded at AS3, BS1 and BS2 respectively while the highest mean concentration was recorded at CS3 (Table 4.6). Sampled site X1 (control) on the other hand recorded no aldrin concentration (Table 4.6). Also the mean concentrations of dieldrin recorded in soil samples at all the three clusters with detectable residue were below the (WHO 2017) MRL of 0.030 µg/g for agricultural soils. Statistically, the concentrations of dieldrin and aldrin recorded in the soil samples were significantly (p = 8.67E-16) different among the various clusters. However, the mean concentrations of dieldrin was slightly significantly higher than that of aldrin in all the soil samples studied and the main reason is that sunlight and bacteria can change aldrin to dieldrin so that we mostly find dieldrin in the environment. Also this could be an indication that there is more dieldrin in the environment compared to aldrin. This observation was supported by the fact that aldrin undergoes photolysis to dieldrin in the environment. These results are in agreement with Akan *et al*. (2013), United States Department of Health and Human services (USDHHS 1993), reported that aldrin is readily and rapidly converted into dieldrin in plant and animal tissues. This is so because dieldrin is extremely non-polar and therefore has a strong tendency to adsorb tightly to lipids such as animal fat and plant waxes. It is for this reason that dieldrin biomagnifies through the terrestrial and aquatic food webs. (Matsumura, 1985) pointed out that dieldrin is one of the most persistent chemicals known. He also reported that dieldrins bioaccumulation in animal tissue is due to its resistance to degradation and biologic metabolism. Similar to DDT and its metabolites, dieldrin is not easily metabolised in water and has limited capacity of being digested and excreted from the body. It is, however, easily absorbed and transported throughout the blood of vertebrates and hemolymph of invertebrates.

Cypermethrin occurs in 2 % of the soil samples analysed, however the mean cypermethrin concentrations in the soil samples ranged from 0.001 µg/g to 0.005 µg/g (Table 4.6). The minimum mean concentration was obtained at CS1 while the maximum mean concentration was recorded at CS3. Samples of soil analyzed from X1 (control) recorded no cypermethrin concentration (Table 4.6). Analysis of variance revealed significant difference (p = 8.67E-16) in cypermethrin among the clusters. Cypermethrin is a very popular synthetic pyrethroids in Ghana, and has been registered for food production in the country by Environmental Protection Agency in 2009. However, the mean cypermethrin concentrations recorded at the various sampled clusters with detectable residues were found to be below the World Health Organization (WHO) Maximum Residue Limit of 0.050 µg/g for agricultural soils. The detection of cypermethrin depicts the current use of the chemical by some farmers in the district. Meanwhile the mean concentration values of cypermethrin recorded in this study were higher than the mean concentration of 0.00025 µg/g reported by Afful *et al*. (2013) in water samples analysed from the Weija Lake in Greater Accra.

Heptachlor occurs in 6 % of the soil samples analysed, however the mean concentrations of heptachlor in the soil samples analyzed ranged from 0.002 µg/g at BS1 to 0.046 µg/g at CS2 (Table 4.6). Samples from AS1, AS2, AS3 and X1 (control) recorded no heptachlor concentration (Table 4.6). Heptachlor-epoxide occurs in 3 % of the soil samples analysed, with mean concentration of the residue in the soil samples ranging from 0.003 µg/g to 0.008 µg/g (Table 4.6). Also the lowest mean concentration was recorded at AS1 and CS3 while the highest mean concentration was recorded at, AS3 (Table 4.6). Again no heptachlor-epoxide residue was detected in soil samples from X1 (control) (Table 4.6). Analysis of variance revealed significant difference (p = 8.67E-16) in heptachlor and its metabolites among the clusters. Meanwhile, heptachlor was present in the southern and western clusters of the soil except the northern cluster and the control soil samples which had no detectable limits, whilst heptachlor-epoxide was detected in all three clusters except soil samples from the control X1. Pesticides are mostly applied as liquids sprayed on the crop or the soil or as a seed treatment by farmers on their farms or at homes in this study area, and these pesticides that reach the soil or plant material in the target area begin to disappear by degradation or dispersion. Persistent organic pollutants may volatilize into the air, runoff or reach into surface water and groundwater, accumulated by plant or soil organisms or stay in the soil. However, the mean concentrations of heptachlor were higher than its oxygenated product, the epoxide, and this could be due to the incomplete breakdown of heptachlor which can be attributed to unfavourable degradation conditions and persistence in the environment though it is among the list of banned pesticides by the Stockholm Convention for use on food (Afful *et al.*, 2010).

4.3.2 Levels of pesticide residues in water samples from the Waanpu Dam

Water samples analysed showed the presence of eight different potential toxic pesticide residues comprising seven organochlorines, one organophosphate, and no synthetic pyrethroid (Table 4.7). The order of percentage of the pesticide residues occurring in the water samples was as follows: Beta-endosulfan (25%) > Dieldrin (14%) > Heptachlor (13%) > Chlorpyrifos (11%) > Aldrin (11%) > Heptachlor-epoxide (11%) > Beta-BHC (9%) > Methoxychlor (6%).

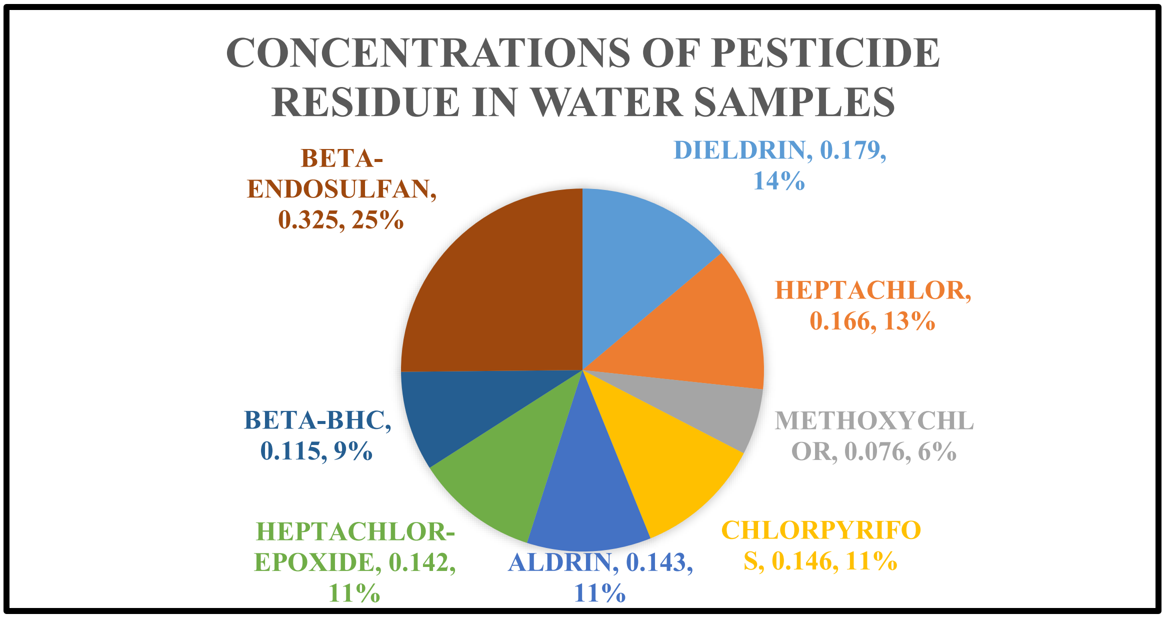

Figure 4.7: Total percentage concentrations of pesticide residues in Water from Bimbilla District

Beta-endosulfan occurs in 25 % of the water samples analysed, and the mean beta-endosulfan concentrations recorded in the four zones of the water samples analysed ranged from a minimum of 0.010 µg/g at N3 to a maximum value of 0.036 µg/g at W3 (Table 4.7). Beta-endosulfan was the only pesticide residue detected in the control sample that is D1 at a mean concentration of 0.001. µg/g. Analysis of variance revealed significant difference (p =3.01E-06) in beta-endosulfan among the four zones in the Waanpu Dam. In addition, beta-endosulfan which is an isomer of the parent chemical endosulfan, was detected in water samples collected at a depth of 0-20cm from the Waanpu Dam. Meanwhile with the exception of water samples from northern and southern zones that is, N1, N2, N3, S1, S2 and S3 which recorded a mean concentration below WHO 2017 MRL value of 0.030 µg/g, the other two zones that is eastern and western zones had detectable beta-endosulfan concentrations mean values above the WHO MRL of 0.030 µg/g for drinking water. In 2009 the Ghanaian Government suspended the use of endosulfan which was banned by the EU since 2006 (PAN, 2008). A total of sixty-two (62) countries have restricted the use of endusulfan (Environmental Justice Foundation) as it has been described by the USEPA 2002 as highly hazardous (EPA, 2010). It was quite surprising to be reported in an interview with Osei-Assibey of the sale of endosulfan in a shop in the Upper West regional capital that is Bolgatanga, which is illegal. In view of this, there is the need to ensure regular monitoring of endosulfan in soils and water. Better still, the mean concentrations of beta-endosulfan in all the samples from the four zones could be inferred from the trend that, there is a continuous use of beta-endosulfan in the area due to its lower cost and effectiveness as well as its broad spectrum activity despite its ban (Amoah *et al*., 2006). The higher mean concentrations could also be attributed to the enormous past uses and due to its longer half-life that is slow degradation and persistence in the environment. The mean residue concentrations of beta-endosulfan in this study were however lower than, the mean values of 3200 µg/g and 0.597 µg/g reported by Idowu et al. (2013) and Okoya *et al*. (2013b) respectively in river water samples analyzed from cocoa producing areas in Ondo State, Nigeria.

Chlorpyrifos occurs in 11 % of the water samples analysed, and the mean concentration of chlorpyrifos in water samples analysed ranged from 0.001 µg/g to 0.027 µg/g as shown in Table 4.7. Analysis of variance revealed significant difference (p =3.01E-06) in chlorpyrifos among the zones in the Waanpu Dam. However, the lowest mean concentration was recorded at W1, W2 and E2 whiles the highest mean concentration was recorded at E3 (Table 4.7). With the exception of water samples from the control sample that is D1, collected at depth of 0-30m from a well near the dam, which had no detectable limits (Table 4.7), all the zones had detectable chlorpyrifos concentrations with mean values below the WHO 2017 MRL value of 0.050 µg/g for portable drinking water. The northern, eastern, southern and western zones that is W1, W2, W3, E1, E2, E3, S1, S2, S3, N1, N2 and N3 recorded mean chlorpyrifos concentrations of 0.001 µg/g 0.001 µg/g, 0.021 µg/g, 0.020µg/g, 0.001 µg/g, 0.027 µg/g, 0.005 µg/g, 0.020 µg/g, and 0.010µg/g respectively which were below the WHO 2017 MRL value of 0.050 µg/g for drinking water. The low mean concentrations of chlorpyrifos in the water samples confirmed the low leaching and run-off of the substance to the dam.

Methoxychlor occurs in 6 % of the water samples analysed, and the mean methoxychlor concentrations in water samples analysed from the Waanpu Dam ranged from a minimum of 0.001 µg/g at W1, W2 and S3 to a maximum of 0.020 µg/g at E2 and N2 (Table 4.7). Methoxychlor residue was however, not detected at D1 (Table 4.7). Statistically, the concentrations of methoxychlor recorded in the water samples were significantly different at (p =3.01E-06) in the four zones in the Waanpu Dam. Additionally, the mean concentrations of methoxychlor recorded at the four zones in the Waanpu Dam with detectable residues, were found to be below the WHO 2017 permissible residue limit of 20.00 µg/g for drinking water. The detection of methoxychlor in the water samples in the four zones depicts the use of pesticides with this chemical as its active ingredient is capable of combating pests and diseases by farmers in the study area as was corroborated by farmers from the field survey.

Dieldrin occurs in 14 % of the water samples analysed, and the concentrations of dieldrin were recorded at all the four zones in the water samples of the Waanpu Dam in the Bimbilla District. Statistically dieldrin and aldrin showed significant differences at all the four zones in the Waanpu Dam at p =3.01E-06. However, the mean dieldrin residues in the water samples analysed ranged from a minimum concentration of 0.002 µg/g at W2 to a maximum concentration of 0.025 µg/g at W1 and S3 (Table 4.7). Aldrin occurs in 11 % of the water samples analysed, and Water samples from W2 recorded the lowest mean concentration of 0.001 µg/g of aldrin whiles E3 recorded the highest mean concentration of 0.021 µg/g (Table 4.7). Meanwhile, water samples from the control (D1) recorded no aldrin and dieldrin residue concentrations (Table 4.7). In fact, according to Miles *et al*., 2009, Aldrin substances degrade to dieldrin compounds. Dieldrin was detected in water samples analysed from all the four zones from the Waanpu Dam, with mean concentrations within the range 0.002 µg/g to 0.025 µg/g, which were all below the WHO 2017 MRL of 0.030 µg/g for drinking water. In addition, the slightly higher detection and levels of dieldrin compared to aldrin may suggest that previous input of aldrin has completely or partially metabolized to dieldrin. Dieldrin is known to be easily absorbed by the lungs, skin and stomach. Also, higher exposure levels of this potential toxic farm chemical may cause endocrine disruptions, reproductive and developmental damage in animals and humans. It can therefore, be concluded that pollution from this pesticide may pose adverse health threat to consumers of the water. Again the presence of dieldrin may suggest a possible degradation of aldrin to dieldrin in the environment, since aldrin, was found to be used by farmers in the study area. However, 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/g and 0.94 µg/g reported by Idowu *et al*. (2013) and Okoya *et al*. (2013b) respectively in river water samples analysed from selected cocoa producing areas in Ondo State, Nigeria.

Table 4.7: Pesticides residues in water samples from the Waanpu Dam.

ZONES	PESTICIDES (µg/g)							
	Dieldrin	Heptachlor	Methoxychlor	Chlorpyrifos	Aldrin	Heptachlor epoxide	Beta BHC	Beta-Endosulfan
W1	0.025	0.021	0.001	0.001	0.015	0.021	0.001	0.031
W2	0.002	0.021	0.001	0.001	0.001	0.015	0.020	0.033
W3	0.020	0.010	0.005	0.021	0.010	0.025	0.020	0.036
E1	0.012	0.025	0.006	0.020	0.010	0.003	0.022	0.032
E2	0.020	0.001	0.020	0.001	0.014	0.011	0.001	0.035
E3	0.010	0.017	0.002	0.027	0.021	0.013	0.001	0.035
S1	0.010	0.001	0.002	0.005	0.009	ND	ND	0.025
S2	0.015	0.010	0.003	0.010	0.009	0.016	0.020	0.024
S3	0.025	0.005	0.001	0.025	0.010	0.015	0.010	0.022
N1	0.010	0.020	0.013	0.005	0.020	0.020	0.010	0.026
N2	0.020	0.010	0.002	0.020	0.004	0.003	0.010	0.015
N3	0.010	0.025	0.020	0.010	0.020	ND	0.001	0.010
D1	ND	ND	ND	ND	ND	ND	ND	0.001
WHO 2017	0.030	0.100	20.000	0.050	0.030	0.030	2.000	0.030

W1: Water sample from western zone one; W2: Water sample from western zone two; W3: Water sample from western zone three; E1: Water sample from eastern zone one; E2: Water sample from eastern zone two; E3: Water sample from eastern zone three; S1: Water sample from southern zone one; S2: Water sample from southern zone two; S3: Water sample from southern zone three; N1: water sample from northern zone one; N2: Water sample from northern zone two; N3: Water sample from northern zone three; Control D1: ND: Non detectable.

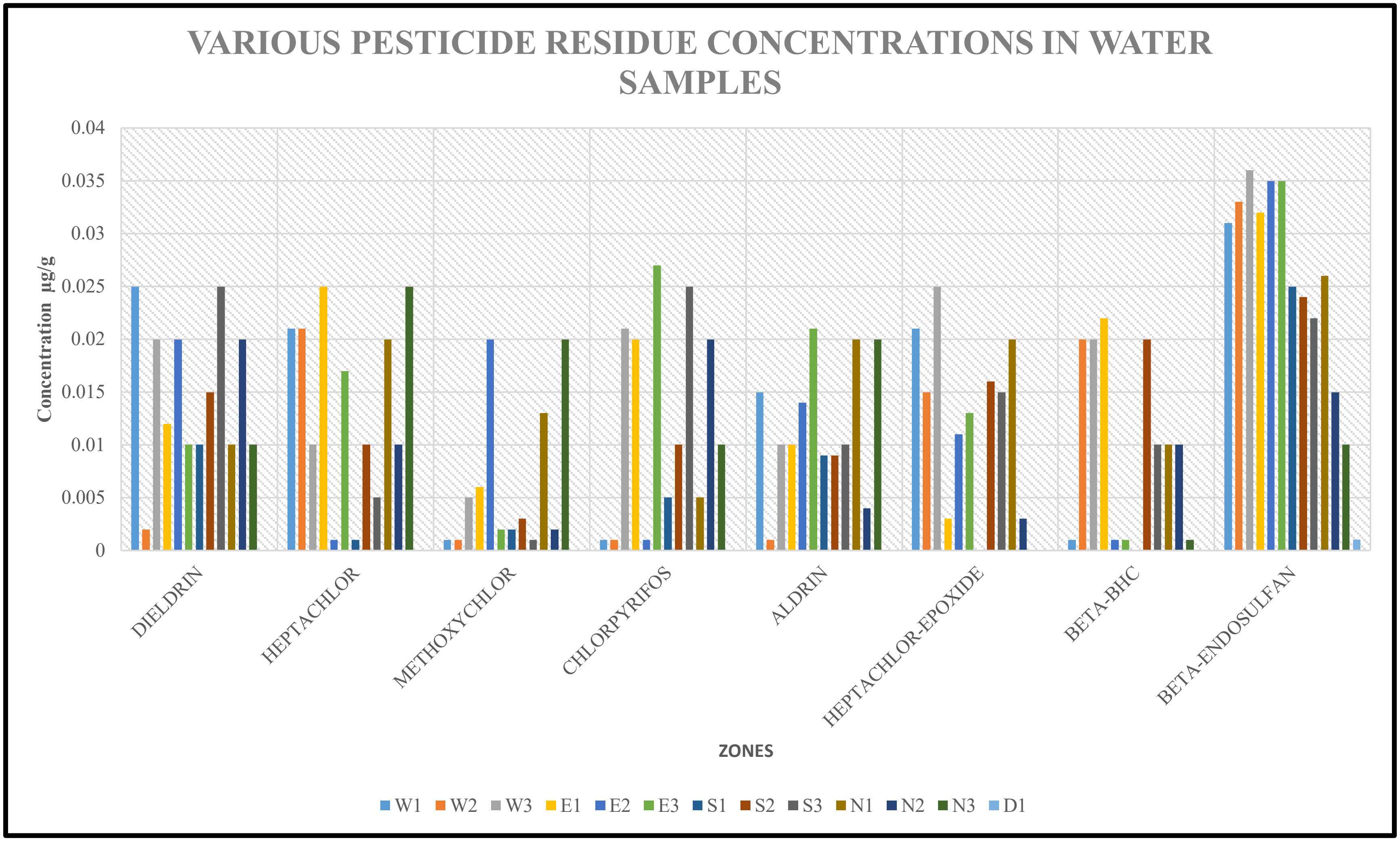

Figure 4.8: Mean concentrations of pesticide residues in Water from the Waanpu Dam, Bimbilla District

Heptachlor occurs in 13 % of the water samples analysed, with the lowest mean concentration of in the water samples recorded at E2 and S1 with a mean value of 0.001 µg/g, whiles the highest mean concentration of 0.025 µg/g recorded at E1 and N3. Heptachlor and its (state the metabolite) was however, not detected at D1 (control) as depicted in Table 4.7. Heptachlor-epoxide occurs in 11 % of the water samples analysed, with mean concentrations in water samples analysed ranging from 0.003 µg/g to 0.025 µg/g (Table 4.7). Statistically heptachlor and its metabolites showed significant differences at all the four zones in the Waanpu Dam at p =3.01E-06. Also, the minimum mean concentration of heptachlor was recorded at E2 and S1 whiles the maximum mean concentration was recorded at E1 and N3 (Table 4.7). Heptachlor-epoxide was however, not detected at D1, N3 and S1. The low mean concentrations of heptachlor, indicate a possible phasing out of this potential toxic organic pollutant in the country. Meanwhile the mean concentrations of heptachlor and its metabolite detected in water samples from the Waanpu Dam at a depth of 0-20cm, were below the WHO 2017 guideline value of 0.100 µg/g of heptachlor and 0.030 µg/g of heptachlor-epoxide for drinking water. Interestingly many OCPs share a lot of remarkable features together with stability against decomposition or degradation in the environment and their very low solubility properties in water, unless oxygen or nitrogen is also present in the molecules. The low occurrence of heptachlor in the water samples suggests the discontinued use of the illegal pesticide by farmers in the Bimbilla environs. Also, the low levels may be attributed to previous non-contamination as well as environmental low persistence from past use 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. Again it was observed that the total mean concentration of heptachlor-epoxide was lower than heptachlor. However, the mean concentrations of heptachlor in this study proved to be higher than the mean value of 0.0067 µg/g for heptachlor in river water samples from collected cocoa farms in Ilawe-Ekiti, Ekiti State, Nigeria, as reported by Olayinka (2013).

Also the isomer of benzene hexachloride (BHC) or hexa-chlorocyclohexane (BHC): beta-BHC was detected in some of the water samples from the Waanpu Dams. Beta-BHC occurs in 9 % of the water samples analysed, however the mean concentration of beta-BHC in water samples ranged from 0.001 µg/g to 0.022 µg/g. The lowest mean concentration was recorded at W1, E2, E3 and N3 respectively whiles the highest mean concentration was recorded at E1 (Table 4.7). D1 and S1 recorded no concentration of beta-BHC (Table 4.7). Analysis of variance revealed significant difference ($p = 3.01E-06$) in beta-BHC among the four zones in the Waanpu Dam. However, the mean concentrations of beta-BHC observed in the water samples at the various zones, that is, northern zone, eastern zone, western zone and southern zone were found to be below the WHO 2017 MRL of 2.00 µg/g for portable drinking water except S1 which recorded no detectable limits. The measured low concentrations of beta-BHC in the studied water can be attributed to the low use of the ϒ-isomer (lindane) which is the only BHC or HCH isomer with powerful insecticidal action as reported by Aiyesanmi and Idowu (2012).

Residues of beta-BHC, Dieldrin, Aldrin, Heptachlor, Heptachlor-epoxide, Methoxychlor, Chlorpyrifos, and Beta-endosulfan showed significant differences at all the four zones in the Waanpu Dam at $p = 3.01E-06$.

CHAPTER FIVE

CONCLUSIONS AND RECOMMENDATIONS

5.1 CONCLUSION

From this study it is palpable that, the Waanpu dam which serves as a source of drinking water and other recreational activities for the people in the area is slightly polluted with pesticide residues. The presence of pesticide residues in the soil and water samples could be as a results of pesticide use by farmers in the study area. Farmers therefore use these chemicals indiscriminately and as such could lead to atmospheric transport of volatilized pesticides or wind drift, direct spillage, leaching, direct overspray and run-off due to application from fields and surroundings. Pesticides detected in the Waanpu Dam and soil of some selected farms in the Bimbilla environs were Beta-endosulfan, chlorpyrifos, deldrin, aldrin, beta-BHC, cypermethrin, methoxychlor, heptachlor and heptachlor-epoxide. The study revealed the presence of most of the selected pesticides at varying concentrations, with Beta-endosulfan and chlorpyrifos recording significant concentrations in both soil and water samples.

Aldrin, Dieldrin, Beta-BHC, Cypermethrin, Methoxychlor, heptachlor and heptachlor-epoxide mean concentrations were found to be below the maximum residue limits of WHO in all the samples analsed in the area, and this could be attributed to their gradual disappearance in the environment. In general, the level of pesticides residue analysed were lower than those reported from other countries and from the southern part of Ghana. Even though some pesticide residues in some of the soils and water samples were slightly higher than the maximum residue limits of the WHO, it was not high enough to pose toxicological and health risks to the people living in the area. Pesticide residues of beta-BHC, Dieldrin, Aldrin, Heptachlor, Heptachlor-epoxide, Methoxychlor, cypermethrin, chlorpyrifos, and beta-endosulfan showed significant differences.

Pesticides may have found their way into the soils via spray drift during treatment of crops, wash-off from treated crops and wrong disposal of left over spray solution, sprayer wash water and pesticide containers. Apart from the potential dangers, pesticides are also known to pose threat to soil organisms, translocation into edible parts of crops and emission into the environment. Farmers in the Bimbilla District depend largely on pesticides as a means to combat weeds and reduce crop loses as it is perceived by these farmers to be more effective, cheaper and time saving. However, it is quite devastating when it comes to handling of these chemicals by these farmers in the area.

5.2 Recommendations

In order to ensure sustainable crop production in the Bimbilla district, the environmental protection agency Extension officers must establish effective and protective measures such as integrated pest management practices, organic farming and reducing the volume of synthetic organic chemical use.

Extension officers should ensure routine monitoring of pesticide residues in the District for the prevention, control, and reduction of environmental pollution, so as to minimize health risks to the people.

Health education programme concerning the safe use of pesticides, effects on the farmers' health when misused and other synthetic organic chemicals in crop production in the area should be conducted by the Extension officers and Ministry of food and agriculture (MOFA) to prevent health risks of farmers

The Extension officers should enact laws to halt the practice where sales agents of these chemicals are the source of advice to farmers on pesticide use. These agents must be forced by the policy to refer farmers and traders to extension officers for advice.

Good agricultural practices must be encouraged by MOFA such as integrated pest management.

Future work should concentrate on sediment samples from the Waanpu Dam in order to compare levels of pesticide residues in soils, water, and sediment samples.

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APPENDIX

Appendix I

CLUSTERS	PESTICIDES (µg/L)									
		Dieldrin	Heptachlor	Methoxychlor	Cypermethrin	Chloropyrifos	Aldrin	Heptachlor epoxide	B-BHC	Beta-Endosulfan
AS1	MEAN	0.003	ND	0.043	0.002	0.06	0.002	0.003	0.001	0.033
	STD.DE	0.001	-	0.021	-	-	-	0.002	-	-
	STD.ERR	0.001	-	0.012	-	-	-	0.001		-
AS2	MEAN	0.004	ND	0.010	0.003	0.062	0.002	0.005	0.045	0.031
	STD.DE	0.001	-	-	-	-	0.001	0.004	0.007	-
	STD.ERR	0.001	-	-	-	-	0.001	0.002	0.004	-
AS3	MEAN	0.003	ND	0.035	0.004	0.052	0.001	0.008	0.040	0.038
	STD.DE	0.002	-	0.021	-	-	-	0.001	0.028	-
	STD.ERR	0.001	-	0.012	-	-	-	0.001	0.016	-
BS1	MEAN	0.011	0.002	0.068	0.004	0.06	0.001	0.004	0.020	0.047
	STD.DE	-	0.001	0.011	-	-	-	0.002	-	-
	STD.ERR	-	0.001	0.006	-	-	-	0.001	-	-
BS2	MEAN	0.004	0.003	0.001	0.004	0.064	0.001	0.005	ND	0.058
	STD.DE	-	-	-	-	-	-	0.001	-	-
	STD.ERR	-	-	-	-	-	-	0.001	-	-
BS3	MEAN	0.024	0.004	0.030	0.004	0.051	0.003	0.005	ND	0.07
	STD.DE	-	>0.001	-	-	-	-	0.004	-	-
	STD.ERR	-	>0.001	-	-	-	-	0.002	-	-
CS1	MEAN	0.003	0.020	0.031	0.001	0.031	0.003	0.005	-	0.062
	STD.DE	>0.001	0.014	0.027	-	-	0.001	0.001	-	-
	STD.ERR	>0.001	0.008	0.016	-	-	0.001	0.001	-	-
CS2	MEAN	0.005	0.046	0.019	0.002	0.028	0.004	0.006	ND	0.059
	STD	0.004	-	0.001	-	0.011	-	0.002	-	-
	STD.ERR	0.002	-	0.001	-	0.006	-	0.001	-	-
CS3	MEAN	0.006	0.014	0.033	0.005	0.024	0.004	0.003	0.020	0.053
	STD.DE	0.001	0.008	0.011	-	-	0.001	0.001	-	-
	STD.ERR	0.001	0.005	0.006	-	-	0.001	0.001	-	-
CONTROL X1	MEAN	ND	ND	ND	ND	ND	ND	ND	ND	0.001
	STD.DE	-	-	-	-	-	-	-	-	-
	STD.ERR	-	-	-	-	-	-	-	-	-

AS1; soil sample from northern cluster one, AS2; soil sample from northern cluster two, AS3; soil sample from northern cluster three, BS1; soil sample from western cluster one, BS2; soil sample from western cluster two, BS3; soil sample from western cluster three, CS1; soil sample from southern cluster one, CS2; soil sample from southern cluster two, CS3; soil sample from southern cluster three, Control X1, ND; Non detectable, Mean, STD.DE; standard deviation, STD.ERR; standard error.

Appendix II

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
DIELDRIN	9	0.063	0.007000	0.000047
HEPTACHLOR	9	0.089	0.009889	0.000233
METHOXYCHLOR	9	0.27	0.03000	0.000376
CYPERMETHRIN	9	0.029	0.003222	1.69E-06
CHLORPYRIFOS	9	0.432	0.048000	0.000254
ALDRIN	9	0.021	0.002333	1.5E-06
HEPTACHLOR-EPOXIDE	9	0.044	0.004889	2.36E-06
BETA-BHC	9	0.126	0.014000	0.000333
BETA-ENDOSULFAN	9	0.451	0.050111	0.000188

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.026167	8	0.003271	20.50694	8.67E-16	2.069832
Within Groups	0.011484	72	0.00016			
Total	0.037652	80				

Appendix III

ZONES	PESTICIDES (µg/L)								
		Dieldrin	Heptachlor	Methoxychlor	Chlorpyrifos	Aldrin	Heptachlor epoxide	Beta BHC	Beta-Endosulfan
W1	MEAN	0.025	0.021	0.001	0.001	0.015	0.021	0.001	0.031
	STD	0.021	0.013	-	-	0.007	0.013	-	0.027
	STD.ERR	0.012	0.008	-	-	0.004	0.006	-	0.016
W2	MEAN	0.002	0.021	0.001	0.001	0.001	0.015	0.020	0.033
	STD	-	0.027	-	-	-	0.003	0.014	0.011
	STD.ERR	-	0.016	-	-	-	0.002	0.008	-
W3	MEAN	0.020	0.010	0.005	0.021	0.010	0.025	0.020	0.036
	STD	-	-	0.001	-	-	0.007	-	-
	STD.ERR	-	-	0.001	-	-	0.004	-	-
E1	MEAN	0.012	0.025	0.006	0.020	0.010	0.003	0.022	0.032
	STD	-	0.007	0.001	-	-	0.001	0.011	0.013
	STD.ERR	-	0.004	0.001	-	-	0.001	0.006	0.006
E2	MEAN	0.020	0.001	0.020	0.001	0.014	0.011	0.001	0.035
	STD	-	-	-	-	0.001	-	-	0.021
	STD.ERR	-	-	-	-	0.001	-	-	0.012
E3	MEAN	0.010	0.017	0.002	0.027	0.021	0.013	0.001	0.035
	STD	-	0.004	-	-	-	-	-	0.004
	STD.ERR	-	0.002	-	-	-	-	-	0.002
S1	MEAN	0.010	0.001	0.002	0.005	0.009	ND	ND	0.025
	STD	-	-	-	0.002	0.008	-	-	-
	STD.ERR	-	-	-	0.001	0.005	-	-	-
S2	MEAN	0.015	0.010	0.003	0.010	0.009	0.016	0.020	0.024
	STD	0.007	-	0.001	-	0.008	-	0.014	-
	STD.ERR	0.004	-	0.001	-	0.005	-	0.008	-
S3	MEAN	0.025	0.005	0.001	0.025	0.010	0.015	0.010	0.022
	STD	0.007	0.001	-	0.007	-	0.007	-	-
	STD.ERR	0.004	0.001	-	0.004	-	0.004	-	-
N1	MEAN	0.010	0.020	0.013	0.005	0.020	0.020	0.010	0.026
	STD	-	-	0.011	0.001	0.014	-	-	-
	STD.ERR	-	-	0.006	0.001	0.008	-	-	-
N2	MEAN	0.020	0.010	0.002	0.020	0.004	0.003	0.010	0.015
	STD	0.014	-	0.001	-	0.001	-	-	-
	STD.ERR	0.008	-	0.001	-	0.001	-	-	-
N3	MEAN	0.010	0.025	0.020	0.010	0.020	ND	0.001	0.01
	STD	-	0.021	-	-	0.014	-	-	-
	STD.ERR	-	0.012	-	-	0.008	-	-	-

APPENDIX III (Cont.)

		Dieldrin	Heptachlor	Methoxychlor	Chlorpyrifos	Aldrin	Heptachlor-epoxide	Beta-BHC	Beta-Endosulfan
CONTROL	MEAN	ND	ND	ND	ND	ND	ND	ND	0.001
D1	STD	-	-	-	-	-	-	-	-
	STD.ERR	-	-	-	-	-	-	-	-

W1; Water sample from western zone one, W2; Water sample from western zone two, W3; Water sample from western zone three, E1; Water sample from eastern zone one, E2; Water sample from eastern zone two, E3; Water sample from eastern zone three, S1; Water sample from southern zone one , S2; Water sample from southern zone two, S3; Water sample from southern zone three, N1; water sample from northern zone 1, N2; Water sample from northern zone two, N3; Water sample from northern zone three; Control D1, ND; Non detectable, Mean ,STD.DE; standard deviation, STD.ERR; standard error.

Appendix IV

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
DIELDRIN	12	0.179	0.014917	5.03E-05
HEPTACHLOR	12	0.166	0.013833	7.74E-05
METHOXYCHLOR	12	0.076	0.006333	5.21E-05
CHLORPYRIFOS	12	0.146	0.012167	9.74E-05
ALDRIN	12	0.143	0.011917	3.97E-05
HEPTACHLOR-EPOXIDE	12	0.142	0.011833	7.27E-05
BETA-BHC	12	0.116	0.009667	7.88E-05
BETA-ENDOSULFAN	12	0.324	0.027000	6.89E-05

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.00309	7	0.000441	6.571985	3.01E-06	2.115472
Within Groups	0.00591	88	6.72E-05			
Total	0.009	95				