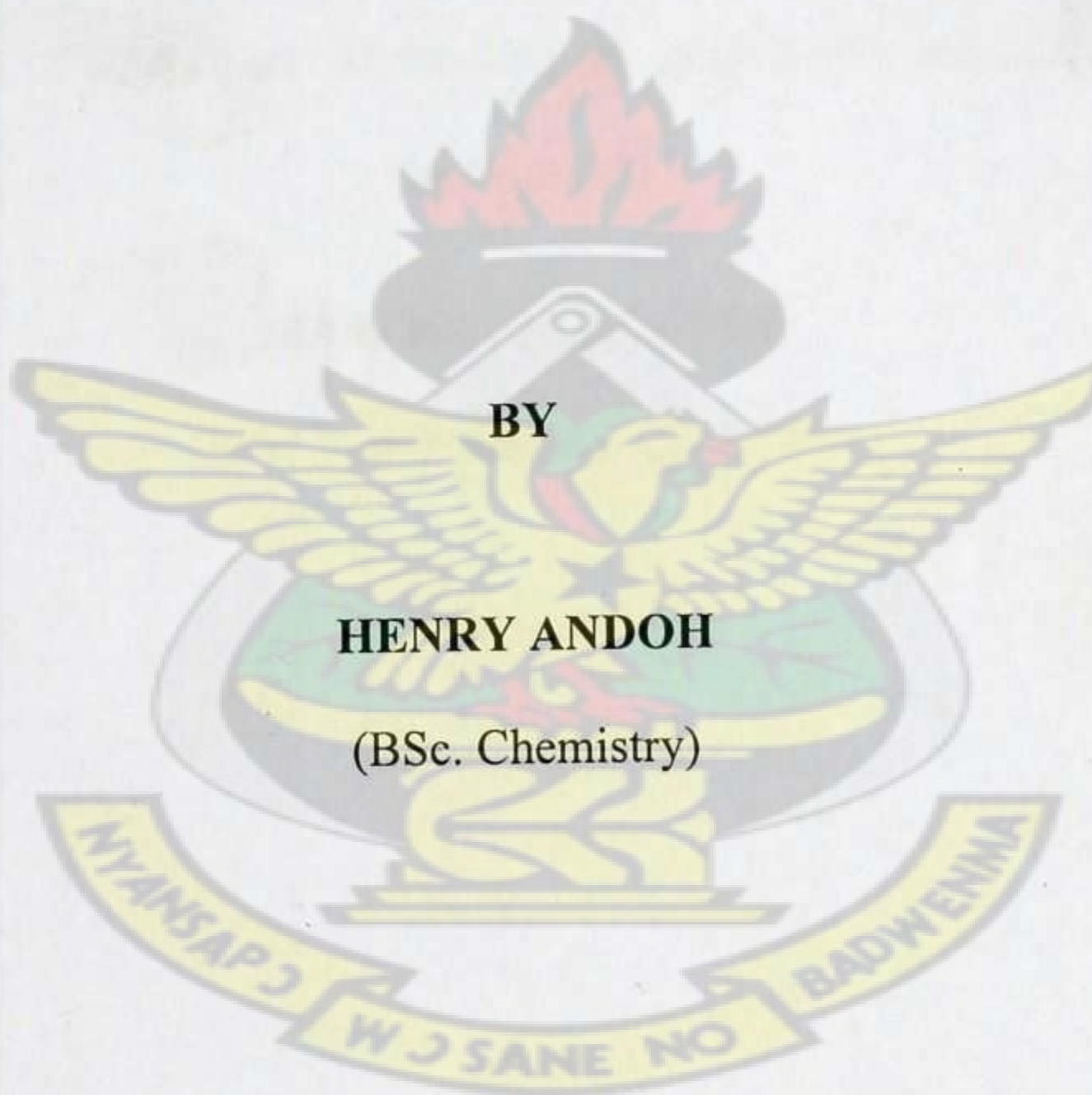# KWAME NKRUMAH UNIVERSITY OF SCIENCE AND TECHNOLOGY, KUMASI

COLLEGE OF SCIENCE

DEPARTMENT OF CHEMISTRY

RESIDUES OF PESTICIDES IN SOIL, MAIZE (*ZEA MAYS*) AND COWPEA (*VIGNA UNGUICULATA*) FROM EJURA, ASHANTI REGION, GHANA

BY

HENRY ANDOH

(BSc. Chemistry)

JUNE, 2013

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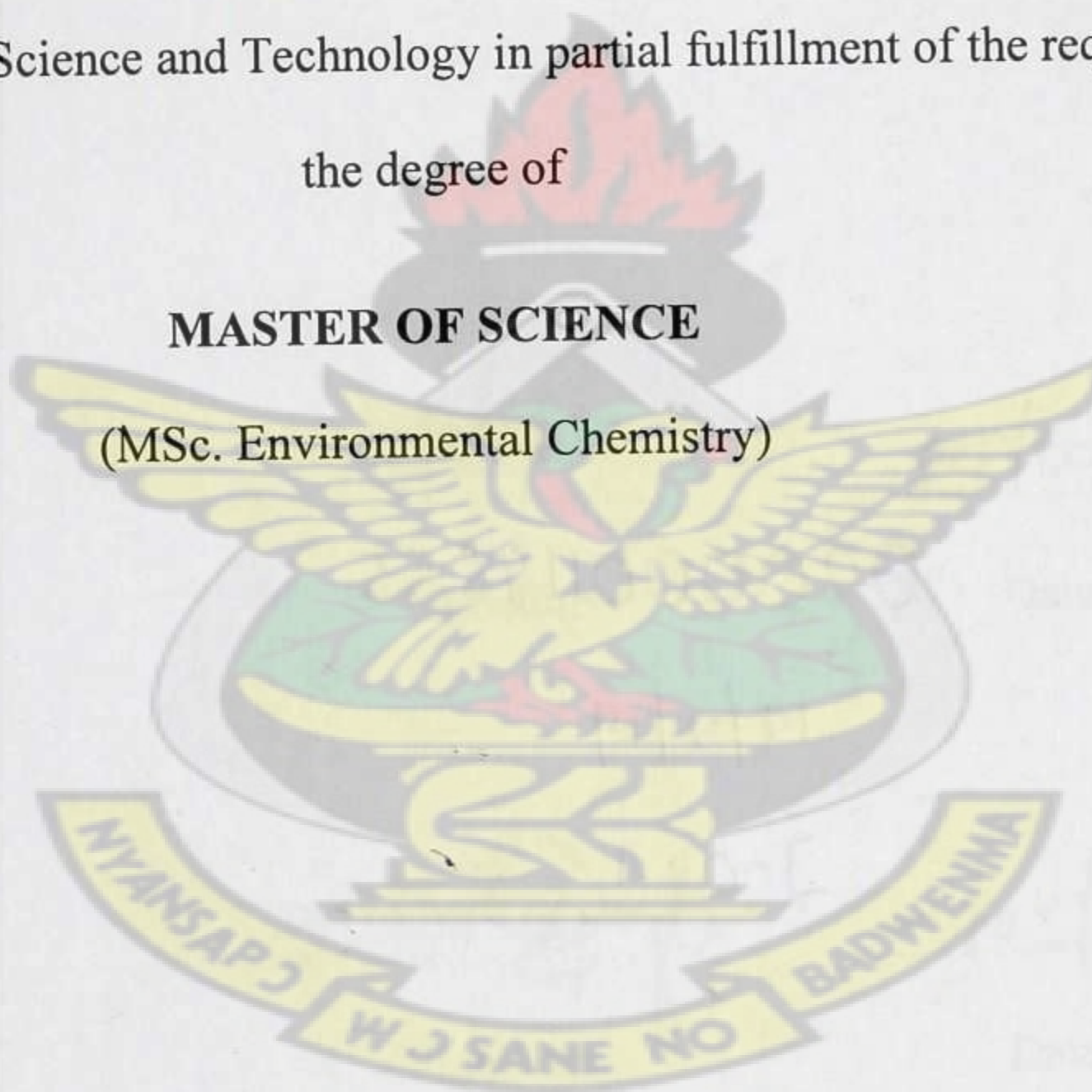
A Thesis

by

HENRY ANDOH

(BSc. Chemistry)

This is submitted to the Office of School of Research and Graduate Studies of Kwame Nkrumah University of Science and Technology in partial fulfillment of the requirement for

the degree of

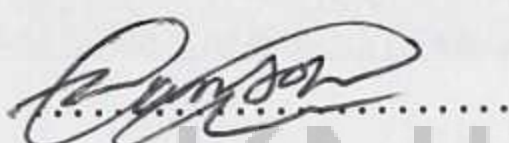**MASTER OF SCIENCE**

(MSc. Environmental Chemistry)

JUNE, 2013

DECLARATION

I hereby declare that this thesis, prepared for the degree of Masters in Chemistry (Environmental Chemistry), which was submitted by me at the Kwame Nkrumah University of Science and Technology, is my own work except where acknowledged. This work has not been submitted for any degree to any other university.

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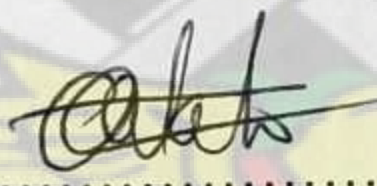
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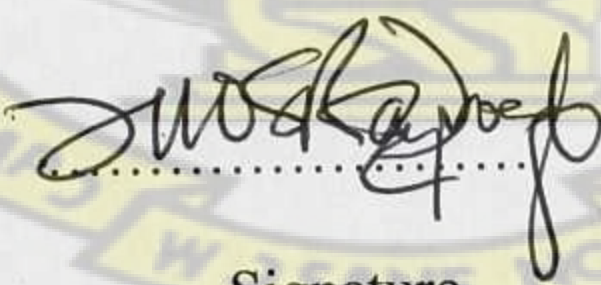
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DEDICATION

This dissertation is dedicated to my wife, Mavis Affedzie, my daughter, Helen Esi Andoh and my son, Hilary Kofi Andoh, for their prayers and support throughout this study.
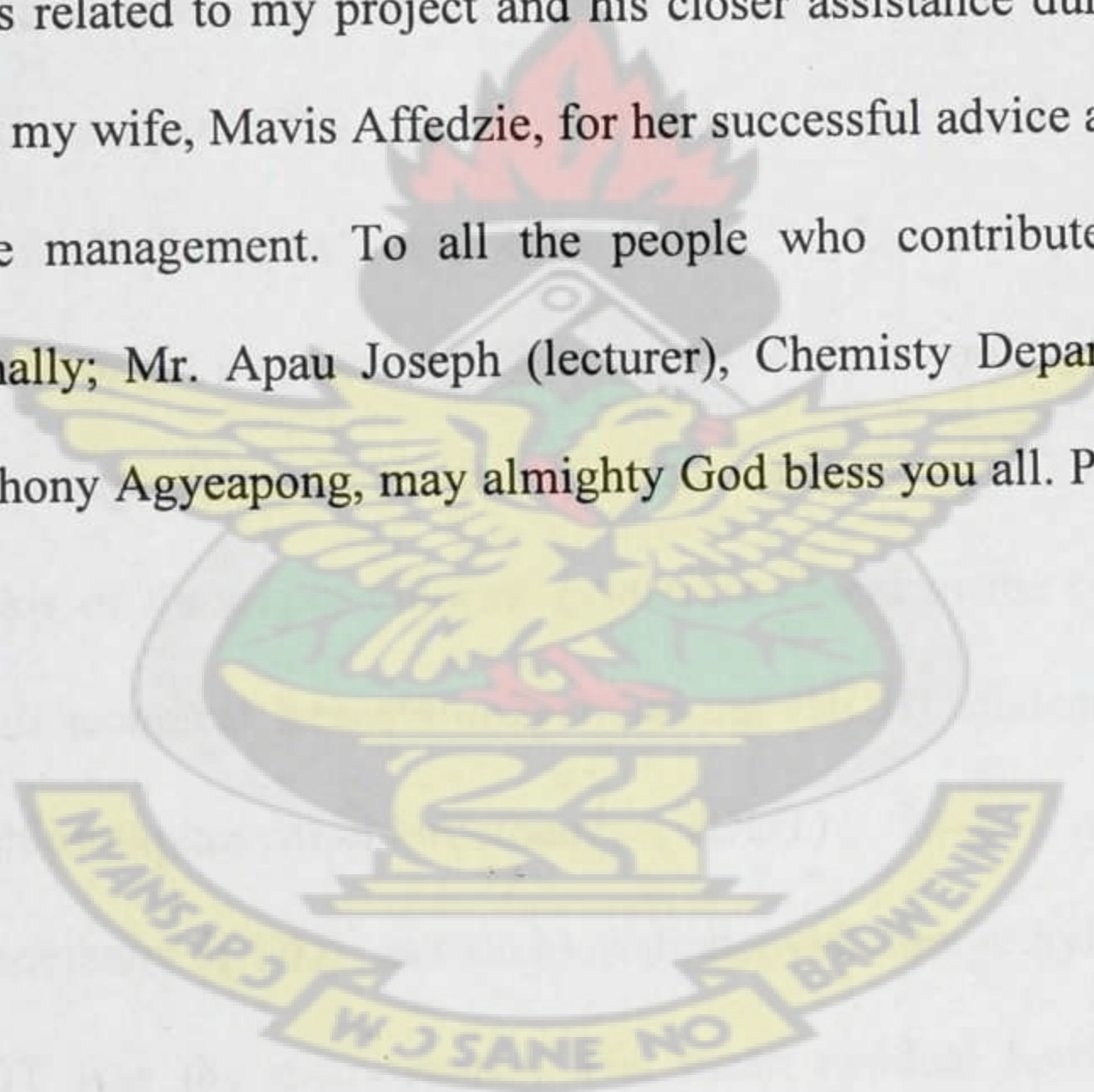
ACKNOWLEDGEMENT

ABSTRACT

Low productivity in agriculture due to damage caused by pests has led to the application of pesticides to control pest infestation. Pesticide application leaves residue on crops which can have chronic effect on the health of humans who consume such products. The aim of this study is to measure the levels of residues of pesticides in soil, maize (*Zea Mays*) and cowpea (*Vigna Unguiculata*). A total of 37 pesticides comprising 15 organochlorines, 13 organophosphorus and 9 pyrethroids, were identified in samples of soil, maize and cowpea from different farms in Ejura. Analytical methods employed included solvent extraction, gas chromatograph equipped with electron capture detector (ECD) and pulse flame photometric detector (PFPD). The extracted residues were clean-up on alumina/activated charcoal (12:1) column before the GC analysis. The results showed that the total concentration of organochlorines (0.246 mg/kg), organophosphorus (0.130 mg/kg) and pyrethroids (0.076 mg/kg) pesticides residues might be cagegorized as light pollute according to the guidelines for the assessment of soil degradation in Central and Eastern Europe (GCP/RER/007/NET – 2000). Isomeric diagnosis of the organochlorine pesticides found in the soil indicated that there was fresh input of technical hexachlorocyclohexane (HCH), endosulfan and aldrin. However, for dichlorodiphenyltrichloroethane (DDT) and its metabolites, dichlorodiphenyldichloroethane (DDD) and dichlorodiphenyldichloroethylene (DDE), past usage of technical DDT was the main source. The mean residual levels of β-HCH, β-endosulfan *p,p'* DDE and *p,p'* DDD in both maize and cowpea were found above their respective maximum residue limits (MRLs) recommended by EU while the levels of fenpropathrin and λ-cyhalothrin in only maize were also found to exceed their MRLs recommended by European Union (EU) in food. The health risk estimates revealed that residues of the investigated pesticides in maize and cowpea were under safe limit. But due to

possible toxicity and bioaccumulation tendency of pesticides by human, the concentration of

pesticides detected in the maize, cowpea and the soil could pose future health problems.

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LIST OF ABBREVIATIONS AND ACRONYMS

AChE	Acetylcholinesterase
ADI	Acceptable Daily Intake
ARfD	Acute Reference Dose
BCPC	British Crop Protection Council
DDD	Dichlorodiphenyldichloroethane
DDE	Dichlorodiphenyldichloroethylene
DDT	Dichlorodiphenyltrichloroethane
EADI	Estimated Average Daily Intake
ECD	Electron Capture Detector
EC	European Commision
EFSA	European Food Safety Authority
EU	European Union
EPA	Environmental Protection Agency
EU	European Union
FAO	Food and Agriculture Organization of the United Nations
GAIN	Global Agricultural Information Network
GAP	Good Agricultural Practice
GC	Gas Chromatograph
GDP	Gross Domestic Products
GSS	Ghana Statistical Service
HCH	Hexachlorocyclohexane
HI	Health Index

IEDIs	International Estimated Daily Intakes
ISRIC	International Soil Reference and Information Centre
IITA	International Institute of Tropical Agriculture
JMPR	Joint FAO/WHO Meeting on Pesticide Residues
LOD	Limit of Detection
mg/kg	Milligram per kilogram
MoFA	Ministry of Food and Agriculture
MRL	Maximum Residue Limit
NOAEL	No-Observed-Adverse-Effect-Level
NPAS	Northern Presbyterian Agriculture Services
OECD	Organisation of Economic Cooperation and Development
PFPD	Pulsed Flame Photometric Detector
SD	Standard deviation
SOVEUR	Soil and Terrian Vulnerability in Central and Eastern Europe
SRID	Statistics, Research and Information Directorate
USEPA	United States of Environmental Protection Agency
WHO	World Health Organization

CHAPTER ONE

1.0. INTRODUCTION

1.1. BACKGROUND OF THE STUDY

The agricultural sector is the backbone of Ghana's economy. It contributes over 34.5% of total Gross Domestic Products (GDP) and employing about 50.8 percent of the national labour force. The crop sub-sector alone contributes about 61.8% of agriculture GDP (MoFA, 2010, 2011). More than 50% of Ghana's population lives in rural areas and their livelihood depend on agriculture and allied activites.

Agriculture in Ghana is associated with low yields due to the damage caused by pests, and diseases (Horna *et al.*, 2008). The damage caused by pests and disease has led to Ghanaian farmers using high doses of pesticides to control pests and diseases. The use of pesticides in Ghana, therefore, continues to increase as several pesticides including insecticides, fungicides, herbicides, fungicides, nematicides and many others have been imported into the country to be used in agricultural production to meet the need for quality and affordable food for the growing population (MoFA, 2010).

Pesticides may be applied in a variety of ways by farmers to kill, to prevent or to control the actions of pests. They may be used on food crops after harvest to prolong their storage life. However residues from these pesticides often remain in or on food and in the environment (Bempah *et al.*, 2011; Armah, 2011; Darko *et al.*, 2008; Ntow, 2001, 2005). Consumers of food crops are therefore exposed to some levels of pesticide residues, either as a result from the direct use of pesticides on the crops or indirectly from farm animals feeding on pesticide treated field, or to a lesser extent from contaminated soils leading to chronic toxicity. Human health risks associated with chronic pesticide toxicity include cancers, neurological damage,

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reproductive effects, immune suppression, birth defects, and diminished intelligence (Calvert et al., 2001; Weiss et al., 2004).

Analysis of pesticide residues in food and in the environment is a key tool for monitoring levels of human exposure to pesticide. Pesticide residues in food are usually monitored with reference to Maximum Residue Limits (MRLs). The MRL is used to monitor whether a pesticide has been used efficiently based on authorized GAP. The MRLs for pesticides are defined as an index that represents the highest concentration of pesticide residue (expressed in mg/kg) that is legally permitted or accepted in a food or animal feed after the application of pesticides (FAO, 2002). The MRLs are always set at a level which should ensure that normally the harvested crop does not exceed the legal limit if the crop was produced according to GAP.

The MRLs are not primarily toxicological safety limits, but reflect the use of minimum quantities of pesticides to achieve effective plant protection and are set at levels where a consumer health risk is not expected. If a pesticide residue found on a given crop to be the same or lower than the MRL, then the crop can be considered safe for consumer health. On the other hand, if a residue exceeds the MRL, it is not necessarily means that the consumer is at risk, but reveals how the pesticide has been used in accordance with GAP (EFSA, 2011; FAO/WHO, 2009).

MRLs might be exceeded in cases where GAP was not respected, such as the use of unauthorized pesticides, the use of pesticides not authorized for a specific crop or the use of authorized pesticides on a crop for which an authorization was granted, but not in compliance with the authorized GAP (e.g. higher application rate or shorter pre-harvest intervals). In

exceptional cases, MRL exceedances have been observed for other reasons, such as; spray drift from neighbouring treated fields, contamination of crops at storage or packaging level and unfavourable weather conditions resulting in a reduced residue decline rate (EFSA, 2011).

For toxicological studies, dietary exposutre and risk assessments have to be performed. Dietary exposure assessment is the qualitative and/or quantitative evaluation of the likely intake of pesticides via food as well as exposure from other sources (FAO, 2006). It is estimated by comparing the expected pesticide exposure with the relevant toxicological reference values, such as the Acceptable Daily Intake (ADI) and Acute Reference Dose (ARfD). If the exposure exceeds the toxicological reference values (ADI and/or ARfD), a potential consumer health risk is identified (EFSA, 2011; FAO/WHO, 2009).

The ADI is the estimated amount of a substance in food (mg/kg body weight/day) that can be ingested daily over a lifetime without appreciable chronic health risk to the consumer (FAO, 2002; EFSA, 2011). The ADI is set on the basis of all known facts at the time of evaluation; taking into account sensitive groups within the population (e.g. children). ADI is obtained from "No-Observed-Adverse-Effect-Level (NOAEL)" for animal studies. NOAEL is the highest dose of the pesticide that does not cause detectable toxic effects on the test organism and is expressed in milligrams per kilogram of body weight per day (FAO, 2002).

The ARfD is the estimated amount of a substance in food, usually expressed in mg/kg on a body weight basis, which can be ingested over a short period of time, usually for one day, without appreciable risk to the consumer. The ARfD is set on the basis of the data produced by appropriate toxicological studies and taking into account the sensitive groups within the

population (e.g. children). An ARfD is set only for active substances which have a potential acute toxicity (EFSA, 2011).

Risk assessment is necessary in order to estimate short-term and long-term hazards posed by pesticides residues in the environment and in food (FAO/WHO, 2009). Risk assessment of pesticides is the evaluation of a known or potential effect resulting from exposure to food borne hazards. It is intended to calculate or estimate the risk to a given target organism, system or (sub) population. Risk assessment processes involve four steps: hazard identification, dose-response assessment, exposure assessment and risk characterization (OECD, 2003).

Hazard identification is the first step in risk assessment and it involves the review and evaluation of a chemical's toxic properties, that is, the extent and the type of inherent adverse health effects that a chemical may have to cause in an organism, system or population (OECD, 2003). Laboratory studies on animals are generally used to define the type of toxic effects caused bya chemical and the exposure levels at which these effects may be seen. In evaluating chemicals, scientists must determine the exposure level at which adverse effects would not be expected to occur. Most of the information on hazards posed by pesticides is available from international organizations such as JMPR for CODEX Alimentarius and EFSA in EU. Recent regulations require that hazard identification be performed before a pesticide can be approved for usage in agriculture or other areas (OECD, 2010). Some of the the hazards that have been identified concerning pesticides include: reproductive and endocrine disruption, neurodevelopmental delays, immune system, cancer and respiratory distress (Gilden, 2010).

Hazard characterization is the description of the inherent properties of an agent or situation having the potential to cause adverse effects. It includes a dose-response assessment. Dose-response assessment considers the toxic properties of a chemical and determines the lowest dose of the chemical the results in an adverse effect. Hazard characterization involves comparing the pesticide exposure concentration with the ADI or the ARfD (OECD, 2003).

Exposure assessment is the process of finding out how people come into contact with the pesticide, how often and for how long they are in contact with the substance, how much of the substance they in contact with. It includes an estimate of people's potential exposure to a chemical at work, at home, or in their diets (OECD, 2003). Exposure may be of short duration (acute, occurring once or for a short time), intermediate duration (subchronic, generally one to three months), or long-term (chronic, generally one year to lifetime). Rates of exposure are determine for breathing (inhalation), eating or drinking (ingestion), or contact with the skin (dermal absorption), depending on the chemical and the ways people may be exposed to it (EFSA, 2011).

The potential intake or consumption of pesticide residues is divided by the body weight and compared to ADI or ARfD in exposure assessment (OECD, 2003). Exposure is basically a function of the amount of consumed food and the concentration of the chemical (e.g. pesticide residue concentration) and can be expressed by the following equation:

$$\text{Dietary exposure} = \frac{(\text{Concentration of pesticide residue} \times \text{food consumption rate})}{\text{body weight}}$$

Food consumption data are essential component of dietary risk assessment. The data used depend upon the type of population being assessed; children, special ethnic groups,

geographical regions and estimation of the quantity of food eaten. Food consumption data may be obtained during food supply surveys (food balance sheets), household inventories, household food use and individual food intake surveys (Hamilton and Crossley, 2004). On an international basis, food balance sheets provide a comprehensive summary of a country's food supply over a defined time period. The food balance sheet compiles the total amount of food on a country-wide basis. The total balanced food supply is then divided by the population to yield a *per capita* consumption estimate.

1.2. STATEMENT OF THE RESEARCH PROBLEM

Although tremendous benefits have been derived from the use of pesticides in agriculture, the fact remains that a very small fraction of all applied pesticides is directly involved in the pesticidal mechanism (Moses *et al.*, 1993, Kaushik *et al.*, 2009). This implies that most of the applied pesticides find their way as 'residue' in the food and in the environment (Winteringham, 1971).

Food is a basic necessity of life and food contaminated with toxic pesticides is associated with sever effects on the human health (USEPA, 1998; Ejaz *et al.*, 2004; Calvert *et al.*, 2001; Mansour, 2004). Food contaminated with toxic pesticides is the main route of human exposure to pesticides (Juraske *et al.*, 2009; Bempah *et al.*, 2011). It is important therefore from health point of view, to systematically carry out monitoring of pesticide residues in foodstuffs and the environment in order to evaluate their health implications. The problem under investigation in this study is to monitor the residues of organochlorine, organophosphorus and synthetic pyrethroid pesticides in soil, maize and cowpea from Ejura, a major food market in Ashanti Region of Ghana.

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1.3. OBJECTIVES OF THE STUDY

1.3.1. General Objective

The main objective of this study is to monitor the residues of organochlorine, organophosphorus and pyrethroid pesticides in cowpea, maize and soil from Ejura, a major farming community in Ashanti Region of Ghana.

1.3.2. Specific Objectives

The specific objectives of this study include:

- to measure the residual levels of organochlorine, organophosphate and pyrethriods pesticides in soil maize and cowpea from Ejura, Ashanti Region, Ghana.

- to find out if the use of organochlorine, organophosphorus and pyrethroids pesticides end up in polluting the farm produce and the soil.

- to determine the possible time of application of organochlorine pesticides in the soil.

- to estimate the dietary intake and human health risks associated with organochlorine, organophosphorus and pyrethroids pesticides residues in maize and cowpea.

1.4. JUSTIFICATION OF RESEARCH

A major concern of human societies has been the attainment of sufficient quantities of food to feed the increasing population. With the development of modern agricultural practices, the use of pesticides has been the major means to ensure an adequate food supply (Kaushik *et al.*, 2009).

Maize (*Zea mays*) and cowpea (*Vigna unguiculata*) are important food and cash crops for small-scale farmers and migrants in the rural and peri-urban areas in Ghana (MoFA, 2010). Maize is a major staple food in Ghana and is the base for several food preparations. Maize is also the main component for poultry and livestock feed. Likewise, cowpea is an important source of protein, containing as much as 25% protein (Yakubu, *et al.*, 2012; Magagular and Maina, 2012). It also provides a cheap source of dietary protein for many people in Ghana, especially in areas where access to animal protein is limiting (MoFA, 2004).

Unfortunately, maize and cowpea are easily attacked by pests, both on the field and during storage. This situation causes drastic reduction in yield and thus a threat to food security (MoFA, 2011). In order to avert the problem of pest, farmers in Ghana have resorted to indiscriminate use of pesticides to reduce damage caused by pests. Farmers sometimes apply as many as 5 - 10 sprays per season, when two or three may be sufficient to control these worrisome pests (Asante and Ntow, 2009; NPAS, 2012). Pesticides used in this way often leave residues of these chemicals in or on food (Gwary *et al.*, 2012; Bempah *et al.*, 2011, 2011; Armah, 2011; Ogah *et al.*, 2011; Mawussi *et al.*, 2009; Darko and Akoto, 2008; Darko and Aquaah, 2007, 2008).

The soil has been the primary reservoir for pesticides used in agriculture, and represents a source from which residues can be released to surface and ground water (Ntow, 2001, 2005; Darko *et al.*, 2008; 2009; Dem *et al.*, 2007; Pandey *et al.*, 2011). When pesticides get in contact with the soil, they may be taken up by plants or ingested by worms and other microorganisms in the soil and thus affect the biodiversity. The pesticide may move down in the soil and either adheres to soil particles or break down via microbial and chemical pathways into other more or less toxic compounds (Menzie, 1972).

In Ghana, there are no many studies conducted to determine the residues of organochlorines, organophosphorus and pyrethroids pesticids in soil, maize and cowpea. However, the monitoring of pesticide residues in maize, cowpea and soil from Ejura (a major food market in the country) is very important in ascertiaing the levels of pesticide residues and their human health risk.

CHAPTER TWO

2.0. LITERATURE REVIEW

2.1. PESTICIDES USE AND HISTORY

Pesticide is substance or mixture of substances intended for preventing, destroying or controlling any pest (FAO, 2002). A pest is any organism that causes damage or annoyance to human beings, their animals, crops and properties. They include vectors of human or animal disease, unwanted species of plants or animals that cause harm during food production, food processing, and food storage or interfere with production and processing of wood and wood products (FAO, 2002).

Crop pests constitute a major constraint to increased food production. It is estimated that, pests can destroy about 30-48% of the world's food production (Hellar, 2002). In Africa, it is estimated that losses in agricultural production due to pests can reach 100% (Abate *et al.*, 2000). Thus, the use of pesticides is very common in agriculture to increase crop productivity in most of the African countries. The use of pesticides in pests control will therefore continue to increase as more food is needed to feed the increasing population. In Ghana, the merits of these pesticides cannot be disputed as they were massively used in the agriculture and public health sectors to curb crop pest and for disease control (Clarke *et al.*, 1997).

Pesticides are also used to control insects such as cockroaches and various flies for public hygiene purposes. In the public health sectors, pesticides are used as veterinary and human medicines (Renwick, 2002). Vector-borne diseases and those with intermediate host are among the major causes of diseases (malaria, chagas, dengue, filariasis and African trypanosomiasis) in many tropical and subtropical countries (WHO, 2010). The use of pesticides has been the most important element in the integrated approach to control vector.

Involvement of pesticides to control malaria has been the greatest achievement. From 1955 to 1970, two billion cases of malaria have been prevented and fifteen million lives saved; however, numerous problems and setbacks such as resistance to insecticides by mosquitoes have resulted from pesticide use (Bull, 1982). Pesticides work through mechanisms of action intended either to kill pests or render them ineffective (Casida, 2009). Widespread use of pesticides in developed and developing countries has contributed to increased crop yields and improved human health (Youm *et al.,* 1990).

Since the beginning of agriculture in about 8000 BC, humans have used many methods to control pests. The ancient Sumerians used elemental sulphur dust to control insects (Goel and Aggrawal, 2007). From that time up to 1860s, substances such as arsenic, soap, plants and animals were used to control worrisome pests. The first synthetic organic pesticide was DDT; synthesized by Ziedler in 1873 (Othmer, 1996), but its insecticidal effect was discovered in 1939 by Paul Muller (Goel and Aggrawal, 2007). Because of its broad-spectrum activity, cheapness and easy to apply, DDT was described as a miraculous substance (Keneth, 1992; Gruzdyer *et al.*, 1983). However, with the recognition that it was a threat to biodiversity, many countries have banned its use (Goel and Aggrawal, 2007).

From 1944 to the 1970s, development of numerous other synthetic organic pesticides such as herbicides including 2,4-D, atrazine and alachlor (1944, 1960s), organophosphate insecticides including parathion and parathion-methyl (1946), and synthetic pyrethroids (allethrin, fenvalerate and permethrin) (1970s) has occurred. The intensive use of pesticides in agriculture is known to be coupled with the "green revolution", which allows the use of pesticide as an agricultural practices (Vocke, 1986).

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2.2. CLASSIFICATION OF PESTICIDES

Since pesticides vary in identity, physical and chemical properties, it is therefore logical to have them classified. Synthetic pesticides can be classified in various ways depending on the needs. However, there are three most popular ways of classifying pesticides which are; classification based on the mode of action, classification based on the target pest species and classification based on the chemical composition of the pesticide (Drum, 1980).

2.2.1. Classification of Pesticides based on the mode of action

Under this type of classification, pesticides are classified based on the way in which they act to bring about the desired effect. In this way pesticides are classified as:

- Physical poisons (examples heavy oils, tar oils etc.)
- Protoplasmic poisons (examples, mercury, copper, arsenics etc.)
- Respiratory poisons (examples, HCN, CO etc.)
- Nerve poisons (examples, organophosphates and carbamates).

2.2.2. Classification of Pesticides based on the mode of entry

Based on the mode of entry pesticides are classified as:

- Stomach poisons: Enter the body through the mouth of the pest. Examples are dieldrin, sulphur, lead arsenate etc.
- Contact poisons: Enter the body through the respiratory system of the pest. They are volatile poisons. Examples are hydrogen cyanide, methyl bromide, carbon tetrachloride, paraquat, diquat dibromide etc.

- Systemic poisons: These are translocated inside the plant body through xylem after the application on absorptive surfaces of plants like leaves, roots etc. examples are phorate, carbofuran, aldicarb, methyl demeton, 2, 4-D and glyphosate (Buchel, 1983).

2.2.3. Classification of Pesticides based on the targeted pest species

In this type of classification, pesticides are named after the name of the corresponding pest in target as shown in table 2.1.

Table 2.1. Classification of pesticides based on the target organisms

Type of Pesticide	Target organism/pest
Insecticides	Insects
Herbicides	Weeds
Rodenticides	Rodents
Fungicides	Fungi
Acaricides and Miticides	Arachides of the order Acarina such as ticks and mites
Molluscides	Mollusks
Bactericides	Bacteria
Avicides	Bird pests
Virucides	Virus
Algicides	Algae

2.2.4. Classification of Pesticides based on the chemical composition

Under chemical classification, pesticides are categorized according to the chemical nature of the active ingredients. This classification is by far the most useful classification to researchers in the field of pesticides and environment. Based on chemical classification, pesticides are classified into four main groups namely; organochlorines, organophosphorous, carbamates and pyrethroids (Buchel, 1983).

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2.2.4.1. Organochlorine Pesticides

Organochlorine pesticides are synthetic organic compounds containing three or more chlorine atoms. They can also be classified into four groups; dichlorodiphenyl (such as DDT), cyclodienes (such as aldrin, endosulfan and heptachlor), chlorinated benzenes (such as hexachlorobenzene) and cyclohexanes (such as lindane). Organochlorines were the first synthetic organic pesticides to be used in agriculture and in public health. Most of them are widely used as insecticides for control of a wide range of insects. The chemical structures of organochlorine compounds (β-HCH, γ-HCH, δ-HCH, heptachlor, methoxychlor, aldrin, dieldrin, endrin, γ-chlordane, α-endosulfan, β-endosulfan, endosulfan sulphate, p,p'-DDT, p,p'-DDE and p,p'-DDD) investigated in this study are given in Appendix 1.

Organochlorine insecticides belong to one of the insecticides classes that affect the nerve system by depolarization of the nerve membranes. They facilitate synaptic transmission and inhibit the γ-aminobutyric acid–chloride channel complex (Narahashi *et al.*, 1992) leading to convulsion and paralysis of the insect and its eventual death. They also cause sensitization of the myocardium to both endogenous as well as exogenous catecholamines and predispose to arrhythmias (Goel and Aggarwal, 2007). Some organochlorine pesticides are endocrine disruptors (Wang *et al.*, 2008; USEPA, 1998).

Chemically, organochlorine pesticides are relatively stable compounds and are characterized by their long-term residual effects in the environment since they are resistant to most chemical and microbial degradations (Rugman and Cosstick, 1990; Ntow, 2001). Organochlorine pesticides are generally insoluble in water and have the tendency to adsorb onto suspended particulate matter in water, on bottom sediments and on organic matter in soil. With their high lipophilicity, organochlorine pesticides tend to accumulate in fatty

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tissues and thus become bio-magnified as they pass along food chains (Jiries *et al.*, 2002; Rugman and Cosstick, 1990).

Because organochlorine pesticides persist in the environment and their toxicity to non-target organisms including humans have been established (U.S-EPA, 1998), many countries including Ghana have banned or restricted the use of organochlorine pesticides. Lindane was phased out in the year 2002 and endosulphan, restricted for cotton pest control is now misused for the control of *capsids* on cocoa and maize, as well as pests on coffee (Asante and Ntow, 2009).

However, recent studies conducted in Ghana have detected the presence of organochlorine pesticide residues in water, sediments (Ntow, 2001, 2005; Darko *et al.*, 2008), fish (Fianko *et al.*, 2011; Afful *et al.*, 2010; Essumang, 2009; Darko *et al.*, 2008), meats (Darko and Acquaah, 2007), vegetables and fruits (Bempah *et al.*, 2011; Darko and Akoto, 2008), fruit-based soft drinks (Bempah et al., 2011), human breast milk (Tutu *et al.*, 2011; Ntow *et al.*, 2007) and blood serum (Ntow *et al.*, 2007). From international point of view a lot of researchers have also reported the occurrence of organochlorine pesticide residues in soil (Wang *et al.*, 2008; Shi *et al.*, 2011), sediments (Pandey *et al.*, 2011), and water (Ize-Lyamu *et al.*, 2007).

2.2.4.2. Organophosphorus Pesticides

The organophosphorus pesticides are synthetic esters, amides, or thiol derivatives of the phosphoric, phosphonic, phosphorothioic, or phosphonothioic acids. The chemical structure of all organophosphorus pesticides consists of a central phosphorus atom, with either a

double bonded oxygen (P=O), which are termed oxon pesticides, or a double bonded sulphur

atom (P=S), which are termed as thion pesticides (Figure 2.1).

$$
\begin{array}{ccc}
\text{O} & & \text{S} \\
\parallel & & \parallel \\
R_1\!\!-\!\!P\!\!-\!\!R_2 & & R_1\!\!-\!\!P\!\!-\!\!R_2 \\
\mid & & \mid \\
X & & X \\
\text{Oxons} & & \text{Thions}
\end{array}
$$
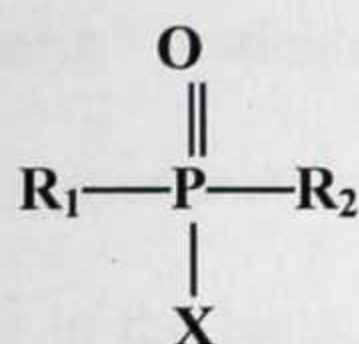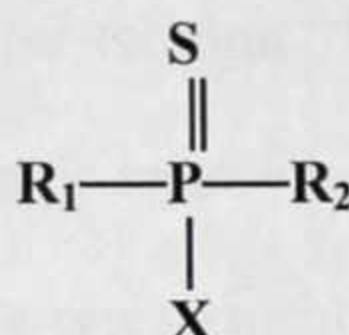
Figure 2.1. General chemical structure of oxon and thion organophosphorus compounds

The R_1 and R_2 generally tend to be methyl or ethyl groups, while X is a labile leaving group

(Sherma, 1995). The chemical structures of organophosphorus compounds (dimethoate,

methamidophos, ethoprophos, phorate, diazinon, fonofos, pirimiphos-methyl,

chlorfenvinphos, chlorpyrifos, malathion, fenitrothion, parathion-ethyl and profenofos) that

were investigated in this study are given in Appendix 2.

Organophosphorus compounds were first synthesized in significant amounts during the

1940s. They are widely used as pesticides that are applied primarily to crops for the control

of agricultural pests. Besides, organophosphorus pesticides are also applied in non-

agricultural sectors such as warehouses, as well as turf and ornamental purposes. Some are

also applied for residential and commercial uses such as termite and mosquito control to

protect public health against diseases such as malaria, dengue fever and encephalitis

(USEPA, 1999).

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The wide use of organophosphorus pesticides is because they are inexpensive and have a broad spectrum property. In general, insects have not developed resistance to organophosphorus pesticides as they have done to some other pesticides (USEPA, 1999). Organophosphorus pesticides have less potential for chronic health effect and less environmental contamination because they usually degrade rapidly in the environment and do not accumulate in the biota; they have been a suitable replacement for the more persistent organochlorine pesticides. Organophosphorus pesticides, however, have higher acute toxicity to humans and most of them are classified by USEPA as toxicity Class I (highly toxic) or toxicity Class II (moderately toxic) (USEPA, 1999).

The main mode of action of the organophosphorus pesticides is inhibition of acetylcholinesterase, the enzyme that terminates the action of acetylcholine neurotransmitter, which is released by nerve stimulation, on postsynaptic cholinergic receptors in the nervous system. As a result, nervous impulses fail to move across the synapse causing a rapid twitching of voluntary muscles and hence paralysis. Organophosphorus pesticides produce an irreversible inhibition to acetylcholinesterase (Goel and Aggrawal, 2007).

Human are commonly exposed to organophosphorus pesticides through food. One of the important aspects for minimizing the potential hazards to human health is the monitoring of pesticides residues in the environment. Studies conducted in Ghana, have demonstrated the presence of organophosphorus pesticide residues in water and fish (Essumang et al., 2007) and vegetables (Darko and Akoto, 2008).

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2.2.4.3. Carbamates Pesticides

Carbamates are organic pesticides derived from carbamic acid with the general formula

$$R^1 - O - \underset{\underset{O}{\parallel}}{C} - N \underset{R^3}{\overset{R^2}{<}}$$
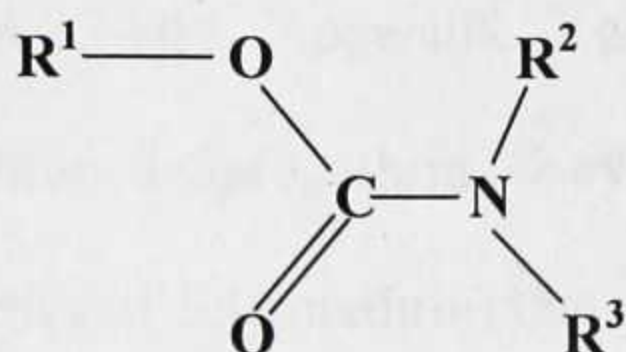
Figure 2.2. General chemical structure of carbamates pesticides

Where, R^1 is an alchohol group, R^2 is a methyl group and R^3 is usually hydrogen. Carbamates have the same presumed primary mechanism of toxicity that characterizes organophosphorus, that is, they inhibit the enzyme acetylcholinesterase (AChE). For this reason, organophosphorus and carbamates are often considered together, but the cholinesterase inhibitions of carbamates differ from that of organophosphorus in that, it is species specific and it is reversible (Drum, 1980).

Carbamates are less toxic but very effective as insecticides, miticides, molluscicides, fungicides, and herbicides (Ogah *et al.*, 2011). Some of the widely used insecticides under this group include carbaryl, carbofuran, methomyl, propoxur and aminocarb. The residual persistence of the carbamate insecticides varies from a few hours to several weeks depending both on the nature of the compound and the conditions of use (Drum, 1980).

2.2.4.4. Pyrethroid Pesticides

Synthetic pyrethroids are synthesized derivatives of naturally occurring pyrethrins; which are obtained from the pyrethrum plant, the oleo resin extract of dried chrysanthemum flowers, but are more stable to light than their natural pyrethrin. Pyrethroids are typically used as

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broad-spectrum insecticides and are known for their fast knocking down effect against insect pests (USEPA, 2009). In general, pyrethroids are less toxic to mammals and are considered good candidates for the replacement of the more toxic organophosphorus insecticides (Seyed and Somashekar, 2010; USEPA, 2009). Appendix 3 shows the chemical structures of pyrethroids compounds (bifenthrin, fenpropathrin, λ-cyhalothrin, permethrin, cyfluthrin, cypermethrin, fenvalerate, allethrin and deltamethrin) that were investigated in this study.

A current study conducted by Bempah *et al.,* (2011), determined pyrethroids residues in fresh fruits and vegetables from Kumasi Metropolis. It was observed that residues of permethrin, cypermethrin, cyfluthrin, deltamethrin and fenvalerate were found contaminating the various fruits and vegetables. Similar to the study done in 2011 by Bempah *et al.,* a study was conducted by Armah (2011) on 9 pyrethroid pesticides (allethrin, bifenthrin, λ-cyhalothrin, fenvalerate 2, cyfluthrin 3, cypermethrin 2, permethrin and deltamethrin) residues in cabbage. Most the residues measured exceeded the MRL for consumption. Also study carried out in India indicated residues of cypermethrin and fenvalerate in samples of grapes (Sayed and Somashekar, 2010; Kumar *et al.,* 2006). A related study carried out in Egypt also indicated residues of 13 pyrethroid insecticides in water, soil, fish and cow milk (Tchounwou *et al.,* 2002).

2.3. TRENDS AND PATTERNS OF PESTICIDE USE IN GHANA

Ghana's total land area is 23,853,910 hectares. About 13,628,179 hectares representing 57.1% of Ghana's total land area is suitable for agriculture. However, the total area under cultivation as at 2010 was 7,846,551 hectares representing 57.6% of the agricultural land area (GSS, 2010). Agriculture is predominantly on a smallholder basis in Ghana. About 90% of farm holdings are less than 2 hectares in size (MoFA, 2010). Most of these farmers depend on

chemical pesticides to control pests and diseases. The uses of pesticides in Ghana's agriculture will therefore, continue to increase as more food is needed to feed the increasing population (Asante and Ntow, 2009).

A study conducted from 1992 to 1994 in the Ashanti, Brong Ahafo, Eastern and Western 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). According to Ghana Statistical Service, in 1993 a total of 3,854,126 kg of pesticides were imported into the country with the following distribution and use as per Figure 2.3 (GSS, 2010).
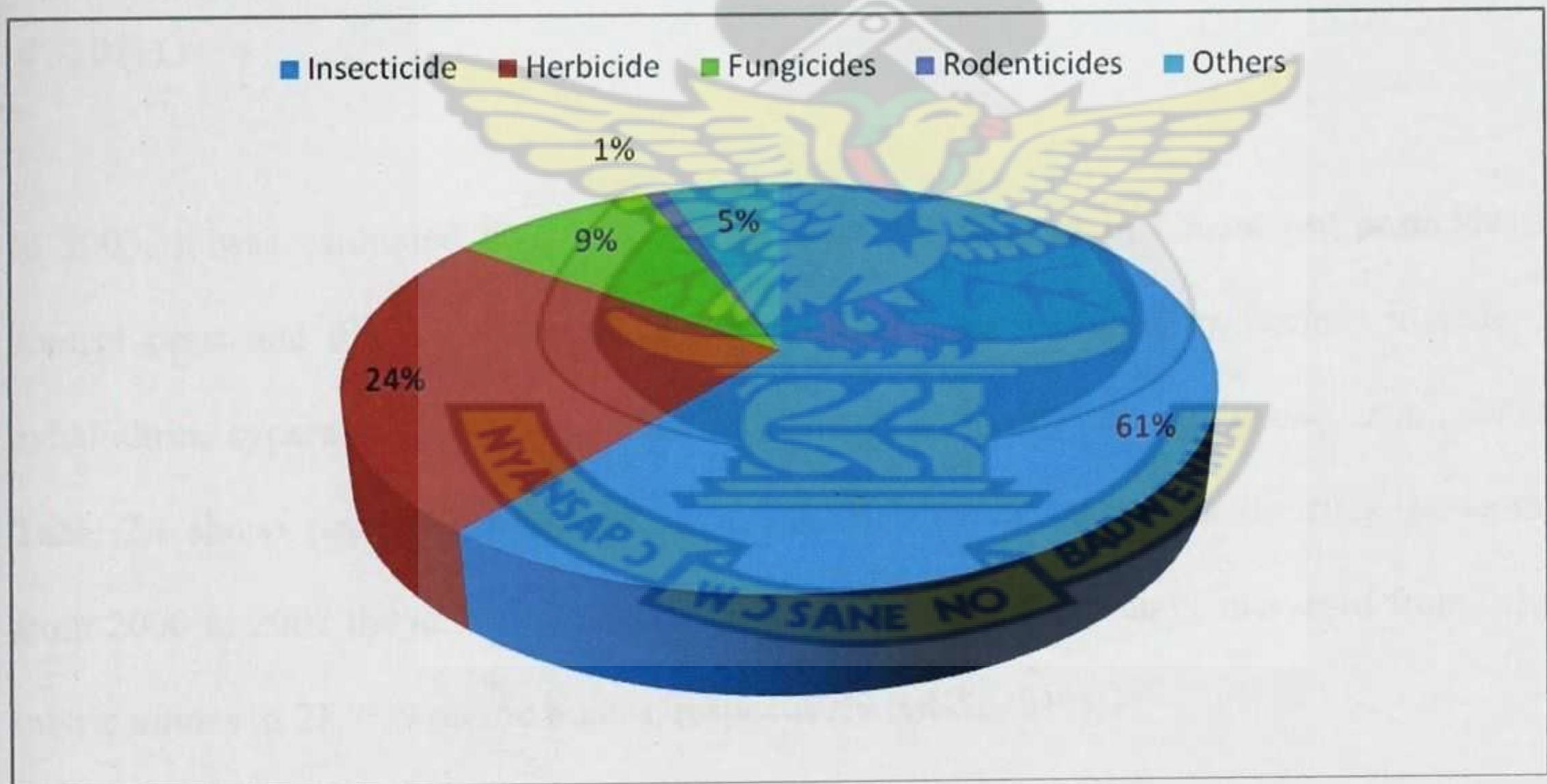
Figure 2.3 Distribution of pesticides imported into Ghana as at 1993

In 2008, Ntow (2008) conducted a survey in vegetable farming areas in Ghana and a total of 43 pesticides were found in use. The pesticides comprised insecticides (33%), fungicides (23%) and herbicides (44%). Data on pesticides as at 2005, from the Environmental

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Protection Agency in Ghana, indicated that about 141 different types of pesticide products have been registered to be used in the country. Of this number of pesticides, 41.84%, 16.31%, 0.43% and 0.01% were insecticides, fungicides, herbicides, respectively and others was 0.01% (EPA-Ghana, 2008).

Pesticide use in Ghana has increased over the years and it is particularly elevated in high value cash crops and vegetable production areas such as Ashanti, Brong Ahafo, Eastern and Western regions (*Horna et al,.* 2007; Asante and Ntow, 2009; Fianko *et al.*, 2011). Among the different types of insecticides known, organochlorine insecticides was the most popular and extensively used by farmers because they are less expensive pesticides and have broad spectrum activity. In Ghana, it is known that lindane was widely used in cocoa plantation, vegetable farms and maize cultivation for control of stem borers (Ntow *et al.*, 2006; Fianko *et al.*, 2011).

In 2003, it was estimated that, about 87% vegetable farmers in Ghana use pesticides to control pests and disease (Dinham, 2003). Pesticides mostly used by farmers include, λ-cyhalothrin, cypermethrin, chlorpyrifos, dimethoate and endosulfan (Yeboah *et al.*, 2004). Table 2.1 shows pesticides imported for use in Ghana as at 2007. The statistics shows that . from 2000 to 2007 the amount of pesticides imported into the country increased from 2,349 metric tonnes to 21, 609 metric tonnes, respectively (GSS, 2010).

Table 2.2. Annual imported pesticides into Ghana from 2000 to 2007 (metric tonnes)

Type of pesticides	Year							
	2000	**2001**	**2002**	**2003**	**2004**	**2005**	**2006**	**2007**
Insecticides	1,195	907	1,090	5,829	610	5,982	6,921	9,979
Fungicides	673	618	1,345	1,673	770	1,713	2,148	2,575
Herbicides	224	598	582	2,472	1,096	5,340	8,780	8,932
Rodenticides	257	384	563	159	NA	13	78	123
Total	**2,349**	**2,507**	**3,580**	**10,133**	**2,476**	**13,048**	**17,927**	**21,609**

*Source: Ministry of Food and Agriculture/ Ghana Statistical Service, 2009.

*NA = Not Available

The use of pesticides in Ghana is governed by Part II of Environmental Protection Agency (EPA) Act No. 490 of 1994. The EPA and in particular its Chemical Control and Management Centre are responsible for pesticides control and management. The agency periodically provides a list of registered pesticides and banned pesticides for public use. Ghana's Environmental Protection Act requires pesticides to be classified as for general use, restricted use, suspended or banned. A pesticide may be suspended or restricted if its application may have unreasonable effects on people, animals or the environment. Currently EPA-Ghana approves the use of 245 pesticides while 26 have been banned and a small number are restricted.

Banned pesticides in Ghana, as at July 2010 include 2,4,5-T and its salts and esters, aldrin, binapacryl, captafol, chlordane, chlordimeform, chlorobenzilate, DDT, dieldrin, dinoseb and its salts and esters, dinitro-otho-cresol and its salts, HCH (mixed isomers), heptachlor, HCB, parathion, pentachlorphenol and its salts and esters, toxaphene, mirex, methamidophos,

methyl-parathion, monocrotophos, phosphamidon, methyl bromide and dustable powder formulation containing a combination of benomyl at or above 7% carbofurna at or above 10% and thiram at or above 15% (EPA-Ghana, 2008; NPAS, 2012).

It has long been known that various restricted or banned pesticides are still being used by farmers in Ghana to grow food crops. In 2008, it was found that 71 tonnes of banned pesticides, most of which were discovered at the warehouses of the Ghana Cocoa Board, the Benso Oil Plantation and the Twifo Oil Palm Plantation (NPAS, 2012). Also, study conducted in 2005 by Amoah et al., (2006) found that lindane and endosulfan, which were then restricted to use on cocoa, coffee and maize, were being used on vegetables, along with DDT, which was banned altogether. It is known that about 7 banned or restricted pesticides (aldrin, dieldrin, endosulfan, lindane, DDT, methylbromide and carbofuran) appear to be still being used by some Ghanaian farmers (NPAS, 2012). Recent survey carried out by NPAS (2012) in Upper East Region found that four banned or restricted pesticides (DDT, aldrin, lindane and dieldrin) were on sale in local agrochemical dealers' shops.

2.4. PESTICIDE RESIDUES IN THE GHANAIAN ENVIRONMENT

Farmers in Ghana have engaged in extensive use of pesticides to control crop loss from pests and diseases (Fianko 2011; Ntow, 2008; Yeboah et al., 2004; Dinham, 2003). Due to application of pesticides on crops for control of pests, their residues are found in the environmental compartments such as soil, water, air and on crops. Pesticide residues found in the environment and on crops are usually accompanied with harmful environmental and public health effects (USEPA, 1998; Mansour, 2004).

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Approximately 90% of agricultural pesticide application never reaches its target organisms but, instead dispersed throughout the environmental compartments such as soil, water and air (Moses et al., 1993). Soil is the principal reservoir of environmental pesticide residues, this representing a source from which residues can be leached into surface and ground water, ultimately becomes the source of drinking water (Shalaby and Abdou, 2010). Pesticide residues found in soil can also be picked up by roots of plants, contaminate food crop and finally be exposed to human (Hamilton and Crossley, 2004; Barriuso et al., 2008).

Organochlorine pesticides are among the major group of chemicals that have long-term residual effect in the environment because they are resistant to most chemical and microbial degradation. In response to their adverse effects seen in wildlife and humans, the production and use of organochlorines have been banned in many countries including Ghana (Ntow, 2001, 2005). Organophosphorus and pyrethroid pesticides are relatively safer as compared to organochlorines as their degradation is much faster in environment. However, long-term exposure has been shown to cause neurotoxic, mutagenic and carcinogenic effect (Das et al., 2007).

Recent studies conducted in Ghana have revealed the presence of pesticide residues in food, water, soil and sediments (Bempah, 2011, 2011, 2010; Fianko et al., 2010; Ntow, 2001, 2005; Essumang et al., 2009; Darko and Aquaah, 2008; Dodoo et al., 2006; Darko et al., 2008). The results of these studies demonstrated the contamination levels of pesticide residues in these substances, even in tropical environment such as Ghana.

The general population is exposed to low levels of pesticides through pesticide residues. There is now overwhelming evidence that some of these pesticides do pose potential risk to

humans and other life forms as well as the environment (Mansour, 2004; Ghimire, 2007). A brief accounts about results of some investigations showing contamination levels of natural ecosystems and different types of food by pesticide residues in Ghana are given below.

2.4.1. Pesticide residues in Soil and Sediments

Ntow (2001) recorded detectable levels of some organochlorine pesticides (lindane; 3.20 μg/kg, α-endosulfan; 0.19 μg/kg, β-endosulfan; 0.13 μg/kg, endosulfan sulphate 0.23 μg/kg, α-HCH; 0.90 μg/kg, heptachlor; 0.63 μg/kg and p,p'-DDE; 0.46 μg/kg) in soil from Akomadan. Generally, the soils were highly contaminated by lindane as reported.

A similar study conducted on top soil samples collected from five cocoa growing districts in the central region contained residues of lindane and propoxur. Generally, lindane residues (range 2.10 - 15.4 mg/kg) occurred in greater amount than propoxur (1.71 – 7.95 mg/kg) (Dodoo et al., 2006).

Sediment samples collected from Volta Lake contained 2.30 μg/kg lindane, 0.21 μg/kg α-endosulfan, 0.17 μg/kg β-endosulfan, 0.36 μg/kg endosulfan sulphate, 9.00 μg/kg p,p'-DDT and 52.30 μg/kg p,p'-DDE (Ntow, 2005). Another studies conducted by Darko et al., (2008) on Lake Bosomtwi also recorded some levels of organochlorine pesticide residues; lindane; 6.56 μg/kg, endosulfan; 9.68 μg/kg, aldrin; 0.07 μg/kg, dieldrin 0.07 μg/kg, p,p'-DDE; 8.34 μg/kg and p,p'-DDT; 4.41 μg/kg.

However, in comparing the two studies, it was found that p,p'-DDE concentration recorded in Volta Lake is about seven folds that recorded in Lake Bosomtwi. It was concluded that the marked difference in p,p'-DDE levels from these two Lakes may be due to the fact that all

major rivers along which most commercial farming activities in the country take place lead to the Volta Lake.

2.4.2. Pesticide residues in Surface and Ground Water

Water samples from rivers and lagoons in Ghana revealed the presence of significant levels of pesticide residues. Water samples taken from the Volta Lake at Akosombo were found to be contaminated with residues of lindane (0.008 mg/kg), α-endosulfan (0.036 mg/kg), β-endosulfan (0.024 mg/kg) and endosulfan sulphate (0.023 mg/kg) (Ntow, 2005). A similar studies conducted by Darko *et al.*, (2008) on Lake Bosomtwi also show some levels of lindane (0.071 ng/g), endosulfan (0.064 ng/kg), *p,p'*-DDE (0.061 ng/g) and *p,p'*-DDT (0.012 ng/g) in the water samples collected from the lake.

Essumang *et al.*, (2009) determined the residues of four organochlorine pesticides (*o,p'*-DDE, *p,p'*-DDD, *p,p'*-DDT and propiconazol) and four organophosphorus pesticides (fenitrothion, chlorpyrifos, dichlorvos and diazinon) in water from four lagoons; Chemu lagoon, Korle lagoon, Fosu lagoo, and Etsii lagoon. Total of the mean pesticide residues contamination from the four lagoons: Chemu, Korle, Fosu and Etsii were found to be 2.6384 mg/L, 0.4992 mg/L, 0.3045 mg/L and 1.3629 mg/L, respectively. This shows some level of exposure of pesticide which would be harmful to humans.

2.4.3. Pesticide residues in Food

Generally, food has been the main exposure route of pesticide residues to human beings (Juraske *et al.*, 2009). Human exposure to pesticide residues through contaminated food accounts for more than 90% of the total exposurer (González-Rodriguez *et al.*, 2008).

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Pesticide residues in food are as a result of direct application of pesticides to crops growing in the field and also to a lesser extent from pesticides residues remaining in the soil (Barriuso *et al.*, 2008). It is therefore of significance to monitor these harmful pesticides in food to control and minimize health risks. In the past few years, a number of academic studies have been carried out to investigate pesticides residues in food. They show the presence of pesticide residues in a number of food commodities in the country.

Bempah *et al.*, (2011) conducted a study to assess the concentration of organochlorines (γ-HCH, methoxychlor, aldrin, dieldrin, endrin, *p,p'*-DDE and *p,p'*-DDT) and pyrethroids (permethrin, cyfluthrin, cypermethrin, fenvalerate and deltamethrin) residues in locally produced fruits and vegetables sold at markets in Kumasi. Out of 350 total samples analysed, organochlorine pesticide residues were present in 59.2% while synthetic pyrethroid pesticide residues were present in 67.2% of the samples. 19% of the samples contain residues that were above the MRL. This means that continuous consumption of such fruits with modest pesticide levels can accumulate and could result in deadly chronic effects.

A similar study by Bempah *et al.*, (2011) also monitored the levels of organochlorine pesticide residues in locally produced fruit-based soft drinks in Ghana. A total of 84 fruit-based soft drink samples were analyzed for organochlorine pesticide residues (γ-HCH, pp-DDT, pp-DDE, endrin, endrin ketone, endrin aldehyde, heptachlor, aldrin, α-endosulfan and γ-chlordane). The data showed that most of the fruit-based soft drink samples analyzed contain residues of the monitored pesticides above the EU MRL level in drinking water. The results obtained also showed that 9.5 % of the fruit-based soft drink samples analyzed contained no detectable level of the monitored pesticides, 14.3 % of the samples contained 1

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pesticide, 20.2 % contained 2 pesticides, 26.2 % contained 3 pesticides and 29.8 % contained 3 or more pesticide residues.

Armah (2011) monitored 21 pesticide residues of which 12 were organophosphorus and 9 were synthetic pyrethroid in cabbage collected from farm during harvest. Out of 40 samples, more than two-thirds were found with residues exceeding the MRLs. The highest residue levels were observed for allethrin (9.566 mg/kg) and phorate (2.077 mg/kg). The level of allethrin in some cabbage samples was higher than the MRL by a factor of 20.

Darko and Akoto (2008) determined the dietary intake of organophosphorus pesticide residues through vegetables (tomatoes, egg plant and pepper) from Kumasi. Dichlorvos was the most frequently detected in all the samples analyzed. Levels of malathion in tomatoes (0.120 ± 0.101 mg/kg) and pepper (0.143 ± 0.042 mg/kg) exceeded the MRL of 0.1 mg/kg. Health risks were found to be associated with methyl-chlorpyrifos, ethyl-chlorpyrifos, and omethioate in tomatoes and methyl-chlorpyrifos, ethyl-chlorpyrifos, dichlorvos, monocrotophos and omethioate in eggplant.

Fianko et al., (2010) conducted a survey on fish from the Densu River Basin. Pesticide residues in fish samples varied greatly; from 0.10 - 30.90 µg/kg. The estimated dose for aldrin, methoxychlor, γ-chlordane, endrin aldehyde, endrin ketone, endrin, p,p'-DDT and δ-HCH do not pose a direct hazard to human health, although present in fish samples since the values were lower than toxic thresholds as well as reference dose. However, γ-HCH, heptachlor, α-endosulfan, endosulfan sulphate, p,p'-DDE and dieldrin levels exceeded the reference dose, indicating a great potential for systemic toxicity in children who are considered to be the most vulnerable population subgroup.

Darko and Acquaah (2007) screened residues of organochlorine pesticides (lindane, endosulfan, aldrin, dieldrin, DDE and DDT) in beef samples from the Kumasi and Buoho abattoirs. The average concentration of residues in lean beef ranged from 0.60 – 11.48 µg/kg at Bouho and 1.43 – 42.93 µg/kg at Kumasi abottior. The average concentration of residues found in fatty beef also ranged from 1.79 – 403.82 µg/kg at Buoho and 2.06 – 545.24 µg/kg at Kumasi abottior.

Darko and Acquaah (2008) studied 6 organochlorine pesticide residues in daily products (milk, yoghurt and cheese). The DDE residues on cheese exceeded the WHO maximum residue limit. The study concluded that bioaccumulation of these residues is likely to pose problems in higher organisms, like humans and therefore there is the need for effective monitoring of these residues in the environment.

2.5. Maize (*Zea mays*)

Maize is one of the world's most important cereal crops. Maize grown in Africa is generally cultivated by small-holder farmers (FAO, 1992). Maize is planted in April/May and harvested in August/September in Ghana for the major season. Maize is grown throughout Ghana but the bulk of maize is produced in the guinea savanna zone (Brong-Ahafo and Northern regions) (Gounou et al., 1993). Maize tends to provide high yield per unit land, which make maize a key crop in ensuring availability of food and promoting food security of the consumers (Brandes, 1992; Mboya et al., 2011).

The production of maize in the country varies with time due to factors which include distribution of rainfall, soil fertility, inefficiency of prevailing crop management practices and biotic factors comprising of diseases and insect pests. In 2002, 1,400 metric tonnes of maize

were produced in Ghana, the amount of maize produced dropped to 1,220 metric tonnes in 2007, and the amount increased from 1,470 metric tonnes to 1,620 metric tonnes in 2008 and 2009, respectively. In 2010, estimates of 1,872 metric tonnes of maize were produced. (MoFA, 2010).

2.5.1. The dietary importance of Maize

Maize is an important staple food crop in Africa (Adeyemo, 1984; Mboya *et al.*, 2011), and that it is the major food crop in Ghana. Maize is used as the base for several food preparations in Ghana. Maize is also the main component for poultry and livestock feed. In addition, maize is becoming a substitute in the malt drink brewing industry (GAIN, 2011). Available data indicate that the per capita consumption rate of maize in Ghana is estimated to be 43.8 kg/head/year (MoFA, 2010). Maize serves as an important food crop not only because it is consumed worldwide, but also due to its nutritive value. Maize provides more carbohydrates than wheat and sorghum, and it is a good source of phosphorus, calcium, iron, thiamine, niacin and fat (Adeyemo, 1984; Brandes, 1992; Mboya *et al.*, 2011).

2.5.2. Major pests and diseases of Maize in Ghana

Maize production in these areas is intensive but numerous diseases and insect pests limit yields. Maize is susceptible to many insects such as bollworms, stalk borers and chilo borers and the ones that suck plant sap such as leafhoppers and maize aphids (Gounou *et al.*, 1993). In Ghana, the most notorious stem borers are *Sesamia calamistis*, *Eldana saccharina* and *Busseola fusca* (MoFA, 2011).

Significant reduction in yield due to stem borers has been reported in all the major maize producing areas in the country (Bowden, 1956, 1976; Girling, 1980). The larvae of stem borers usually cause the damage (Appert, 1970). Estimated yield losses caused by stem borers in West Africa range from 10-100% (Usua, 1968). The story is not different from other parts of Africa where most peasant farmers do not plant the minor season maize due to total loss caused by stem borers (Gounou *et al.,* 1993). *Spodoptera exempta* are known to attack the leaves of maize plant. *Striga*, a parasitic weed that grows on the roots of maize and prevents the crop from growing properly is also found in maize cultivation in Ghana. Streak disease caused by streak virus and transmitted by insects known as leaf hoppers has also been recognized (MoFA, 2011).

2.6. Cowpea (Vigna unguiculata)

Cowpea is a member of the Leguminoseae family. Members of the family include soyabean (*Glycine max*), common beans (*Phaseolus vulgaris*) and mungbean (*Vigna radiate*). Cowpea is the most important grain legume of the world (Soliman, 2011; Akinbo, *et al.*, 2006; Onwueme and Sinha, 1991). Cowpea cultivation is a valuable component of farming systems in many countries including Ghana. Because of its ability to restore soil fertility, it is usually grown in association with cereal crops, notably millet, sorghum and maize (Carsky *et al.,*. 2002; Tarawali *et al.,* 2002; Sanginga *et al.,* 2003; Dugje *et al.,* 2009; MoFA, 2011).

In 1992 world cowpea production was estimated at 12.27 million metric tonnes from 70 million hectares, while in 2002 it was estimated at 4.5 million tonnes on 12 to 14 million hectares (Singh *et al.,* 2002). About 70% of this production occurs in the drier Savanna and Sahelian zones of West and Central Africa (Timko *et al.,* 2007). In 2002 to 2004, 142.3 metric tonnes of cowpea were produced in Ghana and in 2005 to 2007; an estimate of 143.2

metric tonnes of cowpea was produced. In 2008 to 2010, the amount of cowpea that was produced shot to 201.3 metric tonnes (MoFA, 2011).

2.6.1. The dietary importance of Cowpea

Cowpea can be used at all stages of growth as a vegetable crop, and the leaves contain significant nutritional value (Ahenkora et al. 1998). The nutritional content of cowpea grain is important because it provides some amount of high quality protein (25% protein) (Yakubu, 2012) which contains relatively high amount of the essential amino acids such as lysine and tryptophan (Timko et al., 2007), and thus usefully compliments the protein contents of maize, in which the contents of lysine and tryptophan are relatively are poor (Singh and Singh, 1992). Cowpea grain is also a rich source of minerals and vitamins (Hall et al. 2003) and it has high levels of folic acid, a crucial B vitamin (Timko et al., 2007). Due to its low fat and high fiber contents, proteins in cowpea have been shown to reduce low-density lipoproteins that are implicated in heart diseases (Philip et al., 2003; Timko et al., 2007). In addition, because grain legume starch is digested more slowly than starch from cereals and tubers, their consumption produces lesser abrupt changes in blood glucose levels (Philip et al., 2003).

2.6.2. Major pests and diseases of Cowpea in Ghana

Insect pests are major constraints to cowpea production in West Africa. The crop is susceptible to a wide range of insect pests and pathogens that attack the crop at all stages (Dugje, et al,. 2009; Soliman, 2011). According to Ministry of Food and Agriculture, insect pests that normally attack cowpea in Ghana are aphids (Aphis craccivora) and other species; flowers thrips (Megalurothrips sioestedtii), sucking bugs (Anoplocnemis spp., Clavigralla spp., legume pod borers (Maruca vitrata, Euchrysops sp.) and storage weevils (Callosobruchus maculates). Diseases such as anthracnose disease (Colletotrichum

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Lindemuthianum), cowpea mosaic virus diseases and cowpea wilt disease (*Fusarium oxysporum*) have been the major setbacks in cowpea production in Ghana (MoFA, 2011).

2.7. Control of pests and diseases in maize and cowpea cultivation

The integrated pest control is the adopted strategy for the fight against pests in Ghana. However, the use of the integrated combat is not widespread despite the efforts undertaken. Traditionally, in Ghana, pest control has meant the use of chemical pesticides (MoFA, 2011). Pesticides are without any doubt an effective means of killing pests quickly and on demand. No other control methods provide users with an immediate and visibly effective means of response.

Maize and cowpea are probably the most important food crops in the farming systems of Ghana. Cowpea is usually grown in rotation with cereals crops, notably maize. In Ghana, the most damaging pests are flower bud thrips, pod borer, the pod sucking bug (PSB) complex, stem borers, African Armyworms and streak virus. Chemical control via the use of synthetic insecticides remains the most popular control tactic. The development of integrated approaches to managing the maize and cowpea pest complex so as to guarantee increased and sustainable production of these important crops in Ghana has been explored. One combination is the use of host plant resistance alongside reduced insecticide application (MoFA, 2011).

CHAPTER THREE

3.0. MATERIALS AND METHODS

3.1. CHEMICALS AND REAGENTS:

All the solvents and reagents used were of analytical grade: methanol, 99.9% (Sigma-Aldrich), acetone, 99% (Riedel-de Haën), dichloromethane, 100% (AnalaR Normapour), hexane 99% (AnalaR Normapour), alumina (Sigma-Aldrich), anhydrous sodium sulphate (Sigma-Aldrich), sodium chloride (Sigma-Aldrich), and ammonium chloride (Sigma-Aldrich).

The anhydrous sodium sulphate was dried at 500 ^{o}C, aluminum oxide activated at 500 °C for 3 hours while the charcoal was activated at 300 ^{o}C for 3 hours. Cotton wool was washed with a mixture of acetone and hexane (1:1) prior to use.

3.2. SAMPLE COLLECTION

Sampling was carried out in December 2011 from ten different farms located in Ejura in the Ashanti Region of Ghana. The cowpea and maize, not subjected to post-harvest pesticides treatment were sampled from the farms during harvest. The soil samples were also collected from the farms where the maize and cowpea samples were picked.

Maize and cowpea samples were collected directly from five maize farms and five cowpea farms. The samples were code named and packed in a black polyethylene bags. Thereafter, the samples were brought to the laboratory where they were processed to get the grains. The grain samples of maize and cowpea were obtained by pooling the individual samples together. Each grain sample was ground into flour using a Binatone blender (BLG-450) to

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obtain a homogenous composite. The samples were then packed in freezer bags and immediately kept in a refrigerator at 4 °C until further analysis.

Twenty soil samples were collected from a depth of 0 - 10 cm (the root zone) with a graduated hand trowel. Each sample was mixture of at least 4 subsamples collected in one-quarter of the sampling farm. All the soil samples were kept in polythene bags and transported to laboratory as soon as possible for analysis. Soil samples were air-dried at room temperature, passed through a 2 mm mesh to remove stones and other debris. The prepared soil samples were then stored in a refrigerator at 4 °C until further analysis.

3.3. EXTRACTION OF PESTICIDES RESIDUES

3.3.1. Maize and Cowpea samples

Extraction of pesticide residues from maize and cowpea samples was carried out according to the methods developed by Khan et al., (2007) and Riazuddin et al., (2011) with slight modifications. Each sample of 5.0 g of ground maize and cowpea was transferred into a conical flask and 30 mL of acetone-methanol (1:1) extraction solvent was added. The content of the flask were shaken for 3 hours continuously on a mechanical flask shaker. Then the solvent-extracted material was filtered using Buchner funnel fitted with Whatman filter paper # 1001 into a 250 mL suction flask. The filtrate was transferred into a 500 mL separating funnel and 200 ml of sodium sulphate solution (2.5 g per 100 mL) was added together with 25 mL of dichloromethane. The mixture was vigorously hand shaken for 2 minutes. The phases were allowed to separate and the lower dichloromethane layer was collected into a conical flask. Partitioning of the aqueous layer was repeated twice with 15 mL portions of dichloromethane and the combined dichloromethane extracts passed through a bed of 25 g

anhydrous sodium sulphate in glass column to remove moisture. The moisture free extract was concentrated to approximately 2 mL on a rotary evaporator (Buchi, Model V-512) at 35 - 40 °C. The dried extract was then transferred into a 2 mL vial and ready for clean-up.

3.3.2. Soil samples

5.0 g of sieved soil sample was put into a 250 mL conical flask and 15 mL of 0.2 M ammonium chloride as dispersing agent was added. The mixture was swirled and left to stand for 15 minutes and followed by 25 mL of acetone as the solvent for the extraction. The mixture was shaken for 1 hour continuously on a mechanical shaker. The extract was filtered with a Buchner funnel fitted with Whatman filter paper into a suction flask. The extract was washed with another 15 mL portion of fresh acetone. The combined filtrate was transferred into a 500 mL separating funnel and washed with 15 mL of saturated NaCl solution and 150 mL of distilled water. The mixture was then partitioned twice with 50 mL (25 mL each) of dichloromethane and the combined dichloromethane layer was dried over 25 g of anhydrous sodium sulphate. Finally, the dried extract was concentrated to approximately 2 mL using a ratory evaporator and transferred into a 2 mL vial; ready for clean-up.

3.4. CLEAN-UP OF EXTRACTS

A chromatographic column of 38 cm length and 1.6 mm internal diameter was filled with 15 g mixture of alumina and activated charcoal (12:1) and topped up with 2 cm layer of anhydrous sodium sulphate. The alumina-charcoal column was conditioned with 5 mL of dichloromethane. The extract was then transferred onto the column and the sample container rinsed twice with dichloromethane. The extract was eluted with 30 mL (10 mL, 10 mL, and

10 mL) of dichloromethane and then concentrated to 2 mL using a rotary evaporator. The extract was dissolved in 1 mL hexane, transferred into a 2 mL sample vial for GC analysis.

3.5. RECOVERY EXPERIMENT

Before the analysis for pesticide residue concentration, recovery experiments were run for all the three matrices (soil, maize and cowpea samples). Two samples for the various sample types were spiked at two levels, which are 0.1 mg/kg and 0.5 mg/kg levels. The spiked samples were made to stand for at leat 1 hour and extracted and under the same conditions as the samples. The percentage recovery was calculated as:

$$\text{Recovery (\%)} = \frac{\text{Amount of analyte received}}{\text{Amount of analyte spiked}} \times 100$$

3.6. LIMITS OF DETECTION (LOD)

Gas chromatograph equipped with ECD and PFPD were checked for limit of detection. Instrumental limit of detection for GC-ECD was 0.005 mg/kg for organochlorines, 0.01 mg/kg pyrethroids pesticides and 0.001 mg/kg for organophosphorus pesticides.

3.7. ANALYSIS OF PESTICIDE RESIDUE CONTENT

3.7.1. Gas chromatographic conditions

The organochlorine and pyrethroid pesticides residues were analysed on Varian CP-3800 gas chromatograph equipped with a CombiPAL autosampler, an electron capture detector (ECD, ^{63}Ni) and a capillary column (30 m length, 25 mm internal diameter coated with VF-5ms, 0.25 μm film thickness). The oven temperature was programmed from 70 °C, held for 2

minutes then rise to 180 °C at a rate of 25 °C per minute. The injector and detector temperatures were maintained at 300 °C. The carrier gas was nitrogen at a flow rate of 1.0 mL per minute. The injection volume of the sample was 1.0 μL.

The organophosphorus pesticides residues were also analysed on Varian CP-3800 gas chromatograph equipped with a CombiPAL autosampler, pulsed flame photometric detector (PFPD) and a capillary column (30 m length, 0.25 mm inside diameter coated with VF-1701 ms, 0.25μm film thickness). The working conditions include being oven-dried at 70 °C, held for 2 minutes and increased to 200 °C at a rate of 25 °C per minutes and then ramped at 20 °C per minute to 250 °C held for 2 minutes. The carrier gas was nitrogen gas at the flow rate 2 ml per minute. The injector and detector temperature were maintained at 250 °C and 280 °C, respectively. The injection volume of the sample was 2.0 μL.

3.7.2. Identification and quantification of Pesticide residues

For identifying pesticide residiues, sample chromatograms were compared to those of authentic pesticides under the same conditions (external standard method). Peak heights were used for the quantitative determination of residues. Each sample was analyzed three times and the mean values obtained. The pesticide residue concentration of each sample was calculated as:

$$\text{Pesticide residue concentration} = \frac{As \times Vf}{Wts \times CF}$$

Where:

    As = peak area of sample

    Vf = final volume of clean extract

    Wts = weight of sample extracted

    CF = calibration factor

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The CF of each pesticide was calculated as:

$$CF = \frac{Peak\ Area\ of\ Standard}{Total\ amount\ of\ Standard\ identified}$$

3.8. STATISTICAL ANALYSIS

The results obtained from the three matrices were statistically analysed through Statistical

Package for Social Science (SPSS) software (version 16). Elements of descriptive statistics

of samples generated included the mean, range and standard deviations. Correlation analysis

was also performed by using Pearson correlation coefficient for the organochlorine pesticides

to determine relationships between individual pesticides.

3.9. SOIL POLLUTION ASSESSMENT

According to the SOVEUR guidelines for the assessment of soil degradation in Central and

Eastern Europe (GCP/RER/007/NET – 2000) soil pollution by pesticides can be classified as:

having light pollution (concentration of pollutant between A and B-value: 0.1 - 2.0 mg/kg),

moderate pollution (concentration of pollutants between B and C-value: 2.0 - 20 mg/kg) and

strong pollution (concentration of pollutants above C-value: > 20 mg/kg), for total pesticides

(Van-Lynden, 2000). When the soil is classified as having light pollution by pesticides it

means that some indications of degradation are present, but the process is still in an initial

phase. When the soil is moderately polluted, it means that degradation is present, but the

control and full remediation to its current function is still possible with considerable efforts.

If a soil is considered as strongly polluted, it indicates evident signs of degradation and at this

stage it is very difficult to restore, within reasonable limits, the soil properties (Van-Lynden,

2000).

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3.10. MAXIMUM RESIDUE LIMITS

The concentration of organochlorine, organophosphorus and synthetic pyrethroid pesticide residues in maize and cowpea samples were compared with the maximum residue limits (MRLs) recommended by European Union (2011). The MRL of a pesticide is the maximum concentration of its residue that is legally permitted to remain in food after it has been treated with the pesticide. It is not expected to be exceeded in any food if the pesticide was applied in accordance with directions for its safe use. If a pesticide residue is found to exceed the MRL in a given foodstuff, the food commodity is said to be adulterated because it contains an illegal amount of the residue (Nasreddine and Parent-Massin, 2002).

3.11. HUMAN HEALTH RISK ESTIMATION

To evaluate the chronic health risk posed by pesticide exposures, a reference dose such as ADI is commonly used. Human health risk estimates in this study were calculated based on an integration of pesticide analysis data and exposure assumptions. The following assumptions were adapted from the US Environmental Protection Agency's guidelines (US-EPA, 1989, 1996):

1. Hypothetical body weight of 10 kg for children and 70 kg for adults;
2. Maximum absorption rate of 100% and bioavailability rate of 100%.

Food consumption rates were based on the guidelines provided by the Ghana's Ministry of Food and Agriculture (2011). Maize and cowpea consumption rates in Ghana are quoted to be 0.122 kg/day and 0.014 kg/day, respectively.

Hence, for each type of exposure, the estimated lifetime exposure dose (mg/kg/day) was obtained by multiplying the mean pesticide residual concentration (mg/kg) in the food of interest and the food consumption rate (kg/day), and dividing the product by a standard body weight (kg) (US-EPA, 1989, 1996).

$$EADI = \frac{pesticide\ residual\ concentration \times food\ consumption\ rate}{body\ weight}$$

The health risk indices to children and adults were estimated as ratios betwee the EADI, and the FAO/WHO ADIs which are considered to be safe levels of exposure over the lifetime (WHO/FAO, 2010; US-EPA, 1996).

$$Health\ index\ (HI) = \frac{EADI}{ADI}$$

When the HI is greater than the one; eating such food is considered a risk to the concerned consumer. When the HI is less than one, the food is considered as acceptable (no concern) to the concerned consumer (Hamilton and Crossley, 2004).

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CHAPTER FOUR

4.0. RESULTS AND DISCUSSION

Soil, maize and cowpea samples were analysed for residues of 37 pesticides including 15 organochlorines (β-HCH, γ-HCH, δ-HCH, heptachlor, methoxychlor, aldrin, dieldrin, endrin, γ-chlordane, α-endosulfan, β-endosulfan, endosulfan sulphate, p,p'-DDT, p,p'-DDE and p,p'-DDD), 13 organophosphorus (dimethoate, methamidophos, ethoprophos, phorate, diazinon, fonofos, pirimiphos-methyl, chlorfenvinphos and profenofos) and 9 synthetic pyrethroids (bifenthrin, fenopropathrin, λ-cyhalothrin, permethrin, cyfluthrin, cypermethrin, fenvalerate, allethrin and deltamethrin).

4.1. PESTICIDE RESIDUE ANALYSIS IN SOIL

Table 4.1. Concentration and incidence ratio of Organochlorine Pesticide residues in soil (n = 20)

Pesticide	Range (mg/kg)	Mean (mg/kg)	SD	Incidence ratio (%)
β-HCH	0.002 - 0.058	0.021	0.014	95
γ-HCH	0.001 - 0.009	0.004	0.002	95
δ-HCH	0.002 - 0.008	0.004	0.001	95
Heptachlor	0.000 - 0.026	0.006	0.009	75
Endrin	0.001 - 0.005	0.003	0.001	100
γ-Chlordane	0.002 - 0.009	0.006	0.002	95
α-Endosulfan	0.001 - 0.002	0.001	0.001	85
β-Endosulfan	0.002 - 0.052	0.028	0.014	100
Endosulfan sulphate	0.008 - 0.054	0.015	0.012	95
Dieldrin	0.001 - 0.008	0.002	0.002	75
Aldrin	0.001 - 0.015	0.006	0.004	100
p,p'-DDE	0.000 - 0.090	0.028	0.026	100
p,p'-DDD	0.103 - 0.121	0.115	0.006	100
p,p'-DDT	0.002 - 0.090	0.008	0.019	100
Methoxychlor	0.002 - 0.013	0.005	0.003	90

*SD = standard deviation

The increased use of pesticides in agricultural activities has cuased pollution of environmental compartments such soil (Ntow, 2001; Dodoo *et al.*, 2006; Dem *et al.*, 2007; Darko *et al.,* 2008; Al-Wabel *et al.*, 2011), water (Ntow, 2005; Darko *et al.*, 2008; Essumang *et al.*, 2009). The soil has been the primarly reservoir for pesticides used in agriculture. In this study the soil samples collected from Ejura were contaminated with the investigated organochlorine pesticides. Table 4.1 shows the contamination levels of organochlorine pesticide residues detected in the soil.

The mean concentration of the organochlorine pesticide residues measured varied from 0.020 ± 0.014 mg/kg for β-HCH, 0.004 ± 0.002 mg/kg for γ-HCH, 0.004 ± 0.001 mg/kg for δ-HCH, 0.006 ± 0.009 mg/kg for heptachlor, 0.006 ± 0.004 mg/kg for aldrin, 0.006 ± 0.002 mg/kg for γ-chlordane, 0.001 ± 0.001 mg/kg for α-endosulfan, 0.028 ± 0.014 mg/kg for β-endosulfan, 0.015 ± 0.012 mg/kg for endosulfan sulphate, 0.028 ± 0.026 mg/kg for *p,p'*-DDE, 0.115 ± 0.006 mg/kg for *p,p'*-DDD, 0.008 ± 0.019 mg/kg for *p,p*-DDT, 0.005 ± 0.003 mg/kg for methoxychlor, 0.003 ± 0.001 mg/kg for endrin and 0.002 ± 0.002 mg/kg for dieldrin.

Out of 20 soil samples analysed, the most widely detected organochlorine pesticides were endrin, aldrin, β-endosulfan, *p,p*`-DDT, *p,p*`-DDE and *p,p*`-DDD (100% incidence each) followed by β-HCH, γ-HCH, δ-HCH, γ-chlordane, endosulfan sulphate (95% incidence each), methoxychlor (90%), α-endosulfan (85%), heptachlor (75%) and dieldrin (75%). The *p,p'*-DDD concentration (0.115 ± 0.006 mg/kg) was the highest, whereas α-endosulfan concentration (0.001 ± 0.001 mg/kg) was lowest in the soil (Table 4.1).

Since 1985, DDT was banned as an agricultural pesticide (EPA-Ghana, 2008). In soil DDT breaks down slowly to DDD (under anaerobic condition) and DDE (under aerobic condition) by microbial activities (Pandey *et al.*, 2011). The detection of *p,p'*-DDD and *p,p'*-DDE is an indication of degradation of *p,p'*-DDT (Wandiga, 1995). The relatively high concentration of *p,p'*-DDD measured as against *p,p'*-DDE and *p,p'*-DDT in the soil can be explained by the fact that the degradation of DDT previously used in the past has favoured DDD formation (Falandysiz *et al.*, 2011; Xu *et al.*, 2008). The high *p,p'*-DDD residues detected in soil in this study are similar to other reports by Pandey *et al.*, (2011): *p,p'*-DDD (38.81 mg/kg) and *p,p'*-DDE (37.81 mg/kg) and Kishimba and Mihale, (2004): *p,p'*-DDD (0.41 mg/kg) and *p,p'*-DDE (0.11 mg/kg).

Although, organochlorine insecticides have been banned or restricted in most countries, including Ghana, their presence as residues in the environment have been reported by several studies. In Ghana, Ntow (2005) reported the occurrence of γ-HCH (0.023 mg/kg), α-endosulfan (0.021 mg/kg), β-endosulfan (0.017 mg/kg), endosulfan sulphate (0.036 mg/kg), *p,p'*-DDT (0.900 mg/kg) and *p,p'*-DDE (5.230 mg/kg) in the Volta Lake sediments. A similar study conducted by Darko *et al.*, (2008) on sediments from Bosomtwi Lake also recorded the occurrence of lindane (0.656 mg/kg), endosulfan (0.968 mg/kg), aldrin (0.007 mg/kg), dieldrin (0.007 mg/kg), *p,p'*-DDE (0.834 mg/kg) and *p,p'*-DDT (0.441 mg/kg).

At the international stage, several results showing detection of organochlorine pesticide residues in soil, sediments and water have also been reported (Dem *et al.*, 2007; Pandey *et al.*, 2011; Henry and Kishimba, 2002; Wang *et al*, 2007; Wang *et al.*, 2008; Al-Wabel *et al.*, 2011). These findings, including this study, confirmed again the well-known environmental persistence of the organochlorine pesticides and justify its ban from agricultural use.

For several years less persistent classes of pesticides including organophosphorus, pyrethroids and carbamates were widely used in agriculture to substitute organochlorine insecticides. The situation in Ghana is not different, where pesticides such as emamecin bensoate, λ-cyhalothrin, chlorpyrifos, carbofuran, glyphosate and many others, are being used to control pests (Armah, 2011; Yeboah, *et al.,* 2004; Aboagye, 2002). Although the use of organophosphorus, pyrethroid and carbamate pesticides increase crop yield, they also constitute a threat to the environment (Wang *et al.,* 2008).

Table 4.2. Concentration and incidence ratio of Organophosphorus Pesticide residues in soil (n = 20)

Pesticide	Range (mg/kg)	Mean (mg/kg)	SD	Incidence ratio (%)
Dimethoate	0.005 - 0.029	0.013	0.009	40
Methamidophos	0.002 - 0.023	0.007	0.006	50
Ethoprophos	0.000 - 0.001	0.001	0.000	10
Phorate	0.000 - 0.002	0.001	0.001	25
Diazinon	0.001 - 0.002	0.002	0.000	10
Pirimiphos-methyl	0.001 - 0.002	0.001	0.001	15
Chlorpyrifos	0.004 - 0.024	0.012	0.005	85
Malathion	0.000 - 0.032	0.010	0.013	30
Fenitrothion	0.000 - 0.011	0.004	0.004	55
Parathion-methyl	0.001 - 0.003	0.002	0.001	25
Chlorfenvinphos	0.005 - 0.052	0.033	0.012	100
Profenofos	0.006 - 0.113	0.045	0.028	95
Fonofos	0.000 - 0.003	0.002	0.002	10

*SD = standard deviation

From Table 4.2., the mean concentrations and percent incidences of organophosphorus residues measured in soil were respectively, dimethoate: 0.013 ± 0.009 mg/kg and 40%, methamidophos: 0.007 ± 0.006 mg/kg and 50%, ethoprophos: 0.001 ± 0.000 mg/kg and 10%, phorate: 0.001 ± 0.001 mg/kg and 25%, diazinon: 0.002 ± 0.000 mg/kg and 10%, pirimiphos-methyl: 0.001 ± 0.001 mg/kg and 15%, chlorpyrifos: 0.012 ± 0.005 mg/kg in

85%, malathion: 0.010 ± 0.013 mg/kg and 30%, fenirothion: 0.004 ± 0.004 mg/kg and 55%, parathion-methyl: 0.002 ± 0.001 mg/kg and 25%, chlorfenvinphos: 0.033 ± 0.012 mg/kg and 100%, profenofos: 0.045 ± 0.028 mg/kg and 95%, and fonofos: 0.002 ± 0.002 mg/kg and 10%.

Among the organophosphorus pesticides, the residue with highest mean concentration was profenofos (0.045 ± 0.028 mg/kg) while chlorfenvinphos was detected in all the samples. The relatively high residual concentration of profenofos measured can be attributed to its frequent use by farmers in the studied area. It should be noted that if profenofos had been applied in previous years, it would probably have degraded by the time of sampling because its half-life in soil is 7 days (BCPC, 2003), suggesting that is less persistent.

The frequent detection of chlorfenvinphos residue in the soil can be explained by the fact that it is the most commonly used organophosphorus pesticides and is moderately persistent in soil. The half-life of chlorfenvinphos is between 114 - 161 days (Menzie, 1972). The low levels detected for the other organophosphorus pesticides in this study could be probably related to their low soil persistence. The half-lives for these pesticides are: dimethoate (7 - 16 days), cypermethrin (13 weeks), chlorpyrifos (7 - 15 days), diazinon (6 - 84 days), parathion-ethyl (80 days), fenitrothion (54 days), malathion (6 days) (BCPC, 2003; FAO, 2000).

Similar observations of contamination of soil by organophosphorus pesticides have been reported in India by Kumar et al., (2011); phosphomidon: 10.47 ng/g, monocrotophos: 3.45 ng/g, quinolphos: 3.26 ng/g, ethion: 3.23 ng/g and chlorpyrifos: 8.86 ng/g. In Tanzania, a mean chlorpyrifos concentration of 0.125 mg/kg in soil has also been reported (Kihampa et al., 2010). The findings are in full support of the current study.

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Essumang *et al.,* in 2009 also analysed four organophosphorus pesticides (Diazinon, chlorpyrifos, dichlorvos and fenithrothion) contamination in water samples from four lagoons (Etsii, Fosu, Chemu and Korle) in Ghana. The residual concentrations varied from non-detection to 1.5451 mg/L.

Table 4.3. Concentrations and incidence ratios of pyrethroids pesticide residues in soil (n = 20)

Pesticide	Range (mg/kg)	Mean (mg/kg)	SD	Incidence ratio (%)
Bifenthrin	0.001 - 0.016	0.005	0.006	60
Fenpropathrin	0.001 - 0.023	0.010	0.007	85
λ-Cyhalothrin	0.001 - 0.077	0.013	0.018	90
Permethrin	0.000 - 0.011	0.004	0.003	85
Cyfluthrin	0.003 - 0.021	0.010	0.006	80
Cypermethrin	0.002 - 0.017	0.006	0.005	75
Fenvalerate	0.009 - 0.034	0.016	0.007	85
Deltamethrin	0.000 - 0.002	0.001	0.001	55
Allethrin	0.001 - 0.054	0.013	0.015	100

*SD = standard deviation

Table 4.3 shows the concentrations of pyrethroid residues found in the soil. The mean concentration and incidence of occurrence of the pyrethroids are as follows; fenvalerate (0.016 mg/kg, 85%), allethrin (0.013 mg/kg, 100%), λ-cyhalothrin (0.013 mg/kg, 90%), fenpropathrin (0.010 mg/kg, 85%), cyfluthrin (0.010 mg/kg, 80%), cypermethrin (0.006 mg/kg, 75%), bifenthrin (0.005 mg/kg, 60%), permethrin (0.004 mg/kg, 85%) and deltamethrin (0.001 mg/kg, 55%).

Pyrethroid pesticides are less persistent and are easily degraded in soil by light and microorganisms after a few days of application, which makes it difficult to detect due to their low levels in the environment (Shi *et al.,* 2011). Among the pyrethroid pesticides, allethrin

was frequently detected, occurring in all the soil samples analysed. This might be so because allethrin is the most commonly used pyrthroid pesticide used by farmers in the study area.

The present study has showed the presence of organophosphorus and pyrethroid pesticides residues in the soil. This could be an indication of varied emphasis in the use of pesticides in Ghana, where there seen to be a shift from organochlorine pesticides to the more degradable organophosphorus and pyrethroids pesticides

A similar study carried out by Wang *et al.,* (2008) in China, has also proved the occurrence of λ-cyhalothrin (0.002 mg/kg) and cypermethrin (0.001 mg/kg) in soil. The results this study is in agreement with that of Wang *et al.,* 2008, where the presences of pyrethroids pesticide residues were detected.

4.1.1. Soil Pollution Assessment

The total concentration of organochlorine pesticides, organophosphorus pesticides and pyrethroids pesticide residues measured in the soil samples are presented in Table 4.4. The total concentration of all pesticides was found to be 0.452 mg/kg. The pattern of contamination was observed as organochlorine pesticides > organophosphorus pesticides > pyrethroids pesticides. The total concentrations of various pesticides studied were 0.246 mg/kg, 0.130 mg/kg and 0.076 mg/kg for organochlorines, organophosphorus and pyrethroids, respectively.

Table 4.4. Total concentrations of Pesticides residues in the Soil

	Pesticide			
	Organochlorine	Organophosphorus	Pyrethroids	Total
Total concentration (mg/kg)	0.246	0.130	0.076	0.452

By SOVEUR guidelines (GCP/RER/007/NET), the degree of soil pollution by total organochlorines (total concentration of 0.246 mg/kg), total organophosphorus (total concentration of 0.130 mg/kg) and total pyrethroid pesticides (total concentration of 0.076 mg/kg) is classified as Light Pollution (concentration of pollutant between 0.1 to 2.0 mg/kg) (van-Lynden, 2000). Although the extent of pollution by various pesticides clasess reported in this investigation is Light Pollution, there are indications of the presence of degradation (van-Lynden, 2002).

Most pesticides, especially the organochlorines, are not easily degraded and thus tend to accumulate in the soil for a long time (Wang et al., 2008). This was confirmed in this study as high amount of organochlorine pesticides was observed as against organophosphorus and pyrethroids pesticides. Pollutants tend to accumulate in the topsoil where most soil organisms live and also where plants take their nutrients. The pollutants may enter the food crop easily through plant uptake and bioaccumulate in food chains (Hamilton and Crossley, 2004; Jirires et al., 2002).

It is known that organophosphorus and pyrethroids pesticides are readily decomposed in soil by water, light and microbes after application, which makes them difficult to detect (Shi et al., 2011). The results of this study showed relatively low levels of organophosphorus and pyrethroids pesticide residues. In a tropical environment such as Ghana, fast degradation of pesticides is possible, hence, a low level of pollution by these pesticides (van-Lyndan, 2000).

4.1.2. Application time of Organochlorine pesticides in the Soil

Organochlorne pesticides have been of great concern due to their persistent nature and chronic adverse effect on wildlife and humans. From this present study, the soil samples

analysed were contaminated with a spectrum of organochlorine pesticides. The presence of some of the aged banned organochlorine pesticides in the soils is evidence of their persistent nature in the environment.

The composition of organochlorine pesticides and their metabolites can provide a tool for better understanding of the origin and transport pathways of these contaminants in the environment (Kumar *et al.*, 2011; Pandey *et al.*, 2011; Dem *et al.*, 2007; Falandysz *et al.*, 2001; Xu *et al.*, 2007). Isomeric ratios of DDTs, HCHs, endosulfan and aldrin have been presented in Table 4.5. Generally, a ratio greater than 1 is an indication of early time usage of the pesticide in the environment, while a ratio less than 1 suggests recent usage of pesticide (Rapaprt and Eienreich, 1986; Jaga and Dharmani, 2003; Pandey *et al.*, 2009).

Table 4.5. Isomeric ratios of Organochlorine Pesticides

Isomers	$(p,p'\text{-DDE} + p,p'\text{-DDD}) / p,p'\text{-DDT}$	$\beta\text{-HCH} / \gamma\text{-HCH}$	Endosulfan sulphate / β-endosulfan	Dieldrin / Aldrin
Ratio	17.88	5.25	0.54	0.33

4.1.2.1. DDT Isomers in the Soil

Although since 1985 DDT has been banned as an agricultural pesticide in Ghana, (EPA, Ghana; 2008), DDT and its metabolites (DDE and DDD), can still be detected in the environment due to its persistent nature in the environment. The levels of DDTs in soils, sediments and water have been reported in other studies (Ntow, 2001, 2005; Darko *et al.*, 2008; Essumang *et al.*, 2009). In the environment p,p'-DDT degrades slowly into p,p'-DDE under aerobic conditions and to p,p'-DDD under anaerobic conditions by microbial activities (Pandey *et al.*, 2011). From the work, it was found that the concentration of p,p'-DDD and p,p'-DDE in the soils were higher than the parent p,p'-DDT, indicating the degradation of

p,p'-DDT into p,p'-DDE and p,p'-DDD (Sampera *et al.*, 2002). This reflects an input of aged DDT in the soil.

The ratio of p,p'-DDE + p,p'-DDD to p,p'-DDT can also be calculated to determine whether there is recent application of DDT on the studied soil (Rapaprt and Eienreich, 1986; Wang *et al.*, 2007; Xu *et al.*, 2005). In this study the ratio was 17.88, indicating a historical usage of DDT. It is also interesting to know from the results that, the concentration of p,p'-DDD was higher the p,p'-DDE in the soil indicating that the degradation pathway of aged p,p'-DDT in the soil favoured the anaerobic conversion of p,p'-DDT to p,p'-DDD instead of p,p'-DDT to p,p'-DDE (Falandysiz *et al.*, 2001). This finding is also in agreement with other studies reported by Falandysiz *et al.*, (2001) and Pandey *et al.*, (2011).

4.1.2.2. HCH Isomers in the Soil

HCH is a mixture of eight isomers of which five were found in the crude product viz α, β, γ, δ, ε, but only lindane (γ-HCH) has powerful insecticidal properties (Mathur *et al.*, 2005). It is also known that HCH is available in two formulation; technical HCH (α-HCH, β-HCH, γ-HCH, δ-HCH and ε-HCH) and γ-HCH (lindane) (Nhan *et al.* 2001; Qui *et al.* 2004; Kumar *et al.*, 2011). The β-HCH has also been reported to be very stable in the environment than the other isomers due its high vapour pressure and stable structure (Shi *et al.*, 2011). Thus isomers of HCHs easily degrade in soil to form β-HCH, hence increasing their concentration in the soil as has been observed in this study.

Among the HCH isomers, β-HCH, γ-HCH and δ-HCH, which were investigated, the residual concentration of β-HCH (0.021 mg/kg) was the highest followed by δ-HCH (0.004 mg/kg) and γ-HCH (0.004 mg/kg), confirming the stability of β-HCH isomer. In determining the

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possible residence time of HCH isomers in the soil, the ratio β-HCH/γ-HCH was calculated and found to be 5.25 (Table 4.5). This is an indication of historical use of technical γ-HCH (Shi *et al.*, 2011). Also, the presence of relatively high resisual levels of β-HCH as compared to the other isomers, δ-HCH and γ-HCH, in the soil can be attributed to two major sources; fresh use of technical HCH and the degradation of lindane (γ-HCH) to is β-HCH (Shi *et al.*, 2011; Kumar *et al.*, 2011; Henry and Kishimba, 2002).

4.1.2.3. Endosulfan Isomers in the Soil

Endosulfan is among organochlorine pesticides banned in Ghana. Commercial endosulfan consists of a mixture of two isomers, 70% α-endosulfan and 30% β-endosulfan (Kumar *et al.*, 2011; Sunitha *et al.*, 2011). Endosulfan is found to degrade in the environment slowly and often results in the formation of endosulfan sulphate (Henry and Kishimba, 2002; Sunitha *et al.*, 2011). In the soil, β-endosulfan strongly binds to soil particles and persist more in the soil than for the α-endosulfan (Beyers *et al.*, 1965). Thus, the concentration of endosulfan sulphate is expected to be high in the environment through endosulfan degradation.

In this study a very high concentration of β-endosulfan (0.028 mg/kg) was measured, followed by endosulfan sulphate (0.015 mg/kg) and then the α-endosulfan (0.001 mg/kg) (Table 4.1). The occurrence of high amount of β-endosulfan as compared to endosulfan sulphate is an indication of recent application of endosulfan in the study area. The ratio of endosulfan sulphate to β-endosulfan in the soil is also calculated to be 0.54 (Table 4.5), thus, confirming the early time usage of endosulfan in the study area.

4.1.2.4. Dieldrin and Aldrin in the Soil

In the environment, aldrin is gradually converted, through epoxidation, to dieldrin which is more stable; hence dieldrin is expected to be found in relatively higher amount than aldrin in the environment (USEPA, 2003). In this study, the mean concentration of aldrin (0.006 mg/kg) in soil was higher than dieldrin (0.002 mg/kg) (Table 4.1). The high concentration of aldrin in the soil as compared to the dieldrin in this study clearly indicates a recent use of aldrin by the farmers on maize and cowpea farms. Also, the ratio of dieldrin to aldrin observed was 0.33 (Table 4.5.), suggesting a recent input of aldrin by farmers in the studied area.

Although the uses of technical HCH, endosulfan and aldrin have been banned in Ghana, isomerinc ratio analysis clearly indicate that there are recent uses of these chemicals in the study area. Organochlorine pesticides are still being used unofficially in large quantities in many parts of Ghana (NPAS, 2012; Ntow *et al.* 2006). The study has highlighted the fact that there is little respect for the law when it comes to pesticides regulations.

Table 4.6 Matrix of Correlation Coefficients of Organochlorine Pesticide Residues in Soil

	β-HCH	γ-HCH	δ-HCH	Aldrin	Dieldrin	α-Endosulfan	β-Endosulfan	Endosulfan sulphate	p,p'-DDE	p,p'-DDD	p,p'-DDT
β-HCH	1.000										
γ-HCH	0.037	1.000									
δ-HCH	0.140	0.398	1.000								
Aldrin	-0.321	-0.289	0.032	1.000							
Dieldrin	-0.390	-0.15	0.261	0.099	1.000						
α-Endosulfan	0.301	-0.275	-0.002	0.063	-0.011	1.000					
β-Endosulfan	-0.005	0.056	-0.423	0.253	-0.510	0.092	1.000				
Endosulfan sulphate	0.206	-0.164	-0.104	0.084	-0.220	0.385	0.238	1.000			
p,p'-DDE	0.321	-0.101	0.231	0.113	-0.194	0.550*	0.223	0.270	1.000		
p,p'-DDD	0.218	-0.091	0.100	-0.052	-0.250	0.151	-0.165	0.341	0.088	1.000	
p,p'-DDT	-0.312	-0.138	-0.128	0.180	0.004	0.384	0.396	-0.116	0.304	-0.094	1.000

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

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The matrix of correlation coefficients of the organochlorine pesticides in the soil at 0.005 error levels in Table 4.6 showed positive significant correlation for residual levels of *p,p'*-DDE and *α*-endosulfan while no significant differences were observed among the other organochlorine pesticides. The pesticides with significant positive correlation likely shared common sources and were probably affected by related factors in the soil.

4.2. CONCENTRATION OF PESTICIDE RESIDUES IN MAIZE AND COWPEA

Maize and cowpea under study are produced in the country for local consumption. Pesticides are the part of majority of chemicals applied on them. Food treated with pesticides often contains residues of these chemical. The study determined the pesticide residues in maize and cowpea collected from different farms in Ejura. The concentrations of pesticides (organochlorine, organophosphorus and pyrethroid) residues detected in maize and cowpea samples are summarized in Table 4.7 - 4.9.

4.2.1. Concentration of Organochlorine Pesticide residues in Maize and Cowpea

Table 4.7, gives the residual concentrations of organochlorine pesticide residues mearsured in maize and cowpea and their corresponding EU MRLs.

Table 4.7. Concentration of Organochlorine Pesticide residues detected in maize and cowpea and EU MRLs.

Pesticide	Maize			Cowpea		
	Range (mg/kg)	Mean ± SD (mg/kg)	MRL (mg/kg) (EU, 2012)	Range (mg/kg)	Mean ± SD (mg/kg)	MRL (mg/kg) (EU, 2011)
β-HCH	0.016 - 0.062	0.045 ± 0.018	0.020	0.003 - 0.040	0.025 ± 0.014	0.010
γ-HCH	0.001 - 0.001	0.001 ± 0.000	0.010	0.001 - 0.002	0.002 ± 0.001	0.010
δ-HCH	0.002 - 0.002	0.002 ± 0.001	0.020	0.003 - 0.004	0.003 ± 0.001	0.010
Heptachlor	0.001 - 0.011	0.005 ± 0.005	0.010	0.008 - 0.012	0.010 ± 0.002	0.010
Methoxychlor	0.002 - 0.003	0.002 ± 0.002	0.010	0.002 - 0.004	0.003 ± 0.001	0.010
γ-Chlordane	0.003 - 0.007	0.005 ± 0.001	NA	0.002 - 0.003	0.002 ± 0.001	0.010
α-Endosulfan	0.001 - 0.001	0.001 ± 0.001	0.050	0.001 - 0.001	0.001 ± 0.001	0.050
β-Endosulfan	0.028 - 0.274	0.103 ± 0.101	0.050	0.006 - 0.123	0.081 ± 0.045	0.050
Endosulfan sulphate	0.007 - 0.010	0.009 ± 0.002	0.050	0.002 - 0.009	0.006 ± 0.003	0.050
p,p'-DDE	0.010 - 0.091	0.064 ± 0.033	0.050	0.034 - 0.077	0.053 ± 0.018	0.050
p,p'-DDD	0.052 - 0.121	0.102 ± 0.029	0.050	0.108 - 0.118	0.118 ± 0.006	0.050
p,p'-DDT	0.002 - 0.003	0.002 ± 0.001	0.050	0.002 - 0.003	0.003 ± 0.001	0.050
Endrin	0.002 - 0.003	0.002 ± 0.001	0.010	0.001 - 0.002	0.002 ± 0.001	0.010
Aldrin	0.002 - 0.003	0.003 ± 0.000	0.010	0.001 - 0.004	0.003 ± 0.001	0.010
Dieldrin	0.001 - 0.002	0.002 ± 0.000	0.010	0.001 - 0.005	0.003 ± 0.002	0.010
Total (mg/kg)		*0.354 ± 0.169*			*0.314 ± 0.077*	

*SD = standard deviation.

*NA = MRL not available for commodity analysed.

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The mean concentration levels of β-HCH, γ-HCH and δ-HCH isomers recorded in maize samples were 0.045 ± 0.018 mg/kg, 0.001 ± 0.000 mg/kg and 0.002 ± 0.001 mg/kg, respectively, and 0.025 ± 0.014 mg/kg, 0.002 ± 0.000 mg/kg and 0.003 ± 0.001 mg/kg in cowpea, respectively. A similar work conducted in Togo also reported some levels of γ-HCH (lindane) in maize (0.064 ± 0.018 mg/kg) and cowpea (0.050 ± 0.005 mg/kg) (Mawussi et al., 2009). In the environment, HCH isomers easily degraded to form β-HCH isomer due to its high vapour pressure and stable structure (Shi *et al.*, 2011). This proves the high concentrations levels of β-HCH in the environment. Among the HCH isomers investigated, β-HCH concentration in both maize (0.045 mg/kg) and cowpea (0.025 mg/kg) samples were the highest. The results corroborate with the findings of Chen *et al.*, (1984) who detected higher residual levels of β-HCH in fish samples at levels ranging from 3.3 – 8.2 mg/kg as against the γ-HCH isomer, with concentration ranging from 1.4 – 3.5 mg/kg.

Methoxychlor concentrations measured in maize and cowpea were little bit low, perhaps being as a result of historical use of DDT which contain some amount of methoxychlor (Bempah and Donkor, 2010). The mean residual levels of methoxychlor detected ranged from 0.002 ± 0.001 mg/kg in maize and 0.003 ± 0.001 mg/kg in cowpea. Methoxychlor concentrations ranging from 0.009 – 0.003 mg/kg in fish samples collected from the Densu River in Ghana had been reported (Afful *et al.*, 2010). Bempah *et al.*, (2011) also reported mean methoxychlor levels ranging from 0.004 - 0.041 mg/kg in fruits and vegetable samples collected from several local markets around Kumasi metropolis. These concentrations are comparable to the results obtained from this work.

Heptachlor, γ-chlordane and endrin were detected at levels of 0.005 ± 0.005 mg/kg, 0.005 ± 0.001 mg/kg and 0.002 ± 0.00 mg/kg in maize respectively. Likewise in cowpea, heptachlor,

γ-chlordane and endrin levels were and 0.010 ± 0.002 mg/kg, 0.002 ± 0.001 mg/kg and 0.002 ± 0.001 mg/kg respectively. A report by Mawussi *et al.*, (2009) also showed the residual levels of endrin in cowpea (1.316 ± 0.110 mg/kg) and heptachlor in maize (0.072 ± 0.002 mg/kg) and cowpea (0.039 ± 0.060 mg/kg). The findings are all in support of the results of this study.

The residual levels of α-endosulfan, β-endosulfan and endosulfan sulphate measured in maize samples were 0.001 ± 0.001 mg/kg, 0.103 ± 0.101 mg/kg and 0.009 ± 0.002 mg/kg respectively. In cowpea, the levels of the α-endosulfan, β-endosulfan and the endosulfan residues measured were 0.001 ± 0.001 mg/kg, 0.081 ± 0.045 mg/kg and 0.006 ± 0.003 mg/kg, respectively. Commercial endosulfan consists of mixture of α-endosulfan and β-endosulfan. Endosulfan is known to degrade slowly to form endosulfan sulphate in the environment (Kumar *et al.*, 2011; Sunitha *et al.*, 2011). It is obvious from Table 4.7 that, concentrations of β-endosulfan measured in both maize and cowpea were generally higher. This comes as no surprise as β-endosulfan is more persistent in the environment than α-endosulfan (Beyers *et al.*, 1965). The results of this study furthere support the findings of the study carried out in Togo by Mawussi *et al.*, (2009) with residues of α-endosulfan detected in maize (0.035 ± 0.012 mg/kg) and cowpea (0.089 ± 0.012 mg/kg) and β-endosulfan in maize (0.066 ± 0.012 mg/kg) and cowpea (0.099 ± 0.013 mg/kg).

Technical DDT (*p,p'*-DDT) along with its metabolites (*p,p'*-DDE and *p,p'*-DDD) were also detected in the food samples. The mean concentrations varied from 0.002 ± 0.001 mg/kg for *p,p'*-DDT, 0.064 ± 0.033 mg/kg for *p,p'*-DDE and 0.102 ± 0.029 mg/kg for *p,p'*-DDD in maize. Likewise in the cowpea, the residual concentration of *p,p'*-DDT, *p,p'*-DDE and *p,p'*-

DDD ranged from 0,003 ± 0.001 mg/kg, 0.053 ± 0.018 mg/kg and 0.118 ± 0.006 mg/kg, respectively.

Mawussi *et al.*, (2009) also detected levels of DDT and its metaborites at levels ranging from 0.022 ± 0.013 mg/kg in maize and 0.013 ± 0.011 mg/kg in cowpea for *p,p'*-DDT, 0.053 ± 0.003 mg/kg in maize and 0.016 ± 0.012 mg/kg in cowpea, for *p,p'*-DDE, 0.047 ± 0.004 mg/kg in cowpea for *p,p'*-DDD. The findings of other reports on fruits and vegetables (Bempah *et al*, 2011, 2011), fish (Aful *et al.*, 2010; Fianko *et al.*, 2010), beans (Gwary *et al.*, 2012), daily products (Darko and Aquaah, 2008) and water (Ntow, 2005; Essumang, 2009) are in agreement with the results of this study.

Aldrin residual concentrations measured were 0.003 ± 0.000 mg/kg in maize and 0.003 ± 0.001 mg/kg in cowpea, whereas the epoxide form; dieldrin were 0.002 ± 0.000 mg/kg in maize and 0.003 ± 0.002 mg/kg in cowpea. The presence of dieldrin in the food samples declares that, there may be conversion of aldrin to dieldrin by expoxidation in biological systems (USEPA, 2003). A similar result was obtained by Mawussi *et al.*, (2009) on maize and cowpea contamination by residues of aldrin (maize: 0.005 ± 0.001 mg/kg and cowpea: 0.060 ± 0.001 mg/kg) and dieldrin (maize: 0.189 ± 0.012 mg/kg and cowpea: 0.395 ± 0.012 mg/kg). Residual levels of aldrin and dieldrin in fruits and vegetables, meats, fish have also be reported in Ghana (Bempah *et al.*, 2011, 2011; Darko and Aquaah, 2007; Aful *et al.*, 2010). The results are in full agreement with the current study.

The concentration of organochlorine pesticide residues in measured in maize and cowpea samples were compared with the MRLs set forth by European Union (2011). The mean

residual levels of β-HCH, β-endosulfan, p,p'-DDE and p,p'-DDD detected in maize and

cowpea were found exceeding the MRL guidelines (Table 4.7).

Table 4.8. Concentration of Organophosphorus Pesticide residues in Maize and Cowpea compared with EU MRL.

Pesticide	Maize			Cowpea		
	Range (mg/kg)	Mean ± SD (mg/kg)	MRL(mg/kg) (EU, 2012)	Range (mg/kg)	Mean ± SD (mg/kg)	MRL (mg/kg) (EU, 2011)
Dimethoate	0.004 - 0.005	0.004 ± 0.001	0.020	0.004 - 0.011	0.008 ± 0.003	0.020
Methamidophos	0.003 - 0.003	0.003 ± 0.000	0.010	0.003 - 0.008	0.005 ± 0. 003	0.010
Ethoprophos	ND	ND	0.020	ND	ND	0.020
Phorate	ND	ND	0.050	ND	ND	0.050
Diazinon	0.002 - 0.002	0.002 ± .001	0.010	ND	ND	0.010
Pirimiphos-methyl	0.002 - 0.003	0.002 ± 0.001	5.000	ND	ND	0.050
Chlorpyrifos	0.008 - 0.019	0.013 ± 0.004	0.050	0.009- 0.021	0.015 ± 0.007	0.050
Malathion	0.007 - 0.056	0.019 ± 0.021	8.000	0.001 - 0.027	0.014 ± 0.011	0.020
Fenitrothion	0.002 - 0.010	0.006 ± 0.004	0.050	0.0002 - 0.005	0.003 ± 0.004	0.010
Parathion-methyl	0.001- 0.003	0.002 ± 0.001	0.020	0.002 - 0.002	0.002 ± 0.000	0.020
Chlorfenvinphos	0.011 -0.039	0.019 ± 0.011	0.020	0.002 - 0.020	0.009 ± 0.008	0.020
Profenofos	0.005- 0.005	0.005 ± 0.000	0.050	0.005 - 0.012	0.011 ± 0.006	0.050
Fonofos	0.001- 0.001	0.001 ± 0.001	NA	ND	ND	NA
Total (mg/kg)		0.075 ± 0.035			0.067 ± 0.042	

*SD = standard deviation.

*NA = MRL not available for commodity analysed.

*ND = not detected

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Table 4.8, represents a summary of the mean concentrations of organophosphorus pesticide residues found in maize and cowpea. Pesticide residues in maize ranged from 0.005 ± 0.001 mg/kg for dimethoate, 0.003 ± 0.000 mg/kg for methamidophos, 0.013 ± 0.004 mg/kg for chlorpyrifos, 0.019 ± 0.021 mg/kg for malathion, 0.006 ± 0.004 mg/kg for fenitrothion, 0.002 ± 0.001 mg/kg for parathion-methyl, 0.019 ± 0.011 mg/kg for chlorfenvinphos, 0.001 ± 0.000 mg/kg for fonofos, 0.002 ± 0.000 mg/kg for diazinon and 0.002 ± 0.001 mg/kg for pirimiphos-methyl. Likewise in cowpea grain, pesticide residue levels varied from 0.008 ± 0.003 mg/kg for dimethoate, 0.005 ± 0.003 mg/kg for methamidophos, 0.015 ± 0.007 mg/kg for chlorpyrifos, 0.014 ± 0.011 mg/kg for malathion, 0.003 ± 0.004 mg/kg for fenitrothion, 0.002 ± 0.000 mg/kg for parathion-methyl and 0.011 ± 0.006 for profenofos.

For maize, mean concentration o f malathion was 0.019 ± 0.021 mg/kg. This was the highest, value whereas fonofos concentration of 0.001 ± 0.000 mg/kg was the lowest. In the cowpea, the minimum concentration was measured for parathion-ethyl at 0.002 ± 0.000 mg/kg whereas the maximum concentration was also measured for chlorpyrifos at 0.015 ± 0.007 mg/kg. Comparing the concentrations of all the organosphosphorus pesticide residues in both maize and cowpea, it was found that residual concentration were below their respctive MRLs recommended by EU (2011).

For the organophosphorus pesticides investigated, ethoprophos and phorate were not detected in both maize and cowpea. Similarly, diazinon, pirimiphos-methyl and fonofos were not detected in maize but in cowpea. This could be attributed to the fact that farmers do not use pesticide products that contain these active ingredients, or, it may also be due to the fact that these pesticides degrade at a fast rate in a tropical environment such that of Ghana.

A similar work conducted in Nigeria, Ogah et al., (2011) have also reported significant concentration of diazinon (0.0278 mg/kg), pirimiphos-methyl (0.0925 mg/kg) and chlorpyrifos (0.0982 mg/kg) and in beans (*phaseolus vulgaris*). The results support the finding of this study.

Another studies conducted by Darko and Akoto (2008) on vegetables obtained from Kumasi show relatively high levels of dimethoate (tomatoes = 0.228 - 0.978 mg/kg, egg plant = 0.162 - 0.422 mg/kg, pepper = 0.011 - 0.244 mg/kg) and malathion (tomatoes = 0.074 – 2.620, egg plant = 0.176 - 0.340 mg/kg, peper = 0.093 - 0.218 mg/kg). Also, a study carried out by Armah (2011) showed relatively high levels of ethoprophos (1.135 mg/kg), phorate (0.678 mg/kg) and fenitrothion (0.165 mg/kg) in cabbage.

The results of Darko and Akoto, and Armah (2011) appear to contradict the results of this study as relatively higher levels of organophosphorus were measured. The high residual levels of organophosphorus pesticides reported by Armah (2011) and Darko and Akoto (2008) could be attributed to the intensive use of organophosphorus pesticides in fruit and vegetable cultivations in Ghana. It could also be due to early harvest which do not allow most of the applied organophosphorus pesticides to degrade as compared to maize and cowpea cultivation in which the crops are allowed on the field for a longer time to dry before harvest, aiding the degradation process of the pesticides.

Table 4.9 Concentration of Pyrethroids Pesticide residues in Maize and Cowpea compared with EU MRL (2011).

Pesticide	Maize			Cowpea		
	Range (mg/kg)	Mean ± SD (mg/kg)	MRL(mg/kg) (EU)	Range (mg/kg)	Mean ± SD (mg/kg)	MRL(mg/kg) (EU)
Bifenthrin	0.002 - 0.005	0.003 ± 0.001	0.050	0.002 - 0.003	0.002 ± 0.001	0.050
Fenpropathrin	0.002 - 0.060	0.017 ± 0.025	0.010	0.001 - 0.008	0.003 ± 0.003	0.010
λ-Cyhalothrin	0.007 - 0.056	0.028 ± 0.018	0.020	0.001 - 0.083	0.039 ± 0.032	0.050
Permethrin	0.002 - 0.007	0.004 ± 0.002	0.050	0.001 - 0.003	0.001 ± 0.001	0.050
Cyfluthrin	0.004- 0.007	0.005 ± 0.001	0.050	0.002 - 0.018	0.010 ± 0.008	0.020
Allethrin	0.002 - 0.021	0.009 ± 0.007	NA	0.001 - 0.008	0.003 ± 0.003	NA
Cypermethrin	0.004 - 0.006	0.005 ± 0.001	0.300	0.002 - 0.011	0.006 ± 0.004	0.050
Fenvalerate	0.010 - 0.016	0.014 ± 0.002	0.020	0.005 - 0.015	0.009 ± 0.004	0.020
Deltamethrin	0.002 - 0.003	0.002 ± 0.001	2.000	0.003 - 0.013	0.007 ± 0.005	1.000
Total (mg/kg)		*0.087 ± 0.058*			*0.080 ± 0.061*	

*SD = standard deviation

*NA = MRL not available for commodity analysed

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The concentration of pyrethroid residues in maize and cowpea are presented in Table 4.9. In the maize the mean residual concentration ranged from 0.002 - 0.028 mg/kg while in the cowpea, mean concentration ranged from 0.001 - 0.039 mg/kg.

In the maize, the mean residual concentration measured varied from 0.003 ± 0.001 mg/kg for bifenthrin, 0.017 ± 0.025 mg/kg for fenpropathrin, 0.004 ± 0.002 mg/kg for permethrin, 0.028 ± 0.018 mg/kg for λ-cyhalothrin, 0.005 ± 0.001 mg/g for cyfluthrin, 0.005 ± 0.001 mg/kg for cypermethrin, 0.014 ± 0.002 mg/kg for fenvalerate, 0.002 ± 0.001 mg/kg for deltamethrin and 0.009 ± 0.007 mg/kg for allethrin.

Likewise in the cowpea, the residual concentration measured were 0.002 ± 0.001 mg/kg for bifenthrin, 0.003 ± 0.003 mg/kg for fenpropathrin, 0.001 ± 0.001 mg/kg for permethrinin, 0.039 ± 0.032 mg/kg for λ-cyhalothrin, 0.010 ± 0.007 mg/kg for cyfluthrin, 0.006 ± 0.004 mg/kg for cypermethrin, 0.008 ± 0.004 mg/kg for fenvalerate, 0.007 ± 0.005 mg/kg for deltamethrin and 0.003 ± 0.003 mg/kg for allethrin.

The mean residue of λ-cyhalothrin (0.028 mg/kg) occurred highest in maize while deltamethrin was found the lowest at 0.002 mg/kg. Similarly, in the cowpea, the highest concentration was measured for λ-cyhalothrin (0.010 mg/kg) and the lowest for permethrin (0.001 mg/kg). Among the pyrethroid pesticide residues investigated, only residual concentration of λ-cyhalothrin (0.039 mg/kg) and fenpropathrin (0.017 mg/kg) in maize were found exceeding the EU recommended MRL of 0.020 mg/kg and 0.010 mg/kg respectively. With respect to cowpea, all the pyrethroid residues were found to be below their respective EU MRLs values (Table 4.9).

Generally, the total residual concentrations of pesticides detected in this study were higher in maize (organochlorines = 0.354 ± 0.169 mg/kg, organophosphorus = 0.075 ± 0.035 mg/kg, pyrethroids = 0.087 ± 0.058 mg/kg) than in cowpea (organochlorines = 0.314 ± 0.077 mg/kg, organophosphorus = 0.067 ± 0.042 mg/kg, pyrethroids = 0.080 ± 0.061 mg/kg).

A study carried out on fruits and vegetables by Bempah et al., (2011) detected residues of permethrin, cyfluthrin, cypermethrin, fenvalerate and deltamethrin ranging from 0.006 - 0.090 mg/kg, 0.008 - 0.020 mg/kg, 0.004 - 0.060 mg/kg, 0.006 - 0.037 mg/kg, and 0.008 - 0.044 mg/k, respectively. A similar study was also carried by Armah (2011), which indicated residues of allethrin (1.5241 mg/kg), deltamethrin (4.74690 mg/kg), cypermethrin (0.31180 mg/kg), fenvalerate 2 (0.20590 mg/kg), permethrin (0.14700 mg/kg), ethoprophos (1.13544 mg/kg), phorate (0.67820 mg/kg), chlorfenvinp (0.31520 mg/kg) and fenitrothion (0.16500 mg/kg) in cabbage samples.

Also, in South Africa, Dalvie and London (2009) detected residues of cyfluthrin (0.014 mg/kg), fenitrothion (0.117 mg/kg), fenvalerate (0.007 mg/kg), permethrin (0.076 mg/kg) and cypermethrin (0.017 mg/kg) in wheat samples. The results of these studies are in full support of the findings of this study.

4.3. Estimation of Dietary exposure and Health risk assessment of Pesticide residues

The health risk assessment for systemic effects associated with pesticide residues detected in maize and cowpea are summarized in Table 4.10 - 4.15. Health hazard indices were calculated for each pesticide detected in the food.

Table 4.10. Health risk estimation for Organochlorine Pesticide residues in Maize

Pesticde	ADI (mg/kg/day)	EADI (mg/kg/day)	Health Index	Health risk
β-HCH	NA	5.49×10^{-4} (Children)	-	-
		7.84×10^{-5} (Adult)	-	-
γ-HCH	0.0003	1.22×10^{-5} (Children)	0.0410	No
		1.74×10^{-6} (Adult)	0.0100	No
δ-HCH	0.0030	2.44×10^{-5} (Children)	0.0100	No
		3.49×10^{-6} (Adult)	0.0010	No
Heptachlor	0.0001	6.10×10^{-5} (Children)	0.6100	No
		8.71×10^{-6} (Adult)	0.0870	No
Aldrin	0.0001	3.66×10^{-5} (Children)	0.3660	No
		5.23×10^{-6} (Adult)	0.0520	No
γ-Chlordane	0.0005	6.10×10^{-5} (Children)	0.1220	No
		8.71×10^{-6} (Adult)	0.0170	No
α-Endosulfan	0.0060	1.22×10^{-5} (Children)	0.0020	No
		1.74×10^{-6} (Adult)	0.0003	No
β-Endosulfan	0.0060	1.26×10^{-3} (Children)	0.2100	No
		1.80×10^{-4} (Adult)	0.0300	No
Endosulfan sulphate	NA	1.10×10^{-4} (Children)	-	-
		1.57×10^{-5} (Adult)	-	-
p,p'-DDE	0.0200	7.81×10^{-4} (Children)	0.3910	No
		1.12×10^{-4} (Adult)	0.0060	No
p,p'-DDD	0.0200	1.24×10^{-3} (Children)	0.0620	No
		1.77×10^{-4} (Adult)	0.0090	No
p,p'-DDT	0.0200	2.44×10^{-5} (Children)	0.0010	No
		3.49×10^{-6} (Adult)	0.0002	No
Methoxychlor	0.0050	2.44×10^{-5} (Children)	0.0050	No
		3.49×10^{-6} (Adult)	0.0010	No
Endrin	0.0002	2.44×10^{-5} (Children)	0.1220	No
		3.49×10^{-6} (Adult)	0.0170	No
Dieldrin	0.0001	2.44×10^{-5} (Children)	0.2440	No
		3.49×10^{-6} (Adult)	0.0350	No

*NA = ADI not available for the endosulfan sulphate and β-HCH

Table 4.11. Health risk estimation for Organochlorine Pesticide residues in Cowpea

Pesticde	ADI (mg/kg/day)	EADI (mg/kg/day)	Health Index	Health risk
β-HCH	NA	3.50×10^{-5} (Children)	-	-
		5.00×10^{-6} (Adult)	-	-
γ-HCH	0.0003	2.80×10^{-6} (Children)	0.0100	No
		4.00×10^{-7} (Adult)	0.0010	No
δ-HCH	0.0030	4.20×10^{-6} (Children)	0.0010	No
		6.00×10^{-7} (Adult)	0.0002	No
Heptachlor	0.0001	1.40×10^{-5} (Children)	0.1400	No
		2.00×10^{-6} (Adult)	0.0200	No
Aldrin	0.0001	4.20×10^{-6} (Children)	0.0420	No
		6.00×10^{-7} (Adult)	0.0060	No
γ-Chlordane	0.0005	2.80×10^{-6} (Children)	0.0060	No
		4.00×10^{-7} (Adult)	0.0010	No
α-Endosulfan	0.0060	1.40×10^{-5} (Children)	0.0020	No
		2.00×10^{-6} (Adult)	0.0003	No
β-Endosulfan	0.0060	1.13×10^{-4} (Children)	0.0190	No
		1.61×10^{-5} (Adult)	0.0030	No
Endosulfan sulphate	NA	8.40×10^{-6} (Children)	-	-
		1.20×10^{-6} (Adult)	-	-
p,p'-DDE	0.0200	7.42×10^{-5} (Children)	0.0040	No
		1.06×10^{-5} (Adult)	0.0010	No
p,p'-DDD	0.0200	1.32×10^{-2} (Children)	0.6600	No
		1.89×10^{-3} (Adult)	0.0950	No
p,p'-DDT	0.0200	4.20×10^{-6} (Children)	0.0002	No
		6.00×10^{-7} (Adult)	0.0000	No
Methoxychlor	0.0050	4.20×10^{-6} (Children)	0.0010	No
		6.00×10^{-7} (Adult)	0.0001	No
Endrin	0.0002	2.80×10^{-6} (Children)	0.0140	No
		4.00×10^{-7} (Adult)	0.0020	No
Dieldrin	0.0001	4.20×10^{-6} (Children)	0.0420	No
		6.00×10^{-7} (Adult)	0.0060	No

*NA = ADI not available for the endosulfan sulphate and β-HCH

Ttable 4.10 and 4.11, present the health risk for systemic effect associated with residues of organochlorine pesticides in maize and cowpea respectively. Health risk estimate indicate that γ-HCH, δ-HCH, heptachlor, methoxychlor, aldrin, dieldrin, endrin, γ-chlordane, α-endosulfan, β-endosulfan, p,p'-DDT, p,p'-DDE and p,p'-DDD do not pose direct hazard to the health of both children and adult population, although present in maize and cowpea. This is because hazard indices values calculated were less than 1 (Hamilton and Crossley, 2004).

However, in children who are considered to be the most vulnerable population subgroup, hazard indices of heptachlor (0.6100) in maize and p,p'-DDD (0.6600) in cowpea were quite closer to 1, indicating a potential for systemic toxicity on exposure to maize and cowpea.

Organochlorine pesticides are generally persistent, lipohilic and bioaccumulative both in the environment and at each tropic level of the food chain. Contaminants can thus reach high concentrations through biomagnifications in the tissues of human who are high on the food chain (USEPA, 1996).

Table 4.12. Health risk estimation for organophosphorus pesticide residues in maize

Pesticide	ADI (mg/kg/day)	EADI (mg/kg/day)	Hazard index	Health risk
Dimethoate	0.0020	4.88×10^{-5} (Children)	0.0244	No
		6.97×10^{-6} (Adult)	0.0035	No
Methamidophos	0.0010	3.66×10^{-5} (Children)	0.0366	No
		5.23×10^{-6} (Adult)	0.0052	No
Diazinon	0.0050	2.44×10^{-5} (Children)	0.0049	No
		3.49×10^{-6} (Adult)	0.0007	No
Ethoprophos	0.0004	-	-	-
		-	-	-
Phorate	0.0005	-	-	-
		-	-	-
Fonofos	NA	3.66×10^{-5} (Children)	-	-
		5.23×10^{-6} (Adult	-	-
Pirimiphos-methyl	0.0300	2.44×10^{-5} (Children)	0.0008	No
		3.49×10^{-6} (Adult)	0.0001	No
Chlorpyrifos	0.0100	1.57×10^{-4} (Children)	0.0157	No
		2.24×10^{-5} (Adult)	0.0022	No
Malathion	0.0300	2.32×10^{-4} (Children)	0.0008	No
		3.31×10^{-5} (Adult)	0.0011	No
Fenitrothion	0.0060	7.32×10^{-4} (Children)	0.1220	No
		1.05×10^{-5} (Adult)	0.0018	No
Parathion-ethyl	0.0050	2.44×10^{-5} (Children)	0.0049	No
		3.49×10^{-6} (Adult)	0.0007	No
Chlorfenvinphos	0.0005	2.32×10^{-4} (Children)	0.4640	No
		3.31×10^{-5} (Adult)	0.0662	No
Profenofos	0.0300	6.10×10^{-5} (Children)	0.0023	No
		8.71×10^{-6} (Adult)	0.0003	No

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Table 4.13. Health risk estimation for organophosphorus pesticide residues in cowpea

Pesticide	ADI (mg/kg/day)	EADI (mg/kg/day)	Hazard index	Health risk
Dimethoate	0.0020	1.12×10^{-5} (Children)	0.0056	No
		1.60×10^{-6} (Adult)	0.0008	No
Methamidophos	0.0010	7.00×10^{-5} (Children)	0.0700	No
		1.00×10^{-6} (Adult)	0.0010	No
Diazinon	0.0050	- (Children)	-	-
		- (Adult)	-	-
Ethoprophos	0.0004	- (Children)	-	-
		- (Adult)	-	-
Phorate	0.0005	- (Children)	-	-
		- (Adult)	-	-
Fonofos	NA	3.66×10^{-5} (Children)	-	-
		5.23×10^{-6} (Adult	-	-
Pirimiphos-methyl	0.0300	- (Children)	-	-
		- (Adult)	-	-
Chlorpyrifos	0.0100	2.10×10^{-5} (Children)	0.0021	No
		3.00×10^{-6} (Adult)	0.0003	No
Malathion	0.0300	1.96×10^{-5} (Children)	0.0007	No
		2.80×10^{-6} (Adult)	0.0001	No
Fenitrothion	0.0060	4.20×10^{-6} (Children)	0.0007	No
		6.00×10^{-7} (Adult)	0.0001	No
Parathion-ethyl	0.0050	2.80×10^{-6} (Children)	0.0006	No
		4.70×10^{-7} (Adult)	0.0001	No
Chlorfenvinphos	0.0005	1.26×10^{-5} (Children)	0.0252	No
		1.80×10^{-6} (Adult)	0.0036	No
Profenofos	0.0300	1.54×10^{-5} (Children)	0.0005	No
		2.20×10^{-6} (Adult)	0.0001	No

*NA = ADI not available for fonofos

Hazard indices values of the organophosphorus pesticide residues detected in maize and cowpea showed that, all the residues were found to be within safe limits (Table 4.11 and 4.12). Thus, lifetime consumption of maize and cowpea from the study area has no health risk associated with it.

Table 4.14. Health risk estimation for Pyrethroid Pesticide residues in Maize

Pesticide	ADI (mg/kg/day)	EADI (mg/kg/day)	Hazard Index	Health risk
Bifenthrin	0.0100	3.66×10^{-5} (Children)	0.0037	
		5.23×10^{-6} (Adult)	0.0005	No
Fenpropathrin	0.0300	2.07×10^{-4} (Children)	0.0069	
		2.96×10^{-5} (Adult)	0.0010	No
λ-Cyhalothrin	0.0200	3.42×10^{-4} (Children)	0.0171	
		4.89×10^{-5} (Adult)	0.0025	No
Permethrin	0.0500	4.88×10^{-5} (Children)	0.0010	
		6.34×10^{-6} (Adult)	0.0001	No
Cyfluthrin	0.0400	6.10×10^{-5} (Children)	0.0015	
		8.71×10^{-6} (Adult)	0.0002	No
Cypermethrin	0.0500	6.10×10^{-5} (Children)	0.0012	
		8.71×10^{-6} (Adult)	0.0002	No
Fenvalerate	0.0200	1.71×10^{-4} (Children)	0.0086	
		2.44×10^{-5} (Adult)	0.0012	No
Deltamethrin	0.0100	2.44×10^{-5} (Children)	0.0024	
		3.49×10^{-6} (Adult)	0.0005	No
Allethrin	NA	1.10×10^{-4} (Children)	-	-
		1.57×10^{-5} (Adult)	-	-

* NA = ADI not available for allethrin

Table 4.15. Health risk estimation for Pyrethroid Pesticide residues in Cowpea

Pesticide	ADI (mg/kg/day)	EADI (mg/kg/day)	Hazard Index	Health risk
Bifenthrin	0.0100	2.80×10^{-6} (Children)	0.0003	No
		4.00×10^{-7} (Adult)	0.0000	No
Fenpropathrin	0.0300	4.20×10^{-6} (Children)	0.0001	No
		6.00×10^{-7} (Adult)	0.0000	No
λ-Cyhalothrin	0.0200	5.46×10^{-5} (Children)	0.0027	No
		7.80×10^{-6} (Adult)	0.0004	No
Permethrin	0.0500	1.40×10^{-6} (Children)	0.0000	No
		2.00×10^{-7} (Adult)	0.0000	No
Cyfluthrin	0.0400	1.40×10^{-5} (Children)	0.0004	No
		2.00×10^{-6} (Adult)	0.0001	No
Cypermethrin	0.0500	8.40×10^{-6} (Children)	0.0002	No
		1.20×10^{-6} (Adult)	0.0000	No
Fenvalerate	0.0200	1.26×10^{-5} (Children)	0.0006	No
		1.80×10^{-6} (Adult)	0.0001	No
Deltamethrin	0.0100	9.80×10^{-6} (Children)	0.0001	No
		1.40×10^{-6} (Adult)	0.0001	No
Allethrin	NA	4.20×10^{-6} (Children)	-	-
		6.00×10^{-7} (Adult)	-	-

* NA = ADI not available for allethrin

Table 4.14 and 4.15 represents the health risk analysis. The health risk estimates revealed that pyrethroid pesticide residues detected in both maize and cowpea samples have hazard indices values of less than 1.00, representing no health risks to the consumer upon life time consumption.

CHAPTER FIVE

CONCLUSION AND RECOMMENDATION

In conclusion, the study has shown some degree of contamination in soil, maize and cowpea from Ejura by the residues of pesticides investigated. The results showed that, the soil investigated could be classified as lightly polluted. Although the concentration of pesticide residues reported under this study were low, soil pollution can play an important role in the global fate and distribution of pollutants. Soil has been the principal reservoir for pesticides applied in agriculture, from which they may be taken up by plants and may bioaccumulate in the food chain to an extent higher enough to cause chronic adverse health effects to the consumer. The use of organochlorine in agriculture has been banned in Ghana; however residues of organochlorine pesticides were encountered in the soil. This highlighted the fact that organochlorine are by far the most persistent of the pesticides in the environment. For the DDTs, past usage of technical DDT is the main source of their presence. However, new input was shown by endosulfan, aldrin and HCHs.

When compared the residual concentration of the individual pesticides detectd in the food with the European Union MRLs values , the residual levels of β-HCH, β-endosulfan, p,p'-DDE, p,p'-DDD, fenpropathrin and λ-cyhalothrin in maize exceeded their respective MRLs whereas in the cowpea, the residual concentration of β-HCH, β-endosulfan, p,p'-DDE and p,p'-DDD were also found to exceed their respective MRLs values. The findings showed that maize were highly contaminated with the investigaged pesticides than the cowpea. This supports the assumption that maize is more likely to be the principal route of pesticide intake by humans and should give cause for concer.

Data analysis of health risk assessment revealed that residues of the individual pesticides investigated do not pose a direct hazard to human health, although present in the maize and cowpea samples. However, there was no zero risk, because bioaccumulation and bio-concentration of pesticide residues in human are capable of reaching toxic levels even when the exposure is low.

Also, the presence of organophosphorus and synthetic pyrethroid pesticide residues in the investigated samples is an indication of change in usage pattern of insecticides in Ghana, where a shift has taken place from the use of organochlorine pesticides to the easily degradable organophosphorus and pyrethroids pesticides. The research has provided important information on the levels of pesticide residue contamination in soil, maize and cowpea from Ejura in Ashanti Region of Ghana.

On the basis of the above findings, it is recommended that further work on pesticide residues in blood serum of residents of Ejura and its environs and water sources of the study area should be carried out to ascertain the levels of the pesticide residues and its health implications.

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APPENDIX 1: Structures of organophosphlorine compounds monitored in this study
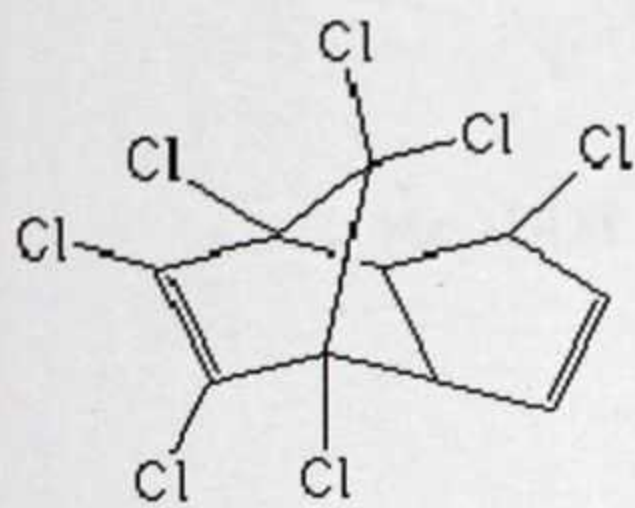
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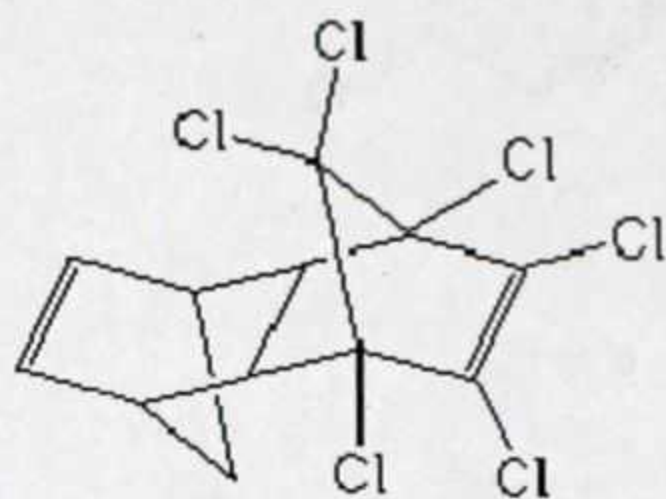
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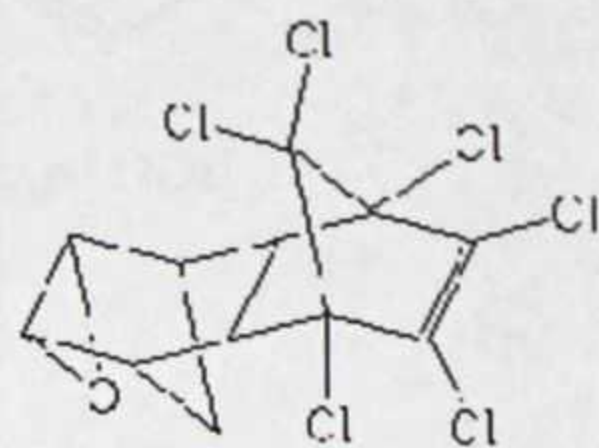
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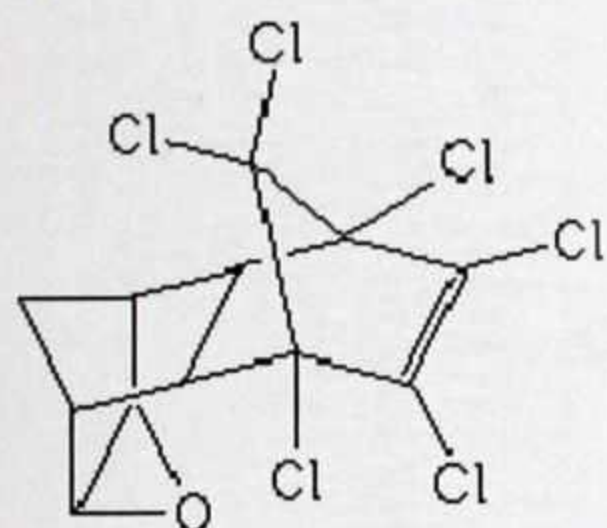
Endrin

Chlordane

Endosulfan sulphate

α-endosulfan

β-endosulfan

δ-HCH

β-HCH
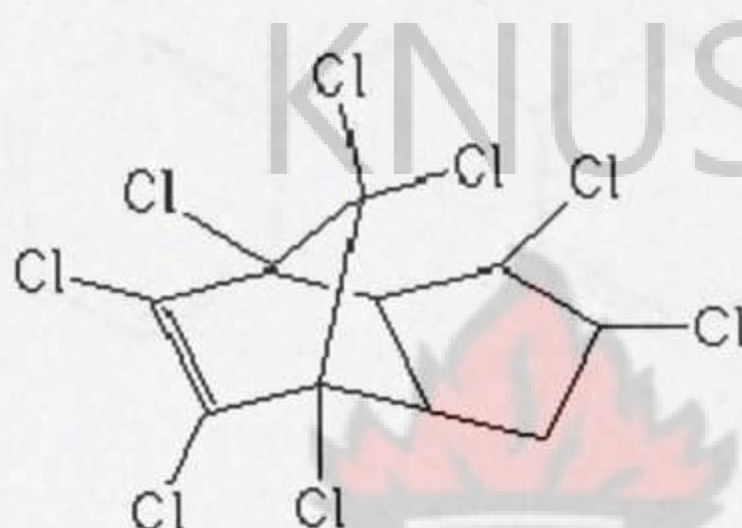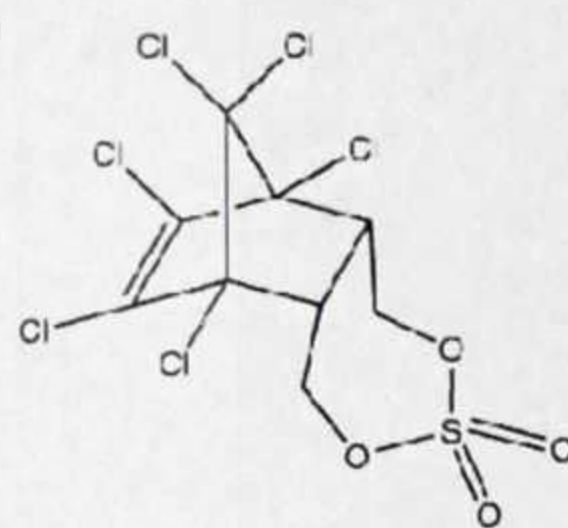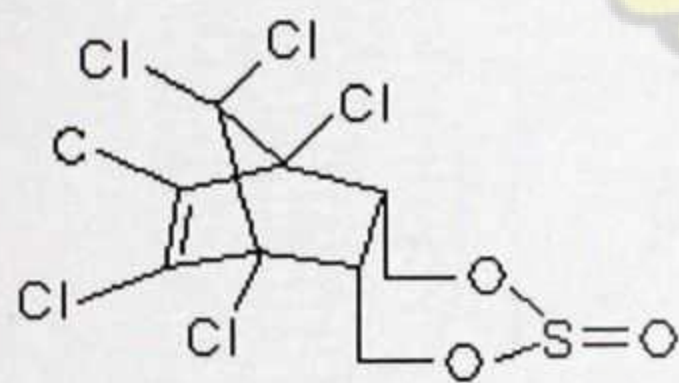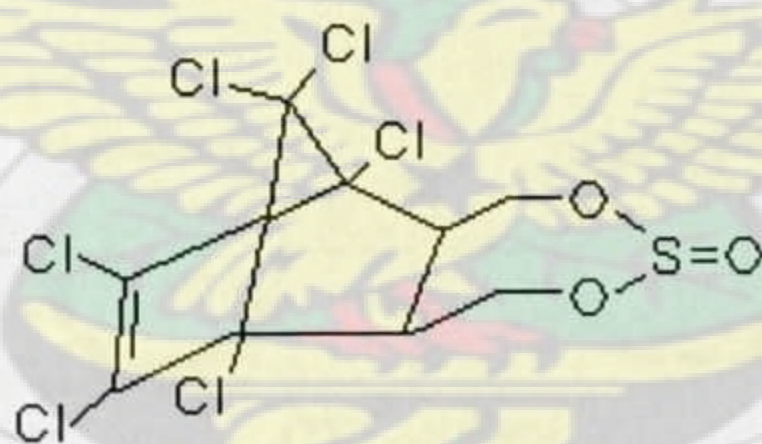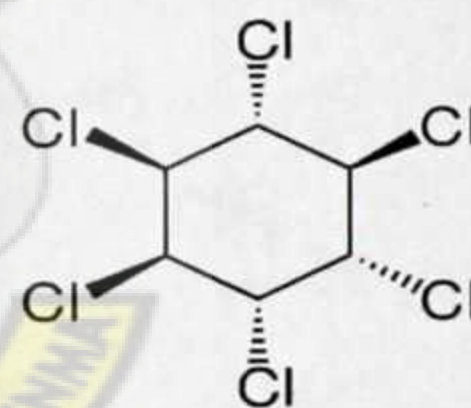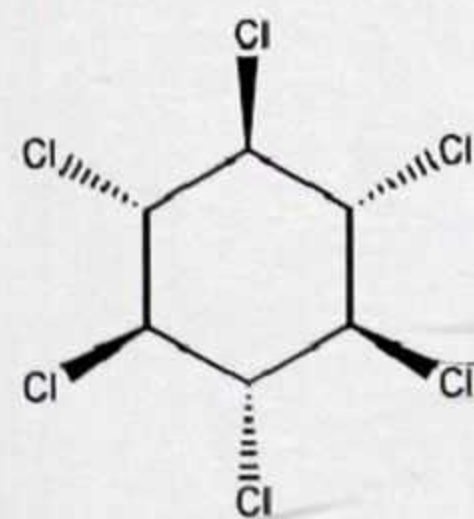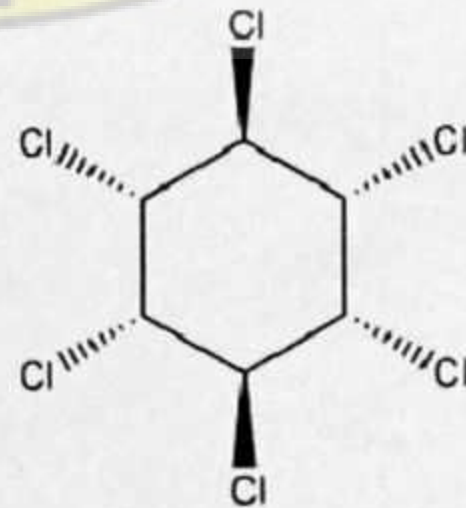
γ -HCH
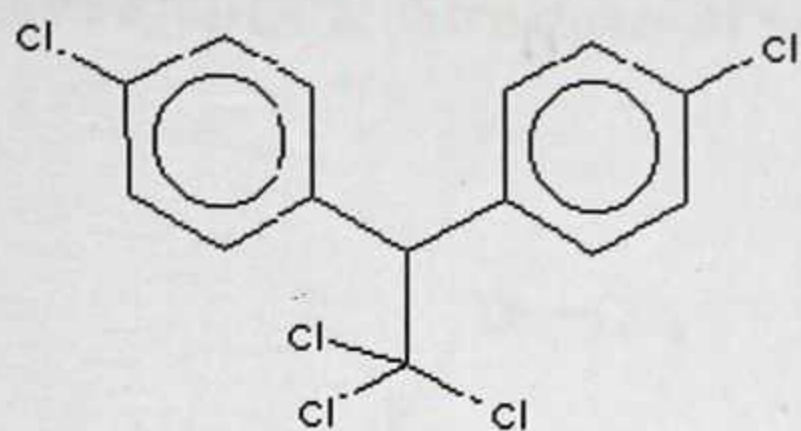
p,p'-DDT
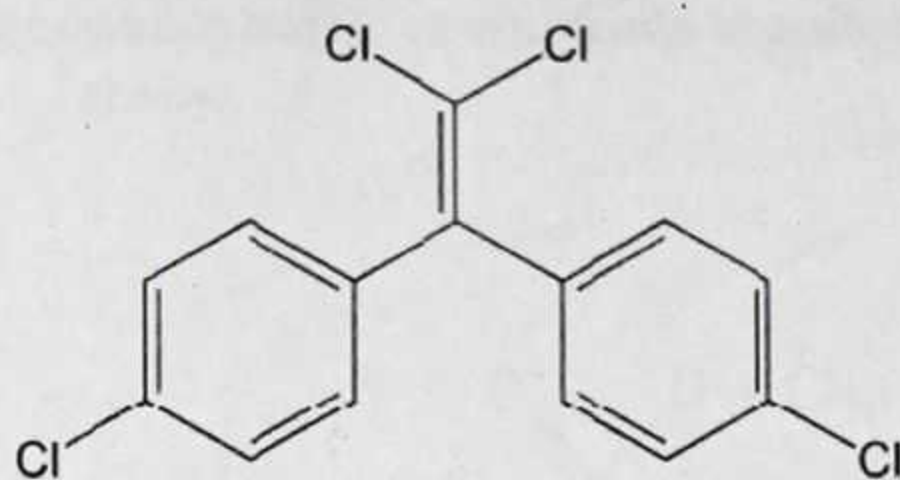
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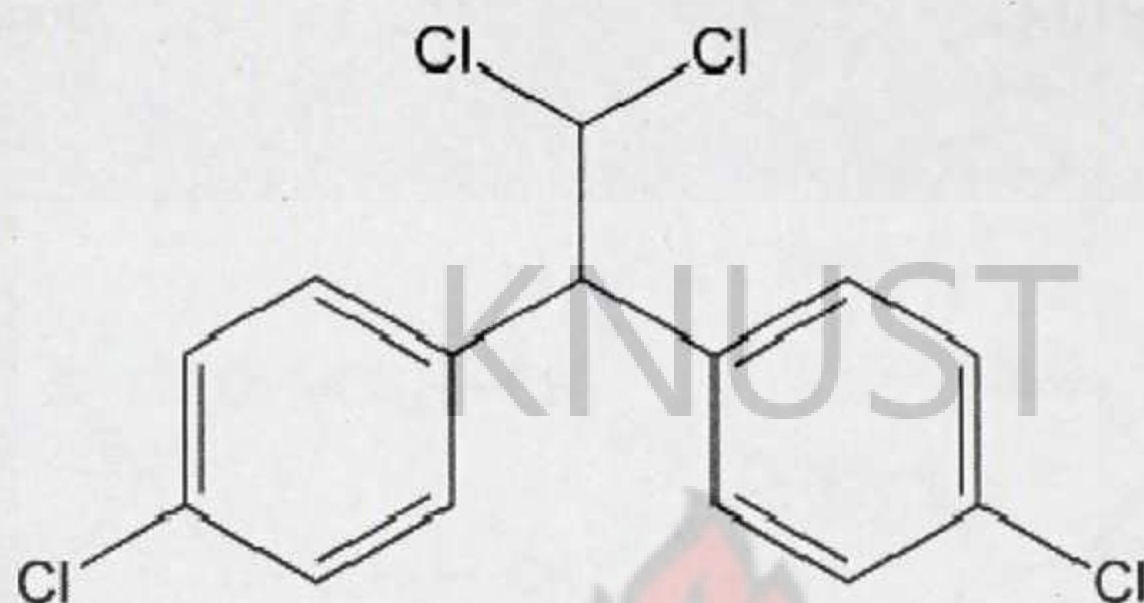
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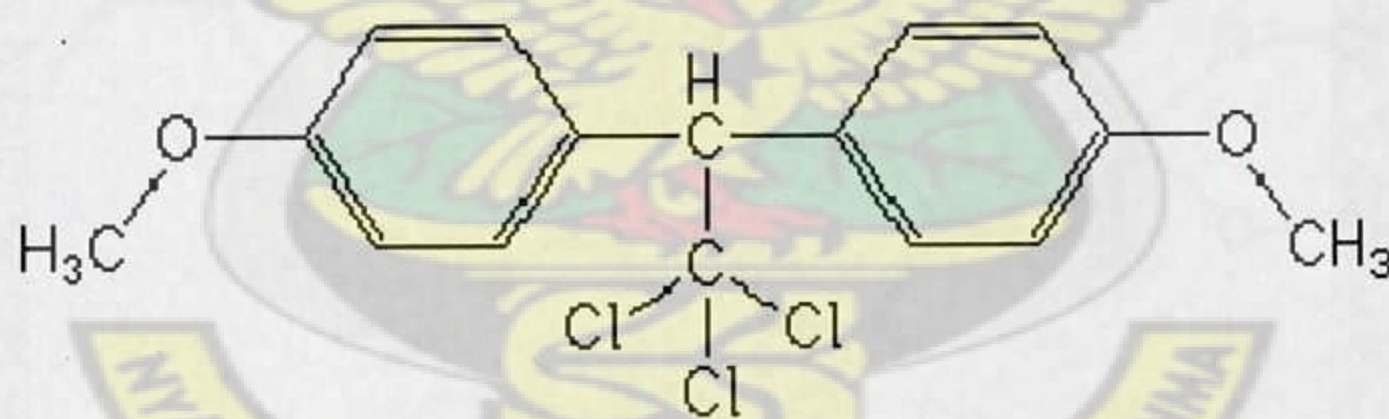
Methoxychlor

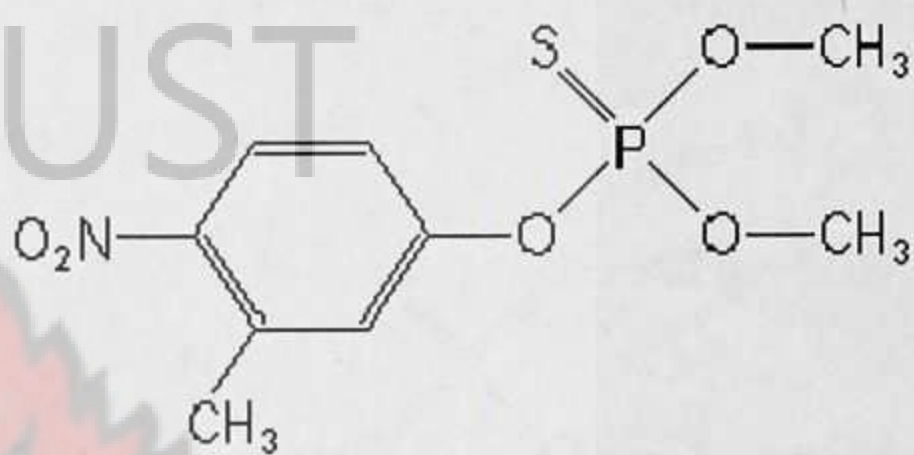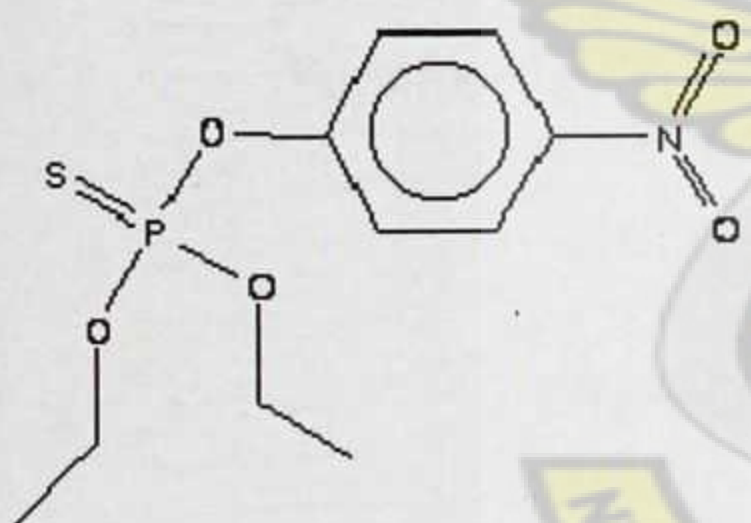# APPENDIX 2: Structures of organophosphorus compounds monitored in this study
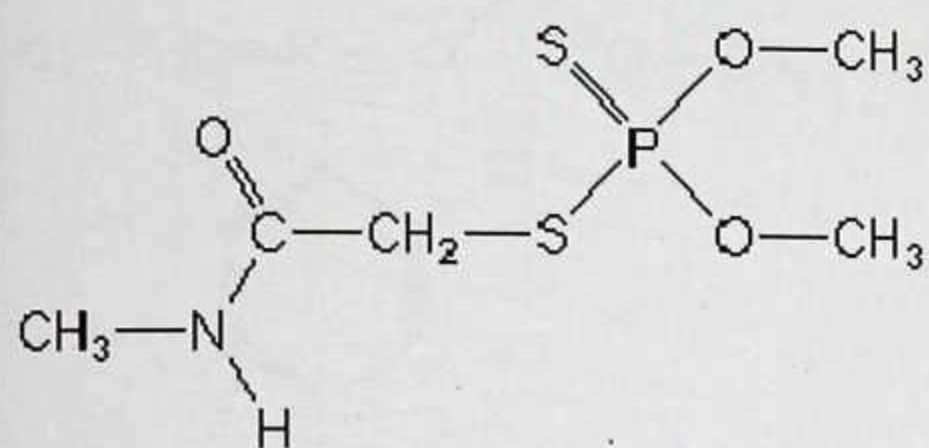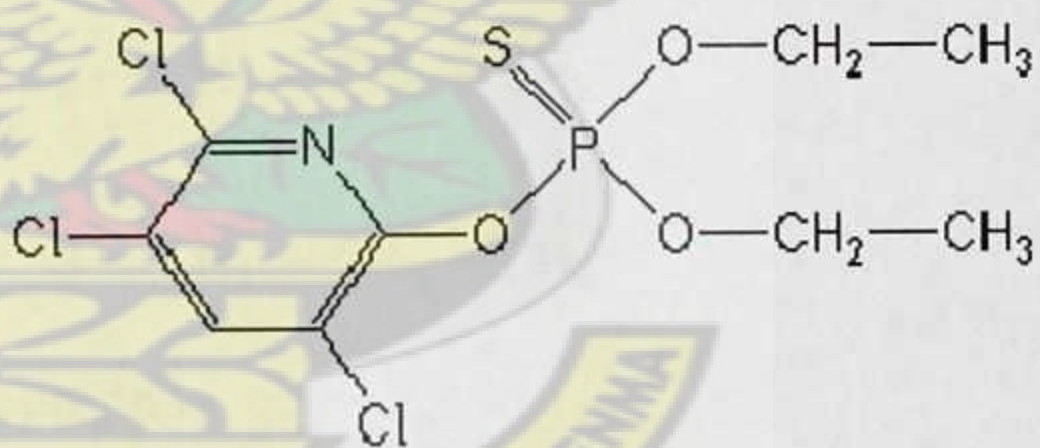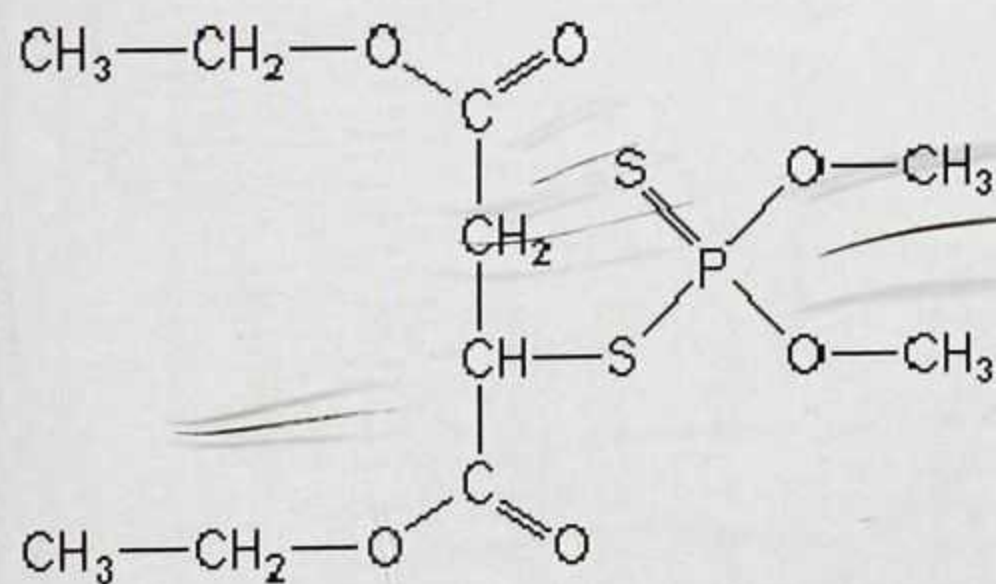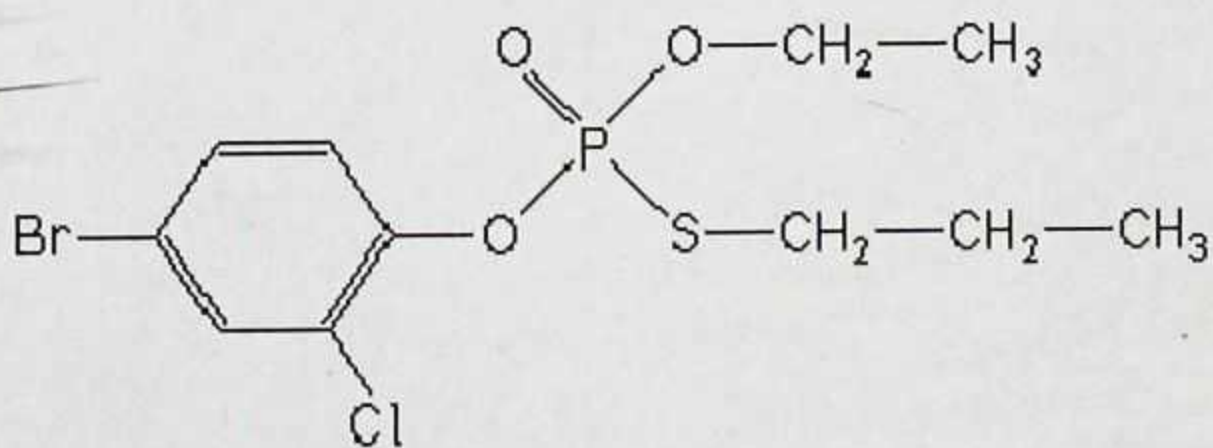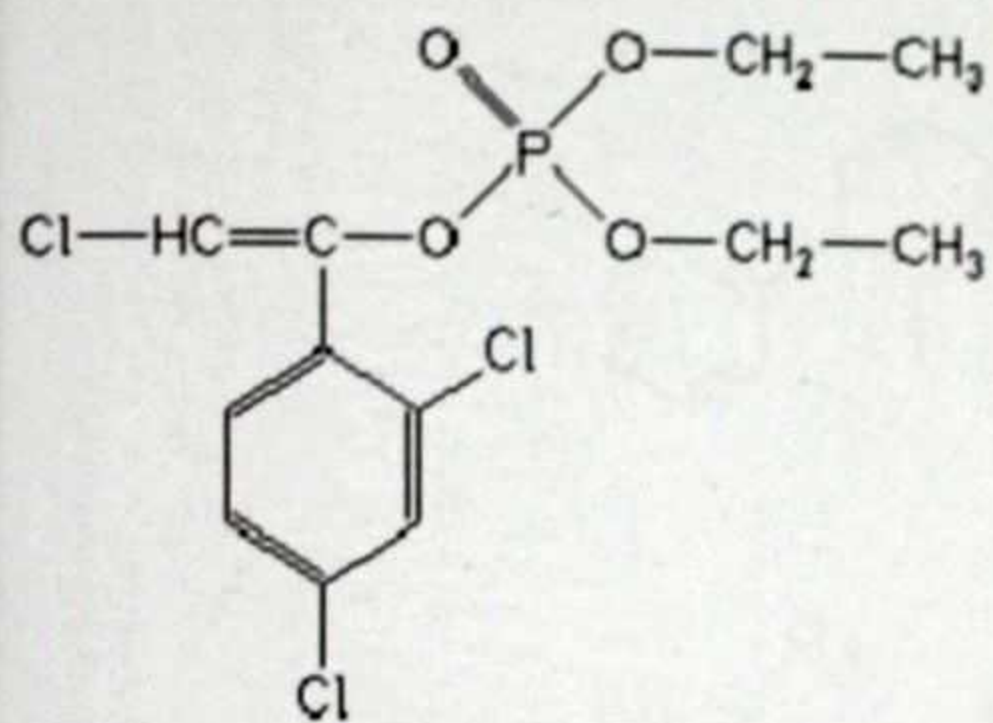

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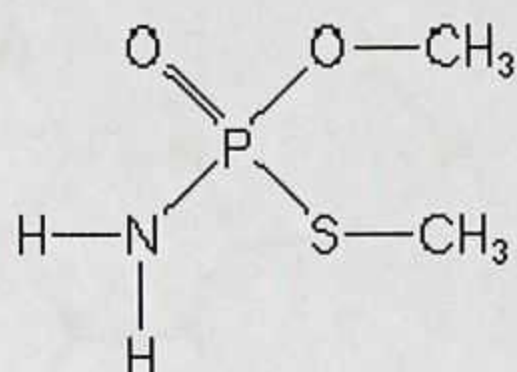
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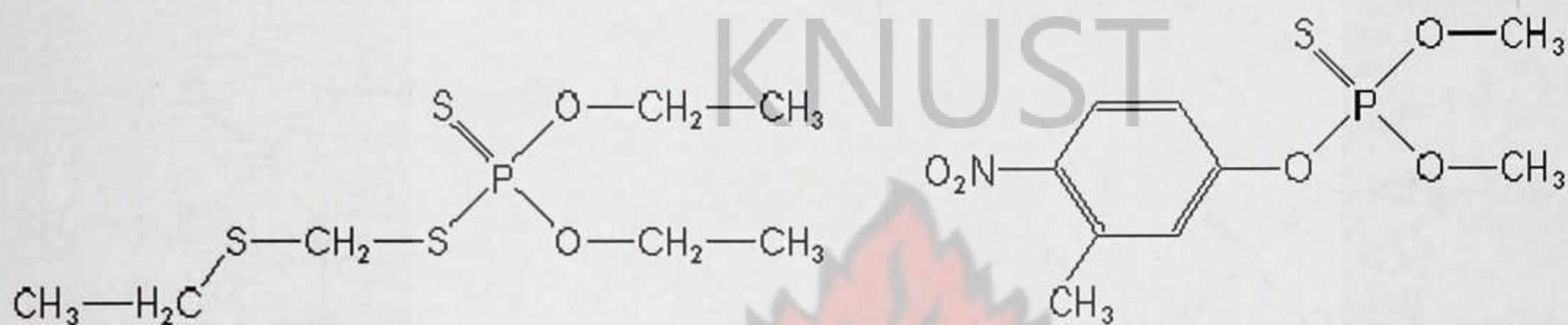
Phorate

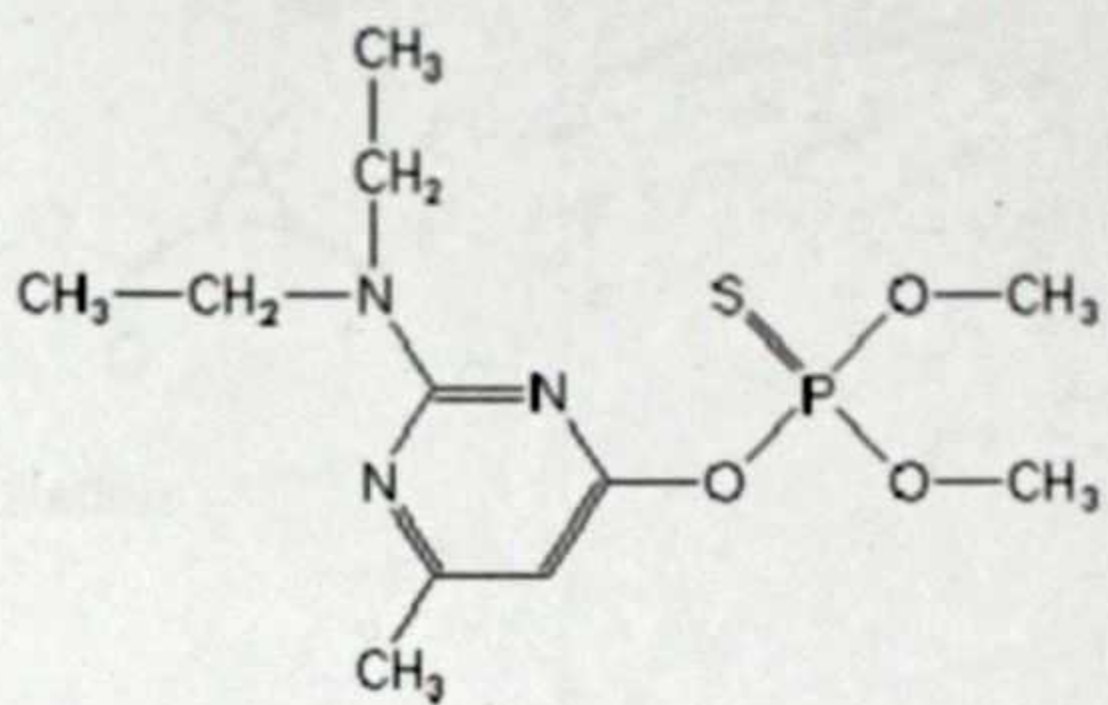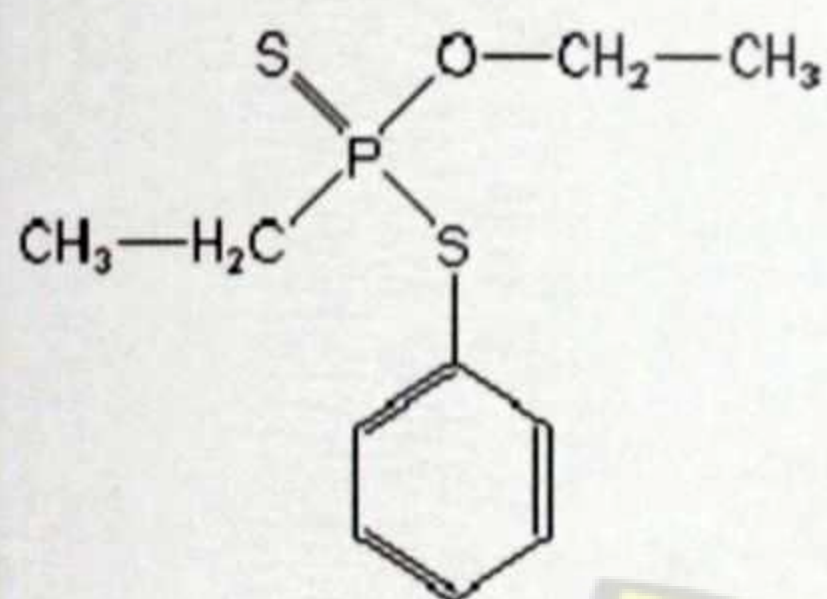Fenitrothion

Parathion-ethyl
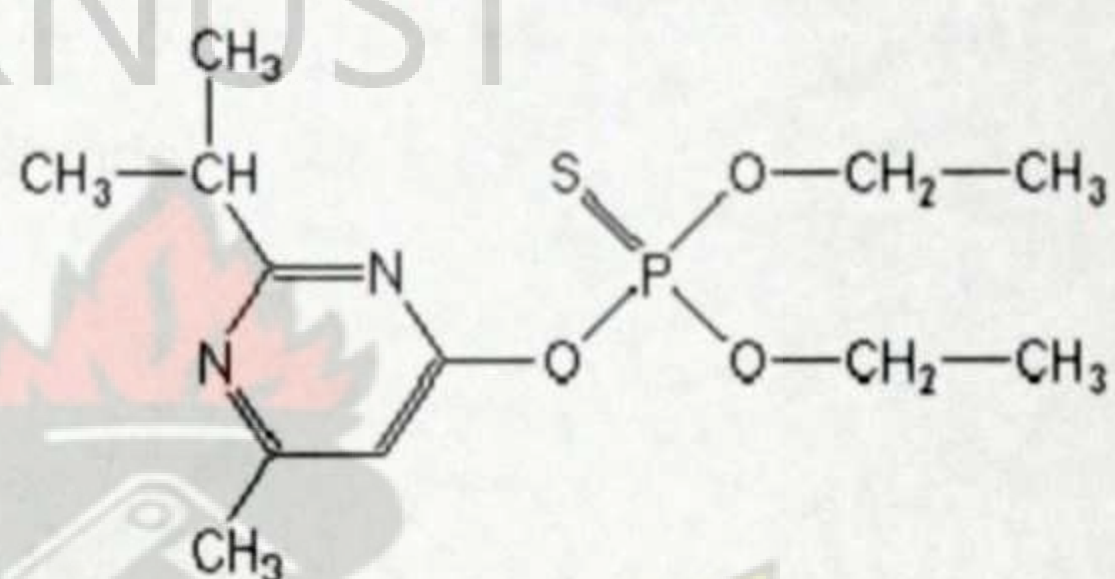
Chlorpyrifos

Malathion
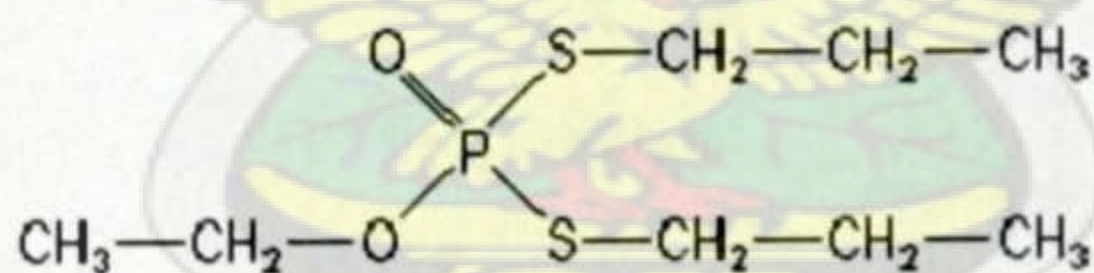
Profenofos

91

Chlorfenvinphos

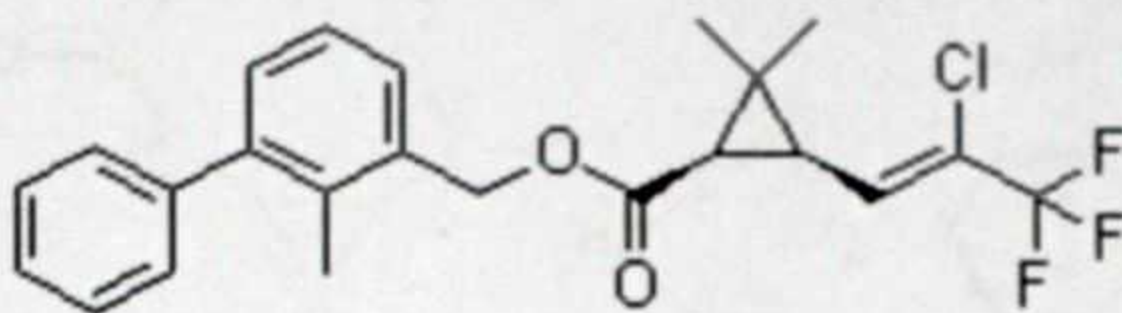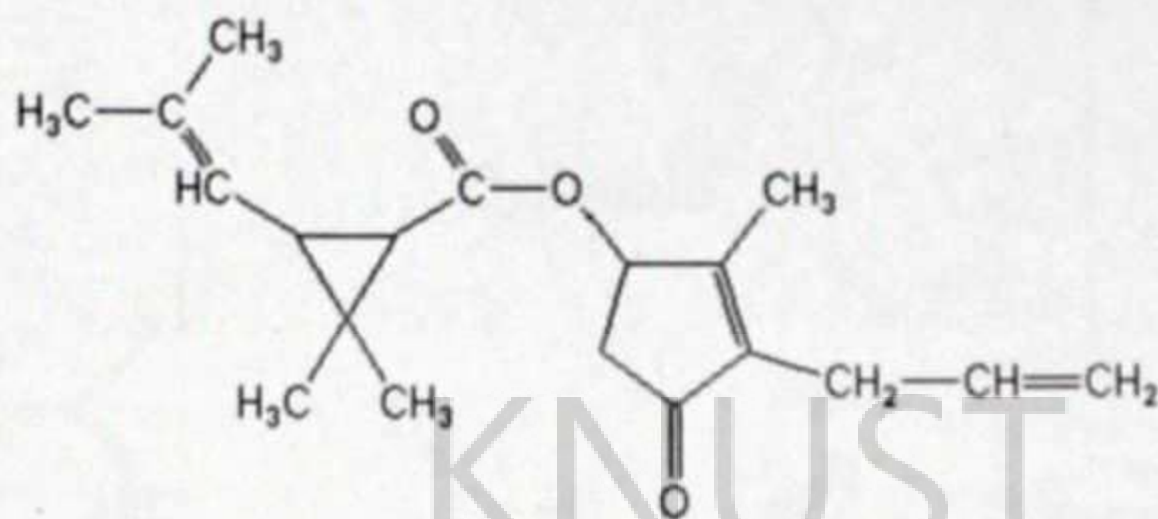

Pirimiphos-methyl

KNUST

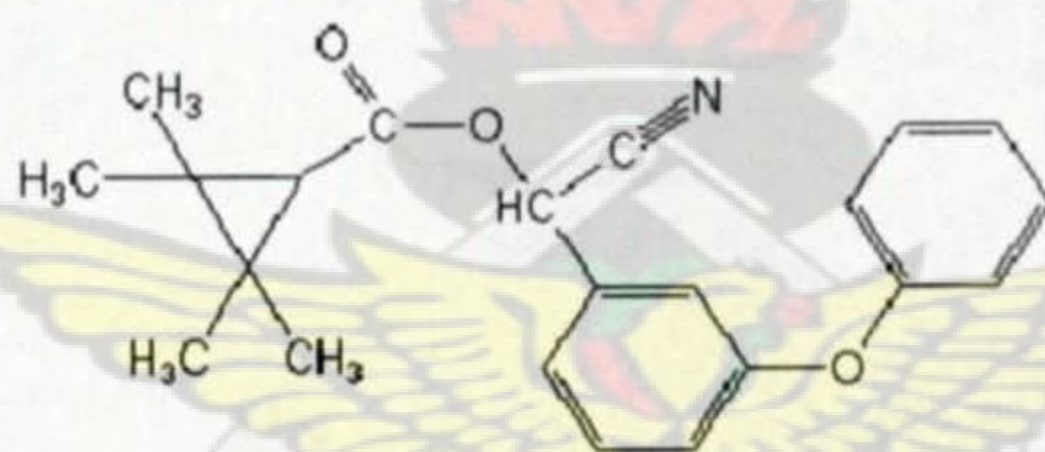Fonofos

Diazinon

Ethoprophos

92

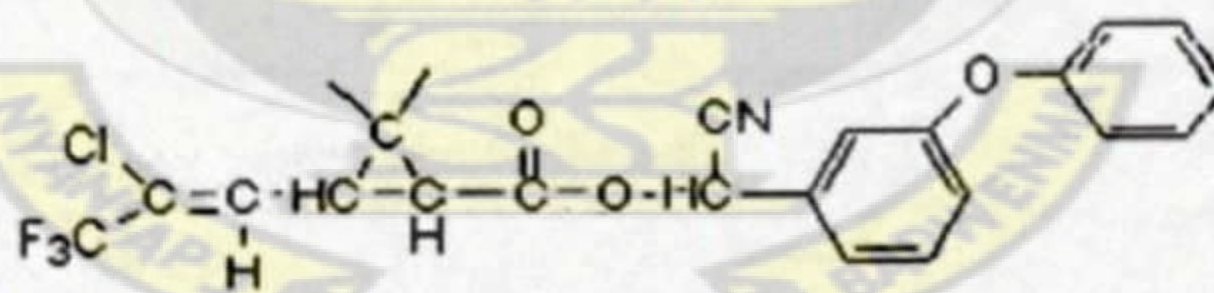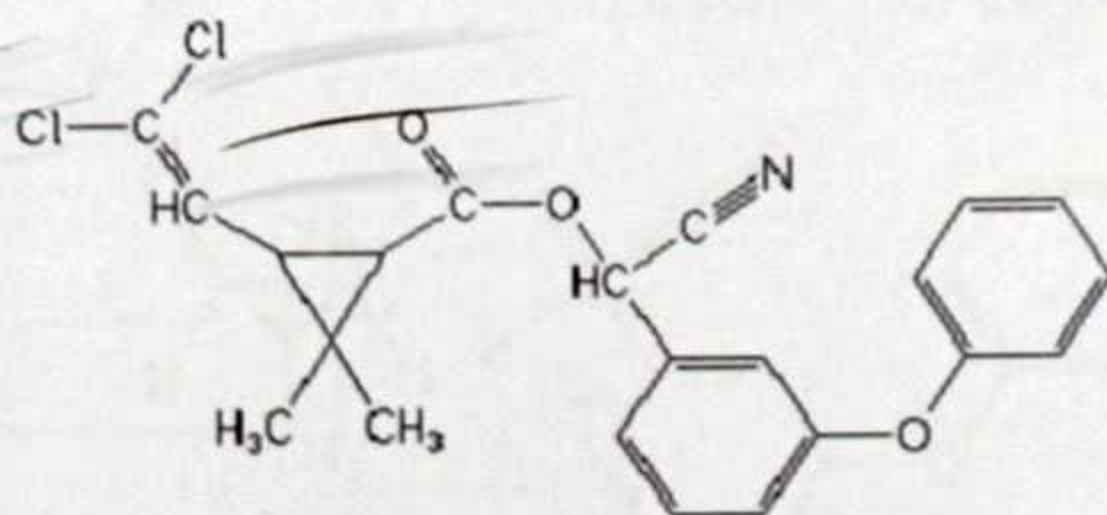# APPENDIX 3: Structures of pyrethroids compounds monitored in this study
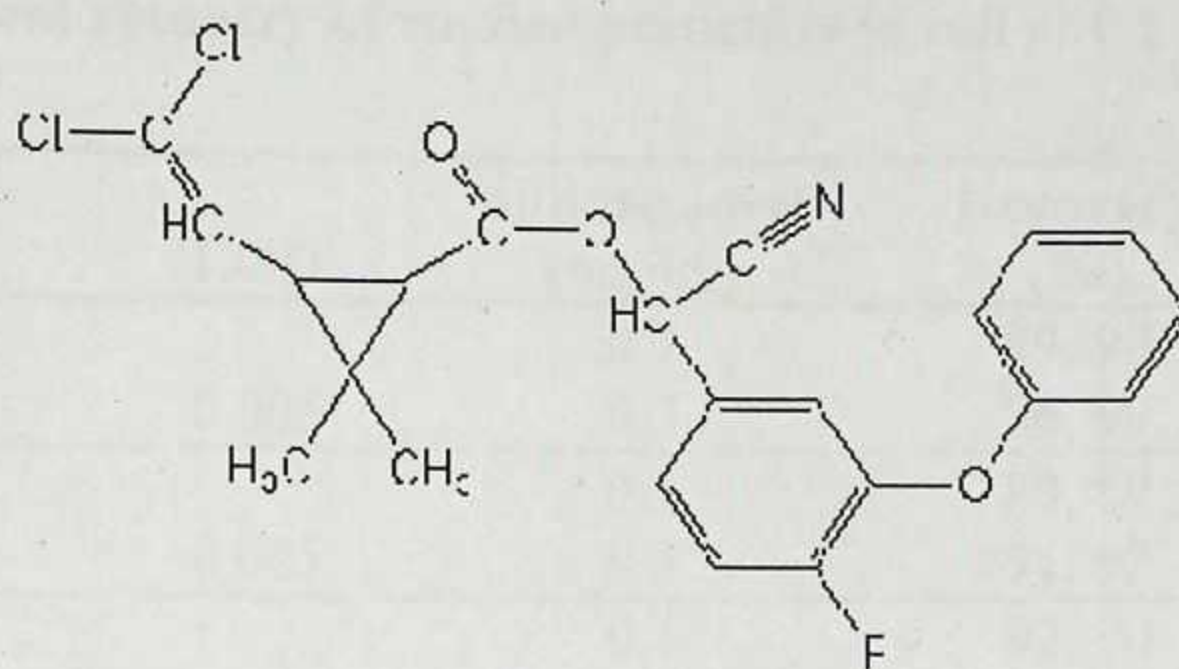

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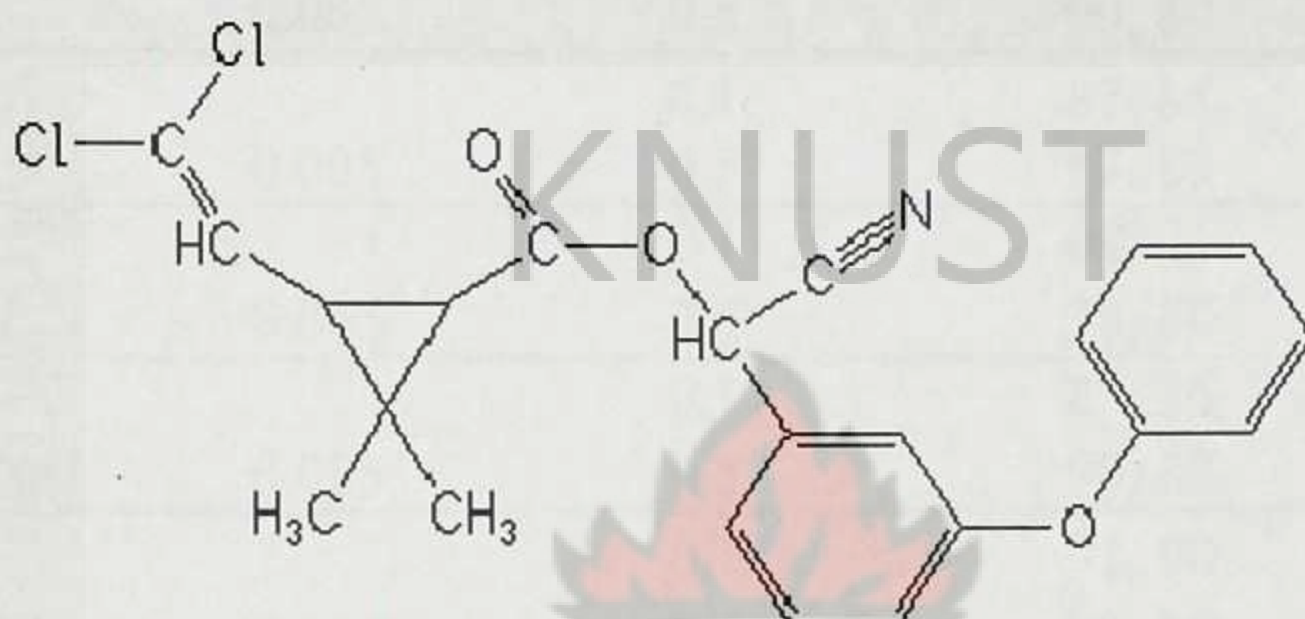

Allethrin

Fenpropathrin

λ-cyhalothrin

Cypermethtrin

Cyfluthrin

Cypermethrin

Fenvalerate

(S)-alcohol (1R)-cis-acid
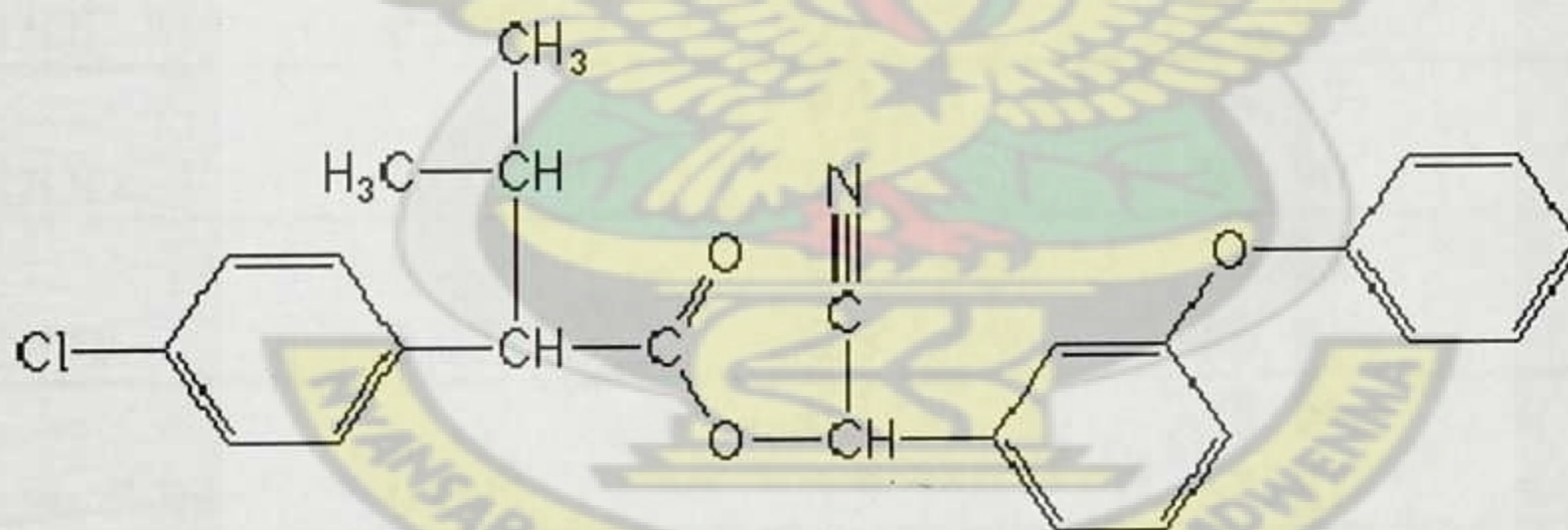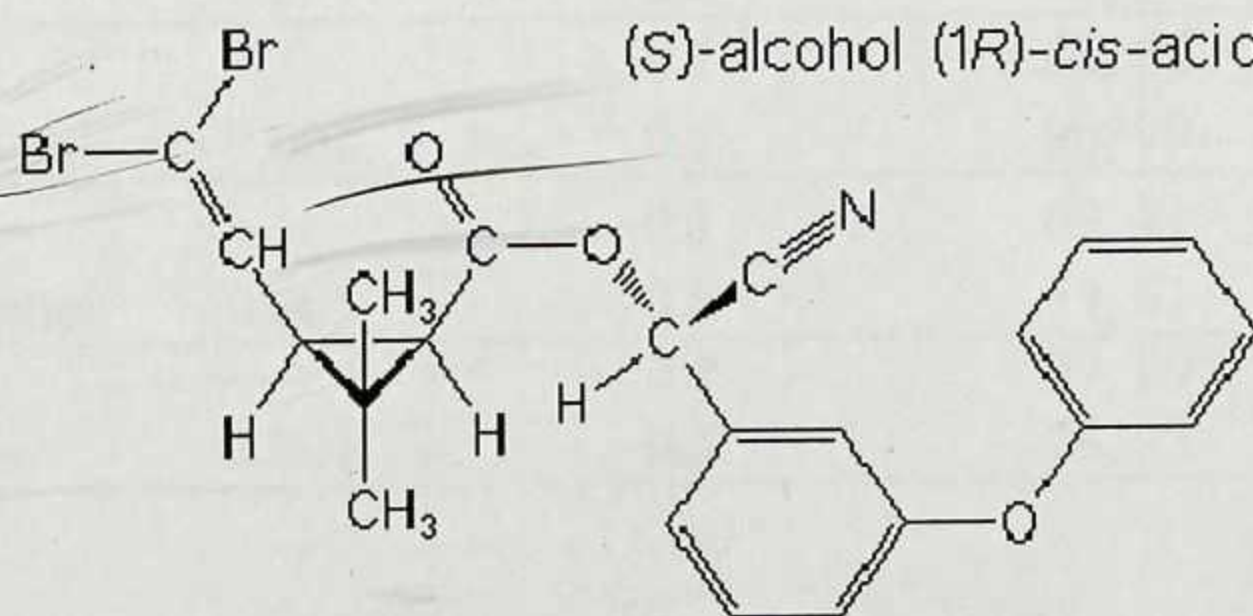
Deltamethrin

Table 1. Percent recovery of studied pesticides in soil at 0.1 and 0.5 mg/kg spiked levels

Pesticide	LOD	Spiking level (mg/kg)	Recovery (%)	Average recovery (%)
β-HCH	0.005	0.1	89, 90	90
		0.5	96, 99	98
γ-HCH	0.005	0.1	89, 89	89
		0.5	91, 92	92
δ-HCH	0.005	0.1	92, 90	91
		0.5	95, 93	94
Heptachlor	0.005	0.1	90, 91	91
		0.5	90, 89	90
Aldrin	0.005	0.1	87, 88	88
		0.5	87, 89	88
γ-chlordane	0.005	0.1	68, 71	70
		0.5	78, 80	79
α-endosulfan	0.005	0.1	83, 86	85
		0.5	90, 89	91
β-endosulfan	0.005	0.1	91, 90	91
		0.5	99, 97	98
Endosulfan sulphate	0.005	0.1	88, 87	88
		0.5	90, 91	91
p,p'-DDE	0.005	0.1	85, 85	85
		0.5	91, 93	92
p,p'-DDD	0.005	0.1	68, 69	69
		0.5	87, 90	89
p,p'-DDT	0.005	0.1	78, 89	84
		0.5	69, 81	75
Methoxychlor	0.005	0.1	78, 56	67
		0.5	57, 81	69
Endrin	0.005	0.1	97, 69	83
		0.5	71, 60	66
Dieldrin	0.005	0.1	91, 65	78
		0.5	85, 59	72
Dimethoate	0.001	0.1	82, 88	85
		0.5	90, 79	85
Methamidophos	0.001	0.1	69, 81	75
		0.5	59, 61	60
Ethoprophos	0.001	0.1	97, 89	93
		0.5	78, 95	87

Continued

Pesticide	LOD	Spiking level (mg/kg)	Recovery (%)	Average recovery (%)
Phorate	0.001	0.1	58, 80	69
		0.5	70, 79	75
Diazinon	0.001	0.1	67, 88	78
		0.5	74, 89	82
Pirimiphos-methyl	0.001	0.1	91, 83	87
		0.5	80, 69	75
Chlorpyrifos	0.001	0.1	97, 80	89
		0.5	101, 98	100
Malathion	0.001	0.1	89, 87	88
		0.5	93, 79	86
Fenitrothion	0.001	0.1	77, 70	74
		0.5	84, 79	82
Parathion-methyl	0.001	0.1	58, 71	65
		0.5	86, 69	78
Chlorfenvinphos	0.001	0.1	96, 89	93
		0.5	78, 99	89
Profenofos	0.001	0.1	67, 89	78
		0.5	90, 78	84
Fonofos	0.001	0.1	96, 98	94
		0.5	80, 78	79
Bifenthrin	0.001	0.1	74, 78	76
		0.5	98, 59	79
Fenpropathrin	0.001	0.1	69, 88	79
		0.5	91, 64	78
λ-cyhalothrin	0.001	0.1	85, 71	78
		0.5	71, 68	70
Permethrin	0.001	0.1	79, 80	80
		0.5	102, 99	101
Cyfluthrin	0.001	0.1	93, 88	91
		0.5	89, 69	79
Cypermethrin	0.001	0.1	94, 92	93
		0.5	93, 82	88
Fenvalerate	0.001	0.1	77, 69	73
		0.5	82, 95	89
Deltamethrin	0.001	0.1	84, 89	87
		0.5	95, 89	92
Allethrin	0.001	0.1	91, 86	89
		0.5	94, 73	84

Table2. Percent recovery of studied pesticides in maize at 0.1 and 0.5 mg/kg spiked levels

Pesticide	LOD	Spiking level (mg/kg)	Recovery (%)	Average recovery (%)
β-HCH	0.005	0.1	77, 91	84
		0.5	96,99	98
γ-HCH	0.005	0.1	102, 96	99
		0.5	87, 92	90
δ-HCH	0.005	0.1	88, 93	91
		0.5	95, 93	94
Heptachlor	0.005	0.1	76, 94	85
		0.5	97, 88	93
Aldrin	0.005	0.1	85, 92	89
		0.5	71, 85	78
γ-chlordane	0.005	0.1	88, 81	85
		0.5	99, 82	91
α-endosulfan	0.005	0.1	88, 89	89
		0.5	99, 89	94
β-endosulfan	0.005	0.1	96, 115	106
		0.5	98, 99	99
Endosulfan sulphate	0.005	0.1	87, 81	84
		0.5	99, 94	97
p,p'-DDE	0.005	0.1	81, 98	90
		0.5	91, 93	92
p,p'-DDD	0.005	0.1	72, 87	80
		0.5	87, 90	89
p,p'-DDT	0.005	0.1	78, 89	84
		0.5	69, 81	75
Methoxychlor	0.005	0.1	78, 69	74
		0.5	57, 81	69
Endrin	0.005	0.1	97, 69	83
		0.5	71, 66	69
Dieldrin	0.005	0.1	91, 65	78
		0.5	85, 59	72
Dimethoate	0.001	0.1	82, 88	85
		0.5	90, 79	85
Methamidophos	0.001	0.1	69, 81	75
		0.5	74, 66	70
Ethoprophos	0.001	0.1	91, 98	95
		0.5	78, 95	87

Continued

Pesticide	LOD	Spiking level (mg/kg)	Recovery (%)	Average recovery (%)
Phorate	0.001	0.1	76, 83	80
		0.5	68, 45	57
Diazinon	0.001	0.1	91, 82	87
		0.5	71, 79	75
Pirimiphos-methyl	0.001	0.1	91, 83	87
		0.5	80, 69	75
Chlorpyrifos	0.001	0.1	87, 60	74
		0.5	98, 99	99
Malathion	0.001	0.1	56, 85	71
		0.5	99, 71	85
Fenitrothion	0.001	0.1	79, 88	83
		0.5	73, 89	81
Parathion-methyl	0.001	0.1	58, 69	64
		0.5	81, 76	79
Chlorfenvinphos	0.001	0.1	68, 88	78
		0.5	78, 59	69
Profenofos	0.001	0.1	62, 79	71
		0.5	98, 72	85
Fonofos	0.001	0.1	89, 71	80
		0.5	69, 72	71
Bifenthrin	0.001	0.1	71, 83	77
		0.5	98, 59	79
Fenpropathrin	0.001	0.1	92, 88	90
		0.5	91, 64	78
λ-cyhalothrin	0.001	0.1	85, 71	78
		0.5	71, 68	70
Permethrin	0.010	0.1	73, 87	80
		0.5	76, 89	83
Cyfluthrin	0.001	0.1	96, 82	89
		0.5	81, 69	75
Cypermethrin	0.001	0.1	76, 91	84
		0.5	83, 79	81
Fenvalerate	0.001	0.1	77, 79	78
		0.5	63, 91	77
Deltamethrin	0.001	0.1	78, 89	84
		0.5	95, 89	92
Allethrin	0.001	0.1	88, 86	84
		0.5	94, 73	84

Table 3. Percent recovery of studied pesticides in cowpea at 0.1 and 0.5 mg/kg spiked levels

Pesticide	LOD	Spiking level (mg/kg)	Recovery (%)	Average recovery (%)
β-HCH	0.005	0.1	98, 88	93
		0.5	80, 99	90
γ-HCH	0.005	0.1	81, 97	89
		0.5	91, 92	92
δ-HCH	0.005	0.1	98, 90	91
		0.5	88, 93	91
Heptachlor	0.005	0.1	90, 91	91
		0.5	90, 89	90
Aldrin	0.005	0.1	87, 88	88
		0.5	87, 89	88
γ-chlordane	0.005	0.1	68, 71	70
		0.5	78, 80	79
α-endosulfan	0.005	0.1	83, 86	85
		0.5	90, 89	91
β-endosulfan	0.005	0.1	91, 90	91
		0.5	99, 97	98
Endosulfan sulphate	0.005	0.1	88, 87	88
		0.5	90, 91	91
p,p'-DDE	0.005	0.1	85, 85	85
		0.5	91, 93	92
p,p'-DDD	0.005	0.1	68, 69	69
		0.5	87, 90	89
p,p'-DDT	0.005	0.1	78, 89	84
		0.5	69, 81	75
Methoxychlor	0.005	0.1	79, 90	85
		0.5	57, 81	69
Endrin	0.005	0.1	97, 69	83
		0.5	75, 81	78
Dieldrin	0.005	0.1	91, 65	78
		0.5	85, 59	72
Dimethoate	0.001	0.1	82, 88	85
		0.5	90, 79	85
Methamidophos	0.001	0.1	64, 89	77
		0.5	78, 61	69
Ethoprophos	0.001	0.1	97, 89	93
		0.5	78, 95	87

Continued

Pesticide	LOD	Spiking level (mg/kg)	Recovery (%)	Average recovery (%)
Phorate	0.001	0.1	67, 84	76
		0.5	74, 98	86
Diazinon	0.001	0.1	78, 59	69
		0.5	74, 89	82
Pirimiphos-methyl	0.001	0.1	68, 84	76
		0.5	73, 69	71
Chlorpyrifos	0.001	0.1	83, 80	82
		0.5	81, 98	90
Malathion	0.001	0.1	81, 85	83
		0.5	73, 79	76
Fenitrothion	0.001	0.1	70, 69	70
		0.5	84, 79	82
Parathion-methyl	0.001	0.1	67, 71	69
		0.5	86, 65	76
Chlorfenvinphos	0.001	0.1	93, 80	87
		0.5	78, 99	89
Profenofos	0.001	0.1	68, 85	77
		0.5	86, 71	79
Fonofos	0.001	0.1	91, 87	89
		0.5	80, 78	79
Bifenthrin	0.001	0.1	70, 78	74
		0.5	98, 59	79
Fenpropathrin	0.001	0.1	69, 85	77
		0.5	87, 64	76
Lambda-cyhalothrin	0.001	0.1	85, 71	78
		0.5	79, 88	83
Permethrin	0.001	0.1	79, 80	80
		0.5	94, 99	97
Cyfluthrin	0.001	0.1	93, 88	91
		0.5	89, 69	79
Cypermethrin	0.001	0.1	99, 92	96
		0.5	93, 82	88
Fenvalerate	0.001	0.1	77, 69	73
		0.5	82, 95	89
Deltamethrin	0.001	0.1	84, 89	87
		0.5	95, 89	92
Allethrin	0.001	0.1	74, 86	80
		0.5	76, 89	83
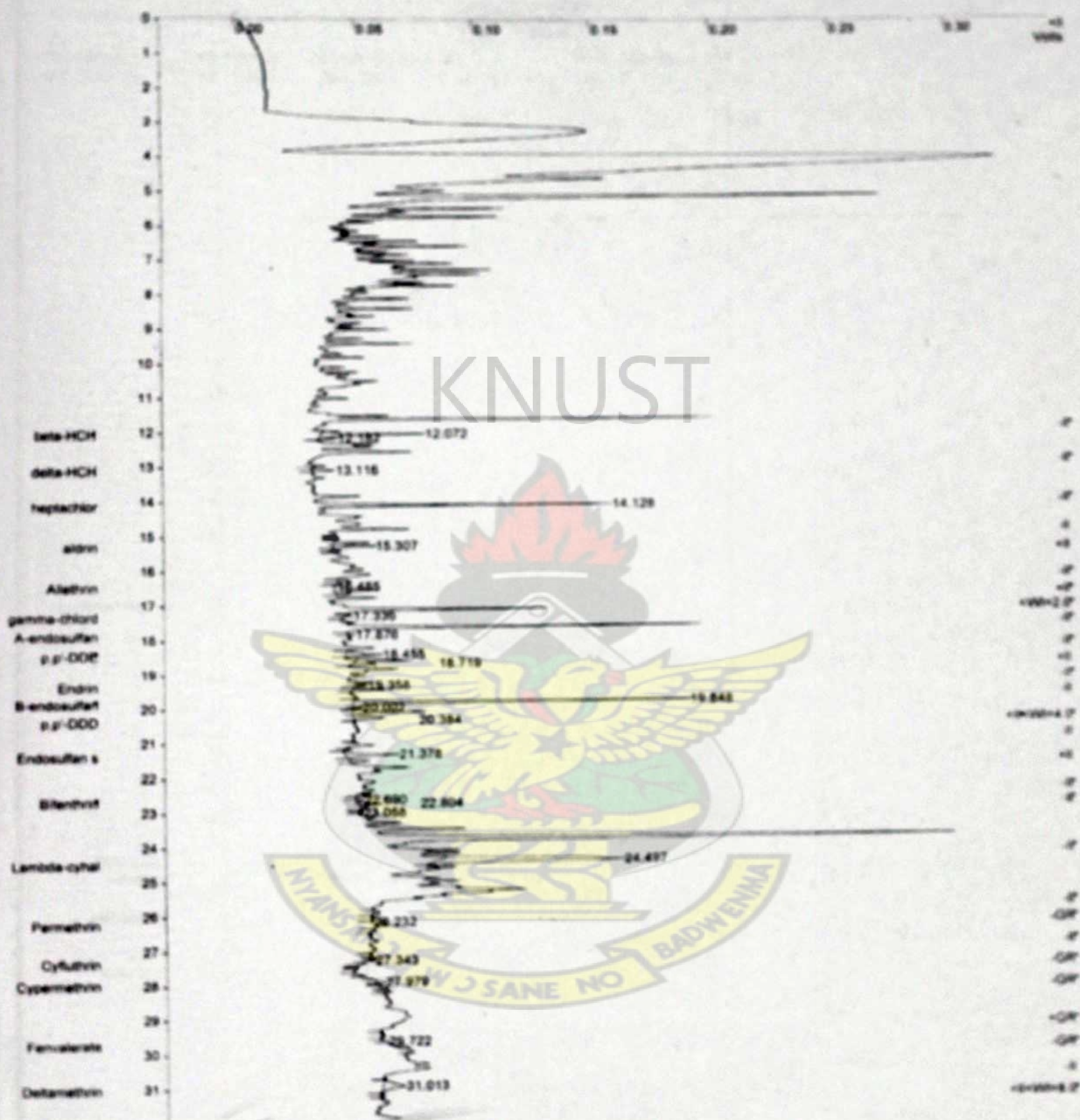
Figure 1. Chromatogram of soil sample showing organochlorine and pyrethroids pesticides detected
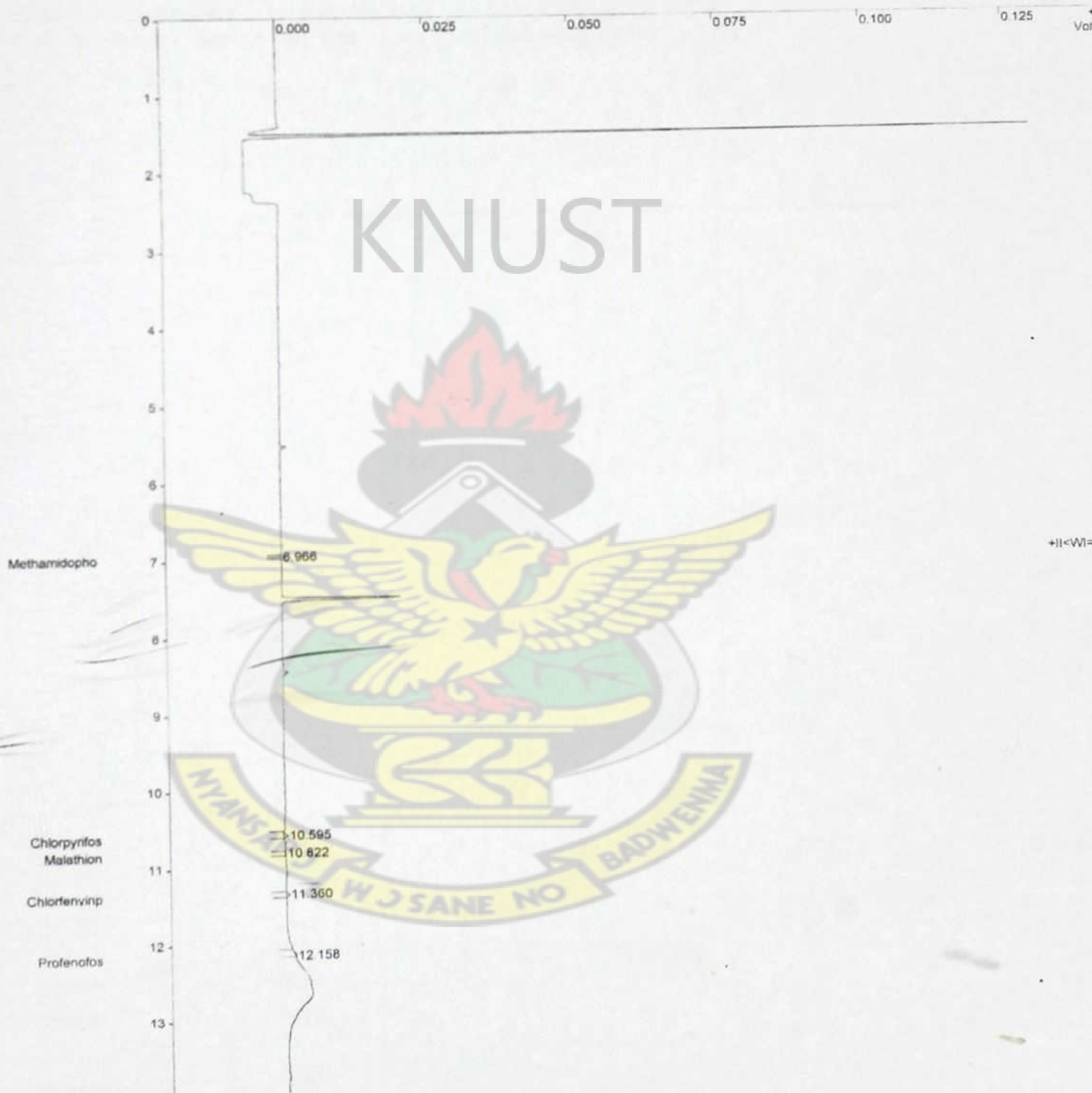
Figure 2. Chromatogram of soil sample showing methamidophos, chlorpyrifos, malathion, chlorfenvinphos and profenofos

Injection Date: 5/28/2012 8:13 PM   Calculation Date: 5/28/2012 8:45 PM

Operator   : Paul   Detector Type: 3800 (10 Volts)
Workstation: OS   Bus Address : 44
Instrument : Varian CP-3800 GC   Sample Rate : 10.00 Hz
Channel   : Middle = ECD   Run Time   : 31.968 min

** GC Workstation Version 6.41 ** 02460-3090-C65-01F4 **

Chart Speed =   0.67 cm/min   Attenuation = 202   Zero Offset = 21%
Start Time =   0.000 min   End Time   = 31.968 min Min / Tick = 1.00
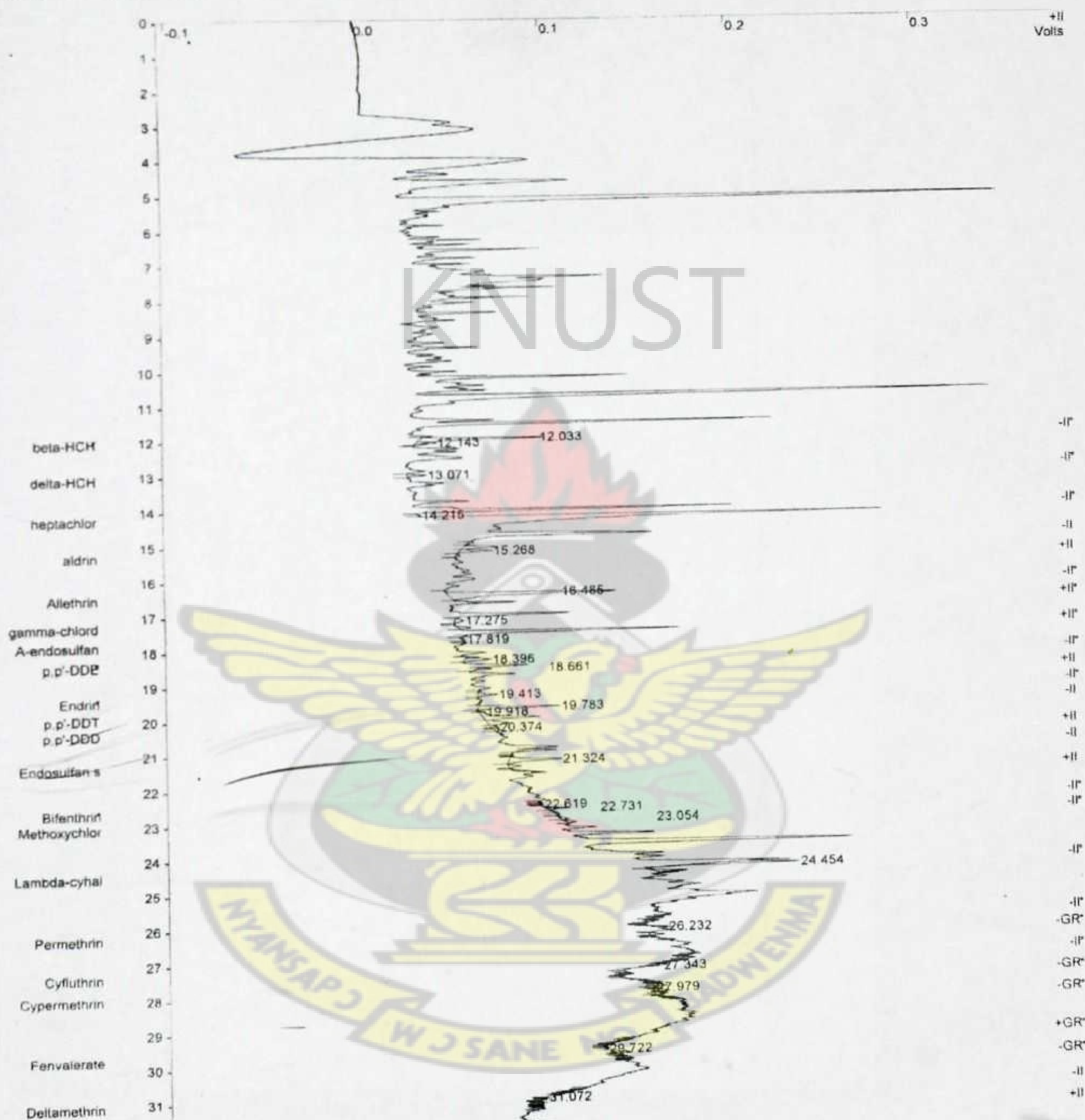
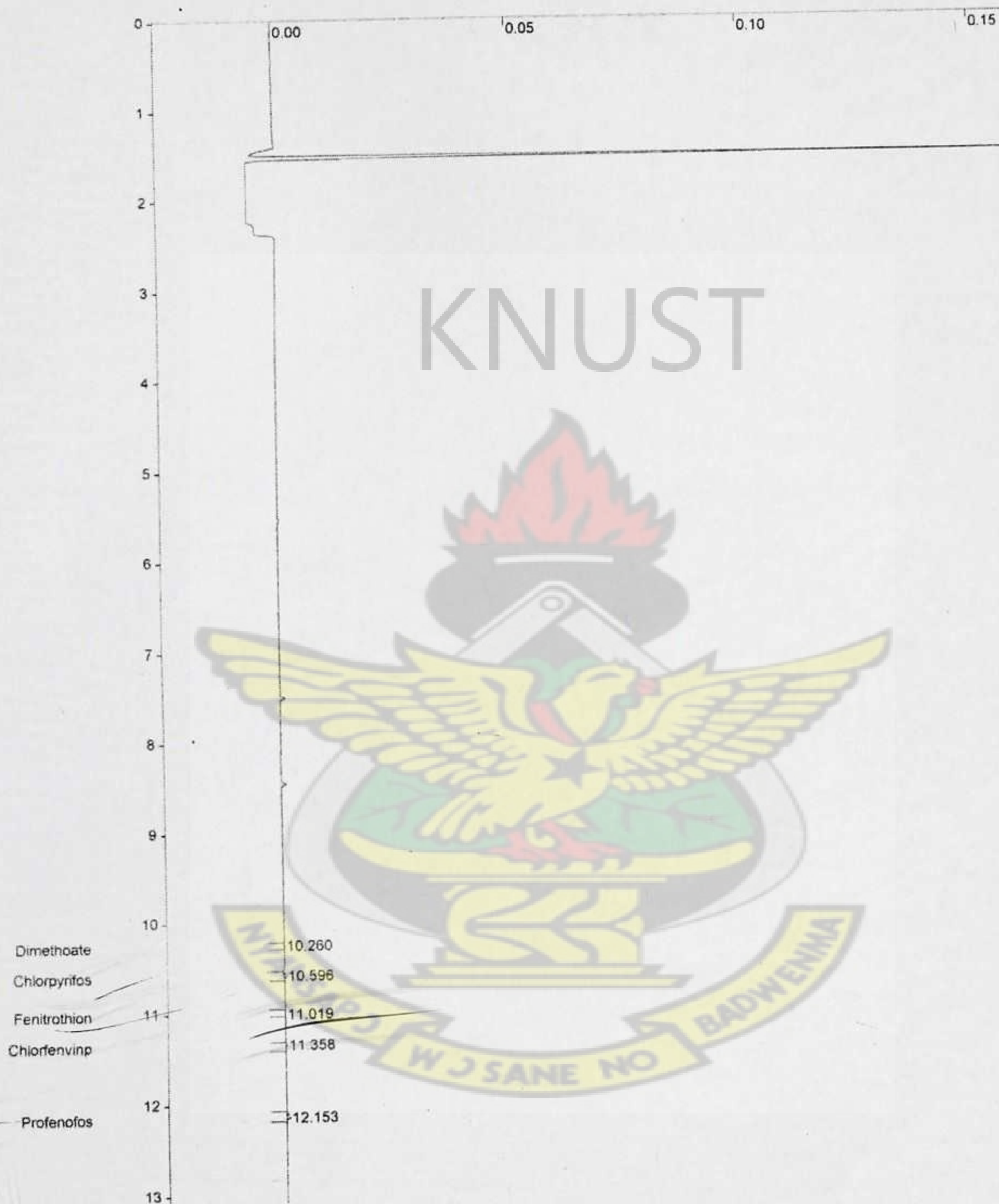Figure 4. Chromatogram of cowpea sample showing organochlorine and pyrethroids
pesticides detected

Figure 5. Chromatogram of maize sample showing dimethoate, chlorpyrifos, fenitrothion, chlorfenvinphos and profenos

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