

**KWAME NKRUMAH UNIVERSITY OF SCIENCE AND TECHNOLOGY
COLLEGE OF AGRICULTURE AND NATURAL RESOURCES,
FACULTY OF RENEWABLE NATURAL RESOURCES**

KNUST

**EFFECTS OF PESTICIDES ON SURFACE AND GROUND WATER QUALITY IN
AGRICULTURE AND FOREST LAND USE SYSTEMS IN AKUMADAN IN THE
OFFINSO DISTRICT**

BY

KUMAKO MICHAEL OCTOBER,

2015

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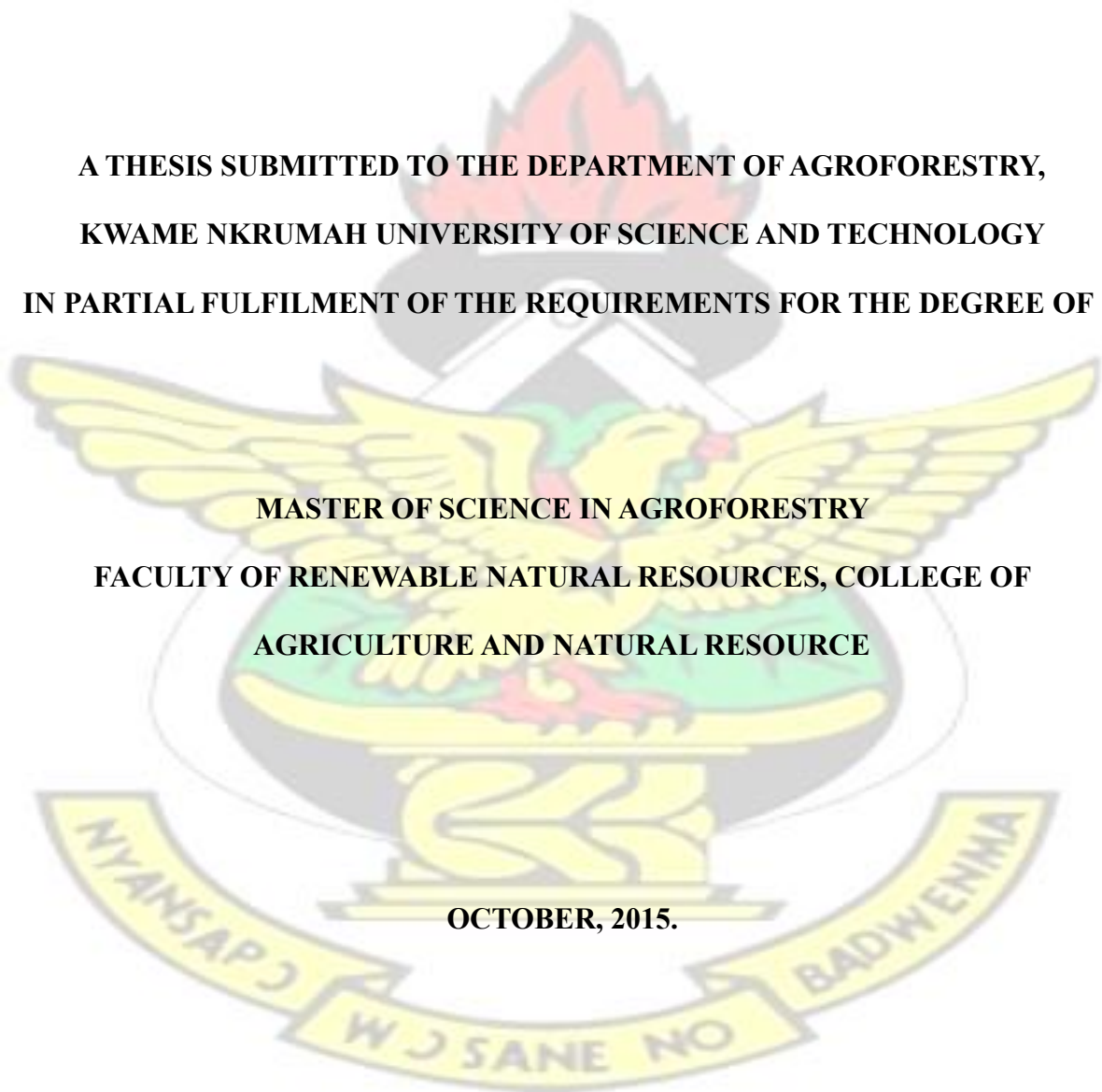
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B.SC. FOREST RESOURCES TECHNOLOGY, (HONS.)

**A THESIS SUBMITTED TO THE DEPARTMENT OF AGROFORESTRY,
KWAME NKRUMAH UNIVERSITY OF SCIENCE AND TECHNOLOGY
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**MASTER OF SCIENCE IN AGROFORESTRY
FACULTY OF RENEWABLE NATURAL RESOURCES, COLLEGE OF
AGRICULTURE AND NATURAL RESOURCE**

OCTOBER, 2015.



CERTIFICATION

I hereby declare that this submission is my own work towards the M.Sc. and that, to the best of my knowledge, it contains no materials previously published by another person nor material which has been accepted for the award of any other degree of the university, except where due acknowledgement has been made in the text.

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DEDICATION

First and foremost, this thesis is dedicated to the Almighty God for having paved the way for my academic pursuits. Finally, I dedicate this work to my bona fide, Linda Quashie and my precious family for their steadfast support and encouragement through it all.

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ABSTRACT

More than 75% of the world's poorest people depend on Agriculture for their livelihoods and survival. Crop production is limited by pests and diseases that must be controlled and pesticides use is the major method available, if farmers are to reduce crop losses. Excessive and misuse of pesticides causes serious contamination of aquifers and surface water bodies, decreasing the quality of water for human consumption. This study was carried out to determine the levels of contamination of ground and surface water bodies with pesticides in Akumadan where farmers apply pesticides in vegetable and other farming operations. Various laboratory equipments were used to test for the physicochemical properties in the samples. The liquid – liquid extraction method was also used for the extraction of the pesticides from water and soil samples and the analysis was done by Gas Chromatograph coupled with electron capture detector. Amongst the physicochemical parameters tested, colour, turbidity and temperature were above the WHO acceptable limits. Five organophosphates were detected namely; Chlorpyrifos, Methamidophos, Ethoprophos, Phorate and Dimethoate. The levels of organophosphate insecticides were below the W.H.O maximum residue limits. This means that the samples were not unduly polluted with organophosphate insecticides. Many organochlorine pesticides were tested for, but those detected were Aldrin, Gamma-chlordane and p,p Dichlorodiphenyldichloroethylene (DDE). Their concentrations in water samples ranged from 0.01µg/L – 0.17µg/L, 0.01µg/L – 1.7µg/L and 0.1µg/L – 0.8µg/L, respectively. In soil sediment the concentrations ranged from 0.02µg/L – 0.22µg/L, 0.1µg/L – 2.0µg/L and 0.1µg/L – 0.9µg/L for aldrin, gamma – chlordane and p,p DDE, respectively. Two pollutant organochlorine insecticides were aldrin and gamma chlordane whose levels were above the W.H.O acceptable limits. Strict restrictions on use of organochlorine insecticides by farmers in the Akumadan area should be undertaken.

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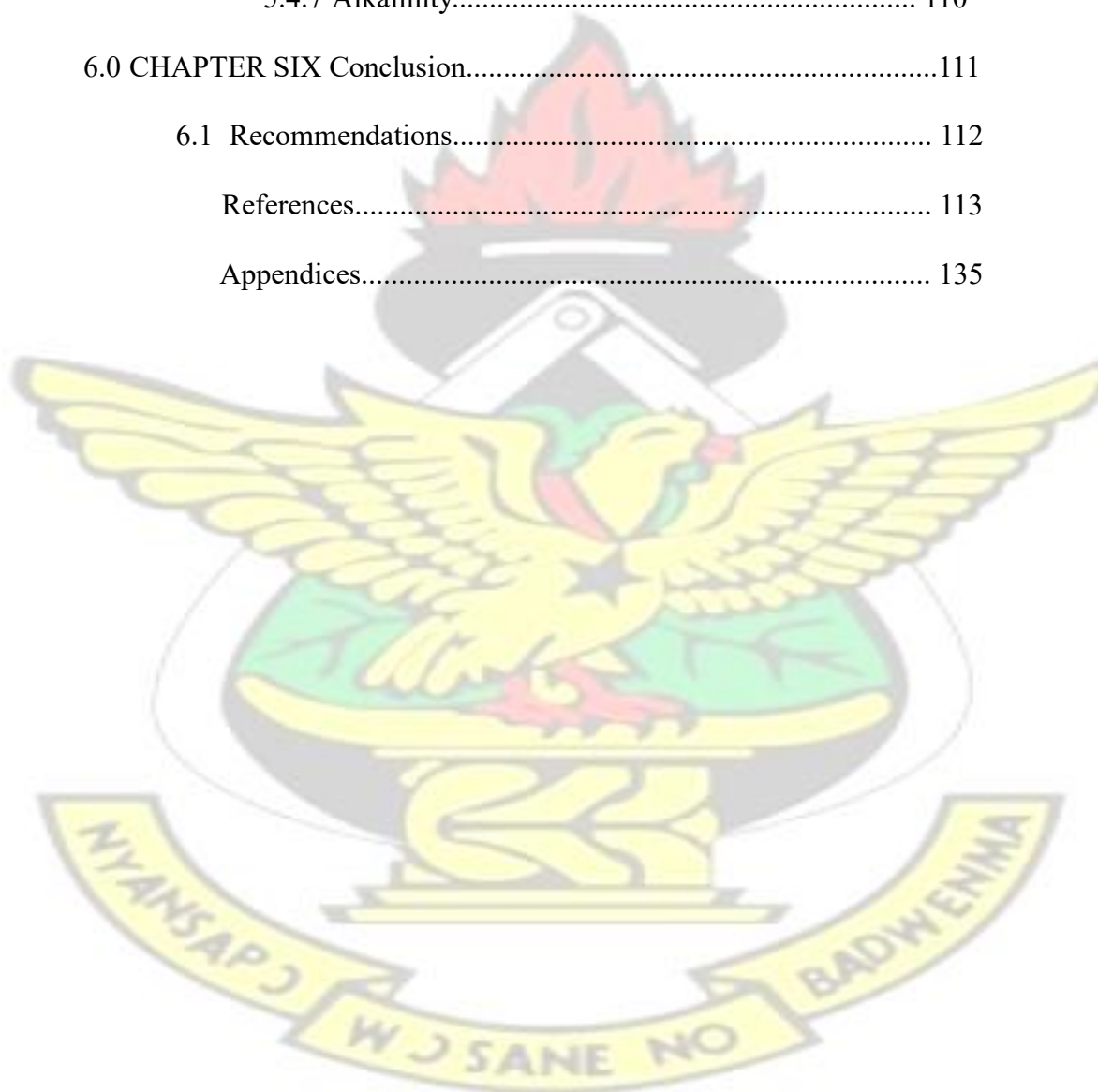
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List of Acronyms

AAS.....	Atomic Absorption Spectrophotometer
ACGIH.....	American Conference of Governmental Industrial Hygienists
ACS.....	American Chemical Society
ADI.....	Annual Allowable Intake
APHA.....	American Public Health Association
CAC.....	Codex Alimentarius Commission

CEPS.....	Customs Exercise and Preventive Service
ECD.....	Electron Capture Detector
EPA.....	Environmental Protection Agency
EU.....	European Union
FAO.....	Food and Agricultural Organization
GC.....	Gas Chromatography
GPHA.....	Ghana Ports and Harbours Authority
GSB.....	Ghana Standards Board
JMPR.....	Joint Meeting on Pesticides Regulation
LD.....	Lethal Dose
MLNR.....	Ministry of Land and Natural Resources
MoFA.....	Ministry of Food and Agriculture
MRL.....	Multi Residue Limits
NIOSH.....	National Institute for Occupational Safety and Health
NIP.....	National Implementation Plan
NPAS.....	Northern Presbyterian Agricultural Service
OC.....	Organochlorine Pesticides
OPP.....	Organophosphate Pesticides
PCMA.....	Pesticides Control and Management Act
POP.....	Persistent Organic Pollutants
PTC.....	Pesticides Technical Committee
RFD.....	Reference Dose
SDWC.....	Safe Drinking Water Committee
TDS.....	Total dissolved solids
UND.....	United Nation Development Program
UNEP.....	United Nations Environmental Programme
UNO.....	United Nations Organisation
USADP.....	United States of America Data Program

USEPA.....United State Environmental Protection Agency

USGS.....United States Geological Service

WHO.....World Health Organisation

WHOPES.....World Health Organization Pesticides Evaluation Scheme

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CHAPTER ONE

1.0 INTRODUCTION

1.1 Background

Pesticides refer to many different kinds of chemicals and mixture of substances that are intended to control, destroy, repel, or attract a pest. Pests can be animals (insects, mice, and deer), unwanted plants (weeds), or microorganisms (F.A.O. 1986). They can be classified by target organism, chemical structure and physical state. Pesticide can also be classified as inorganic (Synthetic) or organic (Biological). Biological pesticides include microbial pesticides and biochemical pesticides. Other types include pests that invade and destroy crops, carry vectors and destroy wood and wood products. These include insects, plant pathogens, rodents, birds and weeds. Some common types of these are antimicrobials, bactericide, algacides, avicides, fungicide, herbicide, fumigant, insecticide, matricides, and nematicides among others.

Pesticides have had a key role in improving productivity to such an extent that India, a former country of famine has quadrupled grain production since 1951 (Dyanatha and Chand, 1999) and now not only feeds itself but exports produce (100m tones in 2003 - Indian export stats). Similarly productivity and outputs have increased dramatically in lots of countries. For example wheat yields in the United Kingdom rose from 2.5 t/ha in 1948 to 7.5 t/ha in 1997 (Austin, 1998). Corn yields in the USA went from 750kg per acre to over 2500kg per acre over the period from 1920 to 1980 (Purdue, 2006). Pesticides are used in the preservation of wood and wood products in the forestry sector and also for land clearing (USEPA, 1999).

In public health, insecticides are used to control the insects that spread deadly diseases such as malaria (Delacollette, 2004) that results in an estimated 5000 deaths each day (Ross, 2005). According to the United State of America Data Programme (2003) pesticides are used to kill mosquitoes that can transmit deadly diseases like West Nile virus, malaria and yellow fever. They also kill bees, ants or wasps that cause allergic reactions and further protect animals from illnesses that could be caused by parasites example of which are fleas. Pesticides can prevent sickness in humans that could be caused by mouldy foods.

Notwithstanding the beneficial effects of pesticides, their bad effects on human health and environmental quality have been well documented worldwide and constitute a major issue that gives rise to concerns at local, regional, national and global scales

(Planas *et al.*, 1997; Kidd *et al.*, 1991; Huber *et al.*, 2000; Cerejeira *et al.*, 2003; Ntow, 2001). Increase accumulation of these chemicals in the food chain may pose serious health hazards in the general populace (Jayashree and Vasudevan, 2007). For example, exposure to organochlorine compounds has been reported to affect thyroid function in preschool children. Low sperm count in males, birth defects, increased in testicular cancer and other reproductive and development effects (Weltman and Norback, 1983) have also been reported as a result of organochlorine contamination.

Residues of pesticides reduce soil and water quality. Pesticides get into water bodies through run offs (surface water) and infiltration (ground water) (Gelbke *et al.*, 2004; Ying *et al.*, 2004). Since these pesticides are insoluble in water, they get in and are unable to dissolve and become a threat to the aquatic ecosystem (Goldman and Koduru, 2001). When pesticides are applied to soil, a number of things may happen, it may be taken up by plants or ingested by animals, worms, insects or microorganisms in the soil. It could

travel downward in the soil and either stick to particles or dissolve (Glover-Amengor *et al.*, 2008). Furthermore, pesticides can be held responsible for contributing to biodiversity losses and deterioration of natural habitats (Sattler *et al.*, 2006).

In Ghana pesticides use is on the ascendency Dinham, (2003) estimates that 87% of farmers in Ghana use chemical pesticides to control pests and diseases on vegetables. In this context, the study area which is the Offinso District is known for widespread usage of these pesticides for both agriculture and agroforestry. Pesticides have therefore become an integral part of Ghanaian agriculture. They are being used on cocoa and cotton plantations, rice fields, vegetable farms, etc. Out of the 87% of the pesticides used, 44% are herbicides, 33% are insecticides and 23% are fungicides

Farmers in the study area often spray hazardous insecticides like organophosphates and organochlorines up to five or more times in a cropping season when perhaps two or three applications may be sufficient (Ntow *et al.*, 2006). It may be possible that runoff of pesticides from the agricultural and agroforestry fields may contaminate water sources i.e. both ground and surface water bodies. The toxic, persistent pesticides may spread within the watershed. Consequently, the quality of such water bodies gradually deteriorates to a level which may jeopardize their use for drinking by humans and that for livestock (Ntow *et al.*, 2006). The questions now are: Do these problems pertain to the study area? What then is the current state of pesticides residue levels in the study area?

1.2 Problem Statement

The bioaccumulation of pesticides through the food web, their highly persistent properties and potential threat to human health has eventually become a risk or threat to both animal and human which demands critical attention. A more recent study has suggested that the incidents of pesticide poisoning may be as high as three million annually (McConnell and Hruska, 1993). In spite of the developed countries using around 80 per cent of the pesticides produced in the world, it has been estimated that 99 per cent of pesticide fatalities occur in the developing world, with just as significant a percentage in the area of non-fatal poisonings. Organochlorine pesticides (OCPs) are widely used throughout the world and frequently detected in surface and ground waters. These compounds are lethal and mostly classified as carcinogens for humans (Sankararamakrishnan *et al.*, 2005; Tanabe *et al.*, 1994).

Institutions are in place to handle some of the problems posed by the use of pesticides but data on the residual effects of pesticides in Ghana and particularly the study area is scanty. This is one of the major set – backs to pesticides management in Ghana. For instance EPA has a dearth of information on the effects of agricultural, agroforestry and forestry pesticides on the environment and public health (EPA, 2009). These are greatly affecting the management of the pesticides. Pesticides such as Atrazine, Aldrin, Carbofuran and Endosulfan among others are in frequent use by farmers but little is known on their effects on water bodies in the study area. Fuseini, (2001) and Fobiaa, (2004) carried out a study in the given area. They considered the impact of pesticides on soil micro flora and fauna and the effects of pesticide use in tomato production on human health and the shelf-life of harvested fruits respectively. The works mentioned leave a gap in identifying the effects of these pesticides on ground and surface water. Fiagbe, (1998) considered the effects of organochlorine pesticides such as aldrin, endosulphan

and Hexachlorobenzene (HCB) on river bodies but this study failed to bridge the gap on ground water and also to identify new trends taken by these pesticides. There are also conflicting views on the presence and pollution of the pesticides in ground and surface water bodies in the study area (Ghanaian Times, 2010).

The use of organochlorine pesticides for agricultural purposes has been banned for about 25 years now in the developed world and some developing nations like Ghana (Ghanaian Times, 2010). However, there are evidence of their continuous usage in many developing nations, like Ghana, due to inadequate regulation and management on the production, trade and use of these chemicals (Darko and Acquah, 2007). The studies above revealed that extensive work has not been done on organochlorine pesticides such as Atrazine, Aldrin, Carbofuran and Endosulfan to really identify whether these pesticides have found their way in the ground and surface water considering their use in some communities even though they have been banned. These problems coupled with the conflicting views on these pesticides affects water quality management.

In addition, farmers who undertake the Taungya agroforestry system in the Asubimah forest reserve use these pesticides in the clearing of land and in the control of weeds and other insects. It may be possible for these pesticides to find their way in the surface and ground water bodies. Lack of adequate research to provide comprehensive information on pesticide effects on surface and ground waters in the study area and Ghana as a whole makes pesticides management very difficult and ineffective.

1.3 Justification

The quality of surface and ground waters is a very sensitive issue. Anthropogenic influences (urban, industrial and agricultural activities) as well as natural processes

(changes in precipitation inputs, erosion and weathering) degrade surface and ground waters. This impairs their use for drinking, agricultural, industrial, recreation or other purposes. Therefore a monitoring program that will provide a representative and reliable estimation on the quality of these water sources is necessary.

It is very important to look into the effects of these pesticides since beside their numerous benefits has side effects which can be very harmful to water bodies and human life as a whole. Also, the extensive use of pesticides in farming and its effects in the study area makes this study important. This will enhance the understanding on effects of these pesticides on water bodies for improved pesticides management

This study therefore seeks to carry out an extensive work on pesticides such as Atrazine, Aldrin, Carbofuran and Endosulfan among others. Identify their presence in ground and surface water and compare them to the W.H.O. standards and making the data available for the institutions involved in their management such as E.P.A Ghana to inform and enhance pesticides management in the country. More so, policy makers and farmers in the study area's understanding of these pesticides will be enhanced at the end of this study to allow for better farming operations.

In addition, a research in the study area to comparing the levels of pesticides in ground and surface water bodies and that of agric and forestry land use systems is necessary since such a study is absent in the area. This research will further serve as baseline information for further research on the subject in the study area. It is against these backgrounds that this research seeks to achieve the following objectives.

1.4 Aim

The general Objective of the study is:

1. To determine the quality of water in terms of the physicochemical qualities and pesticides (Organochlorines and Organophosphates) accumulation in ground and surface water in Akumadan and Asubimah Forest Reserve.

1.5 Objectives

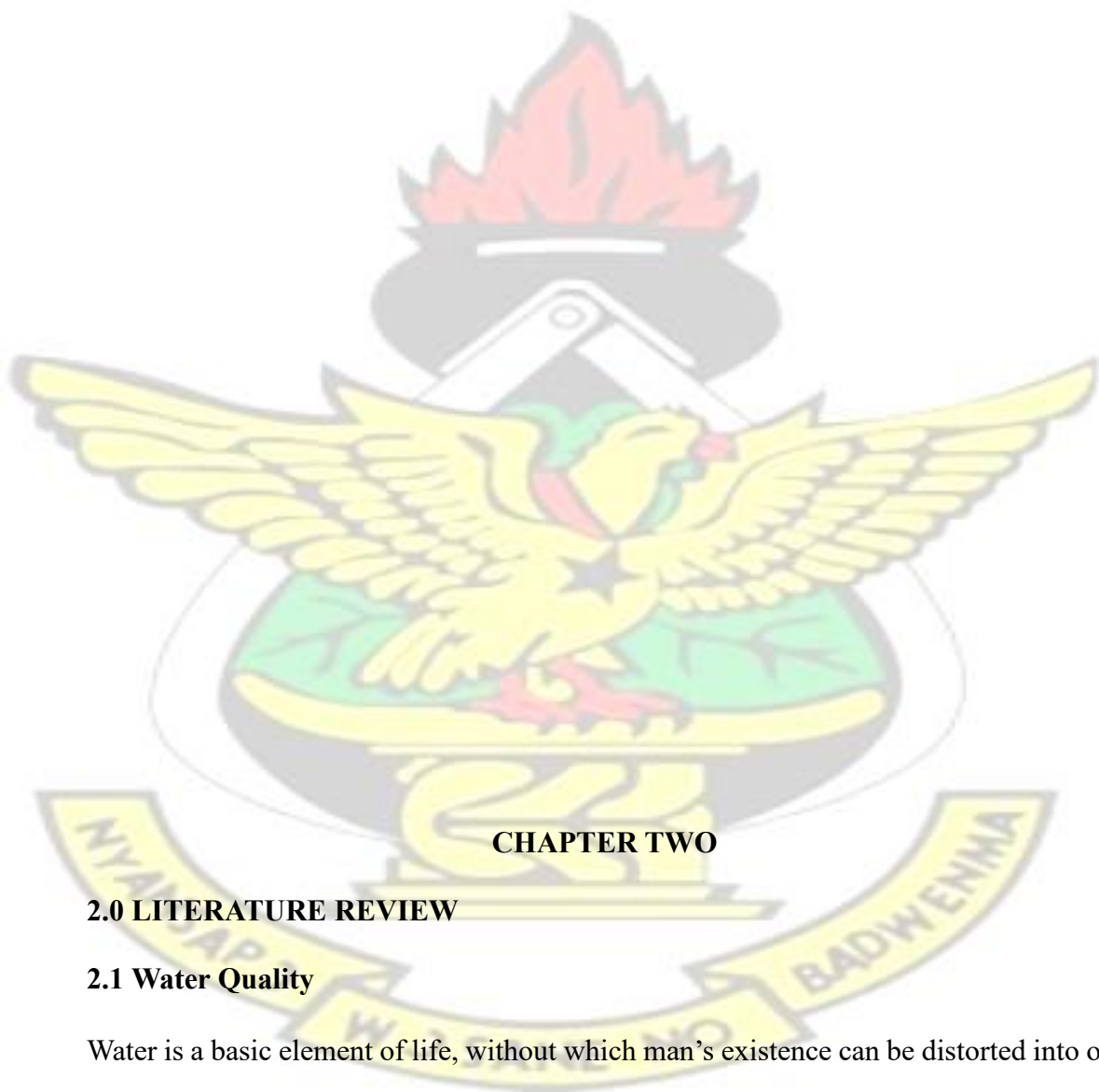
The specific objectives of the study are:

1. To assess the level of pesticides (Atrazine, Carbofuran, Endosulfan and Aldrin) among others in surface and ground water.
2. To compare the level of organochlorine and organophosphate pesticides residues in the ground and surface water bodies in Akumadan with the World Health Organization standards.
3. To determine the physicochemical qualities (conductivity, pH, turbidity, dissolved solids) of surface and ground water in the Akumadan and Asubimah Forest Reserve in Offinso District.

1.6 Hypothesis of the Study

- Pesticide usage can negatively affect the physicochemical properties of ground and surface water.
- The use of pesticides has the potential of contaminating ground and surface water bodies in agricultural and agroforestry land use systems.

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CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 Water Quality

Water is a basic element of life, without which man's existence can be distorted into one continuous liturgy of suffering. Safe drinking-water is an essential need for human development, well-being and health because of this it is an internationally established human right (WHO, 2004). In addition to water availability, water quality is also a

problem, particularly in developing countries. It may be correct to state that the need for a safe domestic water supply is perhaps the greatest threat to the developing world (Witt, 1989). When water supply is low and water treatment inefficient, human health is at its most susceptible point (Feachem, 1983). The worry in many developing countries is centered on a supply of safe and adequate amounts of water for consumption and sanitary purposes.

The United Nations Development Programme (UNDP) approximated that during the period 1988-1991, 70 per cent of the developing world had access to safe water, with the figure dropping to 45 per cent for the least developed countries (UNDP, 1994). In 1992 to approximately 1.3 billion people were without access to safe water (UNDP, 1994). The health repercussions from the inability to supply water of sufficient quality for domestic usage and for other agricultural purposes are tremendous in developing countries. In addition to the direct threats that may flow from consuming water contaminated by pollutants such as chemical agents, the greatest cause of mortality and morbidity is the spread of infectious diseases. In the developing world these account for 72 per cent of the deaths of all children under five years old and 45 per cent of deaths over all (UNEP, 1993). Some guidelines for water quality are shown in the tables below.

Table 2.1: Ghana Water Company Limited guidelines for drinking water quality

Ghana Water Company Limited(GWCL) Guidelines For

Drinking Water Parameter

Parameter	Unit	Value
ph	°C	6.5-8.5
Temperature	Hz	N/A
Colour	NTU Mg/L	0 – 15
Turbidity	µS/cm	0 – 5
Total Dissolved Solids	PSU	1000
Conductivity	Mg/L	N/A
Salinity	Mg/L	N/A
Total Hardness	°C	500
Nitrate		0 – 10
Alkalinity		0

Source: (Ghana Standards Board, 1998)

Table 2.2 Other guidelines for drinking water

Other Guidelines for Drinking Water Quality Parameter				
Parameter	Unit	EU1998	USEPA 1999	WHO 2003
pH		6.5-9.5	6.5-8.5	6.5-8.5
Temperature	°C			25
Colour	Hz	15	15	15
Turbidity	NTU		5	7
Total Dissolved Solids	Mg/L			1000
Conductivity	µS/cm	2500	1500	1500
Salinity	PSU			
Total Hardness	Mg/L			500
Nitrate	Mg/L	500	300	50
Alkalinity	Mg/L	500	200	

WHO (2003)

2.2 What are Pesticides

Pesticides have been defined by the Food and Agricultural Organization (F.A.O) as any substance or mixture of substances intended for preventing, destroying, controlling or repelling any pest. It may be a chemical substance, biological agent (such as virus or bacterium) antimicrobial disinfectant or device used against any pest (WHO/FAO, 2005).

The term includes substances meant for use as a plant-growth regulator, desiccant, defoliant or fruit-thinning agent or agent for preventing the premature fall of fruit and substances applied to crops either before or after harvest to protect the commodity from deterioration during storage and transport. Pests can be animals (insects, mice, and deer), unwanted plants (weeds), or microorganisms.

A lot of pesticides are found around human habitations. These include bleach, ammonia, and many household cleaners as well as ant and roach sprays, no-pest strips, baits and mosquito repellents. Pesticides are used on pets such as flea and tick in the form of collars, powders and shampoos (U.S.EPA, 2001).

2.3 History of Pesticides

Pesticides have been used for ages to protect crops. The first known pesticide is elemental sulphur dusting used in ancient summer about 4,500 years ago in ancient Mesopotamia. In the 17th century, nicotine sulphate was extracted from tobacco leaves for use as an insecticide whereas in the 19th century, there was the addition of two more natural pesticides; pyrethrum which was derived from chrysanthemums, and rotenone also derived from the roots of tropical vegetables. In the period, manufacturers began to produce large amounts of synthetic pesticides and their use became widespread. Some

sources considered 1940s and 1950s to have been the start of the pesticide era. Pesticide use has increased 100-fold since 1950s and 2.3 million tonnes of industrial pesticides are now used each year.

Until the 1950s, the arsenic-based pesticides were dominant. In the 1960s, it was discovered that DDT was preventing many fish-eating birds from reproducing which was a serious threat to biodiversity. Rachel Carson wrote the bestselling book "Silent Spring" about biological magnification. It was a relief to Environmentalist when the Agricultural use of DDT was banned under Stockholm Convention on persistent organic pollutants, but this is still in used in some developing nations. Herbicides became common in the 1960s, led by "triazine and other nitrogen based compounds, carboxylic acids and glyphosphate.

A greater percent of all pesticides in the world i.e. 75% (Seventy five percent) are being used in developed countries, while there is an increasing use in developing countries. According to Holland *et al.*, 1994, organochlorine pesticides such as DDT were dominant but they were replaced in the US by organophosphates and Carbarmates. Since then pyrethrum compounds have become the dominant insecticides. In 2001 EPA stopped reporting pesticide use statistics. The only exhaustive study on pesticide use trends was published in 2003 by the National Science Foundation's Centre for Integrated Pest Management (Dunlap, 1981).

2.4 Classification of Pesticides

Pesticides can be classified in so many ways. Pesticides can be classified by target organism, chemical structure and physical state. Pesticide can also be classified as inorganic (Synthetic) or organic (Biological). Biopesticides include microbial pesticides and biochemical pesticides. Plant – derived pesticides or botanicals have been developing rapidly. These include pyrethroids, rotenoids, and nicotinoids.

Pesticides can be grouped into the chemical families. Prominent among these are organochlorines, organophosphates and carbamates. Pesticides can be classified based upon their biological activity, function or application method. Pesticides move inside plants through absorption by the plants and this movement is outward. Another means of classifying pesticides is the mode of action. This includes stomach poisons (they have to be eaten), contact poisons (they work via the skins), and fumigants (they produce vapour that kills the organism).

Moreover, pesticides are classified based on the target range: Broad spectrum pesticides (chemicals that kill a wide range of pests) Selective pesticides (chemicals that kill only a specific pest or group of pests). Another means of classifying pesticides is based on how it is formulated. This includes: liquid, powders, granules, baits, dust, smoke, generators, and ultra-low volume (ulv) liquids. Pesticides are also classified based on the toxicity class it belongs.

The World Health Organization (WHO) has developed the following toxicity class for chemical pesticides as follows:

- Class 1A: Extremely hazardous ➤ Class 1B: Highly hazardous

- Class II: moderately hazardous
- Class III: slightly hazardous
- Class IV: Product not likely to present severe hazard in normal use

Other WHO classifications include:

- n.e., Not evaluated
- n.a., not available
- PTDI, provisional tolerable daily intake
- (*) One hundred and fifty milligrams per kilogram in kerosene solution □ (**)

Dose able to cause symptoms (*Maroni et al.*, 2000).

Another means of classifying pesticides is whether its use is allowed. These include,

- Registered pesticides
- Banned pesticides (WHO/FAO, 2005).

According to Pesticide Control and Management Act (1996) (Act 528), only the registered products are allowed to be used. Pesticides are also classified according to their persistence, their concentration, how they are used and their container size (OPAC, 2010). The classification of pesticide product is important. It restricts the use of pesticides by people, promotes safe use of pesticides and better protects the environment and human health. It also requires manufacturers to improve pesticide labels to prevent product misuse (WHO/FAO, 2005).

A "Banned" pesticide is defined as a pesticide for which all registered users have been prohibited by final EPA action to protect human health or the environment. It includes pesticides that have been refused approval for first-time use or have been withdrawn by industry. Even though some pesticides have been declared banned, most are still in use in most parts of the world with developing countries being in the lead. Around seven banned or restricted chemical pesticides – aldrin, dieldrin, endosulfan, lindane, DDT, methylbromide and carbofuran (the latter which is banned above a certain level of toxicity) - appear to be still being used by some Ghanaian farmers. A recent study carried out for NPAS in Upper East region found four banned or restricted chemicals were on sale in local agro-dealer shops – DDT, aldrin, lindane and dieldrin. Other dangerous chemical pesticides that the government has cleared for use and failed to ban which are also in use, such as paraquat, atrazine and chlorpyrifos (NPAS, April 2012).

2.5 Uses of Pesticides

Pesticides are used generally to control organisms considered harmful to biodiversity and their products. In the third world countries, the loss of crops due to pests, plants diseases and competition from weeds is enormous. According to the United State of America Data Programme (2003) pesticides are used to kill mosquitoes that can transmit deadly diseases like malaria, West Nile virus and yellow fever. Pesticides can be used to clear roadside weeds, farm weeds and weeds that may cause environmental damage. Pesticides are also commonly applied in ponds and lakes to control algae and plant such

as wiregrasses that can interfere with activities like swimming and fishing and cause the water to look or smell unpleasant.

Pests such as termite which can damage the wooden structures of a house such as ceilings, doors, and window frames may be controlled by pesticides. Pesticides are used in grocery stores and food storage facilities to manage rodents and insects that infest food such as grain thus minimizing post-harvest losses (Clarke *et al.*, 1997). A study conducted by Adeyeye and Osibanjo (1999) found out that not using pesticides reduced crop yields by about 10%. Another study conducted by Repto and Balige (1996) found out that a ban on pesticides in the United States of America may result in a rise of food prices, loss of jobs and an increase in Global hunger.

In public health, insecticides are used to control the insects that spread deadly diseases such as malaria (Delacollette, 2004) that results in an estimated 5000 deaths each day (Ross, 2005). According to the United State of America Data Programme (2003) pesticides are used to kill mosquitoes that can transmit deadly diseases like malaria, West Nile virus and yellow fever. These pesticides can also kill wasps, bees or ants that cause allergic reactions. They could shield animals from illnesses caused by parasites e.g. fleas. Pesticides can prevent human sickness that could be caused by mouldy food.

Pesticides are used extensively in agriculture to sustain and enhance crop yields, and can also be applied in gardens and homes. The yearly application of synthetic pesticides to food crops in the EU exceeds 140,000 tonnes (Carvalho, 2006), an amount that corresponds to 280 grams per EU citizen per year. In spite of European policies to lessen pesticide use, EU data for 1992–2003 indicates that the annual pesticide consumption

has not decreased (Carvalho, 2006). Agrochemicals are important part of modern agriculture production systems around the world. Accordingly, the use of agrochemicals viz fertilizers and pesticides remain a frequent practice particularly in many nations in the tropical world (Carvalho, 2006). Even though World Health Organization has given stronger support to the use of pesticides to fight malaria, each use of the pesticide carries some associated risks.

However, proper pesticide use decreases these associated risks to a level deemed acceptable by Pesticide Regulatory Agencies such as United State Environmental Protection Agency. Widespread use of pesticides therefore is due to the advantages they offer, that is keeping crops healthy and prevent them been wasted by diseases and infestation.

2.5.1 Uses of Pesticides in Ghana

Ghana is a developing country experiencing high economic growth rate in the West African Sub-region (FAO, 2005). As an agriculture-based nation, the use of pesticides contributes much to the national development and public health programmes. Ever since the inception of pesticides, its use to protect crops from pests has significantly reduced losses and improved the yield of crops such as cereals, vegetables, fruits and other crops. Ghana thus, has known a continuous growth of pesticide usage, both in number of chemicals and quantities because of the expansion of area under cultivation for food, vegetables and cash crops (MoFA, 2003)

Pesticide application in Ghana is more concentrated in cocoa, oil palm, cereals, vegetables and fruits sectors. Although purchased physical inputs (tools, agrochemicals and seeds) represent not more than 30% of the total cost of crop production, the use of pesticides is becoming more widespread. For instance, between 1995 and 2000, about 21 different kinds of pesticides were imported into the country for agricultural purposes (FAO, 2004). Its use has been embraced by local communities that are making a living from sale of vegetables and other cash crops. There is ample evidence that this products especially tomatoes are always sprayed and sold immediately after maturity for consumption. This inevitably puts a high risk on consumers who always get their supply directly from the farmers. In Ghana, it is estimated that 87% of farmers who use pesticides, apply any of the following or a combination of pyrethroids, organophosphates, carbamates, organochlorines on vegetables (Ntow, 2001).

Among the different types of pesticides known, organochlorine pesticides are the most popular and extensively used by farmers due to their cost effectiveness and broad spectrum activity. Lindane was widely used in Ghana on cocoa plantations, vegetable farms, and for the control of stem borers in maize (MoFA, 1998). Endosulfan is popularly applied in cotton growing areas, vegetables farms, and coffee plantations in some parts Ghana (FAO, 2004). Pesticides particularly DDT and lindane which are no longer registered for any use in the country were once employed to control ecto-parasites of farm animals and pets in Ghana (Ntow *et al.*, 2006).

Pesticides mostly used to control foliar pests of pineapple in Ghana include dimethoate, chlorpyrifos, diazinon, cymethoate and fenitrothion while the fungicides maneb, carbendazim, imazil, copper hydroxide are used for post-harvest treatment (Boamah and Blay 2000; Cudjoe *et al.*, 2002). Lambda-cyhalothrin, dimethoate, cypermethrin and

endosulfan are also in use by vegetable growers in tomato, pepper, okra, egg-plant, cabbage and lettuce farms. Glyphosate, fluazifop-butyl, ametryne, diuron or bromacil are normally employed in land clearing (Aboagye, 2002). Nonetheless, the most extensively used pesticides in the pepper, tomato, groundnut and beans cultivation are karate, cymbush, thiodine, diathane, lubillite and kocide (Yeboah *et al.*, 2004).

Dinham, (2003), estimates that 87% of farmers in Ghana use chemical pesticides to control pests and diseases on vegetables and fruits. Ntow *et al.*, (2006), gave the proportions of pesticides used popularly on vegetable farms as herbicides (44%), fungicides (23%) and insecticides (33%). In a study encompassing 30 organized farms and 110 kraals distributed throughout the 10 regions of Ghana, Awumbila and Bokuma found that 20 different pesticides were in use with the organochlorine lindane being the most widely distributed and used pesticides, accounting for 35% of those applied on farms. Of the 20 pesticides, 45% were organophosphorous, 30% were pyrethroids, 15% were carbamates and 10% were organochlorines (Awumbila, 1994).

In the public health sector, pesticides, primarily temephos have been used by the Onchocerciasis Programme in the Volta Basin for the control of black flies (*Simulium* spp. Diptera: Simuliidae), which transmit Onchocerciasis (African river blindness, a disease caused by the pathogenic nematode, *Onchocerca volvulus*) to humans and for the control of diseases (Awumbila, 1996) and domestic pests, such as cockroaches, various flies, mosquitoes, ecto-parasites including ticks and other insects (Clarke, 1997). Pesticides have also been used to control black flies along the banks of the

Tano and Pra rivers (Ntow, 2005).

A survey conducted between 1992 and 1994 in the Ashanti, Brong Ahafo, Western and Eastern Regions of Ghana revealed that the most broadly used pesticides by farmers are: copper (II) hydroxide (29.0%), mancozeb (11.0%), fenitrothion (6.0%), dimethoate (11.0%), pirimiphos methyl (11.0%), λ -cyhalothrin (22.0%), and endosulfan (10.0%) (Acquaah and Frempong, 1995). Moreover, it was established that insecticides constituted about 67% of pesticides employed by farmers while fungicides were about 30% and herbicides and other pesticides types form 3% of the total use. On the other hand, it is on record that between 1995 and 2000, an average of 814 tons of pesticides was imported into the country annually, the greatest quantity being insecticides, 70% (FAO, 2004). Updated register of pesticides from the Environmental Protection Agency in Ghana in 2008 indicated that about 141 different types of pesticide products have been registered in the country under the Part II of the Environmental Protection Agency Act, 1994 (Act 490). These consists of insecticides (41.84%), fungicides (16.31%), herbicides (0.43%) and others (0.01%) (Ghana, EPA, 2008).

2.6 Types of Pesticides

There are different types of pests that invade and destroy crops, carry vectors and destroy wood and wood products. These include insects, plant pathogens, rodents, birds and weeds. Some pests are just a nuisance. However, some present health hazard and others may bite or sting. The various types of pesticides and the specific pest each control is shown below:

Tab. 2.3 Types of Pesticides and the Pest controlled

Pesticide type	Pest controlled
Insecticides	Insects
Fungicides	Fungi
Herbicides	Weeds
Avicides	Birds
Bactericides	Bacteria
Matricides	Mites
Molluscicides	Snails
Nematicides	Nematodes
Foeticides or Rodenticides	Rodents
Virucides	Virus
Algaecides	Algae

2.6.1 Herbicides

Herbicides belong to the class of pesticides that are used to control weeds. They are, therefore, also called weed killers. After application of herbicide on target weeds, the active ingredient is gradually lost as a result of breakdown, evaporation and leaching, and the herbicide residue is the amount that remains on the field after application and usage (Afful, 2002). While some herbicides have long residual activity and therefore, persist in the environment for a long time, meanwhile others have low residual activity and disappear from the environment, or produce low residual concentrations (Walker, 1973). The residue level of the herbicide in the soil after application is an important factor to be taken into account when assessing their performance as weed destroyers. There is need to gain information about the duration of phytotoxicity in order to avoid the possibility of damaging a succeeding crop, which may not be tolerant to the herbicide.

2.6.2 Fungicides

Most Fungicides are applied to apples, citrus and other fruit crops (Pimental and Levitan, 1986). Fungicides are extensively used in agriculture, industry, garden and the home for a number of reasons which includes: safeguard of seed grain throughout shipment, germination and storage; protection of matured crops, berries, seedlings, flowers and grasses in the field, in storage and at shipment; suppression of mildews that attack painted surfaces; control of slime in paper pulps; protection of carpet and fabrics in the home. Fungicides differ greatly in the ability to cause unpleasant effects in humans. Previously, some of the catastrophic epidemics of pesticide poisoning happened because of erroneous consumption of seed grain treated with mercury or hexachlorobenzene. However, lots of pesticides currently in use are not likely to cause regular or severe systemic poisonings for numerous reasons. To start with, many have low inherent toxicity in mammals and are inefficiently absorbed. Furthermore, lots of them are formulated as suspensions of wettable powders or granules, from which rapid efficient absorption is unlikely. And lastly, the methods used for application are such that relatively few individuals are greatly exposed. Besides systemic poisoning, fungicides as a class are most likely responsible for the unequal number of irritant injuries to skin and mucous membranes, as well as dermal sensitization (NPAS, 2012).

2.6.3 Rodenticides

A wide variety of materials are used as rodenticides. They pose risks for accidental poisonings for many reasons. First and foremost, as against purposely designed to kill mammals, often their toxicity is very similar for the target rodents and for humans

(Warfarin and other anticoagulant rodenticides were primarily developed to surmount this problem by creating compounds that were highly deadly to rodents, predominantly after recurring exposures, but much less toxic to humans). Second, since rodents usually share environments with humans and other mammals, the risk of inadvertent contact is an integral part of the placement of baits for the rodents. Finally, as rodents have developed resistance to existing rodenticides, there is an incessant need to develop new and potentially more toxic rodenticides. As rodents have become resistant to warfarin baits, e.g. the development of superwarfarins has increased the risks to humans (Mack, 1994; Katona, 1989). It is imperative to be familiar with use patterns and development of more toxic compounds and to make all efforts to recognize the actual agent used in a bid to institute the most fitting management for these poisonings.

2.6.4 Nematicides

Nematodes are non-segmented, bilaterally symmetric worm-like invertebrates that have a body cavity and a complete digestive system but does not have respiratory and circulatory systems. The body wall is made of a multi-layered cuticle, a hypodermis with four longitudinal cords, and internal musculature. The most striking aspect of the nervous system is the nerve ring close to the nematode pharynx. The so-called excretory system has certainly not been linked with removal of metabolic wastes; instead, it functions in osmoregulation or in the secretion of compounds necessary to the life history of the nematode, depending on the species and the developmental stage.

The digestive and reproductive systems comprise much of the body contents. A lot of nematode species are “free-living”; i.e., they feed on microorganisms in water and soil. Although the detection of nematicidal activity in a synthetic chemical dates from the use

of carbon disulfide as a soil fumigant in the second half of the nineteenth century, study on the use of nematicides languish until surplus nerve gas (chloropicrin) became readily available following World War I (Hague *et al.*, 1987). In the 1940s, the discovery that D-D (a mixture of 1, 3-dichloropropene and 1,2dichloropropane) controlled soil populations of phytoparasitic nematodes and led to considerable raise in crop yield and provided a great impetus to the development of other nematicides and hence, the growth of the science of nematology. Consequently, other halogenated hydrocarbons and other volatile compounds were developed as nematocidal soil fumigants. Several of the carbamates and organophosphates are systemic within plants, but it's just one contact nematicide has registered systemic nematocidal activity. For several systemics, the high concentrations needed to retard nematode development within plant roots is not likely to occur under field conditions (Sikora, 1991). Most soil nematicides are also registered as insecticides.

2.6.5 Insecticides (Pesticides affecting insects)

An insecticide is a natural or man-made preparation that is used to kill or otherwise control the population of insects. Instead of killing insects, an insecticide may work to prevent them from reproducing. Insecticides are generally classified as either organic or inorganic. Organic insecticides always contain carbon while inorganic do not contain carbon. Organic insecticides are grouped into synthetic (man – made) and natural insecticides consisting mainly of organochlorine insecticides, organophosphate insecticides, pyrethroids and carbamates.

2.6.5.1 Organophosphate Pesticides (OPP's)

Organophosphate pesticides are chemical compounds formed from atoms of hydrogen, carbon, oxygen with the addition of phosphorus. They degrade easily and are unable to remain in the environment long after application and in organisms long after exposure. The use of OPPs and CMs has increased due to their availability and quick degradation in the environment (Sajjad *et al.*, 2009). There has been evidence of their frequent use in agricultural activities. Currently Organophosphorus pesticides (OPPs) enjoy wide use in the world for the pest control (Aldridge, *et al.*, 1979; ACGIH, 1998) which leads to increased world food production. Some examples of organophosphate pesticides are listed below.

Dimethoate

Dimethoate (CAS No. 60-51-5) is an organophosphate insecticide used to control a broad range of insects in agriculture. It has a half-life of 18 hours to 8 weeks and is not expected to persist in water, although it is relatively stable at pH 2–7. A total daily intake from food of 0.001 µg/kg body weight has been estimated. The permissible limit for Dimethoate is 6µg/L

Chlorpyrifos

Chlorpyrifos (CAS No. 2921-88-2) is a broad-spectrum organophosphate which is used for the control of flies, mosquitoes, various crop pests in soil and on foliage, aquatic larvae and house- hold pests. Even though it is not recommended for addition to water for public health purposes by the WHO Pesticide Evaluation Scheme (WHOPES), it may be used in some countries as an aquatic larvicide for the control of mosquito larvae. Chlorpyrifos is strongly absorbed by soil and does not readily leach from it, degrading slowly by microbial action. It has a low solubility in water and great tendency to partition

from aqueous phases into organic phases in the environment. The permissible limit for Dimethoate is 30µg/L

Methoxychlor

Methoxychlor (CAS No. 72-43-5) is an insecticide used on vegetables, fruit, trees, and fodder and farm animals. It is poorly soluble in water and highly immobile in most agricultural soils. Under normal conditions of use, methoxychlor does not seem to be of environmental concern. Daily intake from food and air is expected to be below 1 µg per person. Environmental metabolites are formed preferentially under anaerobic rather than aerobic conditions and include mainly the dechlorinated and demethylated products. There is some potential for the accumulation of the parent compound and its metabolites in surface water sediments. The permissible limit for Methoxychlor is 20µg/L.

2.6.5.2 Organochlorine pesticides

They are chemical compounds formed from atoms of hydrogen, carbon, oxygen with the addition of chlorine. Their chlorine-carbon bonds are very strong which means that they do not decompose easily thus break down slowly and can remain in the environment long after application and in organisms long after exposure. Organochlorine pesticides comprise of a large group of structurally diverse compounds used to control agricultural pest and vectors of humans (KuranchieMensah et al., 2011). These pesticides have the tendency for long range transport and trans-boundary dispersion and their capacity to bio accumulate in the food chain pose a great threat to human health and the global environment (Laws, 2000).

They are highly insoluble in water, but are lipipholic. Since they oppose metabolism and are readily stored in fatty tissue of any animal ingesting them, they build up in animals in higher trophic levels. This may possibly occur when birds eat fish that have been exposed to the contaminant. It may also have an effect on humans if they drink milk of a dairy cow that has ingested the chemical because the chemical is excreted in its milk fat. This is called biological magnification. The deliberate production and the unintended release have elevated levels of these chemicals in the biosphere far ahead of natural background levels. The most notorious organochlorine is the pesticides dichlorodiphenyltrichloroethane (DDT). Promoted as a 'cure all' insecticide in the 1940s, other commonly known organochlorines include toxaphene and methoxychlor Lindane endosulfan, dicotol, chlordane, heptachlor, Aldrin and dieldrin.

Gibson *et al.*, 1987, revealed that Organochlorine pesticides are mostly used in agriculture to kill insects in vegetables, fruits, cereals, grain and cotton as well as ornamental shrubs, trees and vines. It was also the chemical of choice for the control of mosquitoes until the 1960s. Organochlorine pesticides were extensively used by most Ghanaian farmers due to their low cost, high efficacy and its wide range suitability to plants (Osafo and Frempong, 1998). These pesticides were greatly used in most farming communities in the Ashanti, Brong Ahafo and Western regions of Ghana (Amoah *et al.*, 2006) in vegetable production, cocoa farms and mixed crop farms (Ntow *et al.*, 2006; Gerken *et al.*, 2001). Organochlorine pesticides such as DDT, Lindane and Endosulfan were also employed to control ectoparasites of farm animals and pets in Ghana (Ntow *et al.*, 2006). Pesticides have also been used to control black flies along the banks of the Tano and Pra rivers (Ntow, 2001).

Organochlorines are fairly complex, stable compounds and therefore persist for a long time in the environment either in their original form or as stable metabolites. Their persistence makes them capable of bioaccumulating in the tissues of human beings such as breast milk and blood (William *et al.*, 2008) via the food chain. As a result of its position in the food chain man is greatly exposed to the effect of the micro pollutants by eating foods either from contaminated earth or water (Belta *et al.*, 2006, Raposo and Nilva 2007). They are poorly biodegradable and have high lipid solubility (Mbakaya *et al.*, 1994). Higher levels have been formed in human beings (Ejobi *et al.*, 1996, Skaare *et al.*, 1988, Weisenberg *et al.*, 1985).The organochlorine pesticides are broad spectrum insecticides and are the most widely used in many countries including Nigeria for agricultural purposes and control of mosquitoes (Belta *et al.*, .2006, Blaso *et al.*, 2005). Organochlorine pesticides are very stable compounds and they have been cited that the degradation of DDT (Dichlorodiphenyltrichloroethane) in the soil ranges from 4-30years. Other chlorinated stable compounds also remain for many years after application, due to their high resistance to biological and chemical degradation (Afful *et al.*, 2010). Study by Rajendran and Subramanian, 1997, mentioned that despite the fact that the use of certain organochlorine pesticides is prohibited in many countries including Ghana, these compounds have been detected in the environment

The use of organochlorines has occasionally been accompanied by risks to human health and the environment because of their toxic potential, high persistence, bioconcentration and especially their non-specific toxicity (Barriada Pereira *et al.*, 2005; Krauthacker *et al.*, 1998).

Unfortunately pesticides uses have been abused since most pesticides users are ignorant or have little knowledge about these chemicals. Some farmers are of the view that the more or as often as they apply pesticides the greater the chances of higher yield and also destroying crop pest (Ntow *et al.*, 2006). They have no idea of the halflives of these chemicals or the dangers they pose when misused. The deleterious effects of these organochlorine pesticides on wild life primarily led to their ban from routine use in the US and many other countries in 1970's and 1980's (Dunlap, 1981). With the exception of endosulfan which was considered for restricted use in

2008, Ghana has banned the use of many organochlorine pesticides since 1985. The developed nations like U.S.A, Japan and Western Europe have put in place measures for pesticide control and monitoring in the environment accompanied by continuous regular survey studies and monitoring programmes (Luke *et al.*, 1988, Fontcuberta *et al.*, 2008).

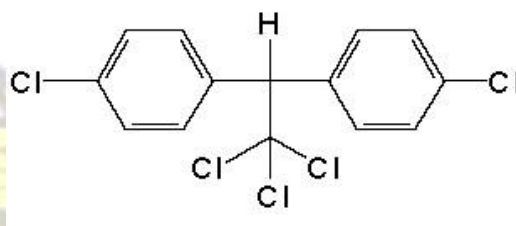
Research by Belta *et al.*, 2006, showed a contrast that, there is very little information on the levels of pesticide usage in developing countries like Ghana. This may be due to lack of financial support for scientific research, environmental policy and regulation for control and monitoring the environment. In countries where they exist, agencies responsible lack the capacity to ensure compliance and enforcement of regulations.

Regrettably, as indicated earlier, even though organochlorines are banned from importation, sales and use, third world nations continue to use them. For example in Ghana, there are evidence of their continued application to crops, vegetables and fruits. Few studies conducted so far in Ghana revealed levels of organochlorine pesticides in water, segments, food and vegetable (Osafo and Frempong, 1998; Ntow, 2001., Darko and Aquaah, 2006), which are emanating from current and past use of these chemicals.

Moreover, pesticide residues in food materials are not properly monitored nor controlled in Ghana and limited information is available for the level of pesticide residues in food. Thus, in Ghana there have been less surveillance programmes for pesticides levels in foods, hence the paucity of data on the dietary intake of pesticides by the Ghanaian population.

Below are some examples of organochlorine pesticides with their chemical make ups DDT and its Metabolites

DDT (originally named dichloro diphenyl trichloroethane) was first synthesized in 1873 by a German graduate student.



This was forgotten about until 1938 when Dr. Paul Muller re-exposed it when he was looking for a lifelong insecticide to combat the clothes moth. It was tremendously effective against flies and mosquitoes and was used at length in North America as a domestic and agricultural pesticide till it was banned by the EPA on January 1, 1973 due to its long residual life and its accumulation in food chains. The terms DDT or DDTs are mostly used to refer to a family of isomers (p,p'-DDT and o,p'-DDT) and their breakdown products (p,p'-DDE, o,p'-DDE, p,p'-DDD, and p,p'-DDD). DDT data are often expressed as the sum of these six components (Maroni *et al.*, 2000).

Metabolites of DDT

DDE

Dichlorodiphenyldichloroethylene (DDE) is a product of the breakdown of DDT in an organism's body. It is produced in most animals when the body tries to rid itself of DDT. One major problem related to contaminants identified in fish-eating birds is the thinning of eggshells which is brought about by the incidence of DDE in female birds. Eggshells comprise of calcium carbonate which is made from calcium and carbon dioxide in the bird's body. This reaction takes an exact enzyme which is repressed by the DDE. Since the eggshell does not have as much calcium carbonate as it should it is thinner than normal and more prone to breakage during incubation by the adult.

DDD (1,1-dichloro-2,2-bis(p-chlorophenyl)ethane)- DDD is produced by metabolism of DDT in some organisms

DDTs (Dichlorodiphenyltrichloroethane)

Chemical Name: 1,1,1,-Trichloro-2,2-bis-(4-chlorophenyl)-ethane (C₁₄H₉Cl₅).

CAS Number: 50-29-3.

Properties: Solubility in water: 1.2-5.5 µg.l⁻¹ at 25°C; vapour pressure: 0.2 x 10⁻⁶ mm Hg at 20°C; log 6.19 for pp-DDT, 5.5 for pp-DDD and 5.7 for pp-DDE.

Discovery/Use: DDT appeared for use during World War II to control insects that spread diseases like dengue fever and typhus. Following this, it was widely used on a variety of agricultural crops. The product is a mixture of about 85% pp-DDT and 15% op-DDT isomers. Persistence/Fate: DDT is highly persistent in soils with a half-life of up to 15 years and 7 days in air. It exhibits high bio concentration factors (in the order of 50 000

for fish and 500 000 for bivalves). In environment, the product is metabolized mainly to DDD and DDE.

Toxicity: The lowest dietary concentration of DDT reported to cause egg shell thinning was 0.6 mg.kg^{-1} black duct. LC_{50} of 1.5 mg.l^{-1} for large mouth and 56 mg.l^{-1} for guppy have been reported. The toxicity of DDT for mammals is moderate with an LD_{50} in rat of 113-118 mg.kg^{-1} body weight. DDT has shown to have an oestrogenlike activity and possible carcinogenic activity in humans. The maximum level in food recommended by WHO/FAO range from 0.02 mg.kg^{-1} milk fat to 5 mg.kg^{-1} meat fat. The Maximum permissible DDT residue level in drinking water (W.H.O.) is

$1.0 \text{ } \mu\text{g.l}^{-1}$.

Aldrin and Dieldrin

Chemical Name: 1,2,3,4,10,10-Hexachloro-1,4,4a,5,8,8a-1,4-endo,exo-5,8dimethano-naphthalene ($\text{C}_{12}\text{H}_8\text{Cl}_6$). CAS Number: 309-00-2

Properties: Solubility in water: $27 \text{ } \mu\text{g.l}^{-1}$ at 25°C ; vapour pressure: $2.3 \times 10^{-5} \text{ mm Hg}$ at 20°C ; $\log K_{ow}$: 5.17-7.

Discovery/Uses: it has been manufactured commercially from 1950, and used over the world up to the early 1970s to manage soil pests such as corn rootworm, rice water weevil, wireworms and grasshoppers. It has also been used to protect wooden structures from termites.

Persistence/Fate: Readily metabolized to dieldrin by both plants and animals. Biodegradation is expected to be slow and it binds strongly to soil particles, and is opposed to leaching into groundwater. Aldrin was classified as moderately persistent with half-life in soil and surface waters ranging from 20 days to 1.6 years.

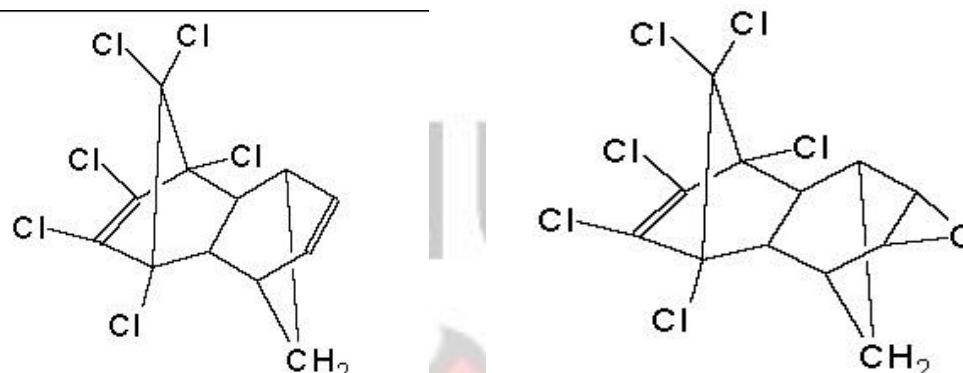
Toxicity: Aldrin is toxic to humans; the lethal dose for an adult has been estimated to be about 80mg.kg⁻¹ body weight. The acute oral LD₅₀ in laboratory animals is in the range of 33 µg.g⁻¹ body weight for guinea pigs to 320 mg.kg⁻¹ body weights for hamsters. The toxicity of aldrin to aquatic organisms is relatively variable, with aquatic insects being the most receptive group of invertebrates. The 96^h LC₅₀ values range from 1-200 µg.L⁻¹ for insects, and from 2.2-53 µg.L⁻¹ for fish. The maximum residue limits in food recommended by FAO/WHO varies from 0.006 mg.kg⁻¹ milk fat to 0.2 mg.kg⁻¹ meat fat. Water quality criteria between 0.1 to 180µg.L⁻¹ have been published.

Aldrin and dieldrin are insecticides with similar structures. Sunlight and bacteria change aldrin to dieldrin so dieldrin is mostly found in the environment. Since 1950-1970, aldrin and dieldrin have been pesticides for crops like cotton and corn. They attach firmly to soil and slowly disappear to the air. Dieldrin is stored in the fat of a body and leaves the body very slowly. Because of apprehension about harm to the environment and the possible harm to human health, EPA banned all uses of aldrin and dieldrin in 1974 but to control termites. Later in 1987, EPA banned all uses.

Heptachlor and heptachlor epoxide

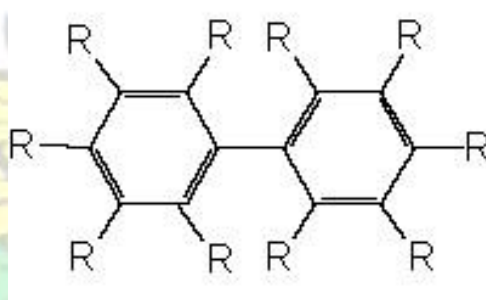
Heptachlor (CAS No. 76-44-8) is a broad-spectrum insecticide, the use of which has been banned or restricted in many countries. At present, the major use of heptachlor is for termite control by subsurface injection into soil. Heptachlor is quite persistent in soil, where it is mainly transformed to its epoxide. Heptachlor epoxide (CAS No. 1024- 57-3) is very resistant to further degradation. Heptachlor and heptachlor epoxide bind to soil particles and migrate very slowly. Heptachlor and heptachlor epoxide have been found in drinking-water at nanogram per litre levels. Diet is considered to represent the major source of exposure to heptachlor, although intake is decreasing significantly, as

its use has substantially declined. The permissible limit for Heptachlor is 20µg/L (Maroni *et al.*, 2000).



Polychlorinated biphenyls (PCBs)

PCBs (polychlorinated biphenyls) were first introduced into commerce in 1929. Because PCBs degrade very slowly in the environment and build up in the food chain, they have been banned from further production in many countries.



There are 209 different PCB compounds called congeners but only about 130 of these are likely to occur in commercial products. A congener may have between 1 and 10 chlorine atoms, which may be located at various positions on the PCB molecule (Maroni *et al.*, 2000).

Chemical Name: Polychlorinated biphenyls ($C_{12}H_{(10-n)}Cl_n$), where n is in the range of 1-10)

CAS Number: Various (e.g. for Aroclor 1242, CAS No.: 53469-21-9; for Aroclor 1254, CAS No.: 11097-1)

Properties: Water solubility decreases with increasing chlorination: 0.01 to $0.0001 \mu\text{g.l}^{-1}$ at 25°C pressure: $1.6-0.003 \times 10^{-6}$ mm Hg at 20°C ; $\log K_{ow}$: $4.3-8.26$.

Discovery/Uses: PCBs were manufactured in different countries under trade names (e.g., Aroclor, Clophen, Phenoclor). They are chemically stable and heat resistant and became widely used in electrical transformers, capacitor oils, lubricating oils, hydraulic and heat exchange fluids, cosmetics, varnishes, inks, carbonless copy paper and pesticides and for general weatherproofing and fire-resistant coatings to wood and plastic.

Persistence/Fate: Most PCB congeners, mainly those deficient of adjacent unsubstituted positions on biphenyl rings (e.g., 2, 4, 5-, 2, 3, 5- or 2, 3, 6-substituted on both rings) are extremely persistent in environment. They are estimated to have half-lives ranging from three weeks to two years in air and, with exception of mono- and dichlorobiphenyls, over six years in aerobic soils and sediments. PCBs also has extremely long half-lives in adult fish, for examples, an eight-year study of eels found that the half-life of CB153 was more than ten years.

Toxicity: LC_{50} for the larval stages of rainbow trout is $0.32 \mu\text{g.l}^{-1}$ with a NOEL of $0.01 \mu\text{g.l}^{-1}$. The acute toxicity of PCB in mammals is generally low and LD_{50} values in rat of 1 g.kg^{-1} bw. IARC has concluded that PCB carcinogenic to laboratory animals and probably also for humans. They have also been classified as substance for which there is evidence of endocrine disruption in an intact organism.

Ortho-PCBs are congeners of PCBs that have one or more chlorines in ortho-position (positions 2 or 6). Non-ortho PCBs can take a totally flat (planar) conformation, which is nearer to that of dioxins. Chlorines in para-positions appear to be more readily

biodegraded, thus ortho-ongeners are available in the environment at higher concentrations than non-ortho congeners.

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Dioxins and furans

Chemical Name: PCDDs ($C_{12}H_{(8-n)}Cl_nO_2$) and PCDFs ($C_{12}H_{(8-n)}Cl_nO$) may contain between 1 and 8 chlorine atoms. Dioxins and furans have 75 and 135 possible positional isomers, respectively.

CAS Number: Various (2,3,7,8-Tetra CDD: 1746-01-6; 2,3,7,8-TetraCDF: 51207-319).

Properties: Solubility in water: in the range $0.43 - 0.0002 \text{ mg.l}^{-1}$ at 25°C ; vapour pressure: $2 - 0.007 \times 10^{-6} \text{ mm Hg}$ at 20°C ; $\log K_{ow}$: in the range 6.60 – 8.20 for tetra- to octa-substituted congeners.

Discovery/Uses: They are by-products resulting from the production of other chemicals and from the low-temperature combustion and incineration processes. They have no identified use.

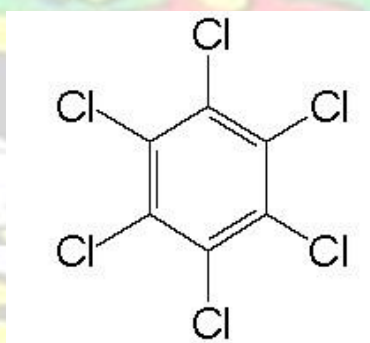
Persistence/Fate: PCDDs/Fs are branded by their fat loving, semi-volatility and resistance to degradation (half-life of TCDD in soil of 10-12 years) and to long-range transport. They are also well-known for their potential to bio-concentrate and biomagnify under typical environmental conditions.

Toxicity: The toxicological effects reported refers to the 2,3,7,8-substituted compounds (17 congeners) that are agonist for the AhR. All the 2,3,7,8-substituted PCDDs and

PCDFs plus coplanar PCBs (with no chlorine substitution at the ortho positions) show the same type of biological and poisonous response. Probable effects consist of dermal toxicity, reproductive effects, immunotoxicity and teratogenicity, endocrine disruption and carcinogenicity. Currently, the only persistent effect linked with dioxin exposure in humans is chloracne. The main sensitive groups are fetus and neonatal infants. Effects on the immune systems in the mouse have been found at doses of $10 \text{ ng.kg}^{-1} \text{ bw. day}^{-1}$, while reproductive effects were seen in rhesus monkeys at $1\text{-}2 \text{ ng.kg}^{-1} \text{ bw.day}^{-1}$. Biochemical effects have been seen in rats down to $0.1 \text{ ng.kg}^{-1} \text{ bw.day}^{-1}$. In a re-evaluation of the TDI for dioxins, furans (and planar PCB), the WHO decided to recommend a range of $1\text{-}4 \text{ TEQ pg.kg}^{-1} \text{ bw}$, although more recently the acceptable intake value has been set monthly at $1\text{-}70 \text{ TEQ pg.kg}^{-1} \text{ bw}$.

HCB (hexachlorobenzene)-

HCB has been used extensively in Australia as a fungicide for the protection of grain in storage. It also exists as a contaminant in the production of other chlorinated solvents (e.g. carbon tetrachloride) and in the production of nitroso-rubber for tires so it can enter the environment via surface run off from road



Chemical Name: Hexachlorobenzene (C_6Cl_6)

CAS Number: 118-74-1

Properties: Solubility in water: $50 \mu\text{g.l}^{-1}$ at 20°C ; vapour pressure: 1.09×10^{-5} mm Hg at 20°C log K_{ow} : 3.93-6.42

Discovery/Uses: It was first introduced in 1945 as fungicide for seed treatments for grain crops, and used to make ammunition, fireworks and synthetic rubber. Today it is chiefly a by-product in the production of a huge number of chlorinated compounds, predominantly lower chlorinated benzenes, solvents and several pesticides, but this problem does not already exist in Europe. HCB is emitted to the atmosphere in flue gases generated by incineration facilities and metallurgical industries.

Persistence/Fate: HCB has an estimated half-life in soils of 2.7-5.7 years and of 0.54.2 years in air. HCB has a relatively high bioaccumulation potential and long half-life in biota.

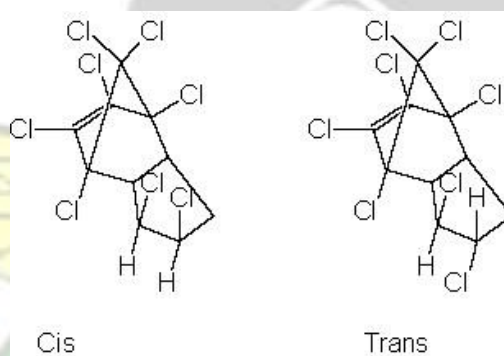
Toxicity: Many of the available acute and chronic aquatic toxicity studies failed to demonstrate effects at or below the solubility limit, but based on validated long-term studies for fish, crustaceans and algae, a 90 days study on the freshwater fish *O. Mykiss* revealed the lowest NOEC of $3.7 \mu\text{g.l}^{-1}$. The acute toxicity of HCB is low with LD_{50} values of 3.5 mg.kg^{-1} for rats. Mild effects of the [rat] live have been observed at a daily dose of 0.25 mg.kg^{-1} bw. HCB is known to cause liver disease in humans (prophyria cutanea tarda) and has been classified as a possible carcinogen to humans by IARC.

Other organochlorines:

Chlordane is a cyclodiene that was used extensively in home and agricultural applications. Chlordane is a word that represents a group of a large number (140) of

individual compounds. A few of them are: cis-nonachlor, trans-nonachlor, cis-chlordane, trans-chlordane, and oxychlordane. Chlordane data are frequently expressed as the sum of several of the most abundant and persistent components and metabolites of the technical chlordane mixture. Like DDT, chlordane compounds are extremely persistent in the environment, resistant to metabolism, biomagnify in aquatic food webs and have a strong affinity for lipid.

Cyclodienes: Cyclodienes were developed after World War II. In general, they are persistent insecticides and are steady in soil. They are used in greater quantity as soil insecticides for the control of termites and soil-borne insects.



Trans-Nonachlor

Trans-Nonachlor is one of the major constituents of the insecticide chlordane. It was used broadly prior to 1983. Its use was cancelled after 1988 due to fear of the threat of cancer. Trans-nonachlor is the most bioaccumulative of the chlordanes.

Chlorophenols

Chlorophenols are synthetic organic compounds which have fungicidal and bactericidal properties. They have primarily been used for long-term wood preservation and for short-term wood protection to control sap stain and mold on freshly cut lumber. Two of

the key members of this family used for wood preservation are pentachlorophenol (PCP) and tetrachlorophenol (TCP).

Other PTS of emerging concern in Europe

Atrazine

Chemical Name: 2-Chloro-4-(ethylamino)-6-(isopropylamino)-s-triazine

(C₁₀H₆Cl₈). CAS Number: 19-12-24-9

Properties: Solubility in water: 28 mg/L at 20°C; vapour pressure: 3.0×10^{-7} mm Hg at 20°C; log K_{ow}: 2.34

Discovery/Uses: Atrazine is a selective triazine herbicide used to control broadleaf and grassy, sorghum, weeds in corn, sugarcane, Christmas trees, pineapple and other crops, and in conifer reforestation plantings. It was discovered and introduced in the late 50's. Atrazine is still widely used today because it is economical and effectively reduces crop losses due to weed interference.

Persistence/Fate: The chemical does not adsorb strongly to soil particles and has a lengthy half-life (60 to > 100 days). Atrazine has a high potential for groundwater contamination despite its moderate solubility in water.

Toxicity: The oral LD₅₀ for atrazine is 3090 mg/kg in rats, 1750 mg/kg in mice, 750 mg/kg in rabbits, and 1000 mg/kg in hamsters. The dermal LD₅₀ in rabbits is 7500 mg/kg and greater than 3000 mg/kg in rats. Atrazine is practically nontoxic to birds. The LD₅₀ is more than 2000 mg/kg in mallard ducks. Atrazine is slightly toxic to fish and other aquatic life. Atrazine has a low level of bioaccumulation in fish. Available data regarding atrazine's carcinogenic potential are inconclusive.

Lindane (γ -HCH)

Chemical Name: 1, 2, 3, 4, 5, 6-Hexachlorocyclohexane (mixed isomers) ($C_6H_6Cl_6$).

CAS Number: 608-73-1 (γ -HCH, lindane: 58-89-9).

Properties: γ -HCH: Solubility in water: 7 mg.l^{-1} at 20°C ; vapour pressure: 3.3×10^{-5} mm Hg at 20°C ; $\log K_{ow}$ 3.8.

Discovery/Uses: There are two principle formulations: ‘technical HCH’, which is a mixture of various isomers including α -HCH (55-80%), β -HCH (5-14%) and γ -HCH (8-15%) and ‘lindane’ which is essentially pure HCH. Historically, lindane was one of the most widely used insecticides in the world. Its insecticides properties were discovered in the early 1940s.

It controls a large range of sucking and chewing insects and has been used for seed treatment and soil application, in household biocidal products, and as textile and wood preservatives.

Persistence/Fate: Lindane and other HCH isomers are relatively persistent in soils and water, and half-life generally greater than 1 and 2 years, respectively. HCH are much less bioaccumulative than other organochlorines because their relatively low lipophilicity. On the contrary, their relatively high vapour pressures, particularly of the α -HCH isomer, determine their long-range in transport in the atmosphere.

Toxicity: Lindane is moderately toxic for invertebrates and fish, with LC_{50} values of 20-90 $\mu\text{g.l}^{-1}$. The acute toxicity for mice and rats is moderate with LD_{50} values in the range

of 60-250 mg.kg⁻¹. Lindane resulted to have no mutagenic potential in a number of studies but an endocrine disrupting activity.

Polyaromatic hydrocarbons (PAHs)

Chemical Name: PAHs is a group of compounds consisting of two or more fused aromatic rings.

CAS Number:

Properties: Solubility in water: 0.00014 -2.1 mg.l⁻¹ at 25°C; vapour pressure: from 0.0015 x 10⁻⁹ to 0.005 Hg at 25°C; log K_{ow}: 4.79-8.20

Discovery/Use: Most of these are formed during incomplete combustion of organic material and composition of PAHs mixture varies with the source(s) and also due to selective weathering effects the environment.

Persistence/Fate: Persistence of the PAHs varies with their molecular weight. The low molecular weight is most easily degraded. The reported half-lives of naphthalene, anthracene and benzo(e)pyrene in sediments are 9, 43 and 83 hours, respectively, whereas for higher molecular weight PAHs, their half-lives are several years in soil/sediments. The BCFs in aquatic organisms frequently range between 100-2 000 increases with increasing molecular size. Due to their wide distribution, environmental pollution by PAH aroused global concern.

Toxicity: The acute toxicity of low PAHs is moderate with an LD₅₀ of naphthalene and anthracene in rat and 18 000 mg.kg⁻¹ body weight respectively, whereas the higher PAHs exhibit higher toxicity and LD₅₀ benzo(a)anthracene in mice is 10mg.kg⁻¹ body weight. In *Daphnia pulex*, LC₅₀ for naphthalene is 1.0mg.kg⁻¹ phenanthrene 0.1 mg.l⁻¹ and for benzo(a)pyrene is 0.005 mg.l⁻¹. The critical effect of many PAHs in man is their

carcinogenic potential. The metabolic action of these substances produces intermediates that covalently with cellular DNA. IARC has classified benz[a]anthracene, benzo[a]pyrene, and dibenzo anthracene as probable carcinogenic to humans. Benzo[b]fluoranthene and indeno[1,2,3-c,d]pyrene classified as possible carcinogens to humans.

Endosulfan

Chemical Name: 6,7,8,10,10-Hexachloro-1,5,5a,6,9,9a-hexahydro-6,9-methano-2,4,3benzo-diaxathiepin-3-oxide (C₉H₆Cl₆O₃S).

CAS Number: 115-29-7.

Properties: Solubility in water: 320 µg.l⁻¹ at 25°C; vapour pressure: 0.17 x 10⁻⁴ mm Hg at 25°C; log K_{ow}: 2.23-3.62.

Discovery/Uses: Endosulfan was first introduced in 1954. It is used as a contact and stomach insecticide and acaricide in a great number of food and nonfood crops (e.g. tea, vegetables, fruits, tobacco, and cotton) and it controls over 100 different insects pests. Endosulfan formulations are used in commercial agriculture and home gardening and for wood preservation. The technical product contains at least 94% of two pure isomers, α- and β-endosulfan.

Persistence/Fate: It is moderately persistent in the soil environment with a reported average field half-life to 50 days. The two isomers have different degradation times in soil (half-lives of 35 and 150 days for α- and β- isomers, respectively, in neutral conditions). It has a moderate capacity to adsorb to soils and it is not likely to leach to groundwater. In plants, endosulfan is rapidly broken down to the corresponding sulphate, on most fruits and vegetables, 50% of the parent residue is lost within 3 to 7 days. Toxicity: Endosulfan is highly to moderately toxic to bird species (Mallards: oral

LD₅₀ 31 – 243 mg.kg⁻¹) and it is very toxic to aquatic organisms (96-hour LC₅₀ rainbow trout 1.5 µg.l⁻¹). It has also shown high toxicity in rats (oral LD₅₀: 18 – 160 mg.kg⁻¹, and dermal: 78 – 359 mg.kg⁻¹).

2.7 Movement of Pesticides in Agric and Forestry Land Use Systems

Pesticides get into surface and ground water through atmospheric precipitation after they have been applied by the human community. They also get into the soil through run-offs, sorption, leaching and evaporation from plants, trees and crops after application. Through Bioaccumulation these pesticides get into the soils and into the water bodies. This is depicted in the framework below.

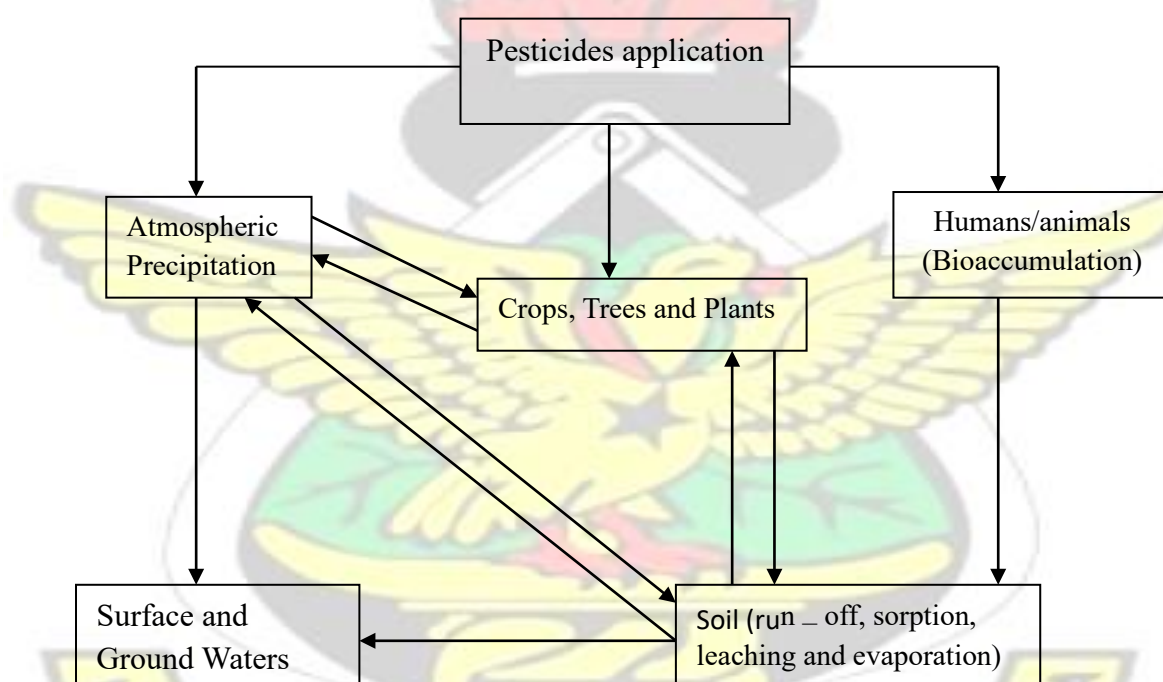


Fig: 2.1 Conceptual Framework of Pesticides Movement in the Agricultural and Forestry Land Uses deduced from theories and concepts (Source: Author's construct).

(Source: Author's construct)

2.8 Sources of Entry of Pesticides in the Environment

Organochlorine insecticides enter the environment as the consequences of human activities in the following ways:

- Deliberate application of the insecticide: This is the major source of environmental contamination.
- The deposits results from the application of chemicals to control agricultural pests and causes public health problems.
- Misplacements and leakage during transportation, sale or storage processes linked to the manufacture of insecticides.

These insecticides enter the environment and are absorbed by various constituents of the environment and transported to other places mainly by air and water movements. They are picked up by various biological systems and are at the same time chemically or biologically transformed to other nontoxic or toxic compounds in the environment (Aroud *et al.*, 2007, Raposo and Nilva, 2007) calculated that roughly 10,000kg/yr of pesticides are transported by the Mississippi river system to the Gulf of Mexico. The widespread use and disposal by farmers, institutions and the general public provides other possible sources of pesticides in the environment. Pesticides which are sprayed can move through the air and eventually end up in other parts of the environment such as in soil or water.

Pesticides which are applied directly to the soil may be washed off the soil to nearby bodies of surface water or may percolate through the soil to lower soil layers and

groundwater. The application of pesticides directly to bodies of water for weed control or indirectly as a result of leaching from runoff may lead to build up of pesticides in water, but may also contribute to the levels through evaporation (Darko and Aquaah, 2006). The persistence of pesticide residues in the soil and their movement in the water–soil system are key aspects in their environmental behaviour. Pesticides are primarily moved from agricultural fields to surface waters in surface run-off (Richards, 2003). The amount lost from fields and transported to surface waters depends on several factors which include soil type, weather, agricultural practices, topography and chemical and environmental properties of individual pesticides (Leonard, 1987 and Wagenet, 1987). This list of possibilities suggests that the movement of pesticides in the environment is very complex with transfers occurring continually among different environmental compartments. In many instances, these exchanges exist not only between areas that are close together (such as a local pond receiving some of the herbicide application on adjacent land) but also may involve transportation of pesticides over long distances. Since, organochlorines are very resistant to degradation by any means and thus remain unchanged in the environment for long periods of time, they can move over long distances (Fleming *et al.*, 1994). Knowledge of organochlorine pesticide movement in the environment is necessary to minimize unnecessary release into the environment.

2.9 Pesticides in Surface and Ground Water Bodies

A fundamental contributor to the “Green Revolution” has been the development and application of pesticides for the control of a wide variety of pests that would otherwise diminish the quantity and quality of food produce (Tariq *et al.*, 2007). Notwithstanding the increased food production, massive use of pesticides has caused serious

contamination of aquifers and surface water bodies, decreasing the quality of water for human consumption (Carvalho, 2006; Camargo and Alonso, 2006).

Pesticide residues have been a catch cry of environmental and consumer groups since the mid -1960's when Rachel Carson 1962, drew the public's attention to the deleterious ecological effects of organochlorine pesticides especially 1, 1, 1-trichloro2, 2-bis-(4'-chlorophenyl) ethane (DDT), which were in widespread use at that time. Pesticides can reach surface water through runoff from treated plants and soil. There is a widespread water contamination by pesticides. The results of a complete set of studies done by the U.S. Geological Survey (USGS) on major river basins across the country in the early to mid- 90s yielded amazing results. Over 90 percent of fish and water samples from all streams had one, or more often, several pesticides (Kole *et al.*, 2001). Pesticides were found in all samples from major rivers with mixed agricultural and urban land use activities (Bortleson and Davis, 1995). The USGS also found that concentrations of insecticides in urban streams commonly exceeded guidelines for protection of aquatic life (USGS, 1999). Twenty-three pesticides were detected in waterways in the Puget Sound Basin, as well as 17 herbicides. Works by the USGS indicated that, lots of pesticides were detected in urban streams than in agricultural streams (US DoI, 1995).

Water samples from rivers in the intensive cocoa growing areas in the Ashanti and Eastern Regions of Ghana have been found to contain lindane and endosulfan (Acquaah, 1997). Water samples from a vegetable farming community in the Ashanti Region (Akumadan) and different areas of Ghana revealed the presence of significant levels of pesticide residues. The Volta Lake was also seen to be slightly contaminated with lindane, DDT, DDE and endosulfan (Ntow, 2005). In Oda, Kowire and Atwetwe rivers in Ghana, mean pesticide concentrations found in water samples for lindane and

endosulfan were 19.4 and 12.4 $\mu\text{g}\cdot\text{L}^{-1}$ (Oda), 16.4 and 17.9 $\mu\text{g}\cdot\text{L}^{-1}$ (Kowire) 20.5 and 21.4 $\mu\text{g}\cdot\text{L}^{-1}$ (Atwetwe), respectively.

Pesticides are able to leach and contaminate ground water. With reference to the USGS, at least 143 different pesticides and 21 transformation products have been found in the ground water, as well as pesticides from every major chemical class. From the past two decades, detections have been found in the ground water of more than 43 states (Waskom, 1994). Contamination of ground water is of worry because ground water supplies most populations with Drinking water (Neil and Raucher, 1998). During one survey in India it has been found that 58% of drinking water samples drawn from various hand pumps and wells around Bhopal are contaminated with Organochlorine pesticides above the EPA standards (Kole and Bagchi, 1995). Once ground water is polluted with poisonous chemicals, it may take a lot of years for the contamination to dissipate. Cleanup may also be very expensive and intricate, if not impossible (US EPA, 2001; Johnson and Ware, 1991 and US EPA, 1999).

2.10 Pesticides in Sediments and Soils

The natural processes that govern the fate and transport of agrochemicals especially pesticides in the environment can be grouped into the broad categories of runoff, leaching, sorption, volatilization, degradation and plant uptake (Goldman and Koduru, 2001). Once applied to soil, a number of things may happen to an agrochemical (Glover-Amengor *et al.*, 2008). It may be taken up by plants or ingested by animals, worms, insects or microorganisms in the soil. It could travel downward in the soil and either stick to particles or dissolve. The pesticide possibly will vaporize and get into the atmosphere, degrade via solar energy or break down via microbial and chemical pathways into other less toxic compounds. Pesticides may leach out of the root zone or

wash off the surface of land by rain or irrigation water, eventually ending in the sediments through the water column. Evaporation of water at the ground surface can lead to upward flow of water and pesticide (Glover-Amengor *et al.*, 2008). The fate of pesticides applied to soil depends largely on two of its properties: persistence and sorption (Carvalho, 2006; Tariq *et al.*, 2007) and Goldman and Koduru, 2001). Two other pathways of pesticide loss are removal in the harvested plant and volatilization into the atmosphere, which subsequently impact water, sediment, soil, and air quality negatively and creating problems for agricultural workers who could be pesticide intoxicated via inhalation at the treated areas.

Studies in Ghana (Ntow, 2005; Darko and Acquaaah, 2008; Glover-Amengor *et al.*, 2008 and Nuerter *et al.*, 2007) have reported the detection of different kinds of pesticides especially organochlorines in soil and sediment in different parts of Ghana. They observed that the pesticides inhibit bacterial population resulting in inhibited nitrification and blockage of other soil microorganisms of both organic and inorganic constituents in the soil, hence decreasing the soil fertility. Pesticide application had a higher effect on fungal population.

Studies of the solubility of pesticides and its sorption on soil are known to be inversely related, increased solubility implies less sorption. One of the most useful indices for quantifying pesticide sorption on soils is the partition coefficient (K_{oc}) defined as the ratio of pesticide concentration in the sorbed state (bound to soil particles) to solution-phase (dissolved in the soil-water), thus, for a known amount of pesticide applied, the lesser the K_{oc} value, the greater the concentration of pesticide in solution. Pesticides with small K_{oc} values are more likely to be leached compared to those with large K_{oc}

values (Mavura and Wangila, 2004). Studies on depletion of herbicides in two soil ecosystems in Ghana by Afful *et al.*, 2008, indicated that the kinetics involved in the process of depletion of the herbicides to a higher degree could be described as first order reaction kinetics and the half-life of herbicides ranged between 14.8 and 32.2 days.

Apoh *et al.*, 1995 in their study of the persistence of lindane in Ghanaian coastal savannah topsoil reported that the dissipation pattern favours second order kinetics and persistence depend on the organic matter content of the soil. Sunlight induced reactions may contribute to the chemical transformation of organic pollutants. Recent evidence (Goldman and Koduru, 2001, Goody *et al.*, 2002, suggests that organic pollutants may react through both direct and indirect photochemical pathways. Many river basins are eutrophic and contain higher amounts of dissolved organic matter (DOM). In connection with these, studies of both DOM and nitrate were shown to help in the degradation of pesticides by sunlight. Moisture and organic matter content was found to facilitate depletion of herbicides in soils (Glover-Amengor *et al.*, 2008; Afful *et al.*, 2008 and Apoh *et al.*, 1995). The degree to which this could occur may highly depend upon the composition and amount of photosensitizers present. Most of the dissolved organic matter in natural waters is comprised of decomposed organic matter and extracellular products as well as amorphous humic substances which may include a variety of chromophoric functional groups that absorb sunlight.

2.11 Toxicity of pesticides

Toxicity of an individual pesticide to the pest is prominently determined by its structure, a different moiety attached to the parent compound, their special arrangement within

molecules, nature of substituent, polarity, symmetry and asymmetry of molecules, the solubility and sorption values (Belta *et al.*, 2004).

Toxicity may be defined as the quality of being poisonous or harmful to animals or plants (FAO/WHO, 1998). Toxicity of pesticides can be measured in several ways but generally based on test results on rats and other animals.

Acute toxicity of a substance is characterized by LD50 (lethal dose) (Berger, 1988). LD50 is the dosage of pesticide (mg/kg body weight) needed to kill 50% of tested animals. The smaller the LD50 the more toxic the chemical is. Toxicity results obtained are only guiding principles. A pesticide that is toxic to rats is not necessarily equally poisonous to people or other animals. It can therefore be used to estimate the hazard of a particular poison. To estimate the lethal dose of humans, the LD50 should be multiplied by the body weight in kg (Berger, 1988). Chronic toxicity is the propensity to cause long term delayed effects, following repeated low level exposure. The most widely used toxicological measurement of chronic toxicity is the reference dose (RFD). The reference dose is derived by taking the highest that has no observable adverse effect in tested animals and declining it by a safety factor typically 100. The results in theory represent doses that exert unappreciable risks to humans, although the uncertainties inherent in extrapolation from animals to humans must be acknowledged. As with the LD50, the smaller the RFD, the more toxic the chemical is (Caudle *et al.*, 2005).

Pesticides due to their great structural variety affect systems of humans and animals in many places through a variety of reaction mechanisms (Jayashree and Vusudevan 2007). Poor nutritional status, extreme physical stress and a high rate of infectious diseases many affect persons detoxification and excretion capacities (Ntow *et al.*, 2008). The United Nations (U.N) has warned that about 30% of pesticides marketed in developing

nations contain toxic substances which pose a serious threat to both human health and the environment (WHO/UNDP, 1990). Organochlorine pesticides have become ubiquitous contaminant and have been implicated in a broad range of deleterious health effects in laboratory animals and man.

The toxic effects include reproductive failure, immune system malfunction (Kolpin *et al.*, 1998), endocrine disruption (Ize *et al.*, 2007) and breast cancer (Garabrant *et al.*, 2001). Studies in developing countries have related long term pesticide exposure to cancer, adverse reproductive effect and damage to the immune system and death (Maroni and Fiat 1993, Repto and Balige, 1996). Twelve farmers in the Upper East Region of Ghana died as a result of misapplication of pesticides (Ghanaian Times, 2010). The WHO has indicated that the total worldwide pesticide poisoning could be as high as 2 million cases a year with twenty thousand poisoning resulting in death (WHO/UNDP, 1990). The social impact of these poisoning fatalities is immeasurable, as it is usually the man who also happens to be the head of the family who is poisoned leaving the woman and children to face destitution.

2.12 Problems Associated with Pesticide Usage in Developing Countries

2.12.1 Exports to Countries without Pesticides Control

Most countries do not have the infrastructure or the resources to adequately regulate and monitor the availability and use of pesticide. The FAO/WHO (1998) study found 81 countries with no detectable pesticide control measures. In 2005, FAO estimated that there were still some 45 countries that have no detectable regulations, though many of these nations are in the process of setting up some form of control (WHO/FAO, 2005). In its drive to increase food production, to feed the growing population, Ghana has been receiving tonnes of pesticides in its various forms for use in agriculture (Afful *et al.*,

2010). These products come into the country in the form of purchased products, donations and /or grants in support of agriculture.

2.12.2 Effects of pesticides on Beneficial, Non – targeted Organisms

When pesticides, toxic to organisms end up in the environment, they may kill non – targeted beneficial organisms. Studies in India showed that mosquito consuming exotic fish species and natural enemies of urinary schistosomiasis cannot survive in the water due to intensive pesticide application (Aroud *et al.*, 2007). Bioaccumulation and biomagnifications usually occurs as the pesticides travel higher up the food chain with detrimental effects on higher organisms especially man (William *et al.*, 2008). The effect on man is compounded by the fact that drinking water is usually taken directly from streams, rivers or lakes, instead of from ground water as is usually the case in Ghana. The presence of pesticides in soil can alter the composition and circulation of nutrient (Ntow, 2001). It may also exert subtle effects on the organism's activities. This may degrade soil fertility, ultimately producing an essentially biological sterile soil (Bariada – Pereira *et al.*, 2005).

2.13 Potential entry into Food Chain

The use of pesticides provide benefits for increasing agricultural production, but by bioaccumulation and biomagnifications through the food web, their highly persistent properties and potential threat to human health can eventually become a risk or threat to both animal and human. Society now pays a high price for its use of pesticides. Pesticide-control measures cost approximately \$4.1 billion annually, not including the in-direct environmental and public-health costs, which total more than \$2.2 billion

annually (Pimentel et al. 1991). Perhaps the most serious social and environmental costs related to pesticide use are the human pesticide poisonings.

Annually approximately 20,000 accidental poisonings occur, mostly from agricultural pesticides, with 2000 cases requiring hospitalization. These poisonings result in approximately 50 fatalities per year. Pesticides are also implicated in numerous other human diseases, including cancer and sterility. An estimated 6000 human cases of pesticide-induced cancer occurs each year (EPA 1987). The threats of pesticides could range from cancers, eye irritations, skin mutation, foetus destruction and many more. These are discussed in details in order to appreciate damages that pesticides could cause when they get into the food web.

2.13.1 Carcinogenicity

Carcinogenicity of pesticides defines the ability of pesticides to cause cancers. Prior to any pesticide receiving its registration from the USEPA, numerous studies must be conducted to determine the hazards of the particular pesticide and its use. For pesticides that will be used on food and some non-food commodities, studies are conducted to determine their potential carcinogenicity. Studies are required in laboratory settings involving both sexes of two species (mice and rats). The results of the studies are peer-reviewed by the Cancer Assessment Review Committee. This committee then recommends a cancer classification for the active ingredient under review. The classification determines how USEPA regulates the pesticide to minimize human risk. These studies may be reviewed again when a pesticide undergoes reregistration and the cancer classification may be re-evaluated, particularly if new studies have been submitted. To indicate possible cancer risk posed by a pesticide, USEPA ranks how

strongly carcinogenic the chemical is and the potential for human exposure. USEPA currently uses a 5-tiered classification system with pesticides that have undergone review since 1999. The classes in this system include:

1. Carcinogenic to humans. USEPA assigns this descriptor to pesticides when there is convincing epidemiologic evidence demonstrating causality between human exposure and cancer. It is based on compelling evidence of carcinogenicity in animals and mechanistic information in animals and humans demonstrating similar mode(s) of carcinogenic action. The only actively registered pesticides in this group are the arsenicals, used for wood treatment. The use of arsenic for wood treatment has been severely restricted since the end of 2003.
2. Likely to be carcinogenic to humans. This class is used when the available tumour effects and other key data for a pesticide are adequate to demonstrate carcinogenic potential to humans. Data within this class range from an association between human exposures to the pesticide and cancer to the weight of experimental evidence showing animal carcinogenicity by a mode of action assumed to be relevant to humans. Imazalil, a postharvest fungicide used in Florida citrus production, fits into this tier.
3. Suggestive evidence of carcinogenicity, but not sufficient to assess human carcinogenic potential. Examples of this assessment may include:
 - Evidence showing a marginal increase in tumours that may be exposure-related;
 - Evidence that is observed only in a single study; or
 - Evidence that is limited to certain high-background tumours in one sex of one species.

In this classification, further studies would be needed to determine human carcinogenic potential. Pyrethrins, insecticides used in a wide array of settings, are an example of active ingredients classed in this category.

4. Data are inadequate for an assessment of human carcinogenic potential. USEPA uses this descriptor whenever there is a lack of pertinent or useful data or where existing evidence is conflicting. For example, some indication is suggestive of carcinogenic effects, but other equally important evidence does not confirm a concern. An example classed in this tier is pyraclostrobin, a biological-based fungicide applied to fruit and vegetable crops.
5. Not possible to be carcinogenic to humans. USEPA places pesticides in this class when the findings of carcinogenicity studies reveal:
 - Evidence that widespread human practice demonstrates the lack of carcinogenic effect;
 - Animal evidence that shows a lack of carcinogenic effects in at least two well-designed and well-conducted studies in two appropriate animal species;
 - Any carcinogenic effects revealed in animals are not considered relevant to humans;
 - Evidence that carcinogenic effects are most likely not caused by a particular route of exposure; and,
 - Proof that carcinogenic effects are not expected below a defined dose range.
- The herbicide glyphosate, used extensively in agricultural, residential and non-crop settings, is an example of a pesticide classed in this tier (Fishel, 2011).

A study conducted in 2001 of Canadian men showed that the risk of non - Hodgkin's lymphoma (a type of cancer) for men exposed to glyphosate more than two days per year was two times greater than the risk for men who were either unexposed or exposed for less than two days per year. The study was conducted at the University of Saskatchewan (Canada), (McDuffie *et al.*, 2001). Another study was undertaken in 2002 of Swedish men showed that glyphosate exposure was significantly associated with an increased risk of non-Hodgkin's lymphoma. The study was conducted by oncologists at Örebro University (Sweden), (Hardell, 2002). A further study in 2003 which reviewed three Midwestern farmers showed that exposure to glyphosate was associated with an increased incidence of non-Hodgkin's lymphoma. These studies were carried out by the National Cancer Institute (De Roos *et al.*, 2003).

2.13.2 Mutagenicity

Mutation refers to changes in cells organisms either by artificial or natural factors. Four laboratory studies published in the late 1990s demonstrated the ability of glyphosate and glyphosate-containing herbicide products to cause genetic damage (mutation), (Bolognesi *et al.*, 1997; Lioi *et al.*, 1998). Two of the studies, both done by scientists at Italy's Istituto Nazionale per la Ricerca sul Cancro exposed mice to glyphosate and a Roundup herbicide by injection (Bolognesi *et al.*, 1997; Peluso *et al.*, 1998). One study also exposed human blood cells to the same chemicals (Bolognesi *et al.*, 1997). The first study showed that in mice both glyphosate and the Roundup herbicide damaged DNA (the genetic material in cells) in the liver and kidney and caused a different kind of genetic damage in bone marrow cells. Both substances also caused a third type of genetic damage in human blood cells. In general, the Roundup used in these experiments was more potent than glyphosate

(Bolognesi *et al.*, 1997).

The second study showed that a Roundup herbicide damaged DNA in the liver and kidney of mice (Peluso *et al.*, 1998). The other two studies were done at the Università della Basilicata (Italy). Both used blood cells, one from cows and the other from humans. Both showed that glyphosate caused a significant increase in the number of abnormal chromosomes (Lioi *et al.*, 1998). A more recent (2004) study from the Institute of Biology and Environmental Sciences (Germany) showed that DNA damage occurred in human connective tissue cells when they were exposed to glyphosate and hydrogen peroxide, a molecule that is commonly found in living things (Lueken *et al.*, 2004). The National Institute for Occupational Safety and Health describes glyphosate as a “mutagen” (NIOSH, 2004).

2.14 Management of Pesticide

Risks associated with the use of pesticides are multifaceted and there is no single effective approach to their resolution. To find effectual solutions, it is significant that activities be considered in the perspective of an overall programme of crop protection and government policy with respect to pesticide use. The International Code of Conduct on the supply and Use of Pesticides were elaborated and contained voluntary standards of conduct to be used, as a point of reference for national legislation.

Furthermore, other international policy mechanisms were adopted to address one or more areas of the pesticide life-cycle. These include the Codex Committee on Pesticide Residues of the Codex Alimentarius, the Montreal Protocol on Substances that Deplete the Ozone Layer, the Basel Convention on the Control of Transboundary Movements of

Hazardous Wastes and their Disposal, the Rotterdam Convention on the Prior Informed Consent Procedure for Certain Hazardous Chemicals and Pesticides in International Trade, and the Stockholm Convention on Persistent Organic Pollutants.

In response to the above a Joint Meeting of the FAO Panel of Experts on the Use of Pesticides in Agriculture and the WHO Expert Committee on Pesticide Residues was held in 1961. The Meeting recommended to the Directors-General of FAO and WHO the assessment of the toxicological and other relevant data on pesticides known to leave residues in food when used. The evaluations could include the estimation of a suitable allowable daily intake (ADI) and an explanation of its derivation. To achieve this recommendation the first Joint Meeting on Pesticide Residues (JMPR) was held in 1963. In 1966, JMPR considered both ADIs and maximum residue limits for the first time. Joint Meetings are held annually, and since 1963 approximately 230 pesticides have been evaluated, many of them on several occasions (F.A.O, 2009).

JMPR serves as a scientific advisory body to FAO and WHO member governments, and to the Codex Alimentarius Commission. All countries must have access to reliable risk assessments of chemicals in food, but comparatively few have the expertise and funds available to undertake separate risk assessments on large numbers of chemicals. JMPR carries out a vital role in providing a reliable source of guidance, and some countries use information from JMPR in formulating their own regulatory programmes. In the same way, CCPR gives recommendations, based on the assessments of JMPR, on suitable standards for pesticide residues in food.

The membership of the JMPR is done by both FAO and WHO. FAO is responsible for choosing members to deal with residue and analytical aspects, while WHO is accountable for selecting members to deal with the toxicological evaluations of the substances under consideration. The choice of members, who serve in their individual capacities as experts, is made only after a cautious deliberation of the scientific credentials of the various candidates. A balance of scientific proficiency and other experience is considered essential. FAO and WHO meet the expenditures of experts' turnout at Joint Meetings (F.A.O, 2010).

Pesticide regulation works to protect health and our environment by promoting safe and proper use of pesticides (Hanson, 1988). Though pesticide regulation varies from country to country, pesticides are marketed across international borders. To deal with inconsistencies in regulations amongst countries, delegates to a conference of the United Nations, food and agricultural organization adopted international code of conduct on the supply and use of pesticide in 1995 to form voluntary standards of pesticide regulations for different countries. The code was updated in 1998 and 2002 (WHO/F.A.O, 2005).

The food and agricultural organization (F.A.O) claims that the code has raised awareness about pesticide hazards and decreased the number of countries without restrictions on pesticide use. (WHO/F.A.O, 2005). Other efforts to improve international trade are United Nations London Guidelines for the exchange of information on chemicals in international trade and limited Codex Alimentarius Commission. The former seeks to execute procedures for ensuring that prior uniformed consent exist between countries buying and selling pesticides whilst the latter seeks to create uniformity for maximum levels for pesticide residue. Both initiatives operate on voluntary basis. Pesticide safety

education and pesticide applicator regulations are designed to protect the public from pesticide misuse but do not eliminate all misuse (Youdeowei, 1989).

2.14.1 Information Exchange and Cooperation

Information management is very vital in sound management of chemicals. Developing countries are often faced with this challenge. Modern information and communication technologies are lacking. The United Nations Environment Programme (UNEP) Chemicals and the United States Environmental Protection Agency (US-EPA) have undertaken a two-year project in Ghana to supply equipment and training on access to chemical information using the Internet. The EPA is the national coordinating agency responsible for obtaining local commitment and organizing the national activities. The CIEN project aims at:

- Enhancing the capacities of countries to gain and disseminate information required for their national decision-making especially in the field of chemical management.
- Creating the framework for the right to use and exchange of information to help national, regional and international activities for proper chemicals management.
- Helping appropriate government organisations in developing countries to access the internet, providing training for chemical managers and appropriate stakeholders on how to get chemical information on the internet.
- Enhancing the establishment of a national/regional network for chemical information swap between chemical management stakeholders.

The project catalyses the building of the national institution's (EPA's) own information database related to chemicals management as the basis of information exchange network that would connect the main agencies involved in chemicals management. Some of the

key institutions involved in the project are CEPS, MoFA, and Ghana Standards Board (GSB). The CIEN project is expected to result in the establishment of infrastructure and technical capabilities to access and exchange chemical information as follows:

- A website in which national and international stakeholders can have access to chemicals information services.
- Train staff in accessing information on chemicals through the internet.
- An institutional kiosk providing information on all actors/stakeholders and their respective informational base.
- Information kiosks and libraries on chemical management, helping the general public to get access to existing bibliographical references about exact subjects and to access them directly from their computers

2.14.2 The Stockholm Convention on Persistent Organic Pollutants

The Stockholm Convention on Persistent Organic Pollutants aims to protect human health and the environment by banning the production and use of some of the most lethal chemicals known to humankind. The Convention became an international law in May 2004, and was ratified by Ghana in 2003. Persistent organic pollutants (POPs) are organic compounds that:

- Do not break down easily in the environment
- Are capable of long-range transport, bioaccumulate in human and animal tissue (and bio magnify in food chains)
- Pose a risk of causing adverse effects to human health and the environment.

There were 12 organochlorine chemicals initially listed as POP's under the Convention in 2004. These are: Pesticides (aldrin, chlordane, DDT, heptachlor, dieldrin, endrin mirex, hexachlorobenzene, and toxaphene), Industrial chemicals – PCBs (polychlorinated biphenyls), (hexachlorobenzene was also used as a pesticide), Unintentional by-products – dioxins and furans (polychlorinated dibenzo-p-dioxins or PCDDs, and polychlorinated dibenzofurans or PCDFs).

An additional nine POP chemicals were listed in 2009. They are: lindane (insecticide with broad applications such as soil, seed and wood treatment, has poisonous effects in laboratory animals and aquatic organisms. Lindane could also be used as a human health pharmaceutical to treat head lice and scabies), alpha hexachlorocyclohexane (HCH) and beta HCH (insecticides, by-products of lindane, potentially carcinogenic to humans and negatively affects wildlife), chlordecone (a pesticide, classified as a possible human carcinogen, is very deadly to aquatic organisms), hexabromobiphenyl (industrial chemical, used as a flame retardant, classified as a possible human carcinogen), tetrabromodiphenyl ether and pentabromodiphenyl ether (commercial pentabromodiphenyl ether) (industrial chemical, used as an additive flame retardant, is toxic for wildlife), hexabromodiphenyl ether and heptabromodiphenyl ether (commercial octabromodiphenyl ether) (industrial chemical, used as an additive flame retardant), pentachlorobenzene (produced unintentionally and used as a chemical intermediate for the production of quintozone, and it is formerly used in dyestuff carriers, as a fungicide and flame retardant and very toxic to aquatic organisms), perfluorooctane sulfonic acid, its salts and perfluorooctane sulfonyl fluoride (an extremely persistent chemical, has many applications e.g., electric and electronic parts, photo imaging, firefighting foam, hydraulic fluids and textiles; binds to proteins in the blood and liver – as opposed to other POPs which partition into fatty tissues).

2.14.3 Implementation of the Stockholm Convention

The Stockholm Convention seeks the elimination or restriction of production and use of all intentionally produced POPs (industrial chemicals and pesticides). It also seeks the continuing minimization and, where possible, eventual elimination of the releases of unintentionally produced POPs such as dioxins and furans. Ghana has prepared and submitted a National Implementation Plan (NIP) for the Stockholm Convention. The NIP assessed Ghana's capacity to implement the Convention and serves as basis for phase out/reduction programmes and ultimately elimination of POPs at the country and global levels (EPA, Ghana, 2009).

2.14.4. Implementation of the Vienna Convention and Montreal Protocol

Under the requirements of the Montreal Protocol, Ghana is expected to stop the use of CFCs by 2010 and to enhance Ghana's compliance with this provision; quotas have been allocated to selected companies.

2.14.5. Implementation of the Basel Convention

The Basel Convention was adopted in 1989 and entered in to force on 5th May 1992 in response to concerns about toxic waste from industrialized countries being dumped in developing countries and countries with economies in transition. The convention controls the passage of harmful waste across international frontiers and adopts a criterion for environmentally sound management of the waste. The EPA of Ghana processes applications for the export and import of hazardous (mostly lead from used batteries) from and into Ghana respectively. Ghana is participating in a number of initiatives for the control of illegal trans-boundary movement of hazardous waste especially e-waste into the country.

2.14.6. Implementation of the Rotterdam Convention

The objective of the Rotterdam Convention is to ensure a mutual responsibility and cooperative efforts among Parties in the international trade of some toxic chemicals in order to guard human health and the environment from potential harm. It is also to add to their environmentally sound use, by enhancing information exchange about their features and to provide for national decision-making process on their import and export and by disseminating these decisions to Parties. Ghana has set a National Action Plan for the Rotterdam Convention and there is a system in place coordinating the preparation of Ghana's import notifications on the chemicals listed in Annex 3 of the Convention as well as reporting (EPA, Ghana, 2009).

2.15 Management of Pesticides in Ghana

In Ghana, pesticide control and management Act (1996) (Act 528) makes the Environmental Protection Agency (EPA) the lead agency responsible for a comprehensive pesticide regulation programme (PCMA, 1996). EPA has the sole authority and responsibility to register all pesticides imported, exported, produced, distributed, advertised, sold and used in Ghana. The Act provides for the control, management and regulation of pesticides in Ghana and to provide for related matters. The objective of regulating pesticides is to protect society from the adverse effects of pesticide without denying access to the benefits of their use. The four main parts of the act are as follows:

- Part I: Regulation of pesticide
- Part II: Licensing of pesticide dealers
- Part III: Enforcement and penalties
- Part IV: General provide

Section 1 of Act 528 states that no person shall import, export, produce, distribute, advertise, sell or use any pesticide in Ghana unless the pesticide has been registered by EPA. Registration enables authorities to exercise control over quality, levels, use, place, labeling, packaging, advertising and disposal of pesticides thus ensuring that the interest of the end users are properly protected. In addition to submitting an application form, the applicant is expected to give a scientific evidence or data in a dossier to support all claim for efficiency and safety of the product to be registered. The dossier must contain sufficient information to effectively address all pertinent issues regarding safety, efficiency, Human toxicology, toxicological labeling, bio efficacy, residue data and ecotoxicology.

Chemical control and management centre of the EPA receives all applications. Subcommittees of Pesticides Technical Committee (PTC) evaluate the applications and submit reports to the PTC. PTC then makes recommendations to the EPA Board based on the report of the subcommittee (PCMA, 1996). EPA Board takes the final decision to register or deny registration of the pesticide. Even though Act 528 was promulgated in 1996, a number of issues prohibited the full and effective implementation of its provisions. Between 2003 and 2004, full operationalization of the Act was initiated. (EPA Ghana, 2008)

Other agencies and organizations that are helping EPA in its implementations are Ghana Ports and Harbors' authority (GPHA), Customs Exercise and Preventive Service (CEPS), Ghana Standards Board (GSB), Ministry of Food and Agriculture (MOFA), Ministry of Lands and Natural Resources (MLNR) and Factory Inspectorate

Department of Ministry of Employment and Social Welfare. According to Youdeowei (1989), the effective control of pesticides in developing countries remains poor due to shortage of personnel, lack of infrastructure, transportation, equipment, very low budgetary allocations and lack of residue analysis facilities. Abate (1996) also pointed out that even though there are regulations concerning the use of pesticides, there are still some pesticides in use that have been restricted in some developing countries.

There is therefore the need to review safety precautions on the use of pesticides in Ghana. The abuse, misuse and the use of a large range of pesticides of moderate to high toxicity in the country, implies high exposures and possible poisoning potentials and would suggest the need for more control and monitoring at national and local levels. An immediate priority in Ghana is an urgent requirement for sustained, low cost and well-targeted training interventions.

2.16. Challenges in the Management of Pesticides in Ghana.

The management of pesticides in the country, aside its success has been faced with some challenges. Prevalent among these are the following:

- The merger of Act 528 with EPA Act 490
- Inadequate facilities for pesticides quality control analysis in food and environmental media.
- Potentially high levels of pesticides due to the free import duties and value added taxes on pesticides
- Inadequate funds to support pesticides inspectors to conduct post registration monitoring and surveillance
- Inadequate number of staff and logistics for monitoring

- Insufficient poisoning information centre to keep institutions updated with poisoning information
- Inadequate resources for training and awareness programmes for farmers and the general public (EPA Ghana, 2009).

KNUST



3.0 METHODOLOGY

3.1 Study Area

3.1.1 Location

Akumadan is a major town in the Offinso District of the Ashanti Region. It is situated on the major road linking the Southern sector to the Northern sector of the country. It is about 65km from Kumasi, a commercial city and the second largest city in the country. Akumadan has a total population of about 20,100 people (Fiagbe, 1998).. The predominant occupation of the people is farming (Fiagbe, 1998).

3.1.2 Relief

The land of Akumadan is a little undulating. It lies in the forest region of the Ashanti plateau between 150 – 460 m above sea level.

3.1.3 Climate

Akumadan lies in the transitional forest zone of Ghana with two rainfall seasons. The major raining season is between April to July with the peak usually occurring in June. A short dry spell occurs in August following a minor rainfall season from September to October. The area is subject to rain events of 150 rainy days per year or more, and an annual precipitation average of 1400 mm (Nurah, 1999). The annual temperature is about 27 °C with March being the hottest and August being the coldest Month. The relative Humidity of the study area is high during the major raining season and reaches a peak of 90% in May and June.

3.1.4 Vegetation

The natural vegetation is of moist semi-deciduous forest type, most of which has been destroyed due to heavy logging activities for both the local markets and the foreign markets as well and also clearing of the land for both cash crop and food crop farming activities.

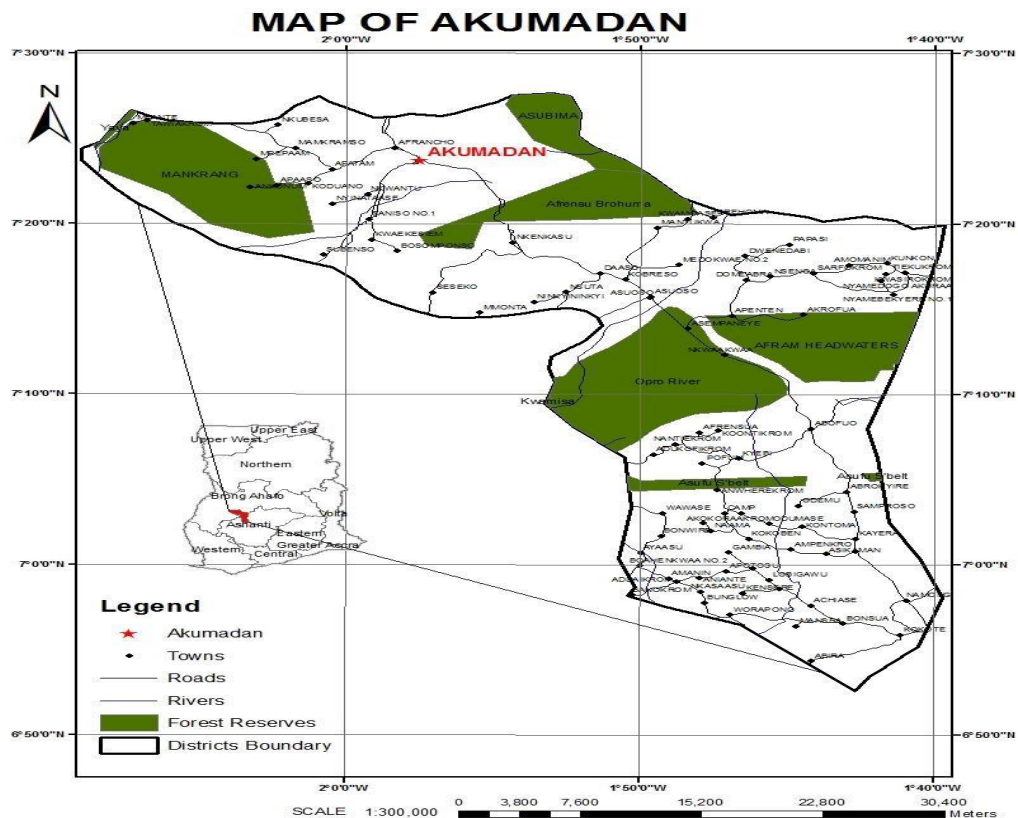


Fig 3.1 Map of Akumadan

3.1.5 Major Land uses

The major land use in the area is agriculture and forest plantation. The forest plantation is done by an NGO by name Form Ghana. This NGO has employed a number of the people in the area which supports their livelihoods. Most of the farmers are into vegetable production to sustain their families. Farmers in the study area do not have problems with water due to the presence of many streams in the area. The area experiences regular annual fires which led Hawthorn and Abu, 2004 to suggest that concerted efforts should be made to protect the area from these fires. Akumadan unlike other tomato producing areas in the country, have four main production seasons and these are:

1. Abriba (major season) March to June

2. Adantemo (mini season) June to September
3. Fube (mid-season) September to December
4. Petra (minor season) December to March

3.1.6. Description of Sampling Site

Water samples were collected from two streams and two wells. The streams are Akumadan and Asubima. This is because Akumadan is an old stream from which the community derived its' name. Also, lots of farming activities take place around its catchment areas. The Asubima stream was selected because it is a matured stream from which the Forest Reserve derives its name and has lots of farming activities going on around it. The wells were selected due to the farming activities surrounding them.

3.2 Data Collection

3.2.1 Sample Collection

The 11 amber glass bottles were used in the collection of the samples. The samples were collected in June, August and October 2012. Four samples (both water and soil sediments) were collected at each sampling date. Samples were collected at three different points and mixed thoroughly to obtain composite samples. The collected samples were preserved on ice and transported to laboratory for analysis. Sediment samples were collected at 30cm depth from the study locations using a stainless-steel grab. Sediment samples were well mixed and stored frozen (20 °C) in pre cleaned aluminum foils until analysis. The sediment was air dried, and then sieved through a 250 µm stainless steel mechanical shaker.

3.2.2 Quality assurance and quality control (QA/QC)

Quality Assurance and Quality Control method was incorporated in the study to enhance the integrity of the samples, boost the confidence of analytical data, and to prevent reporting (“false”) positives caused by contamination. The QA/QC method that was incorporated into the study was a “field blank.” A field blank defines a sample bottle that is prepared with the other bottles, packaged and transported to the sample site, filled with distilled or de-ionized water at the sample site, stored and sent with the other sample bottles, and submitted to the lab for analysis. The resulting expected “non-detected” (ND) analysis would increase the confidence that samples were not contaminated during preparation, field sampling, shipping, storage or analysis.

3.2.3 Reagents and Standards

Reagents used in the study comprised the following: n-hexane (95+% purity, Sigma–Aldrich), Acetone (99.5+%, BDH, England), Ethyl Acetate (99.8%, Sigma Aldrich), Silica gel 70 – 230 mesh (Hopkin and William Ltd. England) Sodium sulphate (Aldrich - Chemie, Germany) and de-ionized water.

3.2.4 Cleaning of Sample Apparatus

All the sampling bottles were rigorously scrubbed with a brush in hot water and detergent. They were again rinsed with acetone and then hexane. The bottles were put in an oven overnight at 180°C. When not in use the bottles were stored in dust-free Cabinets.

3.2.5 Extraction of water samples

Liquid–liquid extraction was used for the determination of pesticide residues. A 50 ml volume of n-hexane was introduced into a 2l separating funnel containing 100ml of filtered water. The mixture was then sonicated for 30 min (Rao and Pillala, 2001). 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 n-hexane. The pooled 150-ml n-hexane extracts were dried over anhydrous sodium sulphate and filtered. The organic fraction was concentrated using rotary evaporator and then cleaned up according to the procedure described below.

3.2.6 Clean Up of Water Samples

A 4 g of activated silica gel was weighed and poured into a column which has been plugged with glass wool and topped with 0.5 g layer of anhydrous sodium sulphate to remove any remaining water from the sample. The sample was then transferred onto the silica gel column and eluted with 20 ml portions of hexane mixtures to recover selected organochlorine pesticides. The eluate was collected into a round bottom flask and evaporated to dryness using a rotary evaporator under vacuum at 40 °C and 350 mbar (Alawi *et al.*, 1995) and dissolved in 15 mL of n – hexane acetone mixture. The eluate was again concentrated and evaporated to dryness using a rotary evaporator under vacuum at 40 °C and 350 mbar (Alawi *et al.*, 2007) and dissolved in 2mL ethyl acetate for Gas Chromatograph analysis.

3.2.7 Extraction of sediment samples

Dry Sediment sample was extracted according to Alawi *et al.*, (2007). A 10 g of airdried sediment sample was transferred into an extraction thimble that had been previously washed with n-hexane and acetone and oven dried. A volume of 20 ml hexane acetone

mixture (1:1) mixture was added to 10.0g air-dried sediment sample in a 250-ml beaker. The mixture was then sonicated for 20 min (Rao and Pillala, 2001). The extract was decanted and filtered through Whatman no. 41 filter paper filled with approx. 2 g of anhydrous sodium sulphate. The previous three steps were repeated twice (Rao and Pillala, 2001). The extract was evaporated to dryness using a rotary evaporator at 40 °C. Each extract was dissolved in 10 ml n-hexane and subjected to clean-up procedure described below.

3.2.8 Clean Up of Sediment Samples

A 4 g of activated silica gel was weighed and poured into a column which has been plugged with glass wool and topped with 0.5 g layer of anhydrous sodium sulphate to remove remaining water from the sample. The sample was then transferred onto the silica gel column and eluted with 15 ml portions of hexane mixtures to recover selected organochlorine pesticides. The eluate was collected into a round bottom flask and evaporated to dryness using a rotary evaporator under vacuum at 40 °C and 350 mbar (Alawi *et al.*, 2007) and dissolved in 15 ml of n – hexane acetone mixture. The eluate was again concentrated and evaporated to dryness using a rotary evaporator under vacuum at 40 °C and 350 mbar (Alawi *et al.*, 2005) and dissolved in 2ml ethyl acetate for Gas Chromatograph analysis.

3.2.9 Instrumental analysis

The Gas Spectrometer was used for the running of the samples because, that was what was used by the Ghana Atomic Energy Commission (GAEC) for such analysis then. A Varian CP-3800 Gas Chromatograph (Varian Associates Inc. USA) equipped with a column injector and electron capture detector was used for GC analysis. Sample extract

of 1 μl aliquots were injected and the separation was performed on a fused silica gel capillary column. The carrier gas was ultra-pure nitrogen at flow rate of 1.0 to 29 ml min^{-1} . The temperature of the injector operating in split less mode and oven temperature were held at 225 $^{\circ}\text{C}$ while the detector temperature was set at 300 $^{\circ}\text{C}$. The column oven temperature was programmed as follows; 60 $^{\circ}\text{C}$ for 2 min. then 180 $^{\circ}\text{C min}^{-1}$ up to 300 $^{\circ}\text{C}$ for 31.80 min. The residues detected by the GC analysis were confirmed by the analysis of the extract on two other columns of different polarities. The first column was coated with ZB-1 (methyl polysiloxane) connected to ECD while the second column was coated with ZB-17 (58% phenyl, methyl polysiloxane) and ECD. The residue of pesticide was identified based on comparison of the measured relative retention times to those of known standards. The residue levels of organochlorine pesticides were quantitatively determined by the external standard method using area under the curve. Measurement was carried out within the linear range of the detector. The peak areas whose retention times coincide with the standards was extrapolated on their corresponding calibration curves to obtain the concentration.

3.3 Laboratory Procedure for Physicochemical Properties

3.3.1 Determination of pH

The pH of a solution is the measure of how acidic or basic that solution is or the concentration of hydrogen ions in that solution. Natural water mostly has a pH of 4-9 and most are slightly basic as a result of bicarbonate and carbonates of the alkali and alkaline earth metals.

Procedure: In the laboratory, pH meter (HANNA model 209) was used to determine the pH of water samples. The pH electrode was cleaned with distilled water and then calibrated in order to give a precise measurement using pH4, pH7 and pH10 standard

buffer solutions before used to measure the water samples. After calibration of the pH electrode, 50 ml of the water sample was poured into a small beaker. The pH electrode was immersed into the water sample and the pH reading was shown on the LCD of the meter. The pH was recorded after the reading stabilized.

3.3.2 Temperature determination

Temperature was measured with a thermometer in degree Celsius or Fahrenheit.

Procedure: This was determined on site at the time of analysis. An aliquot of 50 ml of sample was measured into a 100 ml beaker and a 0-60 °C thermometer immersed in the solution. The reading on the thermometer was then recorded.

3.3.3 Determination of Colour

Water is colourless and to a larger extent, the presence of any colour in water is due to the presence of foreign material such as decaying and suspended organic and inorganic materials.

Procedure: Colour determination was by the Spectrophotometer that was calibrated, using distilled water in a 25 ml nessler cell at a wavelength of 455 nm and platinumcobalt unit of 50 mm. The 25 ml cell was then filled to the mark with water sample and the outside wiped dry with tissue paper to eliminate figure prints and moisture. The cell was inserted into the cell chamber and the lid replaced. After five (5) minutes the measurement of the water colour was read and recorded in Hazen units.

3.3.4 Electrical conductivity (EC) and total dissolved solid (TDS) determination. These were measured with a digital conductivity meter with cell constant of 1.0. The instrument was kept clean and standardized with KCl solution before it was used. Distilled water was used to rinse the electrode and lowered into the water sample contained in a plastic container. The conductivity in $\mu\text{S cm}^{-1}$ of the sample was recorded. The TDS of the samples were also measured by selecting the appropriate TDS key while the electrode remained in the water sample used to measure conductivity and the TDS value was recorded. The conductivity of the water sample was read on the LCD screen of the meter. The probe was rinsed in de-ionized water after final reading was taken. This was repeated for all the water samples at the various sampling sites.

3.3.5 Determination of Turbidity

Turbidity is the term given to anything that is suspended in a water supply. It is most common in surface waters and usually non-existent in ground water except in shallow wells and springs after heavy downpours of rain. Turbidity makes the water looks cloudy in appearance. Materials such as undissolved clay, sand, silt or suspended ions contribute to turbidity.

Procedure: A clean dry cuvette was rinsed three times with the water sample to be tested. The cuvette was filled with the water sample to be analysed and then covered with a light shield cap. The outer surface of the cuvette was wiped dry with a clean tissue paper. It was then pushed firmly into the optical well and the lid replaced. The NTU values were measured by pressing and releasing the arrow and the value was recorded after the display has stopped flashing.

3.3.6 Determination of Total Hardness

Hardness is the measure of capacity of water to react with soap (Gupta, 1999). Hardness of water is caused by the presence of multivalent cations and is largely due to calcium and magnesium ions. Calcium and magnesium combine with bicarbonates, chlorides, sulphates, and nitrates to form salts. The standard measurement for hardness is grains per gallon (gpg) as CaCO_3 . Water with hardness content not more than 0.6 gpg is considered soft.

Procedure: Using a clean pipette, 50 ml of test water sample was dispensed into a clean conical flask and 1.0 ml of 0.5M Ammonium buffer solution ($\text{pH} = 10.0$) and 2 ml of Eriochrome Black-T indicator were added. The content in the conical flask was titrated with 0.01M EDTA solution (Ethylene Diamine Tetra Acetic acid), mixed gently until the colour changed from red to blue. Titration was repeated until a consistent titre was obtained. The average titre value was recorded and total hardness was calculated as:

$$\text{Total Hardness (mg/L)} = \frac{\text{Average titre} \times 1000}{\text{Sample Volume (ml)}}.$$

(APHA, 1998).

3.3.7 Determination of Total Alkalinity

Alkalinity is defined as the ability of water to neutralize acid and it is determined by titration against a known standard acid.

Procedure: A 50 ml sample of test water was measured into a conical flask. Two drops of methyl orange indicator was added. The sample turned pink and was titrated against the standard 0.1M HCL solution to the first permanent pink colour at $\text{pH} 4.5$. The titre value (T_v) was read and recorded. The equation used in the calculation is given below;

$$\text{Alkalinity mg/l (CaCO}_3\text{)} = \frac{A \times N \times 1000}{V} \times 100$$

ml sample x 2

Where A=Titre Value

N= Normality of standard acid used

3.3.8 Salinity Determination

Salinity is the measurement of the mass of dissolved solids present in a given amount of water. In most circumstances, the dissolved solids are used to refer to salts. The salinity was measured with the electric probe thus; a 50 ml well-mixed sample was measured into a beaker. The electric probe was immersed in the sample and its salinity recorded.

3.3.9 Determination of Nitrate

It is one of the major ions in natural water. Most nitrates that occur in drinking water are as a result of contamination of ground water by septic systems, agricultural fertilizers and Feed lots. Nitrates are reduced to nitrite in the body. Reverse osmosis will remove 92-95% of the nitrates. Anion exchange resin will also remove both as will distillation (Alloway and Ayres, 1997).

Procedure: The Wagtech photometer was used to measure nitrate in samples. A clean nitrate test tube was filled with 20ml of water sample. One level spoonful of Nitrate test powder and one tablet of Nitrate test were added, capped and the tube shaken well for a minute and then allowed to stand for another one minute. It was again inverted several times to allow flocculation and then allowed to stand for extra two minutes to enable complete settlement. The clear solution was then decanted into a clean test tube to 10ml mark. One tablet of Nitricol was added, crushed and mixed to dissolve and allowed to stand for an extra 10 minutes for colour development. A wavelength of 570nm was

selected on the Photometer and the tube was inserted into the chamber and reading was then taken.

3.4 Data analysis

Statistical analysis that was incorporated in the work included mean of samples and corresponding standard deviation. Ranges were compiled from minimum and maximum values for levels detected in each individual pesticide residues detected in the study. Data was subjected to a two-way analysis of variance to determine the differences in pesticide residues among the various locations. The statistical software Graph Prism 5 was also used in the analysis.

CHAPTER FOUR

4.0 RESULTS

4.1 Organophosphate Pesticides in Ground and Surface Water in Akumadan

The individual values for Chlorpyrifos in the three sampling periods are shown below.

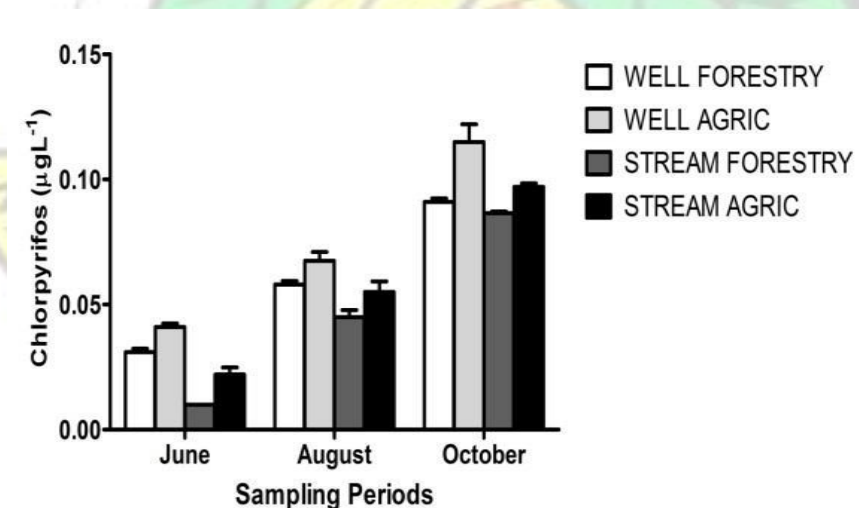


Fig. 4.1a: Chlorpyrifos levels in water in the various sampling sites

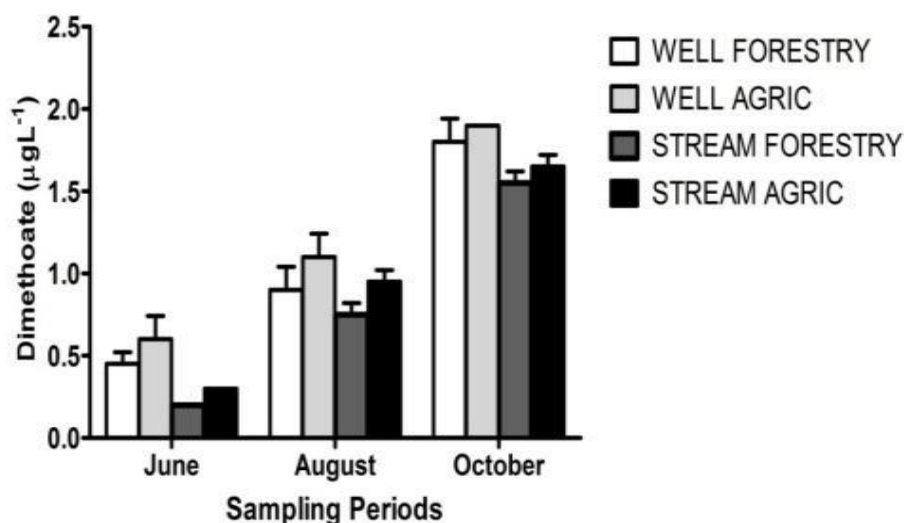


Fig. 4.1b: Dimethoate levels in water at sampling sites

The range of means recorded for Chlorpyrifos in figure 4.3a were between $0.01\mu\text{gL}^{-1}$ – $0.12\mu\text{gL}^{-1}$ for all the three sampling periods. In the first and second sampling periods, well agric recorded the highest Chlorpyrifos levels with the least being recorded from the stream forestry. During the third sampling period well agric again recorded the highest concentrations followed by stream agric with stream forestry recording the least for these sampling periods. It is obvious from the graph that ground water recorded higher values than that of surface water while agricultural land use systems recorded higher values than that of forestry land use systems. These differences were not statistically significant ($F= 0.41$, $d.f = 17$ and $p = 0.74$). Meanwhile there were significant figures between well agric in the second and third sampling periods.

The various Dimethoate levels in figure 4.1b recorded at the individual sampling sites are shown below. The mean values ranged between $0.2\mu\text{gL}^{-1}$ – $2.0\mu\text{gL}^{-1}$. The levels show an increasing trend from the first sampling period through to the third sampling period. It is recorded from above that; well agric had the highest recordings of Dimethoate concentrations with stream forestry recording the least. The graph also depicts

significantly higher values for ground water samples as against surface water samples. It further shows higher values for agricultural land use systems over forestry land use systems meanwhile these differences were not significant

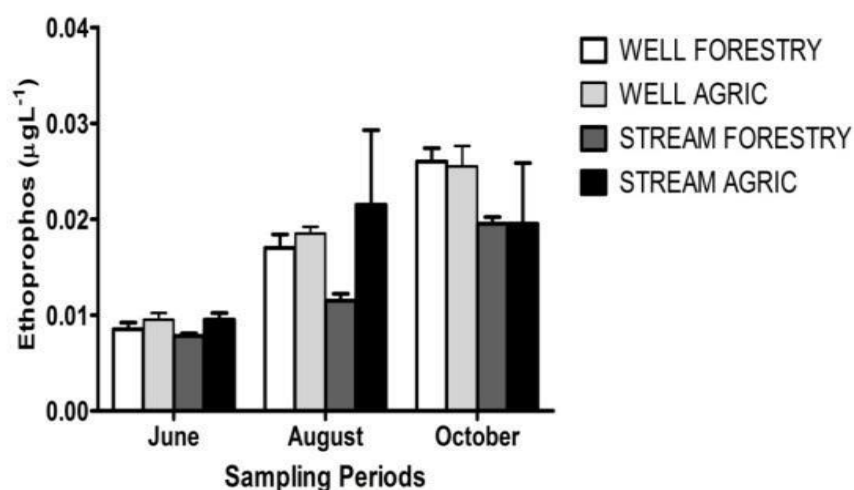


Fig. 4.1c: Ethoprophos concentration in water at sampling sites
Well agric recorded higher values during the first sampling period with stream forestry recording the least value. In the second sampling period, stream agric recorded the highest Ethoprophos concentration with the least being stream forestry while in the third sampling period, well forestry recorded the highest levels with stream forestry lagging behind from (Fig. 4.1c) above. ($F = 0.44$, $d.f = 17$ and $p = 0.72$). Stream Agric recorded significant differences in August and October.

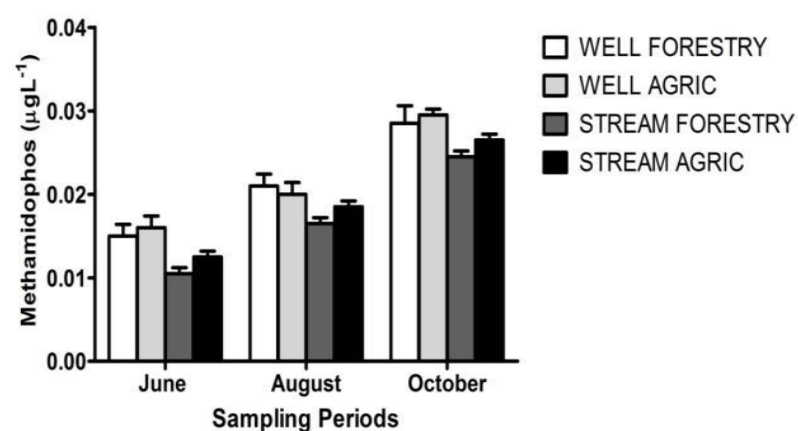


Fig. 4.1d: Methamidophos concentration in water at sampling sites

The Methamidophos values recorded for the three sampling periods is illustrated in the figure 4.1d above. The means ranged from $0.01\mu\text{g/L}$ – $0.03\mu\text{g/L}$. In the first sampling, well agric recorded the highest value followed by well forestry with the least being stream forestry followed by stream agric. The second sampling period recorded higher figures for well forestry followed by well agric and the lowest value was recorded at stream forestry followed by stream agric. In the third sampling period, well agric recorded the highest Methamidophos value followed by well forestry with the least value at stream forestry followed by stream agric. There were no significant difference in these samples ($F= 0.37$, d.f = 17 and $p = 0.77$).

The graph below illustrates the Phorate levels recorded in all the three sampling periods. The means ranged between $0.03\mu\text{g/L}$ – $0.2\mu\text{g/L}$. There was a study increase in levels from the first sampling period to the last. The first sampling revealed highest Phorate levels for well agric followed by well forestry with the least recorded at stream forestry followed by stream agric. In the second sampling, there was a change in trend with the highest value recorded at well agric followed by stream agric and the least value recorded at stream forestry followed by well forestry. The third sampling showed similar trends as the second sampling with higher values being recorded at well agric followed by stream agric and the least at stream forestry followed by well forestry ($F= 0.26$, d.f = 17 and $p = 0.85$).

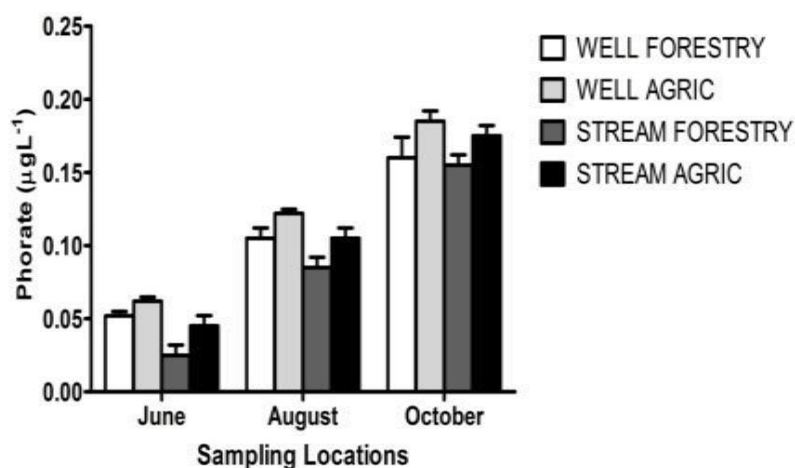


Fig. 4.1e: Phorate levels in water at sampling sites

4.2 Organophosphate Pesticides in Ground and Surface Water Sediments in Akumadan

The various Chlorpyrifos values for the three sampling periods are shown below. The range of means recorded for Chlorpyrifos were between $0.03\mu\text{g kg}^{-1}$ – $0.13\mu\text{gkg}^{-1}$ for all the three sampling periods

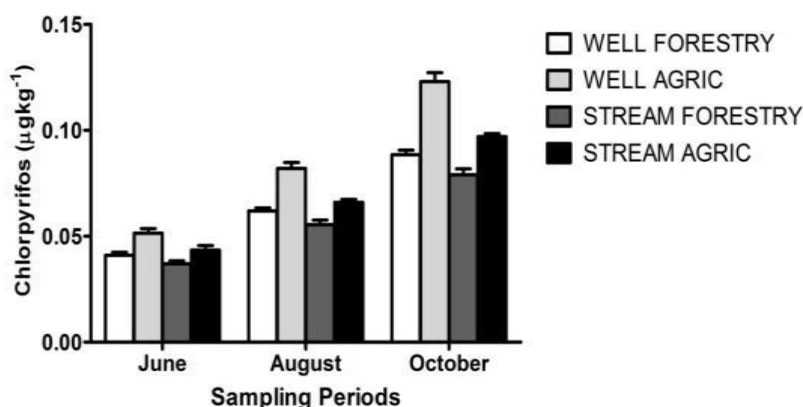


Fig. 4.2a: Chlorpyrifos levels in sediments at sampling sites

In the first sampling, well agric recorded the highest Chlorpyrifos levels followed by stream agric with stream forestry recording the least value. During the second and third sampling periods well agric again recorded the highest concentrations followed by stream agric with stream forestry recording the least followed by well forestry ($F = 0.44$, $d.f = 17$ and $p = 72$).

The Dimethoate concentrations recorded during the study have been illustrated in figure 4.2b. The means of Dimethoate values for all the three sampling periods ranged between $0.4 \mu\text{g kg}^{-1}$ – $3.2 \mu\text{g kg}^{-1}$. Well forestry recorded the highest Dimethoate readings followed by well agric and the least reading was at stream forestry followed by stream agric in the first sampling period. The second sampling period revealed higher values at well agric followed by well forestry and the least figures were recorded at stream forestry followed by stream agric. In the third sampling, well agric still recorded higher values followed by well forestry whilst the least values were recorded at stream forestry and followed by stream agric. The results show that the ground water sediment samples had higher Dimethoate readings as against surface water sediment samples. The graph further shows a higher reading for agricultural land use systems as compared to forestry land use systems. ($F = 0.69$, $d.f = 17$ and $p = 0.57$)

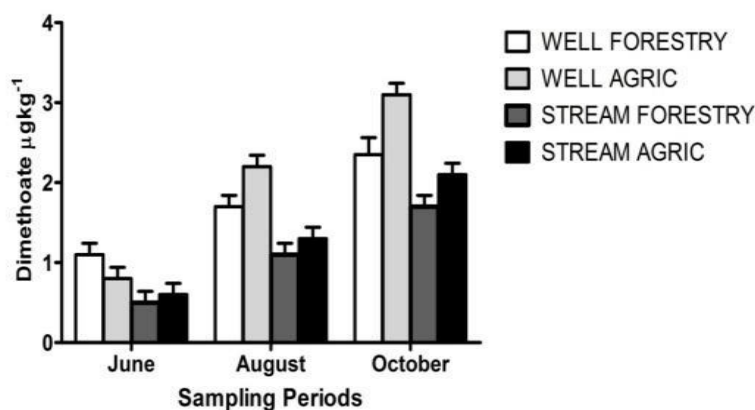


Fig.4.2b: Dimethoate concentrations levels in Sediment at sampling sites

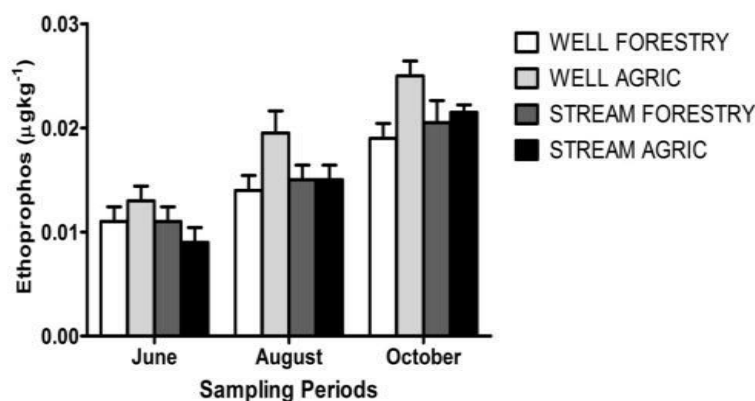


Fig. 4.2c: Ethoprophos levels in Sediment at sampling sites

The Ethoprophos levels recorded during the three sampling periods have been illustrated in figure 4.2c above. The range of means of Ethoprophos values were between $0.01\mu\text{gkg}^{-1}$ – $0.025\mu\text{gkg}^{-1}$ for all the sampling periods. Well agric recorded the highest readings followed by well forestry and stream forestry with the least value at stream agric. In the second sampling, well agric recorded the highest concentrations of Ethoprophos followed by stream forestry and stream agric whiles well forestry recorded the least value. The third sampling reveals higher values for well agric followed by stream agric and the least at well forestry followed by stream forestry ($F=0.27$, $d.f = 17$ and $p = 0.84$).

The Methamidophos values recorded in the sediments in the various sampling sites are shown below. The individual means for the three sampling periods ranged from $0.01\mu\text{gkg}^{-1}$ – $0.03\mu\text{gkg}^{-1}$.

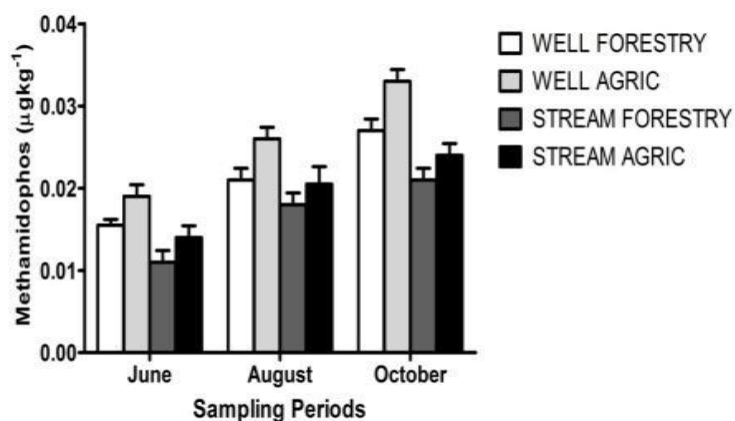


Fig. 4.2d: Methamidophos concentrations in Sediment at sampling sites

During the first sampling, well agric recorded the highest concentration followed by well forestry whiles stream forestry recorded the least followed by stream agric. The second sampling resulted in higher values for well agric followed by well forestry and the least values were recorded at stream forestry followed by stream agric. During the third sampling, the results were in an increasing order of well agric > well forestry > stream agric > stream forestry ($F=1.96$, d.f = 17 and $p = 0.19$).

The graph below illustrates the Phorate levels recorded in the three sampling periods of the study. The means for the individual sampling sites ranged from $0.03\mu\text{gkg}^{-1}$ – $0.20\mu\text{gkg}^{-1}$. In the first sampling period, well agric recorded the highest Phorate values followed by well forestry and stream forestry recorded the least value followed being the highest but this time around followed by stream agric and the least value was also recorded at stream forestry but followed by well forestry. This trend repeated itself in the third sampling period ($F= 0.18$, d.f = 11 and $p = 0.90$).

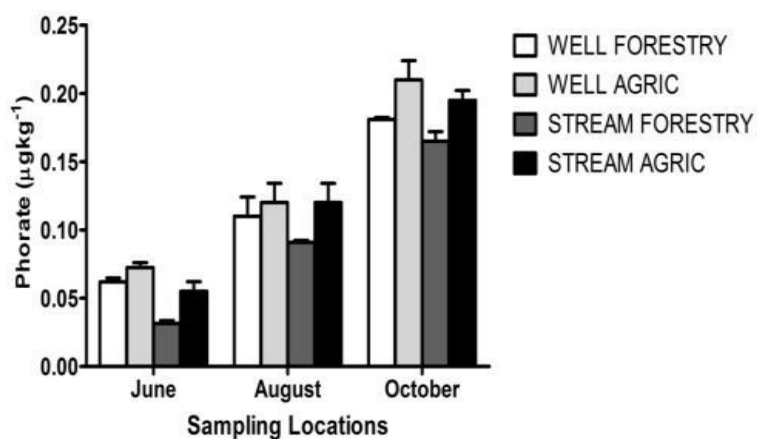


Fig. 4.2e: Phorate levels at sampling sites

4.3 Organochlorine Pesticides (OCP) in Ground and Surface Water in Akumadan

Amongst the various OCP's to be tested for, Aldrin was the only OCP detected. The graphical representation of the Aldrin concentrations for all the three sampling periods has been illustrated below. The means of Aldrin values for the sampling periods were between $0.01\mu\text{g L}^{-1}$ – $0.17\mu\text{g L}^{-1}$.

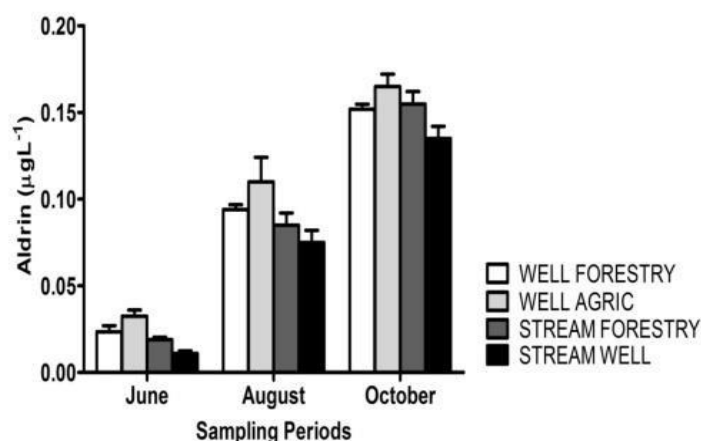


Fig. 4.3a: Aldrin concentrations in water at sampling sites

In the first sampling above, well agric recorded the highest reading followed by well forestry and stream agric recorded the least followed by stream forestry. The second sampling period showed higher values for well agric followed by well forestry with stream agric being the least followed by stream forestry. During the third sampling, well agric recorded the highest readings but with stream forestry being the second highest and stream agric recorded the least followed by well forestry ($F = 0.11$, $d.f = 17$ and $p = 0.94$).

Figure 4.3b shows the Gamma Chlordane values recorded during the study. The range of gamma chlordane mean values ranged from $0.01\mu\text{g/L}$ – $1.7\mu\text{g/L}$ for all the three sampling period. The first sampling period depicted high levels at well agric followed by well forestry and stream forestry and the least value was recorded at stream agric. The second sampling showed greater value for well agric followed by well forestry with the least at stream agric and followed by stream forestry. In the third sampling period, it was recorded that well agric had the highest reading followed by stream forestry and the least at stream agric and followed by well forestry.

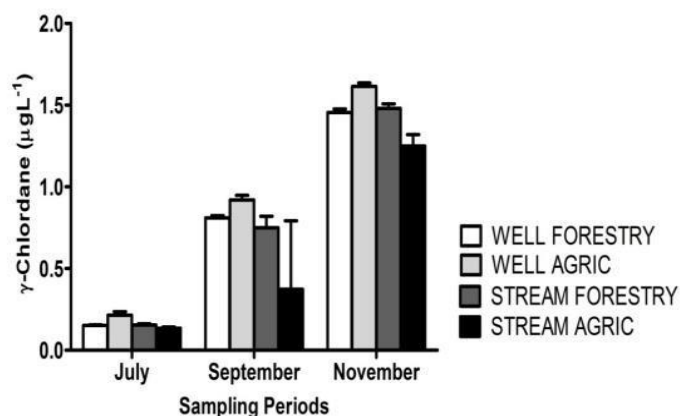


Fig. 4.3b: Gamma Chlordane levels in water at sampling sites

The p,p' DDE concentrations of the three sampling periods have been illustrated in figure 4.3c. The range of the means of the p,p' DDE concentrations were between $0.1\mu\text{g/L} - 0.8\mu\text{g/L}$. In the first sampling period, well agriculture recorded the highest DDE concentration followed by well forestry and the least figure was recorded at stream forestry and followed by stream agric. The second sampling recorded DDE levels that were almost similar with no clear differences in the sampling sites. No DDE concentration was recorded in the third sampling period ($F = 0.02$, $d.f = 17$ and $p = 0.99$).

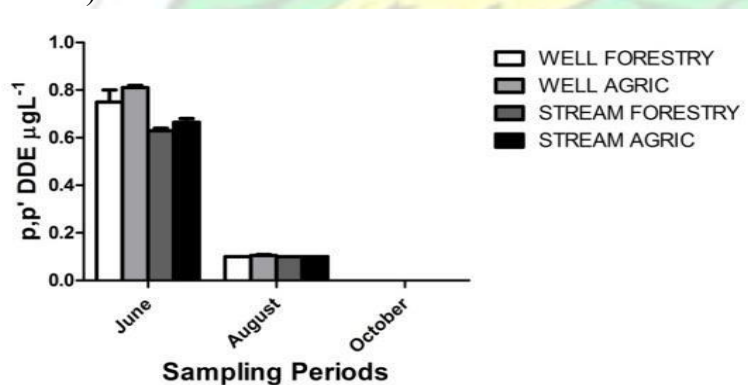


Fig. 4.3c: p,p' DDE concentrations in water at sampling sites

4.4 Organochlorine Pesticides in Ground and Surface Water Sediments in Akumadan

The Aldrin concentrations for all the sampling periods have been shown on the graph below. The range of Aldrin values ranged from $0.02\mu\text{gkg}^{-1}$ – $0.22\mu\text{gkg}^{-1}$ for all the sampling periods. During the first sampling, well agric recorded the highest value followed by stream agric whiles well forestry and stream forestry recorded the least values. In the second sampling, well agric had the highest recordings of Aldrin values with stream agric following. Stream forestry recorded the least value with well forestry following. The graph below shows a clear case of high values for ground water sediments as against surface water sediments. Agricultural land use systems recorded higher values as compared to forestry land use systems ($F= 0.10$, $d.f= 17$ and $p = 0.95$).

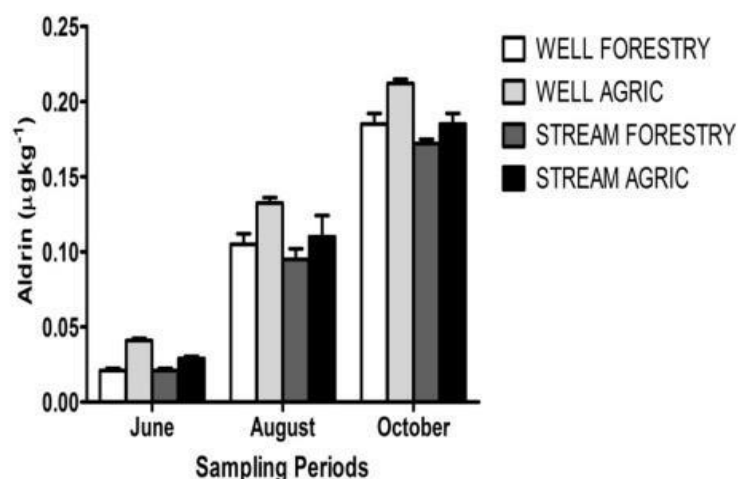


Fig. 4.4a: Aldrin concentrations in sediment at sampling sites

Gamma Chlordane values recorded for the three sampling period has been illustrated by the graph below. The range of gamma chlordane values were between $0.1\mu\text{gkg}^{-1}$ – $2.0\mu\text{gkg}^{-1}$ for all the three sampling periods.

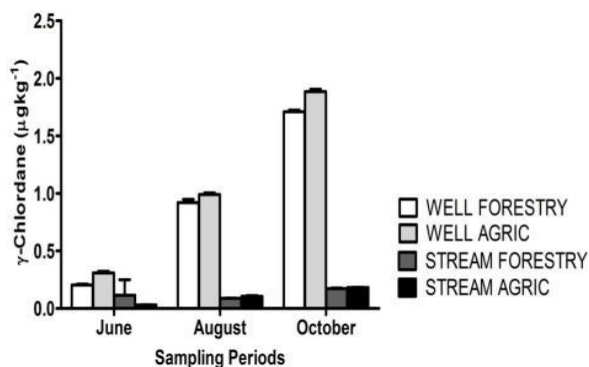


Fig. 4.4b: Gamma Chlordane concentrations in sediment at sampling sites

The first sampling indicated higher values for well agric followed by well forestry and the least values was recorded at stream agric and stream forestry. During the second sampling, well agric had the highest readings followed by well forestry with stream forestry being the least followed by stream agric. In the third sampling, well agric recorded the highest values followed by well forestry stream forestry lagging behind followed by stream agric. The graph above shows higher values for ground water sediments as compared to surface water sediments and higher values for agricultural land use systems as against forestry land use systems ($F= 2.69$, $d.f = 17$ and $p = 0.11$).

The p,p DDE concentrations of the three sampling periods have been illustrated in the graph below. The range of the means of the p,p DDE concentrations were between $0.1\mu\text{gkg}^{-1} - 0.9\mu\text{gkg}^{-1}$. In the first sampling period, well agriculture recorded the highest DDE concentration followed by well forestry and the least figure was recorded at stream forestry and followed by stream agric. The second sampling saw well agric recording the highest levels with well forestry and stream agric recording similar readings. The third sampling period resulted in well agric receiving the highest levels followed by

stream agric and the least value was recorded at well forestry and was followed by stream forestry ($F = 0.05$, $d.f = 17$ and $p = 0.98$).

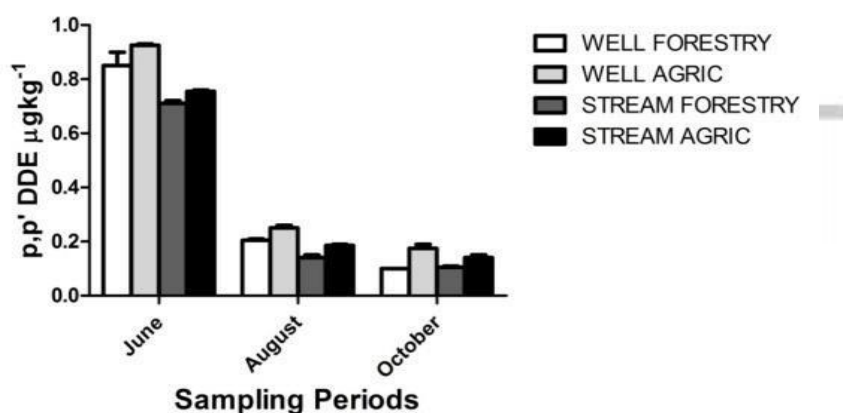


Fig. 4.4c: p,p' DDE levels in sediment at sampling sites

4.5 Physical Parameters of Ground and Surface Water in Akumadan

The temperature readings recorded for the various sampling sites ranged from 26.3°C – 28.9°C (Table 4.5). The highest temperature thus 28.9 °C °C was recorded at agric well with the least 26.3°C being the least in forestry well. The table (4.5) shows higher temperature values in the agricultural water than that of the forestry water. Table 4.5 further indicated higher temperatures for surface water as compared to ground water.

The variations in the land uses and water sample were significantly different (where, $F = 16.9$, $d.f = 11$ and $p = 0.0009$).

Colour levels for the individual samples ranged between 24Hz – 42Hz. (Table 4.5). The highest colour value was recorded at well agric followed by well forestry while the least colour value was recorded at stream forestry followed by stream agric. There were higher colour values at the agricultural land use system than that of the forestry land use system. Comparatively, there were higher colour levels in ground water to that of surface

water meanwhile these differences were not statistically significant ($F=3.09$, d.f = 11 and $p=0.08$).

The individual turbidity values for the various samples were between 6 NTU – 33 NTU. The highest turbidity value was recorded at well agric followed by well forestry while the least temperature value was recorded at stream forestry followed by stream agric.

The turbidity values for the different land uses and that of ground and surface water were the same ($F=1.51$, d.f = 11 and $p= 0.28$).

Table 4.5 Physical Parameters of Samples

		Parameter (Mean \pm SE)	
Sample Site	Temp. ($^{\circ}$C)	Colour (Hz)	Turb. (NTU)
WHO Standards	25	15	7
Mean \pm SE	26.58 ^a \pm 0.28	32 ^a \pm 3.46	21.33 ^a \pm 6.51
Well Forestry			
Mean \pm SE	28.63 ^b \pm 0.25	37.67 ^a \pm 4.51	24.67 ^a \pm 7.64
Well Agric			
Mean \pm SE	27.58 ^a \pm 0.37	28.33 ^a \pm 4.04	13 ^a \pm 7
Stream Forestry			
Mean \pm SE	27.87 ^a \pm 0.50	30.67 ^a \pm 3.51	15.67 ^a \pm 8.50
Stream Agric			

Superscript: Same alphabets means parameters are the same and different alphabets means parameters are different.

4.6 Chemical Parameters of Ground and Surface Water in Akumadan

The pH values ranged from 5.40 to 7.30 with the highest value recorded at the stream forestry followed by well forestry (Table 4.6). The lowest pH value was recorded at the

stream agric followed by well agric. The table indicates alkaline values for forestry land use system with acidic values for agricultural land use system. These differences were significant ($F=9.98$, $d.f = 11$ and $p=0.004$).

The various Total Dissolved Solids (TDS) values for the individual sampling sites ranged from 122mg/L – 234mg/L (Table 4.6). The highest TDS value was recorded at well agric followed by well forestry meanwhile the least TDS figure was recorded at stream forestry followed by stream agric. The table shows higher TDS values for the agricultural land use system with lower TDS values for forestry land use system. There were higher TDS values for ground water relative to surface water from the table below. There were significant difference in both the ground and surface water samples and that of agricultural and forestry land uses systems ($F=9.11$, $d.f = 11$ and $p= 0.005$).

The salinity values for the individual samples ranged between 0.02 PSU – 0.20 PSU (Table 4.6). The highest salinity value was recorded at well agric followed by well forestry whereas the least salinity values were recorded at stream forestry followed by stream agric. The table depicts higher salinity values for the agricultural land use system as compared to that of the forestry land use system. The table also indicates higher salinity levels for ground water as compared to surface water. The differences in the samples were significantly different ($F=4.64$, $d.f = 11$ and $p= 0.03$).

Conductivity levels ranged between 122 μ S/cm–258 μ S/cm (Table 4.6). The highest conductivity level was recorded at well agric followed by well forestry while the least conductivity levels were recorded at stream forestry followed by stream agric. The table

shows conductivity for the two land uses were the same and the water samples too were the same ($F=2.16$, $d.f = 11$ and $p=0.17$).

The various total hardness values for the individual samples were between 25mg/L – 250mg/L (Table 4.6). The highest total hardness value was recorded at well agric followed by well forestry while the least total hardness value was recorded at stream forestry followed by stream agric. The table shows higher total hardness values for the agricultural land use system than that of the forestry land use system and also higher total hardness values for ground water as compared to surface water. The differences between the land uses and the ground and surface water sample were not statistically different ($F=3.49$, $d.f = 11$ and $p= 0.06$).

The nitrate values for the various sampling sites ranged from 0.4mg/L – 2.9mg/L (Table 4.6). The highest nitrate value was recorded at well agric followed by stream agric while the least nitrate value was recorded at well forestry followed by stream forestry. The table shows higher nitrate values for the agricultural land use system than that of the forestry land use system. Also, the table depicted higher values for ground water as compared to the surface water. The variations in the samples were not significantly different ($F=1.33$, $d.f = 11$ and $p= 0.33$).

The alkalinity levels for the individual samples ranged from 10mg/L – 70mg/L (Table 4.6). The highest alkalinity level was recorded at well forestry followed by stream agric while the least alkalinity level was also recorded at well agric followed by stream forestry. The table shows higher alkalinity levels at the forestry land use system as

against agricultural land use system meanwhile there was higher alkalinity levels in ground water as compared to surface water. The differences in the samples were significantly different ($F=34.4$, $d.f = 11$ and $p= 0.0001$).

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Table 4.6: Chemical Parameters of Ground and Surface Water in Akumadan

Parameter	pH	TDS (mg/L)	Salinity (PSU)	Cond. (µS/cm)	Total Hardness (mg/L)	Nitrate (mg/L)	Alkalinity (mg/L)
WHO Standards	6.5 – 8.5	1000		2500	500	50	200
Mean ± SE	6.77 ^a ± 0.40	181 ^a ± 21	0.09 ^a ± 0.05	180 ^a ± 52.55	83.33 ^a ± 35.12	1.21 ^a ± 0.72	61.67 ^a ± 10.41
Well Forestry							
Mean ± SE		224.67 ^a ± 10.07	0.16 ^a ± 0.07	222.33 ^a ± 55.82	160 ^a ± 78.10	2.38 ^a ± 0.65	13.33 ^b ± 5.77
	5.90 ^b ± 0.26						
Well Agric							
Mean ± SE	7.07 ^a ± 0.25	137.33 ^b ± 26.56	0.03 ^b ± 0.01	141 ^a ± 17.35	38.33 ^a ± 12.58	1.42 ^a ± 0.76	21.67 ^a ± 2.89
Stream Forestry							
Mean ± SE	5.83 ^b ± 0.40	168 ^b ± 22.	0.06 ^{a,b} ± 0.02	158 ^a ± 26.23	76.67 ^a ± 37.86	1.77 ^a ± 0.91	38.33 ^b ± 2.89
Stream Agric							

Superscript: Same alphabets means parameters are the same and different alphabets means parameters are different.



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CHAPTER FIVE

5.0 DISCUSSION

5.1 Organophosphate Pesticides in Water and Sediment Samples

The organophosphate pesticides identified in the study ranged from Chlorpyrifos, Methamidophos, Ethoprophos, Dimethoate and Phorate. Pesticides mostly used by vegetable growers in tomato, pepper, okra and pineapple farms in Ghana include dimethoate, chlorpyrifos, diazinon, cymethoate and fenitrothion as asserted by (Boamah and Blay 2000; Cudjoe *et al.*, 2002), affirms the identified pesticides above as being in use in Ghana at Akumadan in the Ashanti Region.

The Chlorpyrifos samples recorded in the study ranged from $0.03\mu\text{gL}^{-1}$ – $0.13\mu\text{gL}^{-1}$ for both ground and surface water. These figures were below the WHO permissible limits of $30\mu\text{gL}^{-1}$. This could be attributed to the frequent use of this organophosphate pesticide for agriculture in the study area as confirmed by (Boamah and Blay, 2000; Cudjoe *et al.*, 2002) above. There were no significant difference in the two samples i.e. ground and surface water even though there were differences in the values recorded. There were higher levels of Chlorpyrifos in sediments than that in water samples. This can be attributed to the fact that some of these pesticides are insoluble in water which is supported by the findings of Alawi *et al.*, 1995 who stated that pesticides concentrations were very low in seawater, as compared to those in sediments which could be interpreted by their lipophilic properties.

The mean concentrations of Methamidophos samples recorded during the study ranged between $0.01\mu\text{gL}^{-1}$ – $0.035\mu\text{gL}^{-1}$. There has not been any established W.H.O. guideline

value for Methamidophos yet. The differences that existed between ground and surface water samples were not statistically different. The higher levels of OPP's in sediment than that of water is due to the fact that the residues are adsorbed onto the sediments than when in water. This affirms the assertion by Tomlin, 1994; Xue *et al.*, 2006 that sediments serve as a primary repository for majority of applied pesticides. Also, sediments represent a source from which residues are re-introduced into the water column and therefore contribute to measurable concentrations in water and biota of many water systems (Iwata *et al.*, 1994; Tanabe *et al.*, 1997; Vagi *et al.*, 2007). Methamidophos being an OPP has the tendency of high degradation and dissipation in the environment hence has little or no health hazards.

The Dimethoate, Ethoprophos and Phorates' mean concentrations recorded during the sampling ranged from $0.4 \mu\text{g/L}^{-1}$ – $3.2 \mu\text{g/L}^{-1}$, 0.01 – $0.025 \mu\text{g/L}$ and 0.03 – $0.20 \mu\text{g/L}$ respectively. The Dimethoate levels were below the W.H.O. guidelines whiles there has not been established guidelines for the other two (2) organophosphates.

5.2 Organochlorine Pesticides (OCP's) in Water and Sediment Samples

The OCP's identified throughout the study were Aldrin, Gamma Chlordane and p,p DDE (a weak metabolite of DDT). This is in agreement with the study carried out by Ntow, 2001, 2005; Darko *et al.*, 2008 whose work identified the three OCP's in addition to HCB, Endosulfan Lindane and Deldrien in freshwater systems in different parts of the country.

The mean concentrations of Aldrin recorded in the study was above the W.H.O guidelines of $0.03 \mu\text{g/L}$. Doong *et al.*, (2002) reported concentration range of 0.05 –

0.15 µg/L for aldrin. From this study however concentrations of aldrin detected was much higher than the reported study. Meanwhile, a study undertaken by Darko *et al.*, (2008) reported higher concentrations of 0.65 µg/L aldrin in Lake Bosomtwi in the Ashanti region of Ghana.

Higher levels of Aldrin were recorded in the sediment samples as compared to the water samples but there were no significant differences in the figures. This could be attributed to the ability of Aldrin to be strongly adsorbs to sediment particles and remain intact for a long period in the aquatic environment as indicated by (Nollet, 2000).

The average values of gamma Chlordane levels recorded during the study ranged between 0.01µg/L – 2.0µg/L. These values were above the W.H.O guideline values of 0.2µg/L. This is an indication that the water and sediment samples collected were polluted with gamma Chlordane. This is in line with a study carried out by Kuranchie *et al.*, 2011 at Weija and Densu rivers where gamma Chlordane was identified. In that study, samples collected from Weija showed levels of gamma-chlordane at 1.95µg/L. Gamma-chlordane was also detected at 1.633 µg/L and 1.325µg/L at Weija and Nsawam respectively. The level of gamma Chlordane in water was higher than that in the sediment.

The mean values of p,p DDE concentrations observed in the study was below the permissible limits by W.H.O. DDT and its metabolites were the least of pesticides expected to be seen in this study even though in very small quantity. The presence of p,p DDE a metabolite of DDT could be due to the length of degradation of the pesticides since there has been a ban on its use for some time now. This is in conformity to the

declaration by Kuranchie *et al.*, 2011 that DDE, a major metabolite of DDT continue to dominate organochlorine pesticide burdens in almost all the aquatic systems.

Moreover, the finding is an indication of the rate of degradation of DDT to DDE in the aquatic environment under the hot, dry climatic conditions which is a feature of tropical waters (Jiries *et al.*, 2002). The results of very small values gives an indication on the restricted use of DDT for agricultural and vector control purposes in Ghana. Long term persistence in the environment of this pesticide has been reported in various publications leading to its subsequent restrictions and ban in many countries (Kidd and James, 1991; Fattore *et al.*, 2002). Low DDE/DDT levels support the assumption that the levels primarily originated from previous contamination and environmental persistence. DDE is generally more persistent.

5.3 Analysis of Physical Parameters

5.3.1 Colour

The standard for colour is set for reasons of appearance and requires that water be virtually colourless. According to WHO standards for drinking water, the colour limit should be 15 Hz. All the water samples collected were above the WHO limit. The colour values for ground water were higher than that in surface water and agricultural land use was also greater than forestry land use systems. There were no significant differences between the samples. Colour in natural water usually results from the leaching of organic materials and is primarily the result of dissolved and colloidal humic substances, primarily humic acid and fluvic acid. Colour is also strongly influenced by the presence of iron and other metals. Potable water should be clear and free from

compounds that can cause colour change (Pritchard *et al*, 2007). Although, colour itself is not usually objectionable from health perspectives, its presence is aesthetically objectionable and suggests that the water may need additional treatment (Safe Drinking Water Committee, 2005) and may lead to greater consumer complaints.

5.3.2 Temperature

All the temperature values recorded throughout the study samples were above the WHO guidelines of 25°C. Temperature values for ground water samples were lower than in surface water sample and also lower in forestry land use systems than in agricultural land use systems.

There were differences between the temperature values for ground and surface water and that of forestry and agricultural land use systems. These relatively low temperatures could be attributed to the fact that all the samples were collected very early in the morning. The temperature of drinking water is most of the time not a major concern to consumers especially in terms of drinking water quality. The quality of water with respect to temperature is usually left to the discretion of the individual based on his taste and preference and there are no set guidelines for drinking water temperature.

5.3.3 Turbidity

All the turbidity figures recorded were above the WHO standards for drinking water of 7NTU meaning the sample are polluted in terms of turbidity. There were no significant differences between the samples. The high turbidity values above the WHO standard for drinking water may be due to suspended matter such as clay, salt, finely divided organic and inorganic matters, planktons, and microscopic organisms as indicated by APHA 1998. The high levels of turbidity in ground water as against the surface water

could be attributed to the stagnant nature of the wells as such any dissolve substances will remain in them for a long time while the streams just wash any materials that get into them away. The difference in the values between forestry and agric could be due to the vegetation cover in the forestry area than that of the agric area. Detergents and emulsifying agents produce stable colloids that could result in turbidity (APHA, 1992). The use of turbid water for domestic properties may constitute a health risk because this could stimulate the growth of bacteria and pathogenic microorganisms (Qadir *et al.*, 2007). Turbidity directly influences the colour of water and there is a general increase in colour with increasing turbidity values. This is a true reflection of the high colour values observed in table 4.1 above. High turbidity values may also increase the possibility of microbiological contamination (DWAF, 1998).

5.4 Analysis of Chemical Parameters

5.4.1 pH

Most of the pH values recorded from the samples were within the WHO (2003) guideline range and the Ghana Standards Board limits (1998) of 6.5 – 8.5. The differences in the pH values recorded were statistically significant. This indicates that most of the samples were safe for drinking in terms of their pH values. Meanwhile high pH levels are not desirable for drinking since they may impart a bitter taste to the water (Safe Drinking Water Committee, 2005)

5.4.2 Total Dissolved Solids (TDS)

The TDS figures recorded were way below the WHO (2003) and Ghana Standards Board (1998) of 1000mg/L. Meanwhile, there were significant difference between ground and surface water and also between agricultural and forestry land use systems. The high TDS values for agricultural land use system could be attributed to the use of

fertilizers and other pesticides for farming. This is in conformity to the assertion by (Pushard, 2005) who revealed that contributions from fertilizers used in farming may affect TDS values. Furthermore, the highest TDS recorded in the agricultural land use could be due to the removal of vegetation cover at the site for agric and other purposes as compared to the forestry area. This is in line with the assertion by WHO (2003), that the primary Sources for TDS in receiving waters include agricultural runoff, industrial wastewater, urban run-off, sewage, and natural sources such as leaves, silt, plankton, and rocks. Bruvold and Ongerth (1969) revealed that palatability of drinking water is related to its TDS. It is rated as excellent, less than 300 mg/L; good, between 300 and 600 mg/L; fair, between 600 and 900 mg/L; Poor, between 900 and 1200 mg/L; and unacceptable, greater than 1200 mg/L. From the grades above it can be stated that the water samples from all the sites were excellent.

5.4.3 Salinity

The mean salinity figures recorded during the study were; 0.09 PSU for well forestry, 0.16PSU for well agric, 0.03 PSU for stream forestry and 0.06 PSU for stream agric. The figures showed significant differences in the samples. The permissible limit for salinity is yet to be ascertained.

5.4.4 Conductivity

The electrical conductivity of water measures the capacity of water to conduct electrical current and it is directly related to the concentration of salts dissolved in water, and therefore to the total dissolved solids (TDS). From (table 4.2) of the study, conductivity values were highest for well agriculture and least for stream forestry.

The individual conductivity values from all the sampling sites were below the (WHO, 2008) guidelines of 2500mg/L. Also, there were no significant differences between the samples. The conductivity values recorded are in consonance with the conductivity values recorded by Arkoli, (2012) whose conductivity values ranged from 120 μ S/cm – 168 μ S/cm and 130 μ S/cm – 201 μ S/cm for Sukyeremma and cool sachet water brands. The higher conductivity values recorded in the agricultural land use system could be attributed to the runoffs from surrounding communities that carry a lot of dissolved ions washed from garages, market areas, roads, laundries, car washing bays etc. into the well since it is situated near the community. Phosphates, nitrates and chloride are some of the possible ion inputs in the well (SDCK Watershed Wiki, 2010). The high conductivity at the agricultural land use sampling site may also be due to the farming activities and the accompanying fertilizers, pesticides and herbicides application. On the other hand, the low conductivity levels at the forestry sampling site could be due to the less human activities at the area. Generally, conductivity of clean water is lower but as it moves down the earth it leaches and dissolves ions from the soil and also picks up organic from biota and detritus (Ferrar, 1989). Basically the conductivity values recorded from all the sampling sites do not pose any potential health risk for consumers since they were all below the acceptable limits set by W.H.O.

5.4.5 Total Hardness

The mean Total Hardness for the sampling sites ranged from 38mg/L to 160mg/L. These figures were below the WHO set guidelines for drinking water. Meanwhile there were no significant differences between ground and surface water and also between agricultural land use and forestry land use systems. The increase in total hardness may

be due to decomposition and mineralization of organic materials (Abida, and Harikrishna, 2008). The use of hard water for domestic purpose leads to excessive use of soaps and detergents and finally leaves spots on glasses, dingy film on laundry and on bathroom fixtures. However hard water provides calcium salts needed by children to make strong bones and teeth (WHO, 2004). According to Sheila (2007) when total hardness in water is too low, the water is referred as fresh, soft water. Waters with a total hardness in the range of 0 to 60 mg/L are termed soft; from 60 to 120 mg/L moderately hard; from 120 to 180 mg/L hard; and above 180 mg/L very hard. Therefore the water at stream forestry was soft with mean hardness of 38 mg/L. Meanwhile stream agric and well forestry waters were moderately hard with mean hardness of 76 mg/L and 83 mg/L respectively whilst the water at well agric was hard. The total hardness may be due to the composition of the minerals present in the earth in which the aquifer containing the water is located, or the underlying bedrock of the river. Here, the hardness of well agric samples is as a result of the activities in the area such as washing around the well. According to Exploring the Water Environment (2004), a streams' hardness reflects the geology of the catchments area and sometimes provides a measure of the influence of human activity in watershed. Hardness of water may not have any health implications but may affect the taste of water as well as influence its lathering ability when used for washing.

5.4.6 Nitrate

Nutrients are needed for survival and growth of aquatic plants. However, if they are present in excess in water, they over stimulate the growth of aquatic plants leading to water quality problems. High concentration of NO_3^- is a potential health risk, particularly in pregnant women and infants under 6 years (blue baby syndrome)

(Kempster *et al.*, 1997). The mean Nitrate values at all the sampling sites were below the drinking water Nitrate guideline value of 50mg/L set by WHO (1998), hence the samples were not nitrate polluted. There were also no significant differences between the samples even though there were differences in the figures. The levels of nitrate recorded at the study area could be as a result of certain natural processes like decomposition of vegetation and activities of nitrogen fixing bacteria and precipitation. Most importantly, the major causes of high nitrate concentration could be due to the human activities that go on around the catchment of the study area as with that of the agric sampling area. This observation is buttressed by the findings of Donald (2012), that elevated levels of nitrate is often noted in streams and rivers draining watersheds with high levels of corn production, nitrogen fertilizer application as well as runoffs from uncontained livestock operations.

5.4.7 Alkalinity

The assertion by (Verma *et al.*, 2000), demonstrated that for a complete quantification of fresh water acidity, the measurement of alkalinity is recommended. In view of this alkalinity was determined for the samples. All the alkalinity figures recorded were below the set guideline for (W.H.O, 1998) which is 200mg/L. The Alkalinity levels were statistically different between ground and surface water samples. Alkalinity may be influenced by rocks and soils, salts and certain industrial wastewater discharges and certain plant activities (US EPA, 2010). This implies, that the above factors could not greatly affect the samples of the study hence their low alkalinity levels. The relatively low alkalinity values means that the water may have a low capacity to neutralize or "buffer" incoming acids and, therefore could be susceptible to acidic pollution since

alkalinity is a measure of all the substances in water that can resist a change in pH when acid is added to the water.

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CHAPTER SIX

6.0 CONCLUSION AND RECCOMENDATIONS

The study revealed the presence of organochlorine pesticides at various concentrations in both water and sediments with sediment generally detecting the highest concentrations. Also, the levels in ground water were higher than those of surface water. Organophosphate pesticides were also detected at varying levels with greater quantities being observed in the sediment samples as against the water samples. The low levels of organochlorine and organophosphate pesticides in water were not astonishing since these pesticides are less soluble in water, thus they readily adsorb to sediment particles and as such are frequently detected in sediment.. In the study, most of the physicochemical properties tested were below the W.H.O guideline limit which is an indication of less contamination of the samples collected. This is seen in the appreciable levels of pesticides observed in the samples being within the W.H.O set limits.

The higher levels of the pesticides detected in agricultural land use system with regard to those of forestry land use systems was obvious due to the high usage of pesticides

for agricultural activities than those of forestry. The pesticides observed in the samples may have originated from various agricultural activities along the banks of the streams and subsequent runoff of the pesticides into the water body.

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6.1 Recommendations

In order to reduce the levels of contamination of water bodies in the study area, it is essential for the EPA to undertake continuous surveillance to get rid of organochlorines.

Furthermore, there is the need for stricter controls at the ports of entry and on the use of pesticides on food crops which later enters the water bodies which makes farmers and their families suffer health problems due to the frequent use of agro-chemicals.

Information regarding the hazards of pesticide usage, recommendation for minimizing each use and alternative measures must be made available to the pesticides users in Akumadan by the Ministry of Food and Agriculture (MoFA).

MoFA should deploy more Agricultural Extension Officers to the Akumadan area to educate and monitor the farmers and agro-chemical dealers on proper use of pesticides.

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APPENDICES

APPENDIX 1

Raw Data for Physical Parameters

June

Parameter	Well Forestry	Well Agric	Stream Forestry	Stream Agric
Temperature	26.3	28.6	27.2	27.4

Turbidity	15	18	6	7
Colour	30	42	24	27

August				
Parameter	Well Forestry	Well Agric	Stream Forestry	Stream Agric
Temperature	26.5	28.4	27.9	28.4
Turbidity	28	33	20	24
Colour	30	33	29	31

October				
Parameter	Well Forestry	Well Agric	Stream Forestry	Stream Agric
Temperature	26.8	28.9	27.6	27.8
Turbidity	21	23	13	16
Colour	36	38	32	34

Raw Data for Chemical Parameters				
June				
Parameter	Well Forestry	Well Agric	Stream Forestry	Stream Agric
ph	6.7	5.7	7.3	5.4
TDS	160	214	122	143
Salinity	0.15	0.20	0.03	0.04

Conductivity	240	258	156	186
Total	50	120	25	50
Hardness	60	120	35	70
Nitrates	1.9	2.6	2.3	2.8
Alkalinity	50	10	20	35

August

Parameter	Well Forestry	Well Agric	Stream Forestry	Stream Agric
pH	6.4	5.8	6.8	6.2
TDS	181	226	122	177
Salinity	0.08	0.20	0.02	0.07
Conductivity	162	251	145	154
Total	120	250	50	120
Hardness	85	150	40	100
Nitrates	0.5	2.9	0.9	1.4
Alkalinity	65	10	20	40

October

Parameter	Well Forestry	Well Agric	Stream Forestry	Stream Agric
pH	7.2	6.2	7.1	5.9
TDS	202	234	168	184
Salinity	0.06	0.08	0.04	0.09
Conductivity	140	158	122	134

Total	80	110	40	60
Hardness	120	250	50	120
Nitrates	1.2	1.7	1.0	1.1
Alkalinity	70	20	25	40



APPENDIX 2

Raw Data for Organophosphate Pesticides in Water (μgL^{-1})

Parameter	June			
	Well Forestry	Well Agric	Stream Forestry	Stream Agric
Phorate	0.05	0.06	0.03	0.05
Dimethoate	0.45	0.60	0.20	0.30
Fonofos	ND	ND	ND	ND

Pirimiphosmethyl	ND	ND	ND	ND
Methamidophos	0.015	0.016	0.010	0.013
Fenitrothion	BDL	BDL	BDL	BDL
Malathion	ND	ND	ND	ND
Chlorpyrifos	0.03	0.04	0.01	0.02
Parathion	ND	ND	ND	ND
Chlorfenvinphos	ND	ND	ND	ND
Profenofos	ND	ND	ND	ND
Ethoprophos	0.008	0.095	0.078	0.095

August

Parameter	Well Forestry	Well Agric	Stream Forestry	Stream Agric
Phorate	0.11	0.12	0.10	0.11
Dimethoate	0.90	1.10	0.75	0.95
Fonofos	ND	ND	ND	ND
Pirimiphosmethyl	ND	ND	ND	ND
Methamidophos	0.021	0.020	0.017	0.019
Fenitrothion	BDL	BDL	BDL	BDL
Malathion	ND	ND	ND	ND
Chlorpyrifos	0.06	0.07	0.05	0.06
Parathion	ND	ND	ND	ND
Chlorfenvinphos	ND	ND	ND	ND
Profenofos	ND	ND	ND	ND
Ethoprophos	0.01	0.02	0.01	0.02

October

Parameter	Well Forestry	Well Agric	Stream Forestry	Stream Agric
Phorate	0.16	0.19	0.15	0.18
Dimethoate	1.80	1.90	1.55	1.65
Fonofos	ND	ND	ND	ND

Pirimiphosmethyl	ND	ND	ND	ND
Methamidophos	0.028	0.029	0.025	0.027
Fenitrothion	BDL	BDL	BDL	BDL
Malathion	ND	ND	ND	ND
Chlorpyrifos	0.09	0.12	0.09	0.10
Parathion	ND	ND	ND	ND
Chlorfenvinphos	ND	ND	ND	ND
Profenofos	ND	ND	ND	ND
Ethoprophos	0.026	0.025	0.020	0.019

Raw Data for Organop

hosphate Pesticides in Sediments (μgkg^{-1})

June				
Parameter	Well Forestry	Well Agric	Stream Forestry	Stream Agric
Phorate	0.06	0.07	0.03	0.05
Dimethoate	1.10	0.80	0.50	0.60
Fonofos	ND	ND	ND	ND
Pirimiphosmethyl	ND	ND	ND	ND
Methamidophos	0.015	0.020	0.010	0.013
Fenitrothion	BDL	BDL	BDL	BDL
Malathion	ND	ND	ND	ND
Chlorpyrifos	0.04	0.05	0.04	0.05
Parathion	ND	ND	ND	ND
Chlorfenvinphos	ND	ND	ND	ND
Profenofos	ND	ND	ND	ND
Ethoprophos	0.012	0.014	0.012	0.009

August

Parameter	Well Forestry	Well Agric	Stream Forestry	Stream Agric
Phorate	0.11	0.12	0.09	0.12

Dimethoate	1.70	2.20	1.10	1.30
Fonofos	ND	ND	ND	ND
Pirimiphosmethyl	ND	ND	ND	ND
Methamidophos	0.020	0.027	0.017	0.019
Fenitrothion	BDL	BDL	BDL	BDL
Malathion	ND	ND	ND	ND
Chlorpyrifos	0.06	0.08	0.06	0.07
Parathion	ND	ND	ND	ND
Chlorfenvinphos	ND	ND	ND	ND
Profenofos	ND	ND	ND	ND
Ethoprophos	0.015	0.018	0.016	0.016

October

Parameter	Well Forestry	Well Agric	Stream Forestry	Stream Agric
Phorate	0.18	0.21	0.17	0.20
Dimethoate	2.40	3.10	1.70	2.10
Fonofos	ND	ND	ND	ND
Pirimiphosmethyl	ND	ND	ND	ND
Methamidophos	0.028	0.034	0.020	0.023
Fenitrothion	BDL	BDL	BDL	BDL
Malathion	ND	ND	ND	ND
Chlorpyrifos	0.09	0.12	0.08	0.10
Parathion	ND	ND	ND	ND
Chlorfenvinphos	ND	ND	ND	ND
Profenofos	ND	ND	ND	ND
Ethoprophos	0.017	0.025	0.018	0.019

Raw Data for Organochlorine Pesticides in Water (μgL^{-1})

June				
Parameter	Well Forestry	Well Agric	Stream Forestry	Stream Agric
Beta-HCH	ND	ND	ND	ND
Delta-HCH	ND	ND	ND	ND
Lindane	BDL	BDL	BDL	BDL
Heptachlor	ND	ND	ND	ND
Aldrin	0.02	0.03	0.02	0.01
Gamma	0.15	0.22	0.16	0.14
Chlordane				
p,p'-DDE	0.75	0.81	0.63	0.67
Dieldrin	ND	ND	ND	ND
Endrin	ND	ND	ND	ND
Alpha-Endosulfan	ND	ND	ND	ND
Beta-Endosulfan	BDL	BDL	BDL	BDL
Endosulfan Sulfate	ND	ND	ND	ND
August				
Parameter	Well Forestry	Well Agric	Stream Forestry	Stream Agric
Beta-HCH	ND	ND	ND	ND
Delta-HCH	ND	ND	ND	ND
Lindane	BDL	BDL	BDL	BDL
Heptachlor	ND	ND	ND	ND
Aldrin	0.09	0.11	0.08	0.07
Gamma	0.81	0.92	0.55	0.71
Chlordane				
p,p'-DDE	0.10	0.10	0.10	0.10
Dieldrin	ND	ND	ND	ND
Endrin	ND	ND	ND	ND
Alpha-Endosulfan	ND	ND	ND	ND
Beta-Endosulfan	BDL	BDL	BDL	BDL
Endosulfan Sulfate	ND	ND	ND	ND

October				
Parameter	Well Forestry	Well Agric	Stream Forestry	Stream Agric
Beta-HCH	ND	ND	ND	ND
Delta-HCH	ND	ND	ND	ND
Lindane	BDL	BDL	BDL	BDL
Heptachlor	ND	ND	ND	ND
Aldrin	0.15	0.17	0.16	0.14
Gamma	1.46	1.62	1.48	1.25
Chlordane				
p,p'-DDE	0.00	0.00	0.00	0.00
Dieldrin	ND	ND	ND	ND
Endrin	ND	ND	ND	ND
Alpha-	ND	ND	ND	ND
Endosulfan				
Beta-	BDL	BDL	BDL	BDL
Endosulfan				
Endosulfan Sulfate	ND	ND	ND	ND

Raw Data for Organochlorine Pesticides in Sediments (μgkg^{-1})

June				
Parameter	Well Forestry	Well Agric	Stream Forestry	Stream Agric
Beta-HCH	ND	ND	ND	ND
Delta-HCH	ND	ND	ND	ND
Lindane	BDL	BDL	BDL	BDL
Heptachlor	ND	ND	ND	ND
Aldrin	0.02	0.04	0.02	0.03
Gamma	0.20	0.30	0.10	0.09
Chlordane				
p,p'-DDE	0.85	0.92	0.71	0.76
Dieldrin	ND	ND	ND	ND
Endrin	ND	ND	ND	ND
Alpha-	ND	ND	ND	ND
Endosulfan				
Beta-	BDL	BDL	BDL	BDL
Endosulfan				
Endosulfan Sulfate	ND	ND	ND	ND

August				
Parameter	Well Forestry	Well Agric	Stream Forestry	Stream Agric
Beta-HCH	ND	ND	ND	ND
Delta-HCH	ND	ND	ND	ND
Lindane	BDL	BDL	BDL	BDL
Heptachlor	ND	ND	ND	ND
Aldrin	0.10	0.13	0.09	0.10
Gamma	0.90	1.00	0.90	0.10
Chlordane				
p,p'-DDE	0.21	0.25	0.14	0.18
Dieldrin	ND	ND	ND	ND
Endrin	ND	ND	ND	ND
Alpha-Endosulfan	ND	ND	ND	ND
Beta-Endosulfan	BDL	BDL	BDL	BDL
Endosulfan Sulfate	ND	ND	ND	ND

October				
Parameter	Well Forestry	Well Agric	Stream Forestry	Stream Agric
Beta-HCH	ND	ND	ND	ND
Delta-HCH	ND	ND	ND	ND
Lindane	BDL	BDL	BDL	BDL
Heptachlor	ND	ND	ND	ND
Aldrin	0.18	0.21	0.17	0.18
Gamma	1.70	1.90	0.17	0.18
Chlordane				
p,p'-DDE	0.10	0.17	0.10	0.14
Dieldrin	ND	ND	ND	ND
Endrin	ND	ND	ND	ND
Alpha-Endosulfan	ND	ND	ND	ND

Beta-Endosulfan	BDL	BDL	BDL	BDL
Endosulfan Sulfate	ND	ND	ND	ND

ND= Non Detected. BDL = Below Detection Limits.

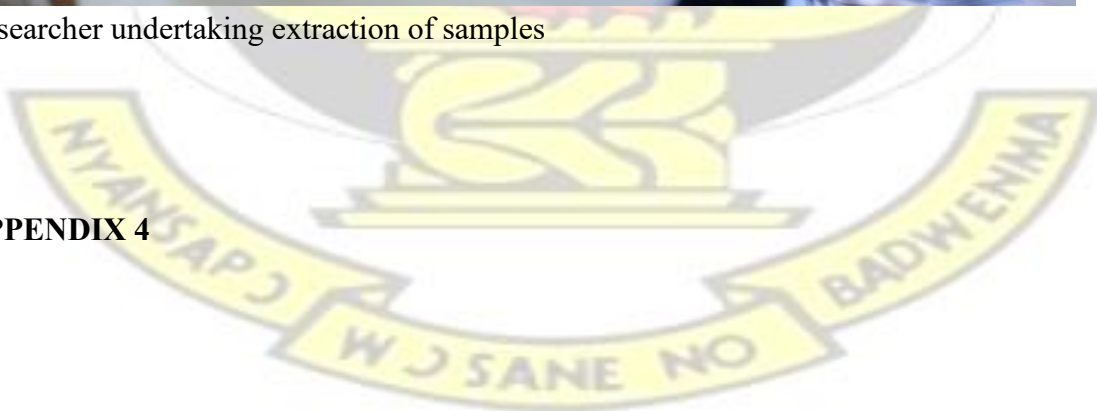
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APPENDIX 3



Researcher undertaking extraction of samples

APPENDIX 4





Researcher carrying out clean up of samples

