PESTICIDE CONTAMINATION OF FRUITS AND VEGETABLES – A MARKET-BASKET SURVEY FROM SELECTED REGIONS IN GHANA.

BY

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DEDICATION

This project is dedicated to my mum Grace Nyarko and my sister, Hannah Asiedu.

DECLARATION

I do hereby declare that, except for references to works of other researchers which have been cited, this work is the result of my own research carried out under the supervision of Prof Robert Kingsford-Adaboh and Dr. Raphael Klake all of Chemistry Department, University of Ghana, and has not been presented previously by anyone anywhere as fulfillment for a degree or any certificate.

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ABSTRACT

A market- basket survey was carried out with the aim of determining the concentration levels of pesticides, in lettuce, garden eggs, pineapple and mango from some selected regions in Ghana and to assess the potential health risk associated with exposure to the pesticide residues from fruits and vegetables consumption. A total of 192 fresh samples of fruits and vegetables were randomly collected under normal purchase conditions from 12 major towns and cities in the three regions of Ghana. The samples were extracted and analyzed for organophosphates, synthetic pyrethroids and organochlorine pesticides. The percentage of samples of fruits and vegetables with pesticide residues in Lettuce, Garden eggs, Pineapple and Mango were 52%, 40%, 45%, 48% respectively and concentrations of pesticides did not vary significantly in samples as well as the sampling areas ($p>0.05$) even though there were differences in residual concentrations of pesticides . The differences in residual concentrations of pesticides could be due to different agricultural practices adopted by farmers and also accessibility of the pesticides. The average residue concentrations range from 0.01-0.45 mg/kg, 0.01-0.30 mg/kg and 0.01-1.27 mg/kg for organophospates, synthetic pyrethroids and organochlorine pesticides respectively. Lindane, chlorpyrifos and cypermethrin were the most frequent organochlorine, organophosphate and synthetic pyrethroid pesticides respectively while lettuce was the most frequently contaminated sample. Comparing the concentration levels of organochlorine pesticides residue with the maximum residue limits (MRLs) adopted by the FAO/WHO Codex Alimentarious Commission shows that some of the fruits and vegetables sold on Ghanaian markets are contaminated even though the levels are generally low. Health risk analysis indicates that heptachlor in particular may be of public concern since its concentration levels exceeded the reference dose in all the four different types of samples analyzed indicating a great potential for systemic toxicity to consumers in Ghana.

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CHAPTER ONE

1.0 INTRODUCTION

1.1 Background

Feeding the ever increasing human population is one of the challenges facing the world today. The high demand for food has led to the use of fertilizers and pesticides in Agriculture in order to boost food production**.** The use of pesticides started with the introduction of arsenical pesticides and organic compounds such as tar, petroleum oils, and dinitrophenol emulsions (Ntow, 2005). Antinnonin (dinitrocresol) is considered the first synthetically produced pesticide for which a patent has been applied. In 1939, after the discovery of insecticidal properties in DDT, a systematic search for synthetic organic products was launched (Kumar, 1987).

Pesticides are widely used in agriculture to increase the yield, improve the quality, and extend the storage life of food crops. Thus pesticides protect food crops in the field against a wide range of pests and diseases. It is estimated that without pesticides, two-thirds of all crops in the field would be lost, depriving many people of food and increasing malnutrition (Botwe, 2006). However, the lack of informed choices, on the use of pesticides has resulted in the repeated and indiscriminate use of pesticides which has exposed farmers and consumers to health hazards due to their toxic residues that persist in foods after application (Biney, 2001). These residues may either cause acute or chronic toxicity in humans after consumption of the treated crop (Ntow, 2005). These toxic effects are more apparent in vegetables and fruits since they are sometimes consumed fresh.

Today many agricultural pesticides are available which are usually organochlorines, carbamates, pyrethroid or phenoxy compounds. The organochlorine pesticides in addition to their toxic nature, resist degradation and persist in the environment for a long time (Botwe, 2007). They are lipophilic and may accumulate in the human body when small amounts are taken up in food. The agricultural use of pesticides (mostly organochlorine pesticides) has been banned or severely restricted in many developed countries due to their adverse effect on human health. The Stockholm convention on persistent organic pollutants (POPs) which was signed in May 2001 is geared towards banning these poisonous chemicals worldwide. Nine out of the twelve chemicals targeted for global elimination under this treaty are organochlorines. The bans and restrictions are not effective and so these pesticides find their way into developing countries and Ghana is no exception (Botwe, 2007).

Though it is of the general opinion that household processing methods such as washing and boiling remove pesticide residues in fruits and vegetables, it is not always so. Washing and boiling may not remove the pesticides (especially the organochlorines) completely (Bull, 1982) and this may be a threat to public health if they exceed the maximum permissive levels. It is therefore necessary to assess the levels of pesticides in the selected fruits and vegetables and to estimate the potential health risk associated with its dietary exposure.

1.2 Problem statement

The increasing demand of vegetables, fruits and other food crops for local use as well as for export has encouraged the use of pesticide in farming for the purpose of controlling and reducing the effect of insects in food production. Organochlorine pesticides are resistant to environmental degradation through chemical, biological and photolytic processes and as a result bio-accumulate in living tissues and in food chains which causes a resultant negative impact on human health and environment. These synthetic organic chemicals therefore contribute to many acute and chronic illnesses such as cancers and hormone disruptions (Amoah *et al*, 2006). As a result of the toxicity associated with Organochlorine pesticides, there is an international effort to eliminate or minimize Organochlorine pesticides and related compounds from the environment.

It is estimated that 87% of farmers in Ghana use pesticides in vegetable and fruit production (Dinham, 2003). In Ghana, even though there is a ban on Organochlorine pesticides such as aldrin, dieldrin, DDT, and lindane (gamma-HCH), due to weak import control and lack of logistics to monitor these pesticides, the ban on these pesticides may be ineffective. Ready made formulations in soft drink bottles and other unlabelled liquid containers sold to farmers may contain some of these restricted or banned pesticides. Thus, even though DDT is highly restricted, DDT residues have been found in some Ghanaian vegetables and fruits (Ntow *et al*, 2001; Amoah *et al*, 2006).

Potential health risk assessment due to dietary exposure to pesticide residue in fruits and vegetables has been undertaken in other parts of the world (National Research Council, 1993). However, in Ghana, very little has been done on health risk assessment, and it is therefore necessary to conduct a health risk assessment on these vegetables and fruits. This study will therefore be a step towards the assessment of health risks due to pesticide residue (especially organochlorine) exposures from consumption of selected vegetables and fruits in Ghana.

1.3 Objectives of the research

The main objectives of the study were to:

- Determine the levels of pesticide residues in the selected fruits and vegetables sold in some Ghanaian markets.
- Estimate the potential health risk associated with the daily intake of the selected fruits and vegetables.

1.4 Hypothesis

H_0: Vegetables and fruits sold on Ghanaian markets are contaminated with pesticide residues.

H_1: Vegetables and fruits sold on Ghanaian markets are not contaminated with pesticide residues

1.5 Justification

Fruits and vegetables form the major component of food consumed by humans because of its high nutritional value for the body and is therefore not surprising to know that many nutritional experts and other health professionals recommend the daily intake of fruits and vegetables.

However, in spite of the benefits gained from the consumption of these fruits and vegetables there have been reports of diseases such as cancer, endocrine disruptions, immunological effects, neurotoxicity and many others which are attributed to continuous use of contaminated fruits and vegetables (Hodgson and Levi, 2003). This incidence of contamination in fruits and vegetables has raised public concern because of its adverse effects on human health.

Many researchers have attributed this contamination in these fruits and vegetables to the continuous use of banned and approved pesticides by farmers during crop production (Ntow, 2005). In Ghana pesticide use in crop production is a common practice and recent studies reveal levels of pesticide residues especially organochlorine in fruits and vegetables from some Ghanaian markets and farms (Bempah *et al*, 2011; Ntow *et al*, 2005). In view of the public health significance of pesticide residues and the uncertainty that exist regarding the long term effects of low dose exposure of these pesticides, this present study therefore becomes relevant in updating data on pesticide residue levels in some selected vegetables and fruits sold in Ghana.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 Introduction

The insurgence of pests, diseases and other plant pathogens has necessitated the use of pesticides. This is to eliminate both pre-harvest and post-harvest losses so as to maintain high yield. The rapid increase in population growth and the need to maintain food security especially in developing countries has increased the use of these pesticides. It has been reported that the use of pesticides has increased massively with an estimated 2.5 million tons (worldwide) used annually (Farag *et al*, 2011).

Pesticides are substances or mixture of substances whose use is supposed to prevent, destroy, repel or mitigate any pest. They may be of biological origin (such as virus or bacterium) or chemical origin (such as DDT or Cypermethrin). Also pesticides can be naturally occurring or manmade with numerous applications. Hill and Walter (1994) stated that pesticides application to the target pest comes in innumerable formulations and delivery systems. Some come in the form of sprays, baits and slow-release diffusions.

Historians have traced the use of pesticides to the time of Homer around 1000 BC. However, the earliest recorded application of pesticides was the burning of sulphur to fumigate Greek homes (Metacalf, 1980). Other inorganic chemical pesticides that emerged around the same time were copper, arsenic and lead. These inorganic pesticides were extensively used until the early 20th century when they were banned due to their high persistence and their non-specific toxicity.

Pesticides are quite toxic to humans and other mammals which sometimes have resulted in deaths (Baird and Cann, 2004).

During and after the Second World War, another form of pesticides evolved. These were the synthetic organic pesticides. The introduction of synthetic organic pesticides was seen as a major effort in the elimination of pests which hitherto had been a major concern in the security of food to the world's population. Unfortunately, the introduction of these synthetic organic pesticides was not very successful. Most pests have become resistant to synthetic organic pesticides. Again, these synthetic organic pesticides have caused a growing number of environmental and health problems (Metcalf, 1980).

Barnett (1997) reported that minimal exposure to pesticides in the environment and result from their residues ingested through food and water has the tendency of causing chronic health effects many years after. Other researchers (Nollet, 2004) have reported a wide range of human health hazards emanating from short term impacts such as headaches and nausea to chronic impacts like cancer, reproductive harm and endocrine disruption.

Indiscriminate use of pesticides especially at the fruiting and pre-harvesting stages; and non-adoption of safe waiting periods have led to pesticides residues accumulating in most consumable vegetables and fruits especially in developing countries. The contamination of vegetables and fruits with pesticides has been reported in many developing countries (Amoah *et al*, 2006). Farmers' quest to get better yield and quality products have resulted in repeated application of pesticides during the entire growing period of vegetables and fruits.

Clarke *et al* (1997) stated that despite the potential health risk derived from the use of pesticides, they have been shown to decrease immensely the volume of crop loss both before and after harvest. In India, Brinjal (*Solanummelongena* L.), an important local vegetable crop grown extensively suffers heavily at the fruiting stage due to attack of shoot and fruit borers causing 70 % loss. The use of pesticides has reduced this loss drastically (Misra and Singh, 1996). Vegetables and fruits are the fresh and edible portions of most plants. Vegetables and fruits have valuable nutrients which build up and repair the body tissue, hence the need to produce them in greater volumes.

2.2 Classification of pesticides

Pesticides are one broad area where so many classes exist depending on what is of interest. For instance US EPA (2008) and Walter (2005) have classified pesticides by their target organisms. In this regard, insecticides, fungicides, herbicides and rodenticides are groups of pesticides that target insects, fungi, herbs (plants) and rodents respectively. In addition to the classes mentioned above, pesticides can also be classified as organic or inorganic pesticides (Baird, 1997).

The inorganic pesticides are made from naturally occurring minerals and have varying modes of action including interfering with conversion of energy within cells which can cause death and desiccation (Agbeve, 2011). Some examples of inorganic pesticides are boric acid (H_3BO_3) silica gel (Na_2SiO_3), sodium fluoride (NaF) and those that contain heavy metals such as mercury, arsenic and lead (Baird, 1997). Organic pesticides consist of compounds containing mainly carbon and hydrogen and may contain other elements such as chlorine, nitrogen, sulphur, tin and phosphorus.

Organic pesticides can further be grouped into synthetic and natural organic pesticides. The synthetic organic pesticide can further be grouped into four major classes as organochlorines, organophosphates, carbamates and synthetic pyrethroids.

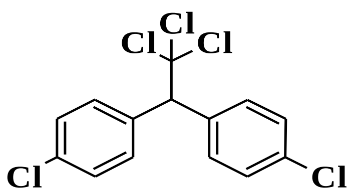
In addition to the classes mentioned above, the Ghana Environmental Protection Agency which is the sole agency responsible for registering pesticides (Act 528 ,1996) has classified pesticides as general use pesticides, restricted use pesticides and suspended or banned pesticides. Pesticides that fall under general use do not have an unreasonable adverse effect on the environment. Banned pesticides have great effects on the environment, humans and crops are therefore not supposed to be used in Ghana. Examples of banned pesticides are DDT, aldrin, dieldrin, heptachlor. Pesticides whose application may lead to unreasonable adverse effects on humans, animals or the environment fall under restricted pesticides. Examples of restricted pesticides used in Ghana include; endosulfan (thiodan), and gamma HCH (Lindane).

2.2:1 Organochlorine pesticides

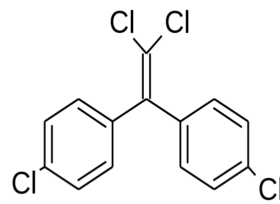
The organochlorine pesticides are synthetic organic pesticides which are made up of predominantly carbon, hydrogen, chlorine and sometimes oxygen and sulphur. They are also known by other names such as chlorinated hydrocarbons, chlorinated organics, chlorinated insecticides and chlorinated synthetics. They were used extensively from the 1940s through the 1960s in agriculture and mosquito control. Generally, there are three major types of organochlorine insecticides and these are: dichlorodiphenylethanes, cyclodienes, chlorinated benzenes or cyclohexanes. The dichlorodiphenylethanes happen to be the oldest group of organochlorines and examples are DDT (dichlorodiphenyltrichloroethane), DDE (dichlorodiphenyldichloroethylene), methoxychlor(1,1,1-trichloro-2-2-bis-(4-methoxyphenyl) ethane, rthothane, dicofol and perthane. Examples of cyclodienes include aldrin, dieldrin, endrin, heptachlor, chlordane and endosulfan(6,7,8,9,10,10-hexachloro-1,5,-5a,6,9,9a-hexahydro-6,9-methano-2,4,3-benzodioxathiepin-3-oxide). The chlorinated benzenes or cyclohexanes also include lindane, toxaphene, mirex, HCH and chlordecone.

In general, many organochlorines and their metabolites have the tendency to bioaccumulate in the food chain due to their low water solubility and high chemical stability. Amongst the organochlorine pesticides, DDT is the most common, harmful chemical and also persists in the environment. Swiss scientist Paul Muller discovered DDT in 1939 as an effective synthetic organic insecticide although it was synthesized before its discovery in 1939. For this momentous work, he received a noble prize in medicine. This is because DDT was found to be very useful in the control of malaria and yellow fever (Dunlap, 1981).

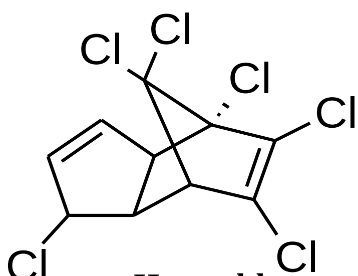
The world health organisation estimates that malaria reduction programs, one component of which was the use of DDT saved the lives of more than five million people (Baird, 1997; Gladwell, 2001). The mode of action of DDT is not clearly established. However it is believed that DDT acts as neurotoxin which disrupts the delicate balance of sodium and potassium ions in nerve cells thereby preventing the normal transmission of nerve impulses in insects and in mammals (Robbins, 1991). Structural formulae of some organochlorine pesticides are shown below.



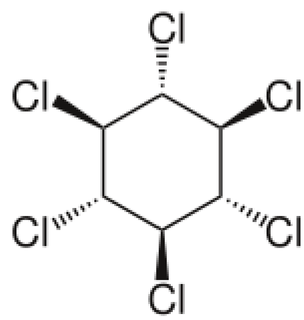
DDT



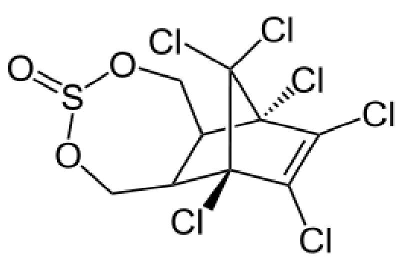
DDE



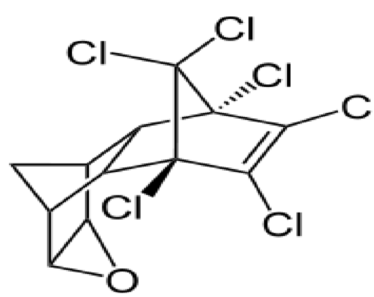
Heptachloro



Hexachlorohexane (HCH)



Endosulfan



Endrin

Figure 2.2.1: Structural formulae of some organochlorine pesticides.

2.2.2 Organophosphate pesticides

Organophosphate pesticides are derivatives of phosphoric acid. They include all insecticides containing phosphorus and are also known as organic phosphates, phosphorus insecticides and phosphoric acid esters. They contain pentavalent phosphorus, carbon, hydrogen, oxygen and sulphur. Organophosphates were discovered in the early 1940s as a replacement for organochlorines for insect control. The largest use of organophosphates is in agriculture but also have much domestic uses (Smith, 1991).

Organophosphates are less persistent or chemically unstable, lasting only a matter of days, months in the environment (Ware, 1983). It is this characteristic that brought them into agricultural use as substitute for persistent organochlorines. The organophosphates work by inhibiting certain important enzymes of the nervous system, namely cholinesterase. The enzyme is said to be phosphorylated when it becomes attached to the phosphorous moiety of the insecticide, a binding that is irreversible. This inhibition brings about the accumulation of acetylcholine at the neuron/muscle junctions or synapses resulting in rapid twitching of voluntary muscles and eventually paralysis (Robbins, 1991).

In spite of the non-persistent nature of organophosphates, most are found to exhibit toxic effects in mammals. Exposure to these chemicals by swallowing, inhalation or absorption through the skin can lead to immediate health problems. There is evidence that organophosphates cause chronic as well as acute health problems especially in children (McKinney and Schoch, 2003). There are three main classes of organophosphates and these are type A, type B, type C as summarised below.

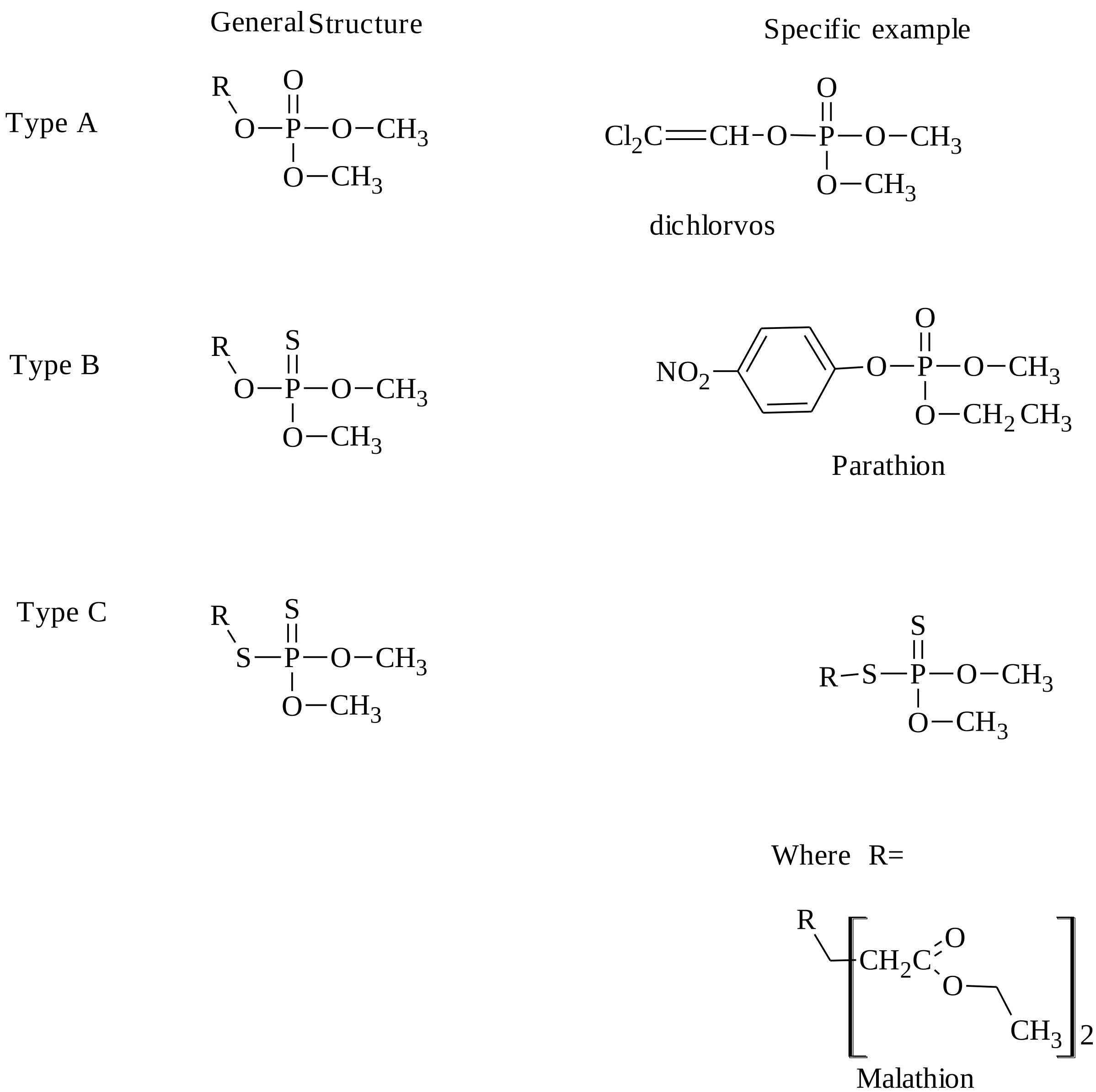


Figure 2.2.3: The three main classes of organophosphates with examples

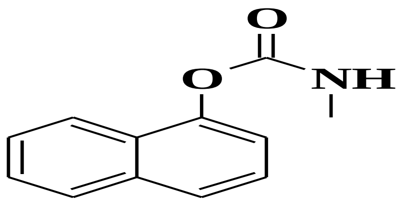
Other specific examples of organophosphates are diazinon, chlorpyrifos, phosmet, fenitrothion, chlorvinphos, azinphos-methyl, profenophos, phorate, methamidophos, ethoprophos, pirimphos-methyl, monocrotophos, mevinphos, acephate, oxydemetonmethyl, isofenphos, sulprofos, famphur and dimethoate (Metcalf, 1980).

2.2.3 Carbamate pesticides

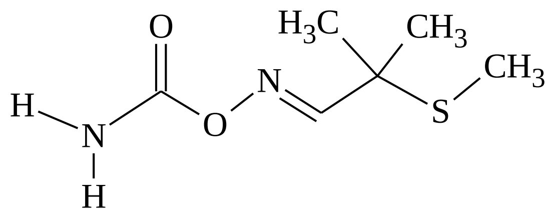
The carbamates are insecticides which are derivatives of carbamic acid H_2NCOOH. An alkyl group usually a methyl replaces one of the hydrogen atoms attached to the nitrogen whereas a longer and more complex organic group replaces the hydrogen atom attached to the oxygen.

In 1956, the first successful carbamate, carbaryl was introduced (Metcalf, 1980). Generally, carbamates have a short-life in the environment and behave just like organophosphates in its mode of action and persistency. The only difference in the mode of action is that the inhibition by carbamates is reversible and when the cholinesterase is inhibited by a carbamate it is said to be carbamylated (Robbins, 1991).

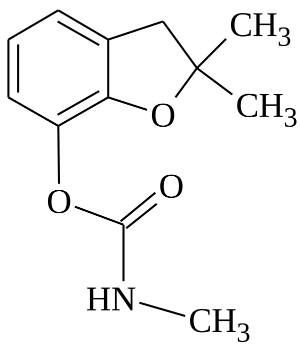
Carbamates react with water and decompose to simple, nontoxic products and are preferred to the organochlorines. However, just like organophosphates, carbamates are a particular problem in developing countries where ignorance about their hazards and failure to use protective clothing has led to sickness and many deaths among agricultural workers (Baird and Cann, 2004). Other examples of carbamate insecticides in addition to carbaryl are methomyl, carbofuran, aldicarb, oxamyl, thiodicarb, methiocarb, propoxur, bendiocarb, carbosulfan, aldoxycarb, promecarb and fenoxycarb (Metcalf, 1980). Structures of some carbamates are shown below.



Carbaryl



Aldicarb



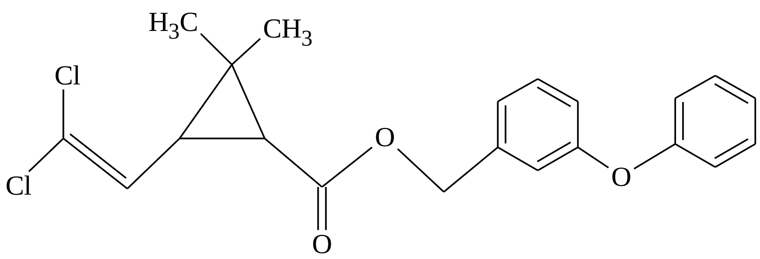
Carbofuran

Figure 2.2.4: Structural formulae of some carbamate pesticides.

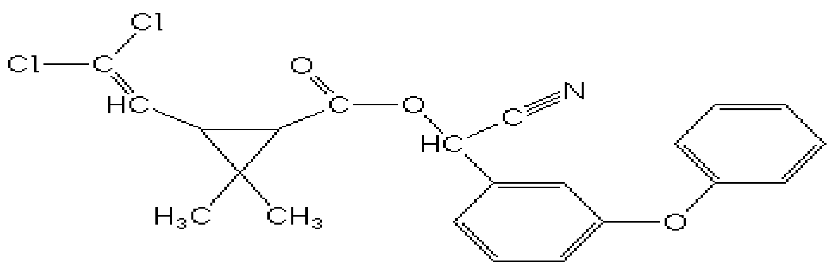
2.2.4 Synthetic pyrethroids pesticides

Synthetic pyrethroids insecticides are man-made insecticides which have a similar chemical structure to natural pyrethrins found in chrysanthemums. They are commonly referred to as pyrethroids, very stable in sunlight and are effective against most agricultural insect pests when used at very low rates (Metcalf, 1980). Pyrethroids have gained considerable popularity since its discovery in the 1970s because of its low toxicity and as a result its usage has increased satisfactorily (Baird and Cann, 2004).

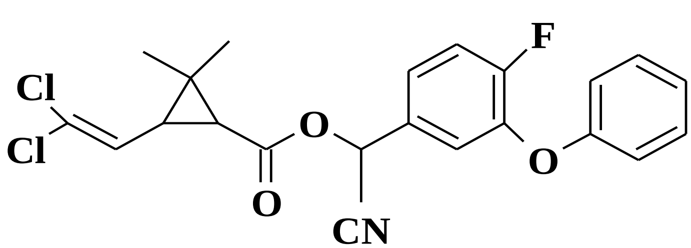
The mode of action of the pyrethroids is similar to that of DDT. They work by keeping the sodium channels open in neuronal membranes. Examples of Synthetic pyrethroids include permethrin, bifenthrin, cypermethrin, deltamethrin, fenpropathrin, allethrin, lambda- cyhalothrin, cyfluthrin, fenvalerate and prallethrin (Metcalf, 1980). Structural examples of some synthetic pyrethroids are shown below.



Permethrin



Cypermethrin



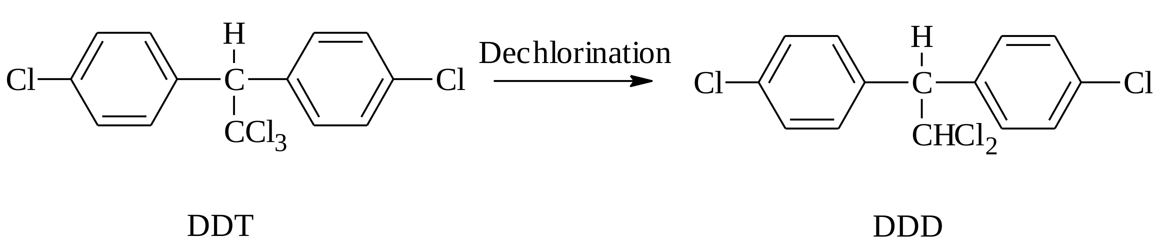
Cyfluthrin

Figure 2.2.5: Structural formulae of some synthetic pyrethroids pesticides.

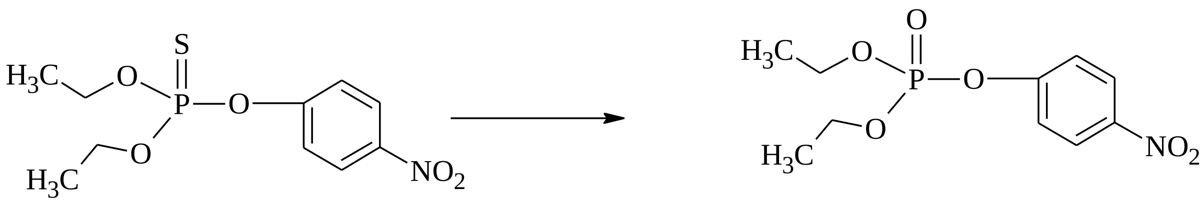
2.3.0 Pesticide metabolites

Metabolites are the products obtained after the original, parent chemical has undergone degradation. This can cause reduction in the concentration of the specific pesticide due to their breakdown to metabolites. The term degradation does not necessarily imply a less potent chemical as metabolites sometimes have an equal or greater toxicity the parent compound (Van Loon and Duffy, 2000). Degradation of pesticides to their metabolites can be caused by chemical reactions in the soil (chemical breakdown), sunlight (photo-degradation) or by microorganisms (microbial breakdown),

Certain degradation reactions produce species with lower toxicity. DDT for instance degrades very slowly in water and soil by dechlorination (removal of chlorine) reactions to a less toxic compound, DDD under reducing conditions. The removal of the chlorine atoms from organochlorine molecules always has a detoxifying effect on these chemicals (Van Loon and Duffy, 2000). The equation for the conversion of DDT (dichlorodiphenyltrichloroethane) to DDD (dichlorodiphenyldichloroethane) through microbial breakdown is shown below.



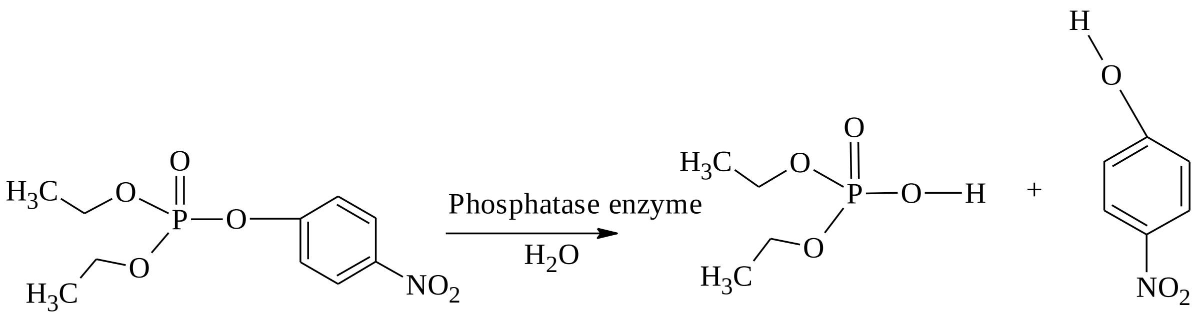
Whereas most organochlorines degrade to produce less toxic compounds, degradation products of some organophosphosphate exhibit high toxicity. For instance organophosphate compound like parathion is properly called phosphorothioate because of the presence of the P=S group. Inside cells, oxygenating enzymes convert this group to P=O as shown below.



Parathion Paraoxon

The phosphorus atom in the oxygenated product, paraoxon, then reacts with the acetylcholinesterase (AcE) forming a stable complex that inhibits the ability of AcE to catalyse acetylcholine hydrolysis during transmission of nerve impulses. This interference with the neurotransmission accounts for the activity of paraoxon as pesticide; which is also a serious potential health hazard to other organisms including humans (Bempah, 2008)

Both paraoxon and parathion are subject to degradation via hydrolysis reactions, in which water acts as a nucleophile. These reactions are catalyzed in organisms by various phosphatase enzymes. However, the presence of sulfur (S) attached to phosphorus (P) in parathion



Paraoxon

instead of the oxygen (O) in the paraoxon reduces the tendency for reaction with the nucleophile and therefore the S analogue is less toxic. Consequently it is of environmental concern when the more toxic oxygen-containing forms of these organophophorus compounds are produced by oxidation outside the target organism (Bempah, 2008). Two breakdown products of the herbicide atrazine are 2-chloro-4-ethylamino-6-amino-*s*-triazine and 2-chloro-4-amino-6-isopropylamino-*s*-triazine commonly referred to as deisopropylatrazine (DIA) and deethylatrazine (DEA), respectively. These metabolites are typically found and used as a marker for interaction between surface and ground water (Bempah 2008).While these metabolites are phytotoxic and somewhat equally potent, 2-[(2,6-diethylphenyl)(methoxymethyl) amino]-2-oxoethanesulfonic acid, the ethane sulfonic acid (ESA) metabolite of alachlor, possesses greater stability than the parent compound but retains no herbicidal activity (Bempah, 2008).

Generally pesticides metabolites are more stable and have a greater degree of polarity than the parent chemical. The breakdown products (metabolites) usually have a lower molecular mass than the parent compound and are more completely oxidized. These differences make them the metabolites more water soluble thereby increasing mobility and likelihood of transport (Barret, 1996).

2.3.1 Trends in pesticide use in Ghana

It is estimated that 87% of farmers in Ghana use pesticides in vegetable and fruit production (Dinham, 2003). From 1970 to 1990 for example, the use of insecticides alone increased rapidly from 270,000 litres to 1,900000 litres, an annual rate increase of 30% (Ntow, 2001, Botwe, 2007). Before the early 1980s, annual pesticide product imports into Ghana were worth less than

US $ 5 million. However over the last two decades, imports have increased significantly reaching more than US $ 30 million in 1999 (Ntow, 2001; Botwe, 2007).

The government of Ghana in an attempt to regulate the importation, registration, distribution, application and disposal of pesticides promulgated the Pesticide Control and Management Act (Act 528). Under this Act, it is a criminal offence to import, distribute, manufacture or sell unregistered pesticides. Lindane (gamma-HCH) and thiodan (endosulfan) are recommended only for particular crops and pests and therefore have restricted use. For instance lindane is registered for capsid control cocoa on plantations, on vegetable farms, and for the control of stem borers in maize. Endosulfan is popularly used in cotton growing areas, on vegetables farms, and on coffee plantations (Ntow, 2001).

Herbicides are the predominant pesticide type used in vegetable production in Ghana probably due to the farmers' perception of weed control. They reason as long as it is profitable, and no better alternatives are available, the spraying of pesticide is a good investment. More so, chemical control method is very effective, rapid in curative action, adaptable in most situations, flexible in meeting changing agronomic and ecological and economical conditions (Bempah, 2008). The table below shows the summary of imported insecticides, fungicides, herbicides imported from 1995 up to 1999.

Table 2.0: Volume of pesticide products (tons) imported into Ghana from 2002-2006

Pesticide	2002	2003	2004	2005	2006	Average	Percent
Insecticides	4,130	5,974	8,418	10,006	12,728	8,251	49
Fungicides	1,079	1,249	2,402	2,205	3,195	2,026	12
Herbicides	2,186	2,939	4,578	8,566	10,718	5,797	35
Others	368	498	544	707	1,224	672	4
Total	7763	10658	15942	21484	27886	16746	100

Source: Godfred Darko, Dietary intake of organophosphate pesticide residues through vegetables from Kumasi, Ghana, February 2009. p.3, http//tpsalliance.org

2.3.2 Studies on pesticides in Ghana

Various studies in Ghana and other parts of the world have focused much on the analysis of only organochlorine pesticides because of their persistence, lipophilicity, toxicity and bioaccumulation. Nevertheless, regular survey studies and monitoring programmes of the other different types of pesticides have been carried out (MAFF, 1989; Luke *et al*; 1988; Yamaguchi *et al*, 2003) .In a study encompassing 30 organized farms and 110 kraals distributed throughout the 10 regions of Ghana, Awumbila and Bokuma (1994) found that 20 different pesticides were in use with lindane being the most widely distributed and used pesticides accounting for 35% of those applied on farms and 85% of those used as herbicides. Of the 20 pesticides, 45% were organophosphates, 30% were pyrethroids, 15% were carbamates and 10% were organochlorines, (Awumibila and Bokuma, 1994).

In 1997, Clarke *et al* studied the knowledge attitudes and practices of 123 farm workers on three irrigation project areas in the Afram plains regarding the safe handling and use of pesticides. They found moderate levels of knowledge of pesticides absorption routes and of potential symptoms following exposure. However, farm workers knowledge for personal protective measures was poor to moderate and their use of personal protective equipment was minimal primarily due to financial constraints. They concluded that, training of agriculture and health workers in safety precautions in safety precautions, recognition and management of pesticides poisoning was a matter of urgency.

Aboagye *et al* (2002) analysed pesticide residue in exportable quality cocoa beans collected from selected cocoa growing districts in the middle belt of Ghana and two shipping ports at Tema and Takoradi. Analysis of the extract by gas liquid chromatography showed detectable amount of lindane residue but the level was about 10% of maximum residue level of 0.1 mg/kg permitted by Codex Alimentarious Commission. The results of the research indicated that Ghana's exportable cocoa beans were of no immediate danger of being rejected by importing countries due to the presence of lindane pesticide residues.

Amoah *et al* (2005) carried out a study on pesticide residues levels in a total of 180 vegetable samples(lettuce, cabbage and spring onion) which were randomly collected under normal purchase conditions from 9 major markets and 12 specialized selling points in 3 major Ghanaian cities: Accra, Kumasi and Tamale. The samples were analyzed for pesticide residues on all three vegetables. Chlopyrifos (Dursban) was detected on 78% of the samples, lindane (Gamalin 20) on 31% of the samples, endosulfan (thiodan) on 36% of the samples, lambdacyhalothrin (karate) on 11% of samples and dichloro-diphenyl-trichloroethane on 33% of samples. Most of the residues recorded exceeded the maximum residue limit for consumption. Ntow (2001) also reported residues of lindane and other organochlorine pesticides in different samples. A total of 208 samples of water, sediment, tomato, other crops, farmer's blood and milk of women in Akumadan area in Ashanti region of Ghana were analysed. The results of the water and sediments analysed showed significant levels of lindane and endosulfan.

There have been few reports on pesticides residues and the dangers they pose. The farmer's field survey carried out by Gerken *et al* 2001 in Ghana identified headache, general weakness and dizziness, body pains, nausea and vomiting, stomach ache and diarrhoea as acute poisoning symptoms through pesticides application. In March 1999, three children in Ghana died after consuming fruits containing high residue of carbamates (Gerken *et al,* 2001). In late October, 1998 children aged between 3-4 years were served with milk contaminated with the organophosphate insecticide, parathion in peru. They began vomiting and convulsing within half an hour of eating contaminated breakfast. Twenty four children died and another twenty one were treated at hospital and discharged (Aboagye, 2002).

2.4 Health impacts of pesticides

The harmful effects of pesticide usage cannot be ignored despite its numerous benefits.

Pesticides can cause injury to human health as well as the environment. Exposure to hazardous pesticides is associated with a wide range of adverse effects in humans. Pesticide residues in food can cause short term or acute effect such as dizziness, diarrhoea and death. They can also result in long term or chronic health effects which can occur months or years after exposure. Chronic health effects include cancer, tumours, brain and nervous system damage, birth defects, infertility and other reproductive system deformities, body organ damage, mild cognitive dysfunction and damage to the immune system (Botwe, 2007).

2.4.1 Toxicity to Humans

Humans can be exposed to pesticides through many ways. Exposure to pesticides may be minimal or excessive. Excessive exposure normally occurs through ground application of insecticides in farm fields. In most developing countries, like Ghana and Egypt a very large number of workers, laborers, and spray workers are involved in spraying of agriculture fields a number of times each season. In most cases, they are often not equipped with protective clothes or masks. In addition, many thousands including children working on farms are exposed to insecticide residues. Eventually, this may affect majority of them resulting in exposure to pesticide intoxication in many nations (Mansour, 2004).

In the United States for instance, about 45,000 accidental poisonings occur annually leading to about 50 deaths per year. Many more are believed to die of cancer caused by pesticide exposure (Bempah, 2008), whereas in Egypt reports indicate, incidence of pesticide poisoning during the period 1966-1982 was 5913. Moreover in Egypt, the other exposed populations suffered from dermatitis, neuropsychiatries, topical eye changes, gastrointestinal, genitourinary manifestations, as well as hepatomegaly and ventilatory function changes were significantly manifested among exposed group. Sensory hypothesia and abnormal deep reflexes were also noticed among the workers (Mansour, 2004).

2.4.2 Pesticide accumulation in biological systems

Many organochlorine compounds are found in the tissues of fish in concentrations that are orders of magnitude higher than those in the waters in which they swim. Hydrophobic (water-hating) substances like DDT are particularly liable to exhibit this phenomenon. There are several reasons for this bioaccumulation of chemicals in biological systems (Baird and Cann, 2005). Some of the reasons include low water solubility, high lipophilicity and high chemical stability of the pesticides.

2.4.3 Biomagnification

Several aquatic organisms such as fish may accumulate organic chemicals from the food they eat and from their intake of particulates in water and sediments onto which the chemicals have been adsorbed. In many cases, the chemicals are not metabolized by the fish: the substance simply accumulates in the fatty tissue of the fish, where its concentration increases with time. For example, the concentration of DDT in trout from Lake Ontario increases almost linearly with the age of the fish (Bempah, 2008).

The average concentration of many chemicals also increases dramatically as one proceeds up a food chain, which is a sequence of species, each one of which feeds on the one preceding it in the chain. Over a lifetime, a fish eats many times its weight in food from the lower levels of the food chain, but it retains rather than eliminates most organochlorine chemicals from these meals. A chemical whose concentration increases along a food chain is said to be biomagnified. In essence, the biomagnification results from a sequence of bioaccumulation steps that occur along the chain.

2.4.4 Toxicology

Toxicity is the degree to which a substance can damage an organism. It also refers to the harmfulness of a substance to an organism such as organochlorine pesticides. Toxicity of a substance can be affected by a number of factors such as the pathway of administration (whether the toxin is applied to the skin, ingested, inhaled or injected), the time of exposure (Botwe, 2007).

Toxicological data concerning the harmfulness of a substance to an organism, such as Organochlorine pesticide or heavy metal, are gathered most easily by determining its acute toxicity, which is the rapid onset of symptoms including death at the extreme limit following the intake of a dose of the substance. For example, experiments show that it takes only a few tenths of 1 microgram of the most acutely toxic synthetic compound, the dioxin kills most rodents within a few hours after it is administered orally to them (Bairn and Cann 2005; Bempah, 2008).

Although the acute toxicity of a substance is of interest when we are exposed accidently to pure chemicals, in environmental toxicology we are usually more concerned about chronic (continuous, long-term) exposures at relatively low individual doses of a toxic chemical that is present in the air we breathe, the water we drink, or the food we eat. Generally speaking, any effects whether cancer, birth defects, etc. of such continuing exposures are also long-lasting and therefore also classified as chronic. (Bairn and Cann 2005; Bempah, 2008).

The same chemical may give rise to both acute and chronic effects in the same organism, although usually by different physiological mechanisms. For example, a symptom of acute toxicity in humans of exposure to many organochlorines is a skin irritation that leads to chloracne, a persistent, disfiguring, and painful analog to common acne, and there is the fear that persistent exposure to much lower individual doses than those that produce skin disease could eventually lead to cancer (Bairn and Cann 2005; Bempah, 2008).

2.4.5 Dose – Response Relationship

The dose of the substance administered in toxicity tests is usually expressed as the mass of the chemical, usually in milligrams, per unit of the test animal's body weight, usually expressed in kilograms, thus giving units of milligrams per kilogram. The division by body weight is necessary because the toxicity of a given amount of a substance usually decreases as the size of the individual increases. Normally the toxicity of a substance increases with increasing dose, although exceptions are known (Bairn and Cann 2005).

Individuals differ significantly in their susceptibility to a given chemical: some respond to it even at very low doses whereas others require a much higher dose before they respond. For this reason scientists have created dose – response relationships for toxic substances, including environmental agents (Bairn and Cann 2005; Bempah, 2008). Usually, the response effect on the test animals that is used to construct dose – response curve is death. The dose that proves to be lethal to 50% of the population of the test animals is called the LD_{50} value of the substance; its determination from a dose – response curve. The smaller the value of LD_{50}, the more potent (i.e., more toxic) the chemical, since less of it is required to affect the animal. A chemical much less toxic than that would have a sigmoidal curve shifted to the right of the one shown (Bairn and Cann 2005; Bempah, 2008).

Many sources quote values for the LD_{50}, the lethal oral dose, when the chemical has been administered orally to the test animals, as opposed to dermal or some other means of administration. For example, the LD_{50} value for DDT for rats is about 110 mg/kg. As mentioned previously, the presumption is usually made that LD_{50} values are approximately transferable between species. In the case of DDT, for example, humans are known to have survived doses of about 10 mg/kg, so presumably the LD_{50} value for humans is greater than 10 mg/kg. However, we have no direct evidence that the 110 mg/kg value for rats is also valid for humans (Bairn and Cann 2005; Bempah, 2008)

In the dose – response curves for some substances there exists a dose below which none of the animals are affected; this is called the threshold. The highest dose at which no effects are seen lies slightly below it and is called the no observable effects level (NOEL), although sometimes the two terms are used interchangeably (Bairn and Cann 2005; Bempah, 2008)

2.5 Risk Assessment

The health risk associated with a particular pesticide is a function of both exposure and toxicity. Toxicities associated with the different pesticides (especially organochlorines) may however differ significantly. To protect public health from pesticide residues, most countries have specified and enforced maximum residues levels (MRLs) allowed to remain in foods. The MRLs may differ for different countries due to differences in food consumption patterns and agricultural practices. In Ghana, there are no set maximum residues levels (MRLs) and therefore MRLs by international bodies such as the Codex Alimentarius Commission and acceptable daily intake (ADI) values established by the world health organization (WHO) are often used as bench marks. Generally risk = exposure x toxicity

Therefore in performing a risk assessment, an attempt is made to estimate the exposure of the affected population first. For example for chemicals whose mode of exposure is primarily through drinking water, regulatory agencies such as the U.S. EPA consider a hypothetical average person who drinks about 2 litres of water daily and whose body weight averages 70 kg 9154 Ib) through life. If the ADI (or RfD) is 0.0020 mg/kg/day, then for the 70 kg person, the mass of substance that can be consumed per day is 0.0020 X 70 = 0.14 mg/day. Thus the maximum allowable concentration of the chemical in water would be 0.12 mg/2L = 0.07 ppm. Of course, if there are other significant sources for the substance, they must be taken into account in determining the drinking water standard. Also, exposure to several chemicals of the same type (e.g, several organochlorines) might lead to additive effects, so the standard for each one should presumably be lowed to take this into consideration (Bairn and Cann,2005)

2.6 Analytical methods for pesticide residue analysis

Different analytical methods exist for the analysis of pesticide residues in fruits and vegetables and new analytical methods are being developed continually. The analytical methods used at a particular time depends on the pesticide residues of interest, the sample matrix, the time required for analysis, the expected concentrations of pesticide residues and the materials and equipments available to the experimenter (Botwe, 2007). Basically, the process of pesticide residue analysis consists of the following steps:

- Sampling
- Extraction
- Clean up on interfering materials / Extract Purification
- Concentration of samples
- Identification and quantification of pesticide residue.

2.6.1 Sampling

A representative sample should be collected into appropriate containers. Containers such as glass bottles, Teflon and aluminium foils have been proven to be the most suitable materials to come into contact with the sample for pesticide residue analysis. Pesticides may be lost by degradation, adsorption to the wall of the container and sometimes by volatilization. This occurrence can be prevented or reduced by sealing samples in airtight containers and storing them in a deep freezer until analysis (Akerblom, 1995).

2.6.2 Extraction

Extraction is an important technique in the process of pesticide residue analysis and therefore when choosing an extraction method, one should take into consideration the chemical and physical properties of the analytes and the type of matrix in which they are present (Zwir-Ferenc, 2004). In vegetables and fruits, pesticide residues are normally present in low concentrations and therefore residues need to be concentrated first before the analysis is carried out. This is achieved by partitioning the residues to appropriate organic solvents or different solvent combinations (Akerblom, 1995; Yeboah, 2001). Among the many techniques that exist for isolating pesticides and PCBs (polychlorinated biphenyls) from food samples, the most frequently used are:

- Solvent extraction by shaking (LE)
- Solvent extraction in a soxhlet apparatus
- Ultra sonication extraction (USE)
- Microwave-assisted extraction (MAE)
- Focused microwave –assisted solvent extraction(FMASE)
- Supercritical fluid extraction techniques(SFE)

- Accelerated solvent extraction (ASE)
- Membrane extraction techniques
- Solid-based extraction techniques

2.6.2.1 Solvent extraction by shaking

Solvent extraction aided by shaking is based on the partitioning of analytes between liquid and solid phases (in the case of classical liquid-liquid extraction (LLE), between two immiscible liquids), which occurs when analyte move from the sample matrix into the properly selected solvent (Bempah, 2008). This technique has so many disadvantages. For instance it is laborious and time consuming, expensive and apt to form emulsion, it may require the evaporation of large volumes of solvent and the disposal of toxic and flammable chemicals. Moreover, a relatively large amount of matrix is required. Smaller sample size becomes important when dealing with real life problems, such as consumer complaints and alleged chemical contamination (Bayer and Biziuk, 2008).

2.6.2.2 Solvent extraction by soxhlet apparatus

Extraction in soxhlet apparatus is one of the new, less expensive techniques which has replaced the old process of liquid-liquid extraction. The sample is repeatedly brought closer to a fresh solvent with high temperature. One major advantage of this technique is that no filtration is required. However, the main disadvantages of this method are that it still requires large amount solvent and is time consuming. An improved version of soxhlet apparatus which allows for shortening of the extraction time even to one hour with a simultaneous reduction of solvent usage is soxtec apparatus. Extraction in soxtec is a two-step procedure, involving a boiling and rinsing step which drastically reduces the total time of extraction. Soxtec extraction has been used in many applications to extract organochlorine pesticide residues from samples with high lipid content such as fish (Falandysz *et al*, 2004; Bempah 2008).

2.6.2.3 Ultrasonication extraction (USE)

Ultrasonication extraction is a common conventional technique which has been widely applied for the extraction of pesticides and PCBs from various environmental samples (Ahmed, 2003). The application of ultrasonication extraction is to enhance food washing. The prominent mechanism for this washing is mechanical and includes the abrasion of suspended food particles in solvent leading to the removal of contaminants and improved solvent leaching of contaminants from the interior of the particles. Like the technique mentioned above, this technique requires the application of a lot of solvents (Mason *et al*, 2004).

2.6.2.4 Microwave-assisted extraction (MAE)

Another extraction technique is the microwave assisted extraction. In this phenomenon, the microwave energy absorption is applied. The microwave energy causes molecular movement and liquid rotation with permanent dipole, leading to a very fast heating of the solvent and the sample. The microwave assisted extraction's requires low temperature treatment, high extraction rate, automation and the possibility of simultaneously extracting different samples at the same time without interferences (Camel, 2000)

Microwave extraction is becoming the choice for the extraction of a diverse array of solid matrices for organic analyte analysis by GC, GC-MS, HPLC, and other analytical techniques. Since it operates at a far higher temperature and pressure than traditional soxhlet and sonication techniques, it can be applied to a broader range of samples. One of the biggest benefits is realized in the reduced amount of time the extraction takes for multiple samples in a single extraction operation. With microwave extraction, samples are enclosed in high quality Teflon vessels together with solvent and heated to a controlled temperature with microwave power. With the flexibility of vessel options, choices of sample size, temperature/pressure, amounts of solvent, and number of samples make this an attractive technique for high-throughput sample preparation as well as the ability to process more difficult samples. This technology can also be applied to open-vessel applications depending on the matrix and substrate analyzed. One of the major benefits with this approach is moving to solvent-free applications (Camel, 2000; Bempah, 2008).

2.6.2.5 Focused microwave –assisted solvent extraction (FMASE)

The use of focused microwave –assisted soxhlet extraction (FMASE) has proved to be an alternative to soxhlet extraction. This process requires small amount of solvents and hence minimizes environmental pollution. (Luque-Garcia and Luque de Castro, 2004). Focused microwave –assisted solvent extraction has been used in many applications to extract pesticide residues from samples with high fat content and sunflower seeds (Prados-Rosales *et al*, 2003).

2.6.2.6 Supercritical fluid extraction techniques (SFE)

Extraction is a diffusion-based process, with the solvent required to diffuse into the matrix, and the extracted material to diffuse out of the matrix into the solvent. Diffusivities are much faster in supercritical fluids than in liquids, and therefore extraction can occur faster. Also, surface tension and viscosities are much lower than in liquids, so the solvent can penetrate into small pores within the matrix inaccessible to liquids. Both the higher diffusivity and lower viscosity significantly increase the speed of the extraction: An extraction using an organic liquid may take several hours, whereas supercritical fluid extraction can be completed in 10 to 60 minutes (Skoog, 2007). The requirement for high pressures would increase the cost compared to conventional liquid extraction, therefore SFE may be used where there are significant advantages. Carbon dioxide itself is non-polar, and has somewhat limited dissolving power, hence it cannot be always used as a solvent on its own, particularly for polar solutes. The use of modifiers increases the range of materials which can be extracted. Food grade modifiers such as ethanol are often used, and can also help in the collection of the extracted material, but this reduces some of the benefits of using a solvent which is gaseous at room temperature (Bempah, 2008).

2.6.2.7 Accelerated solvent extraction (ASE)

Accelerated solvent extraction is one the newly developed extraction techniques. This method utilizes solvents that are raised to near supercritical region, where they display better extraction properties. The rate of extraction increases at high temperatures because the viscosity and the surface tension decreases while its solubility and diffusion rate into the sample increase. As a result, pressure keeps the solvent below its boiling point and forces its penetration into the pores of the sample (Mendiola *et al*, 2007). The use of both high temperatures and pressures provides a relatively faster extraction process. Additionally, smaller amounts of solvents are required. In accelerated solvent extraction, the time required for extraction is independent on the mass of the sample and the efficiency of extraction is mainly dependent on temperature. The main advantages of accelerated solvent extraction are reduction in solvent consumption and extraction time. However the major disadvantage with this method is that it is very expensive (Mendiola *et al*, 2007).

2.6.2.8 Membrane extraction techniques

Membrane extraction technique is one of the most recently developed methods of extraction of pesticides. The selective nature of membranes has made them a unique alternative to solvent extraction for sample clean up (Cordero *et al*, 2000; Jonsson *et al*, 2000, Bempah, 2008). This technique allows the preparation of samples that have a complex matrix by means of simple and easily automated equipments (Jakubowska *et al*, 2005). Also, membrane extraction technique can be coupled with the chromatographic system with significant advantages such as direct introduction of untreated samples, analyte pre-concentration and elimination of interferences. Additionally, there is also the possibility of recirculating the sample through the membrane cell, thereby allowing the extraction procedure to be applied even in cases where only limited amounts of sample are available (Carabias-Martinez *et al*, 2000).

2.6.2.8 Solid-based extraction techniques

Another way of extracting analyte is using a solid adsorbent material. A sorbent with strong affinity towards some target analytes will retain and concentrate those compounds from the sample solution. Widely applied to many matrices, including food, solid – phase – based extraction techniques are matrix solid – phase dispersion (MSPD), solid – phase extraction (SPE), solid-phase micro-extraction (SPME) and stir-bar sorptive extraction (SBSE). Current trends in these techniques for pesticides determination in food and the environment are presented in an up-to-date review (Bempah, 2008).

2.6.3 Clean-up of sample extract

During the process of extraction, some constituents of the sample (fruit / vegetable) other than the target analytes can also be extracted into the solvent and interfere with the analysis and this is known as matrix-effect (Plimmer, 1995). These co-extractives have the effect of obscuring peaks in the chromatogram, damaging analytical columns and sensitive detectors used in the residue analysis. Co-extracted compounds often require tedious clean-up process for their removal to avoid matrix effect and ensure more consistent detector response and better baseline from instrument (Bacci *et al*, 1988; Botwe, 2007). When undertaking a clean- up process for an extract, care must be taken to ensure that target pesticides are not lost.

Different methods have been developed to separate pesticides from co-extractives, and many are applied to different group of pesticides. Column adsorption chromatography and gel permeation chromatography techniques are two common techniques that have been widely used for clean up (Miglioranza *et al*, 1997). In column adsorption chromatography, the extract is applied to a column packed with a solid material such as florisil, alumina or silica gel for the components to be adsorbed (Jiang *et al*, 2005). The adsorption is followed by elution of the components of interest with solvents or solvent mixtures with increasing polarity. Separation of components is achieved based on difference in polarity of the components. As are result, polar compounds are eluted with polar solvents while non-polar are eluted with non-polar solvents (Hess *et al*, 1995).

Adsorbent materials with relatively close particle size distribution packed in disposable polypropylene cartridges-solid phase extraction columns have also been used during clean up.

When analysing the techniques for determining pesticides and PCBs in food, a single, universal procedure, applicable to all types of samples does not exist. Because a combination of different techniques is often required, the aim of any analytical procedure should be achieved in as few steps as possible (Focant *et al,* 2001). The table below shows a summary of sample extraction and clean up procedures.

Table 2.1: Methods of sample extraction and clean-up (Zwir-Ferenc *et al*, 2004).

Technique	Extraction	Clean-up	Characteristics
LLE	+	+	Foods, liquids, crops, plant material. High consumption of organic solvents, risk of emulsion creation, universal
SPE Catridge Membrane extraction disc GCB	+	-	Foods, liquids, crops, plant material No emulsion, low consumption of organic solvents, automated, universal.
SPME	+	-	Foods, liquids, crops. No organic solvents automated, universal
MSPDE	+	+	Plant material, food, liquids feed No emulsions, direct on-line clean up, universal.
SFE	+	+	Cereals, plant materials. Use ecologically nontoxic fluid (CO_2). Optimization of modifier, automated, expensive instrumentation, small extractions.
ASE	+	-	Foods, crops, plant material. Low use of solvents, automated, expensive instrumentation.
Colum AC			Foods, crops, plant material, fatty foods
Florisil column	+	-	
Alumina column	+	-	
Silica gel column	+	-	
PGC column	+	-	Samples with high content of fat, oil Automated, economical, universal.
Soxhlet extraction	+	-	Foods, crops, plant material fatty foods Time consuming, high consumption of organic solvents.

+, Main application; -, secondary application Abbreviation : LLE, liquid-liquid extraction; SPE, solid-phase extraction; SPME, solid-phase micro extraction ; MSPDE, matrix solid-phase dispersion extraction; SPE, supercritical fluid extraction; ASE, accelerated solvent extraction; MAE, microwave-assisted extraction; column AC, ;PGC, porous graphitic carbon.

2.6.4 Identification and quantification of Pesticide Residue

2.6.4 .1 Chromatography methods

Currently, gas chromatography has proved to most versatile and easiet method for pesticide residue analysis due to its high sensitivity. The replacement of glass or metal by columns of Teflon was suggested because of the fact that a metallic column can decompose the analyte. Detectors such as electron capture (ECD), nitrogen-phosphorous (NDP), flame photometric (FPD) and Mass spectrometer are normally used. Mass spectrometry (MS) is currently the often used detection technique; this is due to its ability to provide information on the compounds molecular structure. It is also highly sensitive when used in the single ion monitoring mode. GC-MS is the most accepted confirmatory technique (Torres *et al,* 1996).

Nitrogen Phosphorous Detectors or GC-NPD, otherwise known as Thermionic Specific Detector or TSD, is a technique used to analyse nitrogen or phosphorous containing organic compounds. It is commonly used for pesticides, pharmaceuticals, food and environmental determinations due to its selectivity for phosphorous and nitrogen. Similar to a Flame Ionization Detector, a NPD uses a Hydrogen/Air flame through which the sample is passed. However a NPD uses a rubidium or cesium chloride alkali bead which is heated by a coil, over which the carrier gas mixed with Hydrogen passes (Torres *et al,* 1996).

The hot bead emits electrons by thermionic emissions which are collected at the anode and provides the background current. When a component containing nitrogen or phosphorous exits the column, the partially combusted nitrogen and phosphorous materials are adsorbed on the surface of the bead. This then increases the emission of electrons and the current which is then measured.

Electron Capture Detectors (ECDs) are often used in pesticide residue determination. It has a very high sensitivity to polychlorinated hydrocarbons and other halogenated pesticides.). When electronegative compounds enter the ECD cell from the column, they immediately combine with some of the free electrons, temporarily reducing the number remaining in the electron cloud. When the electron population is decreased, the pulse rate is increased to maintain a constant current equal to the standing current. The pulse rate is converted to an analog output, which is acquired by the Peak Simple data system. Unlike other detectors which measure an increase in signal response, the ECD detector electronics measure the pulse rate needed to maintain the standing current (Bempah, 2008). It's disadvantaged to selectivity because all kinds of electron attracting functional groups such as nitro groups and aromatic structures also give response. (Torres *et al*, 1996)

Gas Chromatography – Flame Photometric Detector or GC-FPD is a technique used to analyse sulphur or phosphorous containing compounds and metals such as tin, boron, arsenic and chromium. An FPD uses a Hydrogen/Air flame into which the sample is passed. Phosphorous and sulphur containing hydrocarbons generate chemiluminescene at specific wavelengths which when passed into a photo-multiplier gives an electrical signal which can then be measured. (Torres *et al*, 1996).

High Performance Liquid Chromatography - High performance liquid chromatography is basically a highly improved form of column chromatography. Instead of a solvent being allowed to drip through a column under gravity, it is forced through under high pressures of up to 400 atmospheres. That makes it much faster and also allows you to use a very much smaller particle size for the column packing material which gives a much greater surface area for interactions between the stationary phase and the molecules flowing past it. This allows a much better separation of the components of the mixture.

CHAPTER THREE

3.0 METHODOLOGY

3.1 Study Area

The study was undertaken in three regions of Ghana namely Greater Accra, Eastern and Central Regions. These regions are linked together in the southern part of Ghana where there is abundant of rainfall and good climatic conditions necessary for crop production especially fruits and vegetables. As a result, the use of pesticides is a common practice as well as probable use of restricted or banned pesticides which get into the country through unapproved routes. There may also be deposition of pesticide residues especially organochlorine pesticides at the study area (markets) as a result of long range air transport from their application sites. These factors are the reasons for the selection of those areas for the study.

In each region, four large urban markets were targeted. These include the regional capitals and other towns where these fruits and vegetables are mostly cultivated and sold since majority of the populace obtains their fresh vegetables and fruits from such markets.

MAP SHOWING STUDY AREAS

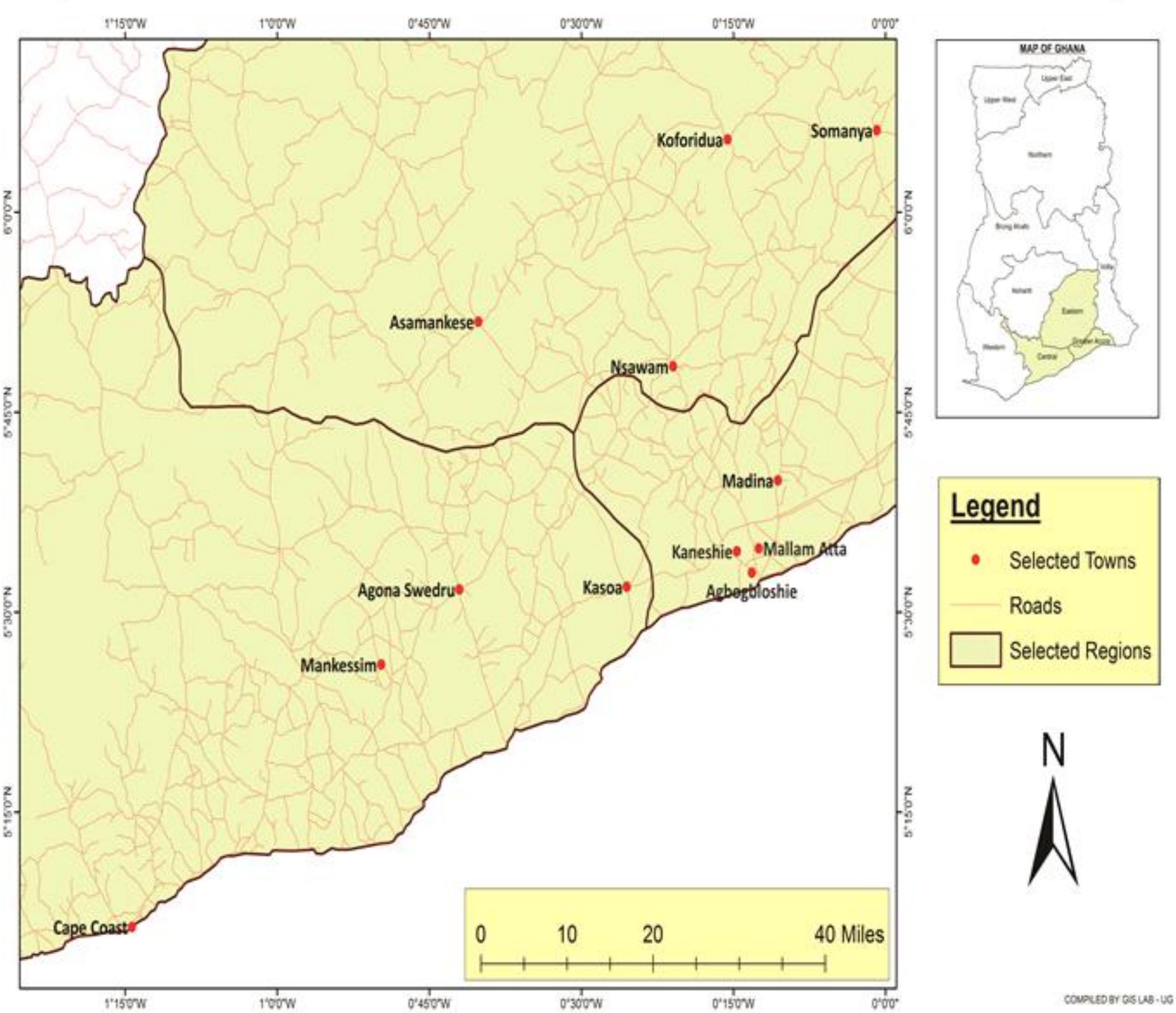


Figure 3.1: Map showing the study areas

3.1.2 Sampling and storage

A total of 192 samples of fruits and vegetables were purchased from major market centers in three regions of Ghana within the months of January and February. The fruits and vegetables sampled were lettuce, garden eggs, mango and pineapple. In Greater Accra, samples were purchased from Mallam Atta, Agbobloshie, Kaneshie and Madina markets. For Central Region, samples were obtained from Cape Coast, Kasoa, Mankesim and Agona Swedru markets. In Eastern region, samples were purchased from Koforidua, Nsawam, Somanya and Asamankese markets. In every market, fresh samples were purchased from different sellers in order to have a true representation. After collection, the samples were sealed in polyethylene bags, labeled appropriately and transported to the laboratory and kept in a refrigerator for further analysis.

3.1.3 Reagents

Pesticide grade ethyl acetate, analytical grade acetone were supplied by Labscan (Dublin,Ireland), sodium hydrogen carbonate and sodium sulfate were purchased from E.Merck (Germany). Disposable solid-phase florisil cartridges (500mg/8mL) were obtained from Sigma-Aldrich Chemicals USA. Pesticide reference standards were obtained from Dr, Ehrenstofer GmbHm (Germany) and stored in the freezer to minimize degradation.

3.1.4 Apparatus

The following lists of apparatus were used for laboratory analysis:Gas chromatograph (GC): Helwet Packard 5890 series ii with electron capture detector nickel source Column: 30m capillary column,0.53mm ID, fused silica coated with DB-5, Integrator: Helwet Packard 3396, Homogenizer-Foss 2096 based on tecator technology, Weighing balance-Metler Toledo PG

1003-5, Macerator- Ultra-turax macerator, type t- 25 generator, Centrifuge-CRI multifunction Thermo Electron Industries SAS (France), Rotary vacuum evaporator-Buchi RE-200 (Buchi Labortechnic AG, Postfach, Switzerland), graduated pipettes, Round bottom flasks (250ml and 100ml), aluminum foils, oven, auto sampler vials (2ml) ,chromatographic columns.

3.1.5 Cleaning of glass wares

Glass wares were soaked in soapy water for two days after which they were thoroughly washed with detergent. After washing, the glass wares were rinsed six times with tap water followed by deionized water and then dried in an oven at 100 ^{o}C for about one hour. The glass wares were then removed from the oven and allowed to cool down ready to be used.

3.1.6 Preparation of pesticide (organochlorine) mixture standard solution

0.1mL each of o,p' DDE, endrin, p,p' DDT, heptachlor, chlordane, alpha -endosulfan, beta-endosulfan, methoxychlor, HCH, and aldrin were accurately pippeted into a 50ml volumetric flask and 48.4ml of ethyl acetate was added to give organochlorine mix. Standard solution with concentration 2.0µg/ml was made for the calibration curve.

3.1.7 Extraction

The extraction procedure was according to methods described by Netherlands analytical methods of pesticide residues and foodstuffs (Ministry of Public Health, Welfare and Sports, Netherlands, 2007). Frozen vegetables and fruits were allowed to thaw to room temperature, shredded and homogenized. Approximately 20 g of the homogenized sample was macerated with 40ml of ethyl acetate. 5 g of sodium hydrogen carbonate and 20 g of anhydrous sodium sulfate were added to remove moisture present and macerated for 3 minutes till a consistent mixture was attained using the ultra-turax macerator. The samples were centrifuged for 5 minutes at 3000 rpm to separate the two phases. The solvent was filtered through a No. 1 filter paper into 250 ml conical flask. After this the residue was taken through the same process two more times and added to the original filtrate. A drop of isodrin was added to the combined filtrate and evaporated to dryness on a vacuum rotary evaporator.

3.1.8 Solid-phase extraction (SPE) clean-up of extract

About 3 g of activated silica was weighed and poured into a glass column which has been plugged with a glass wool at the end followed by 2 g of anhydrous sodium sulfate. The silica packed column was clamped using a retort stand after which it was conditioned with 10ml ethyl acetate. A receiving flask was placed under the column to collect the eluate. The sample was then transferred onto the silica column and eluted two times first with 10 ml of ethyl acetate and again with 5 ml of ethyl acetate using Pasteur pipette. The eluate was collected into a round bottomed flask and evaporated to dryness using a rotary evaporator fitted to a vacuum pump. The residue was dissolved with 2 ml of ethyl acetate using Pasteur pipette into glass vials for Gas Chromatographic analysis.

3.1.9 Calibration curve

Calibration curve was prepared from the stock solutions containing the individual pesticide standards to check for the linearity of the system. Ethyl acetate (9975 µl) was added to 25 µl of pesticide standards solution (2 µg/ml). Serial dilutions of concentrations of 0.20 µg/ml, 0.02 µg/ml, 0.01 µg/ml and 0.005 µg/ml were prepared. 1.0 µl of each concentration was injected into the injection port of the GC-ECD and the responses were recorded. A calibration curve was constructed by plotting the concentration against their respective peak areas.

3.2 Gas Chromatographic Analysis

A Varian CP-3800 Gas Chromatograph (Varian Associates Inc. USA) equipped with ^{63}Ni electron capture detector was used for the analysis. A volume of about 1 µL of the extract was injected and the separation was performed on a fused silica gel capillary column coated with VF-5ms, 40m long with internal diameter and film thickness of 0.25 mm and 0.25 µm respectively. The carrier gas and make up gas were nitrogen at a flow rate of 1.0 and 29 ml/min respectively. The injector and detector temperatures were 270 ^{o}C and 300 ^{o}C respectively. The column oven temperature was programmed as follows: 80^{o}C for 1min to 18^{o}C at 25 ^{o}C/min and up to 300 ^{o}C at 5 ^{o}C/min held for 1min.

3.2.1 Quantification of pesticides results

An external standard method was used for determining the quantities of residues in the sample extracts. A standard mixture containing known amounts of pesticides was run and the response of the detector for each compound was determined. The area of the corresponding peak in the sample was compared with that of the known standard.

3.2.2 Quality control and quality assurance

Quality control and quality assurance were incorporated into the analytical scheme. Samples were carefully handled carefully to avoid contamination. Analytical grade reagents were used in the sample preparations and treatments and deionized water was used throughout the study.

3.2.3 Recovery Test

Loss of target compounds could occur during sample preparation, extraction and analysis. The extent of analyte losses especially during extraction was assessed by performing a recovery test. This was done by spiking the samples with 0.5ppm of an internal standard (isodrin) before extraction to evaluate the recovery of the compounds. The recovery was determined using the formula:

$$\% \text{ Recovery} = \frac{\text{Pesticide (ppm) recovered from fortified sample}}{\text{Amount of pesticide (ppm) added}} \times 100$$

3.2.4 Limit of detection (LOD)

The extracts of the fortified samples were serially diluted by a factor of two to give different concentrations. 1.0µL of each concentration was injected and the least concentration that gave response was noted. The limit of detection was calculated by the formula:

$$\text{LOD} = \frac{V_1\ (\mu l)}{V_2\ (\mu l)} \text{ X Concentration fortified}$$

Where V_1=volume injected and V_2=final volume of fortified extract

3.2.5 Data analysis

Statistical analysis incorporated in the work include mean of samples and corresponding standard deviations. Ranges were compiled from minimum and maximum values for levels of pesticides residues detected in the study. Data was subjected to one-way analysis of variance to determine the differences in pesticide residue among the samples as well as the different areas from which they were sampled. All tests were regarded as statistically significant when $p<0.05$. All these calculations were done using Microsoft excel 2007.

CHAPTER FOUR

4.0 RESULTS AND DISCUSSION

4.1: Introduction

The concentrations of organophosphates, synthetic pyrethroids and organochlorine pesticide residues were measured in four different samples namely, lettuce, garden eggs, pineapple and mango from the selected regions in Ghana. Analysis of the samples revealed varying concentrations of pesticide residues. Tables 4:12- 4.19 show the results of the various pesticide residues detected in samples from the different sampling areas.

Data was subjected to one-way analysis of variance (one-way ANOVA) to determine whether the pesticides concentrations vary among the samples (lettuce. garden eggs, pineapple and mango) as well as the different areas (the three regions) from which they were sampled. All tests were regarded as statistically significant when $p<0.05$. These are summarized in Appendices A-D. Again, the results of the pesticide residues were compared with the WHO/FAO codex Alimentarious Commission Maximum Residues Levels (MRLs) for fruits and vegetables. Health risk estimation was computed for each organochlorine pesticide and is presented in tables 4.21-4.24 and the results discussed.

4.1.1: Percentage of samples of fruits and vegetables with pesticide residues.

The percentage of samples of fruits and vegetables with pesticide residues are presented in the table 4.11. In all, a total of 192 fresh samples of fresh fruits and vegetables were purchased from major market centers in the three regions of Ghana within the months of January and February 2013. The percentage of samples of fruits and vegetables with pesticide residues in Lettuce, Garden eggs, Pineapple and Mango were 52%, 40%, 45%, 48% respectively and details are discussed below.

Table 4.11: **Percentage of samples with one or more pesticide residues.**

Vegetable/fruit	Scientific name	Number of samples	% with one or more residues
Lettuce	*Lactuca sativa*	48	52
Garden eggs	*Solanum melongena*	48	40
Pineapple	*Ananas comosus*	48	45
Mango	*Magnifera indica*	48	48
Total		192	

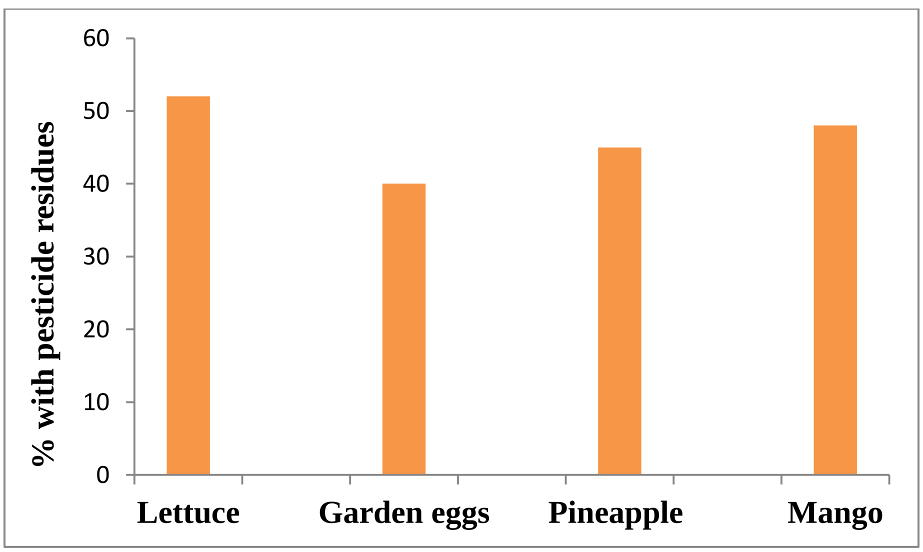


Fig 4.11: Graph showing the percentage of samples with one or more pesticide residues

4.1.2: Occurrence and distribution of organophosphates and synthetic pyrethroids in samples from the Greater Accra Region

Table 4.12 and Figures 4.12a-4.12f show the levels of organophosphates and synthetic pyrethroids in samples from the Greater Accra Region. Total samples analyzed show the presence of sixteen different pesticides residues comprising nine organophosphates and seven synthetic pyrethroids being the region with the highest number of recorded synthetic pyrthroids pesticide residues. The different organophosphates pesticides detected were dimethoate, pirimiphos-methyl, malathion, fenitrothion, parathion ethyl, chlorfenvinphos, profenofos, methamidophos, and chlorpyrifos. Phorate and ethoprophos were not detected in any of the samples analyzed.

Generally most organophosphates pesticides recorded high concentrations except profenofos and dimethoate with total mean concentrations of 0.02 mg/kg and 0.04 mg/kg respectively in all samples. The highest concentration of organophosphate in lettuce was recorded for malathion with mean concentration of 0.26 mg/kg while dimethoate, profenofos and chlorpyrifos recorded lowest mean concentrations of 0.02 mg/kg (Fig 4.12c). Again, the highest concentration of organophosphate in garden eggs was recorded for chlorpyrifos while the lowest was recorded for pirimiphos-methyl with mean concentrations of 0.45 mg/kg and 0.01mg/kg respectively (Fig 4.12d).

In pineapple, the highest concentration of organophosphate was observed for parathion ethyl/malathion with mean concentration of 0.10 mg/kg while the lowest was recorded for chlorfenvinphos with mean concentrations of 0.02 mg/kg (Fig 4.12e). Mango showed the highest concentration of organophosphate for methamidophos with mean concentration of 0.78 mg/kg while the lowest was recorded for chlorfenvinphos/parathion-ethyl/profenofos/ chlorpyrifos with mean concentration of 0.02 mg/kg (Fig 4.12f). Statistically, the concentration of organophosphates in the samples of lettuce, garden eggs, pineapple did not vary significantly ($p>0.05$ or $p=0.525$, appendix a) suggesting a common route of contamination.

Also, the seven different synthetic pyrethroids pesticides detected were allethrin, lambda-cyhalothrin, permethrin, cyfluthrin, deltamethrin, cypermethrin and bifenthrin. The results show low levels of synthetic pyrethroids except for cypermethrin, cyfluthrin and bifenthrin with mean concentrations of 0.26 mg/kg, 0.07 mg/kg and 0.13 mg/kg respectively. The highest concentration of synthetic pyrethroids in lettuce was observed for lambda-cyhalothrin with mean concentration of 0.18 mg/kg while the lowest concentration was observed for permethrin with mean concentration of 0.02 mg/kg (Fig4.12c). The highest concentration of synthetic pyrethroids in garden eggs was recorded for cypermethrin with mean concentration of 0.36 mg/kg while the lowest concentration was observed for lambda-cyhalothrin/ cyfluthrin, with each recording a mean concentration of 0.03 mg/kg (Fig 4.12d).

The highest concentration of synthetic pyrethroid found in pineapple and mango was cypermethrin with mean concentrations of 0.21 mg/kg and 0.36 mg/kg in pineapple and mango respectively while the lowest concentration was recorded for cyfluthrin with mean concentrations of 0.15 mg/kg and 0.05 mg/kg for pineapple and mango respectively (Fig 4.12e and 4.12f). Statistically, the differences in concentrations of synthetic pyrethroids in the samples of lettuce, garden eggs, pineapple and mango varied significantly ($p<0.05$ or $p= 0.0015$, appendix a) suggesting different route of contamination.

The high levels of organophosphates and synthetic pyrethroids in samples from Greater Accra Region suggest that farmers who supply vegetables and fruits to these markets centers do use organophosphates and synthetic pyrethroids in significant quantities.

Table 4.12: Concentrations (mg/kg) of organophosphates and synthetic pyrethroids in samples from the Greater Accra Region

Pesticide	Lettuce			Garden eggs			Pineapple			Mango		
	Mean	*SD*	*Range*	*Mean*	*SD*	*Range*	*Mean*	*SD*	*Range*	*Mean*	*SD*	*Range*
Dimethoate	0.02	-	0-0.02	0.05	-	0-0.05	0.05	-	0-0.05	0.03	-	0-0.03
Pirimiphos-m	0.09	-	0-0.09	0.01	-	0-0.01	0.05	-	0-0.02	0.56	-	0-0.56
Malathion	0.26	-	0-0.26	0.13	-	0-0.13	0.1	0.07	0-0.17	0.12	-	0-0.56
Fenitrothion	0.08	0.06	0-0.13	0.12	-	0-0.12	0.04	0.02	0-0.05	0.05	-	0-0.05
Parathion ethyl	0.08	-	-	0.07	0.05	0-0.12	0.10	0.05	0-0.14	0.02	-	0-0.02
Chlorfenvinp	0.03	0.01	0-0.04	0.19	-	0-0.09	0.02	-	0-0.02	0.02	-	0-0.02
Profenofos	0.02	0.02	-	0.02	-	0-0.02	0.03	-	0-0.03	0.02	-	0-0.02
Methamidop	0.08	-	-	0.03	0.01	0-0.04	0.06	-	0-0.02	0.78	-	0-0.78
Chlorpyrifos	0.02	0.01	0-0.02	0.45	0.02	0.09-1.36	0.07	0.03	0-0.09	0.02	-	0-0.02
Allethrin [a]	<0.01	-	-	0.05	0.02	0-0.08	<0.01	-	-	ND	-	-
Lambda-cyhal [a]	0.08	0.02	0-0.13	0.03	-	0-0.03	ND	-	-	ND	-	-
Permethrin [a]	0.02	-	-	0.08	-	0-0.08	<0.01	-	-	ND	-	-
Cyfluthrin [a]	0.04	0.04	0-0.06	0.03	-	0-0.03	0.15	-	0-0.15	0.05	0.03	0-0.03
Deltamethrin [a]	<0.01	-	-	0.04	-	0-0.04	ND	-	-	ND	-	-
Cypermethrin [a]	0.04	0.04	0-0.04	0.41	0.22	0-0.63	0.21	-	0-0.21	0.36	-	0-0.02
Bifenthrin [a]	ND	-	-	0.13	-	0-0.13	ND	-	-	ND	-	-

[a] - Synthetic Pyrethroids , Limit of detection for all pesticides = 0.01 mg/kg, ND=not detected, SD =standard deviation,

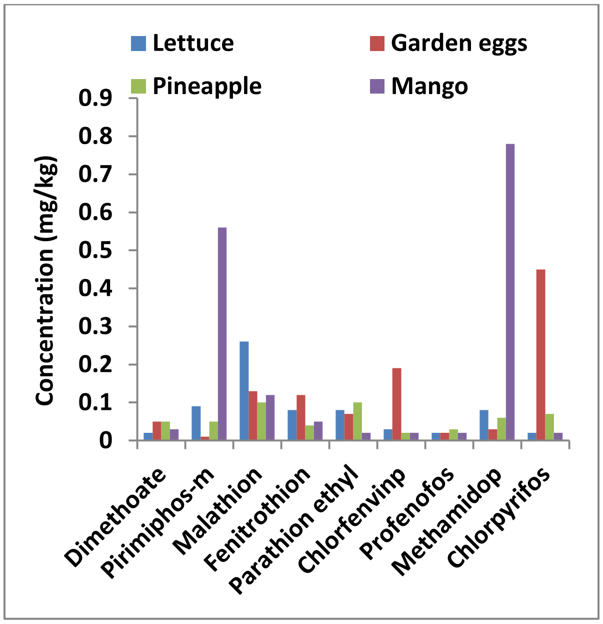


Fig 4.12a: Mean concentration levels of organophosphates in fruits and vegetables from the Greater Accra Region.

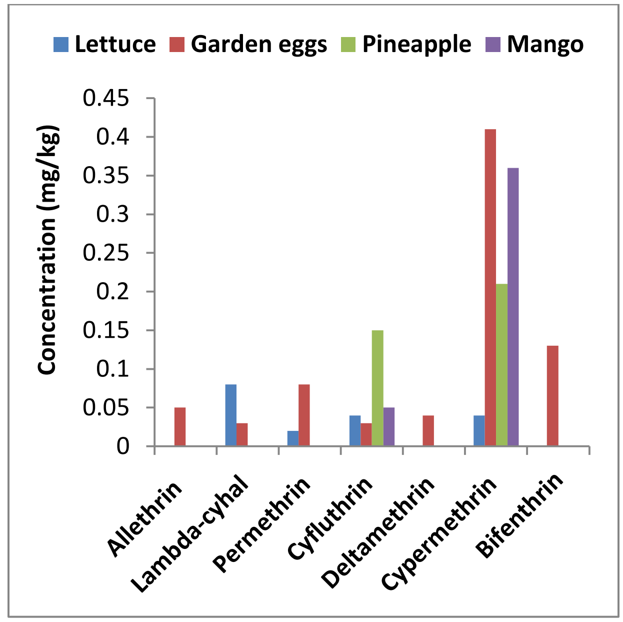


Fig 4.12b: Mean concentration levels of synthetic pyrethroids in fruits and vegetables from the Greater Accra Region.

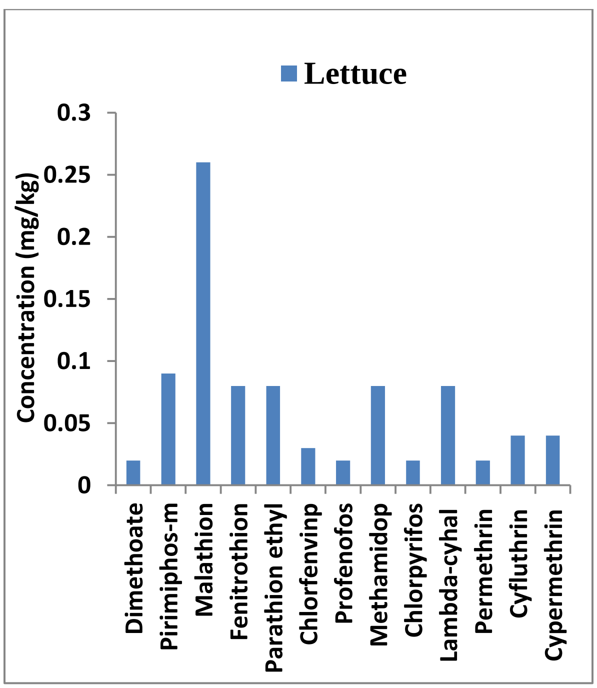


Fig 4.12c: Mean concentration levels of organophosphates and synthetic pyrethroids in lettuce from the Greater Accra Region.

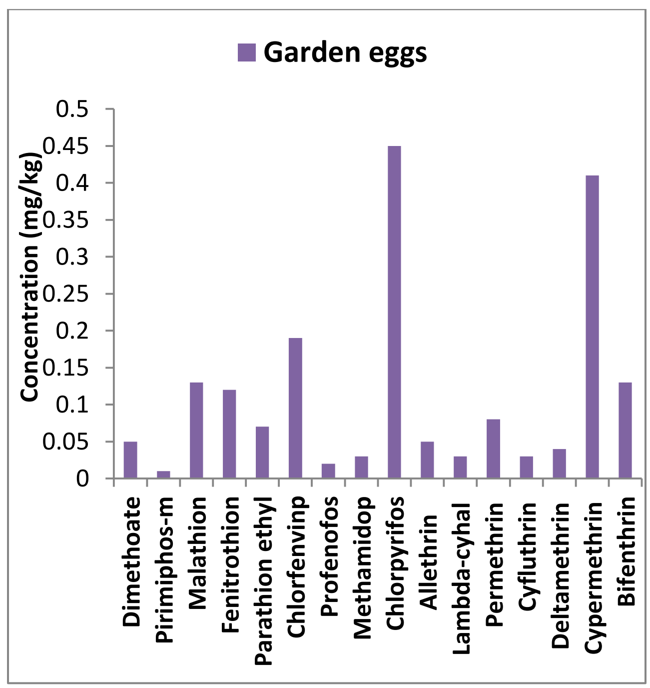


Fig 4.12d: Mean concentration levels of organophosphates and synthetic pyrethroids in garden eggs from the Greater Accra Region.

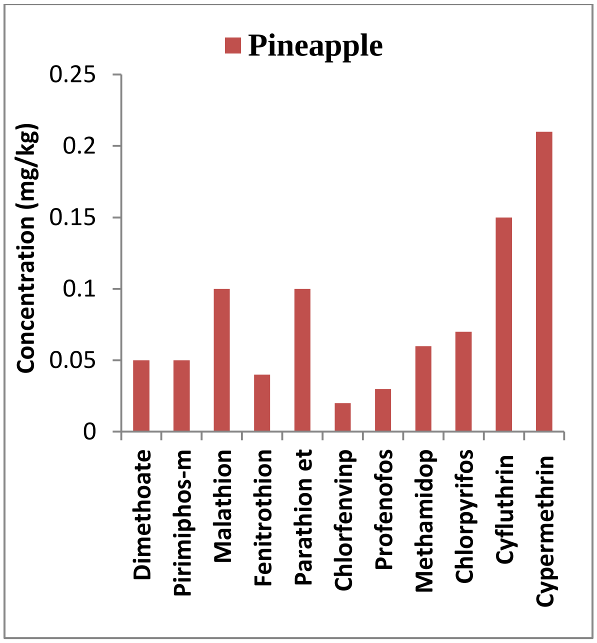


Fig 4.12e: Mean concentration levels of organophosphates and synthetic pyrethroids in pineapple from the Greater Accra Region.

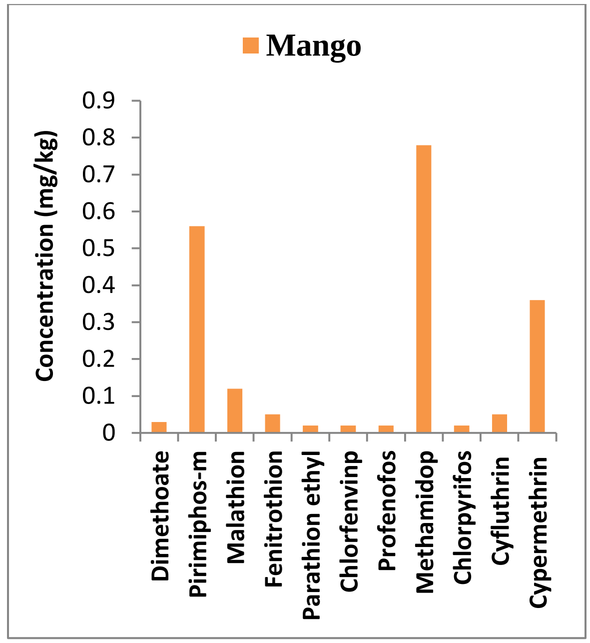


Fig 4.12f: Mean concentration levels of organophosphates and synthetic pyrethroids in mango from the Greater Accra Region.

4.1.3: Occurrence and distribution of organophosphates and synthetic pyrethroids in samples from the Central Region

The mean, standard deviation and the range of values obtained from the analysis done on all samples from the Central Region are shown in table 4.13. The results from the samples analyzed showed the presence of thirteen different pesticides residues comprising eight organophosphates and five synthetic pyrethroids being the region with the least number of recorded organophosphates pesticide residue. The organophosphates pesticides detected were dimethoate, fenitrothion, chlorfenvinphos, profenofos, methamidophos, ethoprophos and chlorpyrifos.

In the Central Region, the highest concentration of organophosphate in lettuce was recorded for methamidophos with mean concentration of 0.05 mg/kg while the lowest concentration was recorded for fenitrothion with mean concentration of 0.02 mg/kg (Fig4.13c). Phorate and ethoprophos recorded concentrations below the detection limit. Again the highest concentration of organophosphate in garden eggs was observed for chlorpyrifos with mean concentration of 0.17 mg/kg while the lowest concentration was obtained for both dimethoate and chlorfenvinphos with mean concentration of 0.01 mg/kg each (Fig4.13d). Fenitrothion and profenofos were not detected in any of the garden eggs samples analyzed.

In pineapple, the highest concentration of organophosphate was obtained for methamidophos with mean concentrations of 0.11 mg/kg while the lowest concentration was obtained for dimethoate and chlorfenvinphos with concentrations of 0.01 mg/kg each (Fig4.13e). Fenitrothion and profenofos were not detected in any of the garden eggs samples while phorate and ethoprophos recorded concentration levels below the detection limit.

The highest concentration of organophosphate in mango was observed for chlorpyrifos with mean concentration of 0.34 mg/kg while the lowest concentration was observed for phorate/profenofos at concentrations of 0.04 mg/kg each (Fig4.13f). Fenitrothion and ethoprophos were not detected in any of the pineapple samples analyzed while dimethoate concentrations were below the detection limit. Generally, most organophoshates recorded low concentrations levels except methamidophos and chlorpyrifos with mean concentrations of 0.08 mg/kg and 0.15 mg/kg respectively in all samples. Parathion ethyl, malathion, pirimphos methyl were not detected in samples from the Central Region. The concentration of the organophosphates in the fruits and vegetables varied significantly ($p < 0.05$ or $p=0.011$, appendix b).

Also, the five different synthetic pyrethroids pesticides detected were lambda-cyhalothrin, permethrin, cyfluthrin, deltamethrin and cypermethrin. The results indicate low levels of synthetic pyrethroids except for cypermethrin, cyfluthrin and lambda-cyhalothrin with mean concentrations of 1.67 mg/kg, 0.13 mg/kg and 0.12 mg/kg respectively. The highest concentration of synthetic pyrethroids in lettuce, garden eggs, and pineapple mango was obtained for cypermethrin with mean concentrations of 1.34 mg/kg, 1.7 mg/kg, and 1.52 mg/kg and 2.11 mg/kg respectively (Fig 4.13a - 4.13f). The lowest concentration of synthetic pyrethroids in lettuce and garden eggs was observed for allethrin with mean concentrations of 0.04 mg/kg and 0/03 mg/kg respectively (Fig 4.13c and 4.13d). The lowest concentration of synthetic pyrethroids in pineapple and mango was observed for lambda-cyhalothrin with each recording mean concentrations of 0.01 mg/kg (Fig 4.13e and 4.13f). The difference in the concentration of synthetic pyrethroids in the samples of lettuce, garden eggs, pineapple and mango from the Central Region was not significant (statistically, $p>0.05$ or $p= 0.991$, appendix b). Deltamethrin was absent in both lettuce and garden eggs while allethrin was absent in both pineapple and mango. Cyfluthrin was not detected in any of the pineapple samples analyzed. The relatively low levels of organophosphates and high levels of synthetic pyrethroids especially cypermethrin in samples from **the** Central Region shows that farmers in this region use cypermethrin extensively.

Table 4.13: Concentrations (mg/kg) of organophosphates and synthetic pyrethroids in samples from the Central Region

Pesticide	**Lettuce**			**Garden eggs**			**Pineapple**			**Mango**		
	Mean	***SD***	***Range***	***Mean***	***SD***	***Range***	***Mean***	***SD***	***Range***	***Mean***	***SD***	***Range***
Dimethoate	0.05	0.01	0-0.06	0.01	-	0-0.01	0.01	-	-	<0.01	-	-
Fenitrothion	0.02	-	-	ND	-	-	ND	-	-	ND	-	-
Chlorfenvinphos	0.03	-	-	0.01	-	0-0.01	0.01	-	0-0.01	0.05	0.03	0-0.08
Profenofos	0.03	-	0-0.03	ND	-	-	ND	-	-	0.04	-	-
Phorate	<0.01	-	-	0.02	-	0-0.12	<0.01	-	-	0.04	0.02	0-0.06
Methamidophos	0.05	0.01	0-0.07	0.09	0.02	0-0.11	0.11	-	0-0.11	0.06	-	0-0.06
Ethoprophos	<0.01	-	-	0.02	-	0-0.02	<0.01	-	-	ND	-	-
Chlorpyrifos	0.04	0.02	0-0.06	0.17	0.1	0-0.27	0.04	0.02	0-0.07	0.34	-	-
Allethrin [a]	0.04	0.01	0-0.06	0.03	0.02	0-0.04	ND	-	-	ND	-	-
Lambda-cyhal [a]	0.41	0.22	0-0.71	0.50	0.48	0-1.17	0.01	-	0-0.01	0.01	-	0-0.01
Permethrin [a]	0.11	0.08	0.05-0.25	0.05	0.03	0.02-0.09	0.07	0.07	0-0.16	0.13	-	0-0.13
Cyfluthrin [a]	0.29	0.08	0-0.41	0.08	0.01	0-0.08	ND	-	-	0.03	-	0-0.03
Deltamethrin [a]	ND	-	-	ND	-	-	0.10	-	-	0.05	- 0.02	0-0.06
Cypermethrin [a]	1.34	0.32	1.34-2.41	1.70	0.43	1.34-2.41	1.52	0.30	1.19-1.91	2.11	0.90	1.41-3.39

[a] - Synthetic Pyrethroids , Limit of detection for all pesticides = 0.01 mg/kg, ND=not detected, SD =standard deviation,

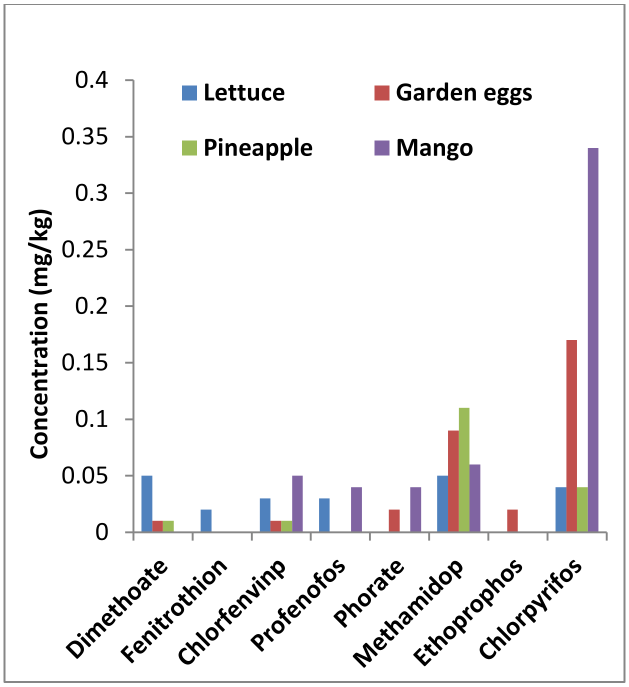


Fig 4.13a: Mean concentration levels of organophosphates in fruits and vegetables from the Central Region.

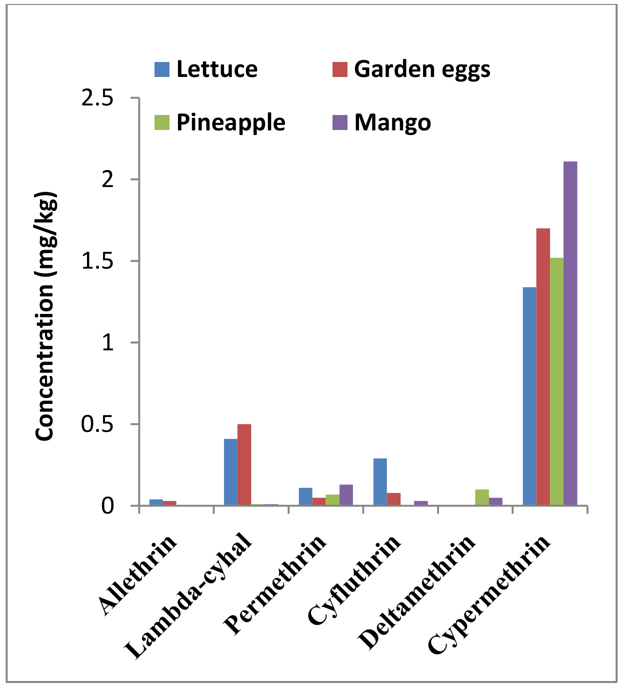


Fig 4.13b: Mean concentration levels of synthetic pyrethroids in fruits and vegetables from the Central Region.

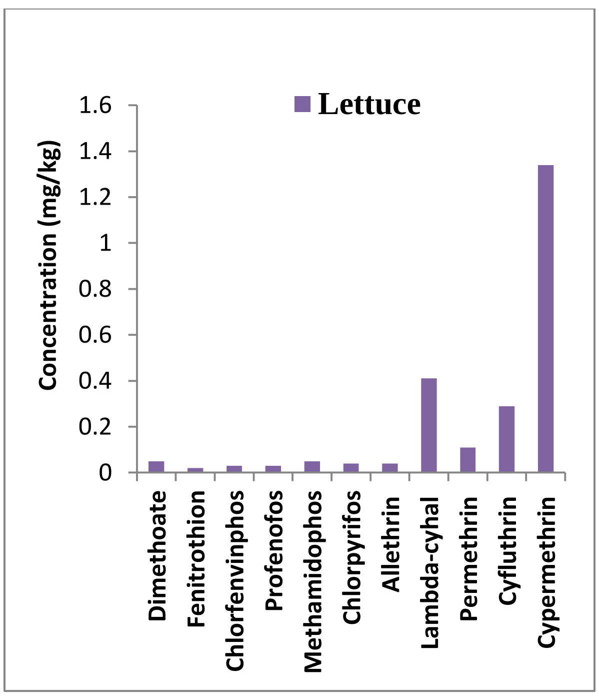


Fig 4.13c: Mean concentration levels of organophosphates and synthetic pyrethroids in lettuce from the Central Region.

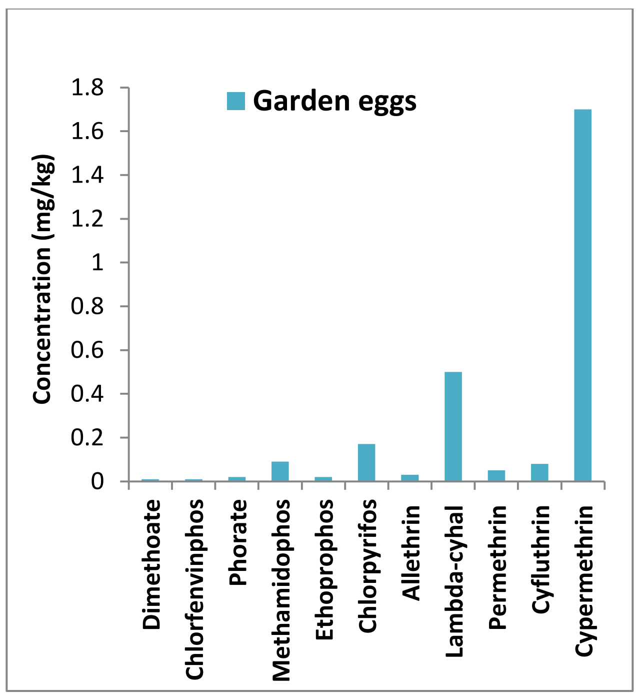


Fig 4.13d: Mean concentration levels of organophosphates and synthetic pyrethroids in garden eggs from the Central Region.

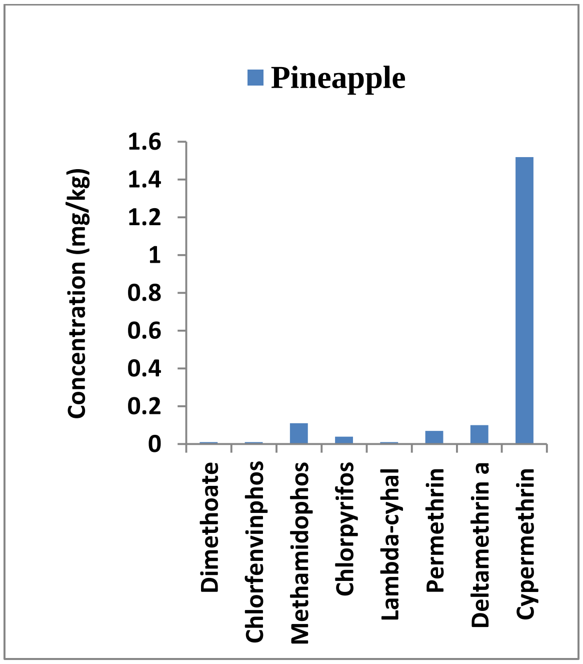


Fig 4.13e: Mean concentration levels of organophosphates and synthetic pyrethroids in pineapple from the Central Region.

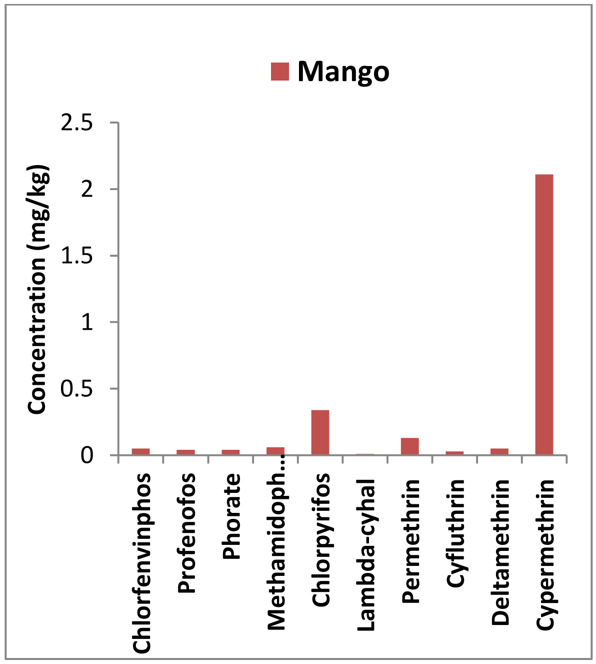


Fig 4.13f: Mean concentration levels of organophosphates and synthetic pyrethroids in mango from the Central Region.

4.14: Occurrence and distribution of organophosphates and synthetic pyrethroids in samples from the Eastern Region

The results obtained from the analysis of samples from the Eastern Region are shown in table 4.14 and graphically represented in Fig4.14a-4.14f. Total samples analyzed show the presence of eleven organophosphates and five synthetic pyrethroids. This region recorded the highest number organophosphate pesticide residues. The different organophosphate pesticides detected were dimethoate, pirimiphos-methyl, malathion, fenitrothion, parathion ethyl, chlorfenvinphos, profenofos, methamidophos, chlorpyrifos, phorate and ethoprophos.

The most predominant organophosphate pesticide in lettuce, garden eggs, pineapple and mango was chlorpyrifos with mean concentrations of 0.19 mg/kg 0.14 mg/kg 0.08 mg/kg 0.30 mg/kg (Fig4.14a-4.14f). The high levels of chlorpyrifos in most samples suggest that farmers in this region use a lot of chlorpyrifos as pesticides. These results confirm earlier findings by Ntow *et al* (2005) that a lot of farmers in Ghana use Dursban (chlorpyrifos) in vegetable production especially lettuce and cabbage.

The least predominant organophosphate pesticides in lettuce was obtained for dimethoate, parathion ethyl, chlorfenvinphos and phorate all recording a mean concentration of 0.02 mg/kg (Fig 4.14c). Malathion was not detected in any of the lettuce samples analyzed. The lowest concentration of organophosphates pesticides in garden eggs was observed for ethoprophos with a mean concentration of 0.02 mg/kg (Fig 4.14d). Chlorfenvinphos was not detected in any of the garden egg samples analyzed while pirimiphos-methyl concentration was below the detection limit.

Again the lowest concentration of organophosphate pesticides in pineapple was recorded for phorate and dimethoate with a mean concentration of 0.01 mg/kg (Fig 4.14e). Comparably, these values are not different from those detected in pineapple sampled from the Central Region suggesting similar route of contamination. Pirimiphos-methyl, Chlorfenvinphos and profenofos were not detected in any of the pineapple samples analyzed indicating that farmers in this region do not use these pesticides in pineapple production or could be to the fact that farmers are seriously following extension officer's guidelines as regards pesticide application. In mango, the lowest concentration of organophosphates pesticides was recorded for phorate with a mean concentration of 0.01 mg/kg (Fig 4.14e). Generally most organophosphates pesticides recorded high concentrations except phorate and methamidophos with total mean concentrations of 0.02 mg/kg and 0.04 mg/kg respectively in all samples. The concentration of the organophosphates in the fruits and vegetables varied significantly ($p < 0.05$ or $p = 0.013$, appendix b).

Also, five synthetic pyrethroids pesticides were detected and they include lambda-cyhalothrin, permethrin, cyfluthrin, deltamethrin and cypermethrin. Allethrin and bifenthrin were not detected. From the results, it was observed that high levels of synthetic pyrethroids were detected except for deltamethrin, with a mean concentration of 0.04 mg/kg. The highest concentration of synthetic pyrethroids in lettuce, garden eggs, pineapple and mango was cypermethrin with mean concentrations of 1.55 mg/kg, 0.67 mg/kg, 1.52 mg/kg and 1.35 mg/kg respectively. (Fig 4.14b and 4.14e). Interestingly, this observation is no different from that of the Central Region.

The lowest concentration of synthetic pyrethroid in lettuce was obtained for lambda-cyhalothrin with a mean concentration of 0.05 mg/kg (Fig 4.14a). Deltamethrin was not detected in any of the lettuce samples analyzed. The lowest concentration of synthetic pyrethroid in garden eggs was observed for allethrin with a mean concentration of 0.03 mg/kg (Fig 4.14c). Lambda-cyhalothrin was not detected in any of the garden eggs samples analyzed. Statistically, the difference in concentration of synthetic pyrethroids in the samples of lettuce, garden eggs, pineapple and mango was not significant ($p > 0.05$ or $p = 0.938$, appendix c)

In pineapple, the lowest concentration of synthetic pyrethroid was observed for cyfluthrin with a mean concentration of 0.01 mg/kg (Fig 4.14e). Lambda-cyhalothrin was not detected in any of the pineapple samples analyzed while allethrin concentration was below detection limit.In mango; the lowest concentration of synthetic pyrethroid was recorded for deltamethrin with a mean concentration of 0.04 mg/kg (Fig 4.14f). This observation was not different from concentration levels of lambda-cyhalothrin recorded in samples from the Greater Accra Region.

The absence of lambda-cyhalothrin in both pineapple and mango suggest proper use of these pesticides or farmers do not use these pesticides in pineapple and mango production in this region. In addition, the high levels of organophosphates and synthetic pyrethroids in samples from the Eastern Region suggests that farmers who supply vegetables and fruits to these markets use organophosphates and synthetic pyrethroids in significant quantities.

Table 4.14: Concentrations (mg/kg) of organophosphates and synthetic pyrethroids in samples from the Eastern Region

Pesticide	Lettuce			Garden eggs			Pineapple			Mango		
	Mean	*SD*	*Range*	*Mean*	*SD*	*Range*	*Mean*	*SD*	*Range*	*Mean*	*SD*	*Range*
Dimethoate	0.02	0.01	0-0.02	0.03	0.01	0-0.05	0.01	-	-	0.08	0.06	0-0.10
Pirimiphos-m	0.04	-	0-0.04	<0.01	-	-	ND	-	-	0.09	-	0-0.15
Malathion	ND	-	-	0.13	-	0-0.13	0.2	-	0-0.02	0.23	-	0-0.23
Fenitrothion	0.04	0.02	0-0.05	0.02	-	0-0.02	0.02	-	0-0.02	0.07	-	0-0.07
Parathion ethyl	0.02	-	-	0.04	-	0-0.04	0.04	0.05	0-0.06	0.05	0.07	0-0.08
Chlorfenvinphos	0.02	0.01	0-0.02	ND	-	-	ND	-	-	0.23	0.56	0-0.42
Profenofos	0.05	0.01	0-0.06	0.03	0.03	0-0.06	ND	-	0-0.03	0.13	0.02	0-0.13
Phorate	0.02	-	0-0.02	0.03	0.01	0-0.04	0.01	-	0-0.01	0.01	-	0-0.01
Methamidophos	0.04	-	0-0.04	0.04	-	0-0.06	0.03	0.02	0-0.04	0.05	0.01	0-0.06
Ethoprophos	0.07	-	0-0.07	0.02	-	0-0.02	0.22	0.56	0-0.35	0.26	-	-
Chlorpyrifos	0.19	0.57	0.04-0.42	0.14	055	0.02-0.24	0.08	0.30	0.04-0.13	0.3	0.15	0-0.56
Allethrin [a]	0.07	0.03	0-0.12	0.03	0.01	0-0.03	<0.01	-	-	0.18	0.05	0-0.24
Lambda-cyhal [a]	0.05	0.01	0-0.07	<0.01	-	-	ND	-	-	ND	-	-
Permethrin [a]	0.17	0.45	0-0.37	0.09	0.34	0-0.13	0.23	0.04	0-0.16	0.13	0.06	0-0.15
Cyflu [a]	0.15	0.32	0-0.67	0.12	0.41	0.02-0.35	0.01	-	0-0.01	0.08	-	-
Deltamethrin [a]	ND	-	-	0.04	-	0-0.04	0.04	-	0-0.04	0.04	0.05	0-0.08
Cypermethrin [a]	1.55	0.41	0.89-2.56	0.67	0.38	0.06-0.32	1.52	0.34	1.18-1.86	1.35	0.45	0-61

[a] - Synthetic Pyrethroids , Limit of detection for all pesticides = 0.01 mg/kg, ND=not detected, SD =standard deviation,

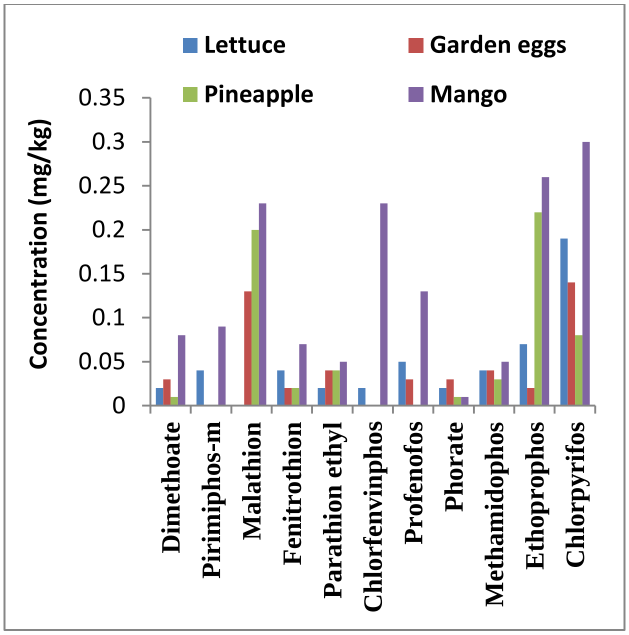


Fig 4.14a: Mean concentration levels of organophosphates in fruits and vegetables from the Eastern Region.

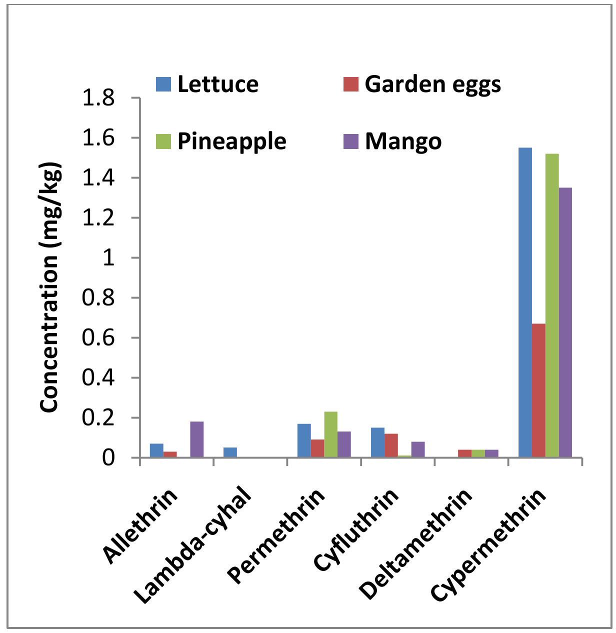


Fig 4.14b: Mean concentration levels of synthetic pyrethroids in fruits and vegetables from the Eastern Region.

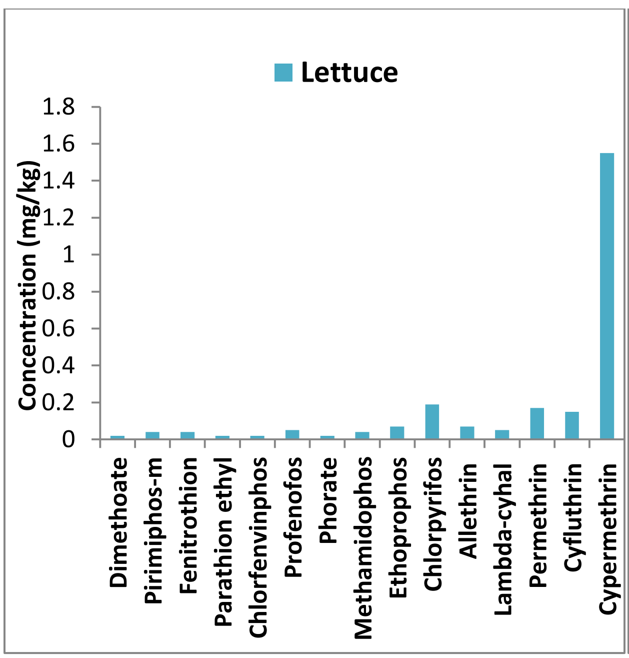


Fig 4.14c: Mean concentration levels of organophosphates and synthetic pyrethroids in lettuce from the Eastern Region.

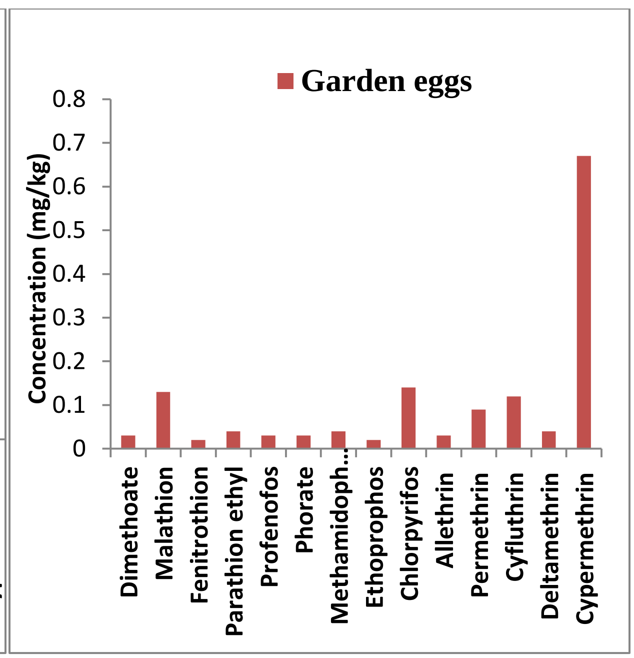


Fig 4.14d: Mean concentration levels of organophosphates and synthetic pyrethroids in garden eggs from the Eastern Region.

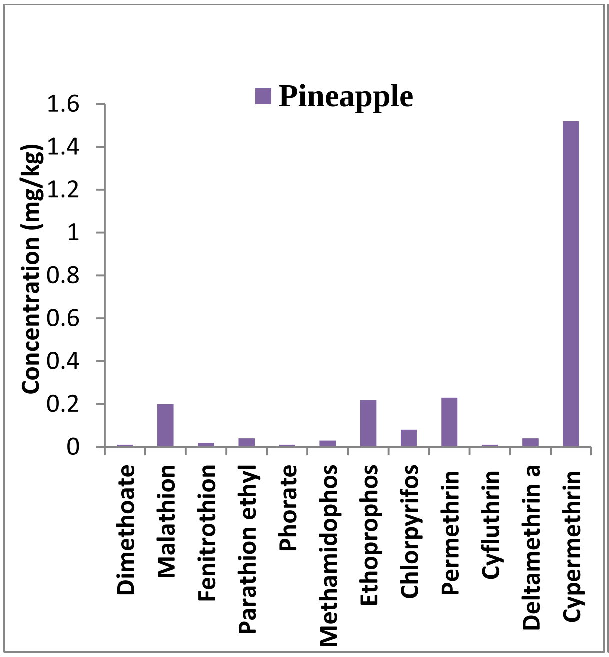


Fig 4.14e: Mean concentration levels of organophosphates and synthetic pyrethroids in pineapple from the Eastern Region.

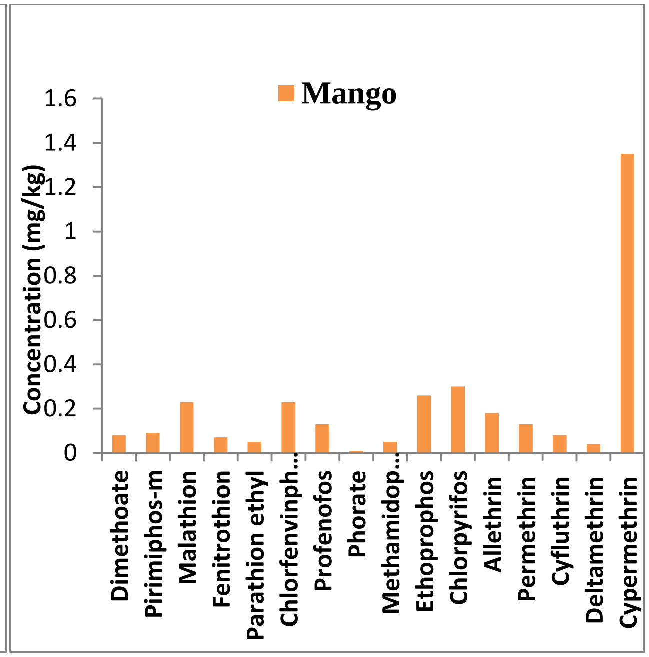


Fig 4.14f: Mean concentration levels of organophosphates and synthetic pyrethroids in mango from the Eastern Region.

4.15: Occurrence and distribution of organophosphates and synthetic pyrethroids in samples from all the sampling areas

Fig 4.15a-4.15j show the overall distribution of the various organophosphates and synthetic pyrethroids levels detected in lettuce, garden eggs, pineapple, mango from the various sampling areas. Table 4.15 also shows the mean concentration levels of organophosphates and synthetic pyrethroids in samples from all sampling areas. In all, a total of eighteen pesticides including eleven organophosphates and seven synthetic pyrethroids were detected in the samples. The eleven organophosphates comprise dimethoate, pirimiphos-methyl, malathion, fenitrothion, parathion ethyl, chlorfenvinphos, profenofos, methamidophos, chlorpyrifos, phorate and ethoprophos. The seven different synthetic pyrethroid pesticides detected were allethrin, lambda-cyhalothrin, permethrin, cyfluthrin, deltamethrin, cypermethrin and bifenthrin.

The highest concentration of organophosphate in lettuce was recorded for malathion with a mean concentration of 0.26 mg/kg while the lowest concentration was recorded for parathion ethyl and phorate with a mean concentration of 0.02 mg/kg (Fig 4.15c). In garden eggs, the highest concentration of organophosphate was obtained for chlorpyrifos with a mean concentration of 0.25 mg/kg while the lowest concentration was recorded for ethoprophos with a mean concentration of 0.02 mg/kg (Fig 4.15d). The highest concentration of organophosphate in pineapple was obtained for ethoprophos with a mean concentration of 0.22 mg/kg while the lowest concentration was phorate with a mean concentration of 0.01 mg/kg (Fig 4.15e). In mango, the highest concentration of organophosphate was observed for pirimiphos-methyl with a mean concentration of 0.32 mg/kg while the lowest concentration was observed for phorate with a mean concentration of 0.02 mg/kg (Fig 4.15f). The concentration of the organophosphates in the fruits and vegetables varied significantly among the sampling areas ($p < 0.05$ or $p = 0.039$, appendix d).

Among the synthetic pyrethroids, cypermethrin levels were all highest in lettuce, garden eggs, pineapple and mango with mean concentrations of 0.97 mg/kg, 0.93 mg/kg, 1.08 mg/kg and 1.27 mg/kg respectively (Fig 4.15g - 4.15j). The lowest concentration of synthetic pyrethroids in lettuce and garden eggs was recorded for allethrin with mean concentration of 0.06 mg/kg and 0.03 mg/kg respectively while the lowest concentration in pineapple and mango was lambda-cyhalothrin with a mean concentration of 0.01 mg/kg respectively (Fig 4.15g - 4.15j). Bifenmethrin was not detected in any of the samples analyzed from all the three regions. The difference in concentrations of synthetic pyrethroids in the samples of lettuce, garden eggs, pineapple and mango from all the sampling areas was not significant (statistically, $p>0.05$ or $p= 0.996$, appendix d).

The most occurring organophosphate in samples was chlorpyrifos while the most occurring synthetic pyrethroid was cypermethrin with mean concentrations of 0.15 mg/kg and 1.10 mg/kg respectively. Comparing these values with the maximum residue limits (MRLs) set forth by the FAO/WHO Codex Alimentarius Commission, cypermethrin and chlorpyrifos exceeds the limit of 0.05 mg/kg for both pesticides.

The concentrations of lamda-cyhalothrin in lettuce range from 0.01-0.18 mg/kg while that of chlopyrifos range from 0.01-0.19 mg/kg. These values are far lower than those reported by Ntow (Ntow *et al*, 2005) who obtained 0.01-1.4 mg/kg and 0.4-6.0 mg/kg for lamda-cyhalothrin and chlorpyrifos respectively. About 90% of cypermethrin (marketed as Ammo or Cymbush) manufactured worldwide is used to combat pests feeding on crops (WHO, 1989) and is therefore its high levels in fruits and vegetables. From the results, it can be deduced that some organophosphates and synthetic pyrethroids levels detected in lettuce, garden eggs, pineapple, mango from the various sampling areas were above the maximum residue limits (MRLs) set forth by the FAO/WHO Codex Alimentarius Commission.

Generally, the high frequent and high levels of organophosphates and synthetic pyrethroids in the fruits and vegetables analyzed is an indication that most of the modern pesticides used by farmers in Ghana contain these high organophosphates and synthetic pyrethroids and farmers may misuse or misapply them causing serious contamination.

Table 4.15: Concentrations (mg/kg) of organophosphates and synthetic pyrethroids in samples from all the sampling areas

Pesticide	Lettuce			Garden eggs			Pineapple			Mango		
	Mean	*SD*	*Range*	*Mean*	*SD*	*Range*	*Mean*	*SD*	*Range*	*Mean*	*SD*	*Range*
Dimethoate	0.03	0.03	0-0.06	0.03	0.02	0-0.05	0.02	0.34	0-0.05	0.06	0.07	0-0.10
Pirimiphos-m	0.07	-	0-0.07	0.03	-	0-0.03	0.05	-	0-0.05	0.32	-	0-0.32
Malathion	0.26	-	0-0.26	0.13	-	0-0.13	0.12	0.01	0-0.20	0.18	0.03	0-0.23
Fenitrothion	0.05	0.04	0-0.13	0.07	0.32	0-0.12	0.03	0.02	0-0.05	0.06	0.01	0-0.07
Parathion ethyl	0.02	-	0-0.02	0.04	-	0-0.04	0.04	0.06	0-0.06	0.05	0.02	0-0.08
Chlorfenvinp	0.03	0.6	0-0.04	0.1	0.20	0-0.19	0.03	0.34	0-0.09	0.10	0.09	0-0.42
Profenofos	0.03	0.02	0-0.06	0.03	0.04	0-0.06	0.03	-	0-0.03	0.06	0.03	0-0.13
Phorate	0.02	-	0-0.02	0.03	0.02	0-0.04	0.01	-	0-0.01	0.03	0.01	0-0.04
Methamidophos	0.06	0.43	0-0.08	0.05	0.03	0-0.11	0.07	0.03	0-0.11	0.30	0.03	0-0.78
Ethoprophos	0.07	-	0-0.7	0.02	-	0-0.02	0.22	0.33	0-0.50	0.26	-	0-0.26
Chlorpyrifos	0.08	0.04	0-0.42	0.25	0.02	0-1.36	0.06	-	0-0.06	0.22	0.06	0-0.34
Allethrin [a]	0.06	0.21	0-0.12	0.03	0.04	0-0.08	0.04	0.57	0-0.60	0.18	0.01	0-0.24
Lambda-cyhal [a]	0.18	0.04	0-0.35	0.19	0.67	0-1.17	0.01	-	0-0.01	0.01	-	0-0.01
Permethrin [a]	0.1	0.50	0-0.37	0.07	0.43	0-0.13	0.15	0.01	0-0.16	0.13	0.01	0-0.15
Cyfluthrin [a]	0.16	0.42	0-1.30	0.08	0.42	0-1.6	0.08	0.02	0-1.19	0.05	0.01	0-0.08
Deltamethrin [a]	<0.01	-	-	0.04	-	0-0.04	0.07	0.02	0-0.10	0.05	0.06	0-0.08
Cypermethrin [a]	0.97	0.45	0-2.56	0.93	0.50	0-2.41	1.08	0.35	0-1.91	1.27	0.50	0-3.39
Bifenthrin [a]	<0.01	-	-	0.13	-	0-0.13	ND	-	-	0.05	-	0-0.05

[a] - Synthetic Pyrethroids , Limit of detection for all pesticides = 0.01 mg/kg, ND=not detected, SD =standard deviation,

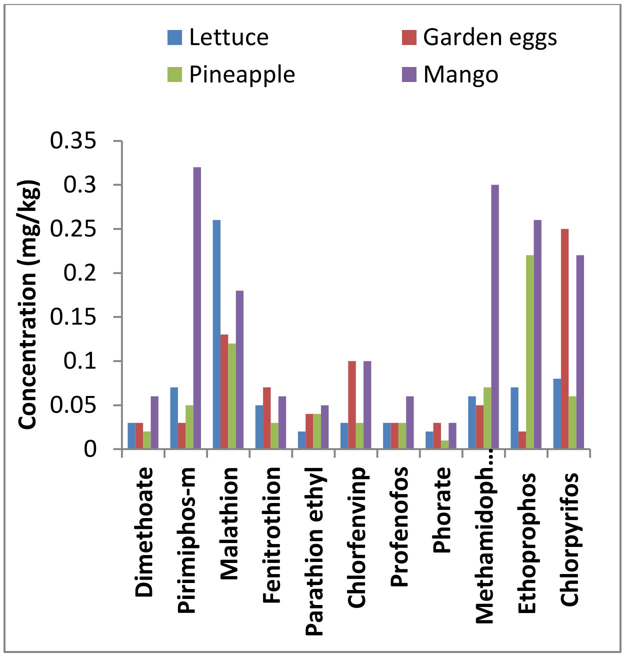


Fig 4.15a: Mean concentration levels of organophosphates in fruits and vegetables from all the sampling areas.

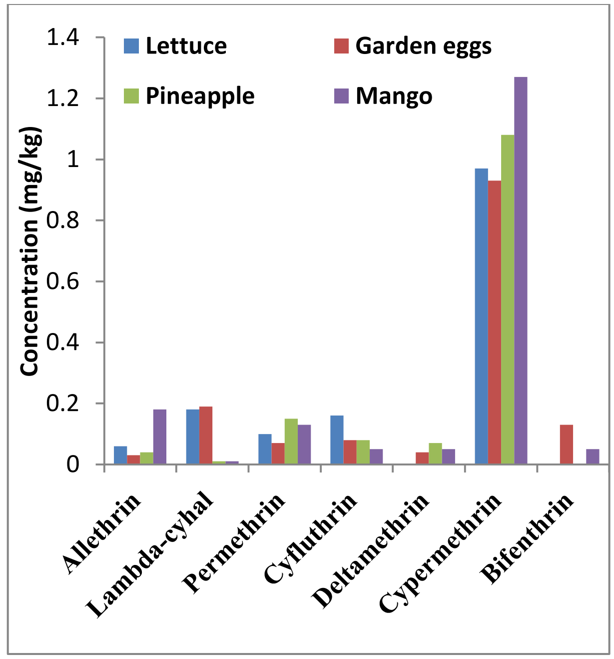


Fig 4.15b: Mean concentration levels of synthetic pyrethroids in fruits and vegetables from all the sampling areas.

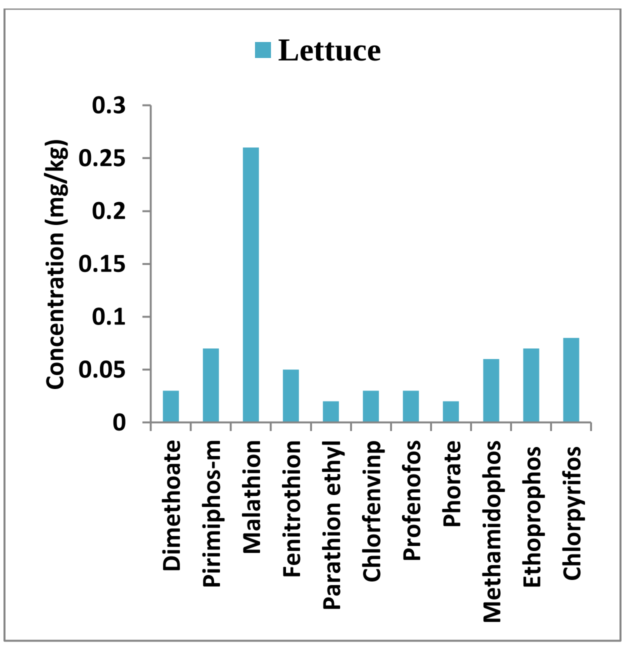


Fig 4.15c: Mean concentration levels of organophosphates in lettuce from all the sampling areas.

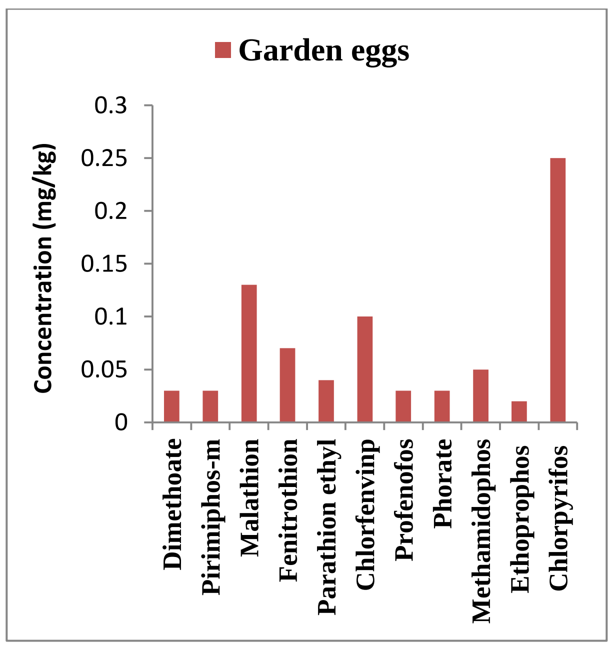


Fig 4.15d: Mean concentration levels of organophosphates in garden eggs from all the sampling areas.

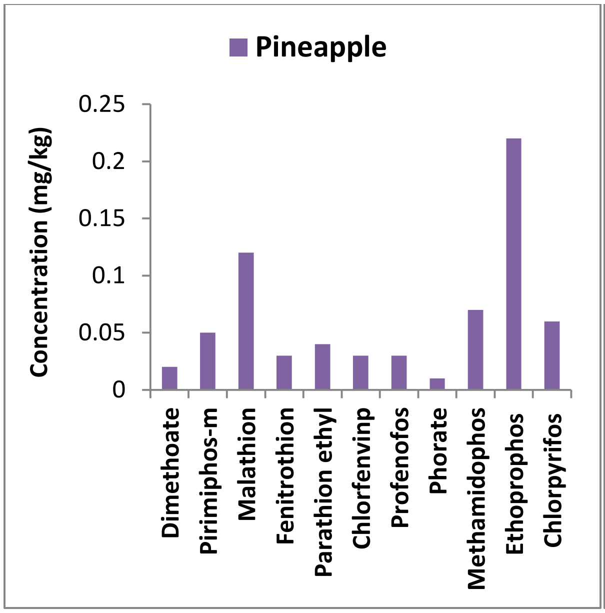


Fig 4.15e: Mean concentration levels of organophosphates in pineapple from all the sampling areas.

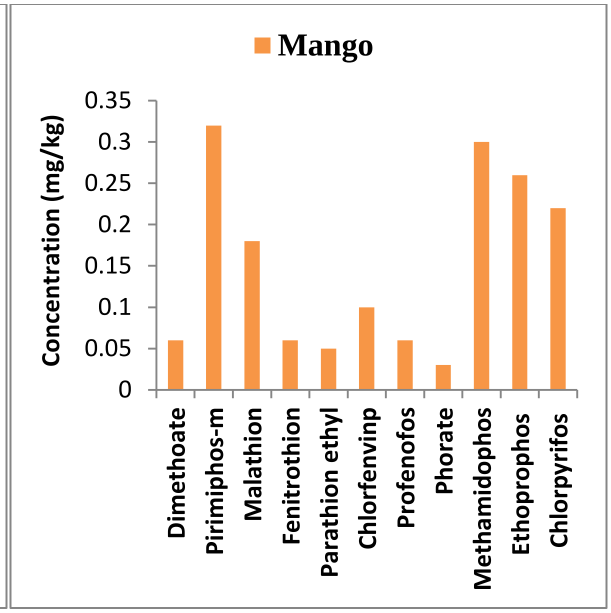


Fig 4.15f:Mean concentration levels of organophosphates in mango from all the sampling areas.

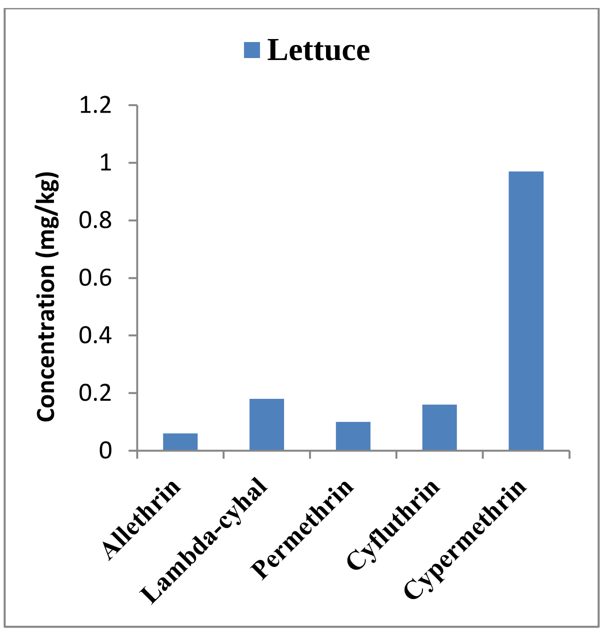


Fig 4.15g: Mean concentration levels of synthetic pyrethroids in lettuce from all the sampling areas.

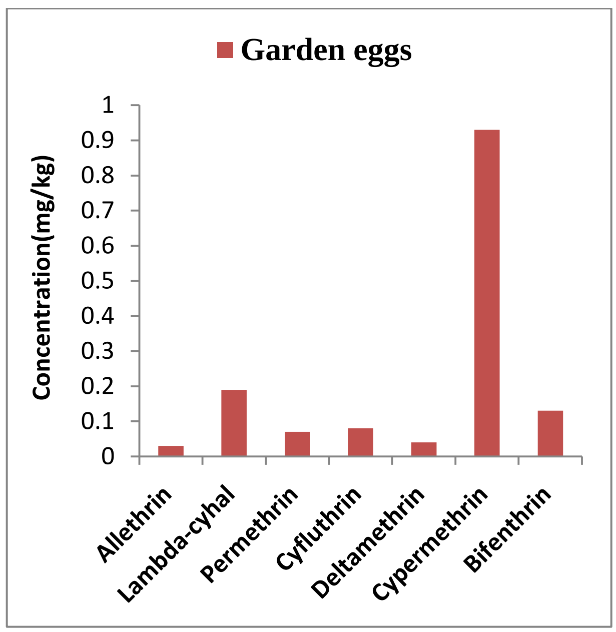


Fig 4.15h: Mean concentration levels of synthetic pyrethroids in garden eggs from all the sampling areas.

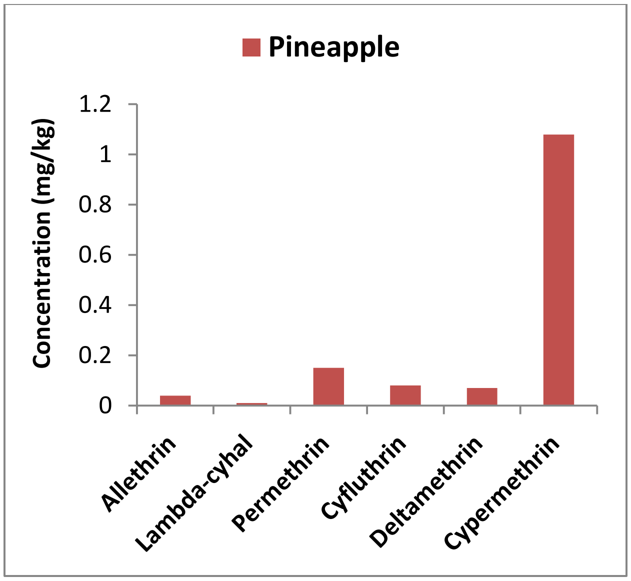


Fig 4.15i: Mean concentration levels of synthetic pyrethroids in pineapple from all the sampling areas.

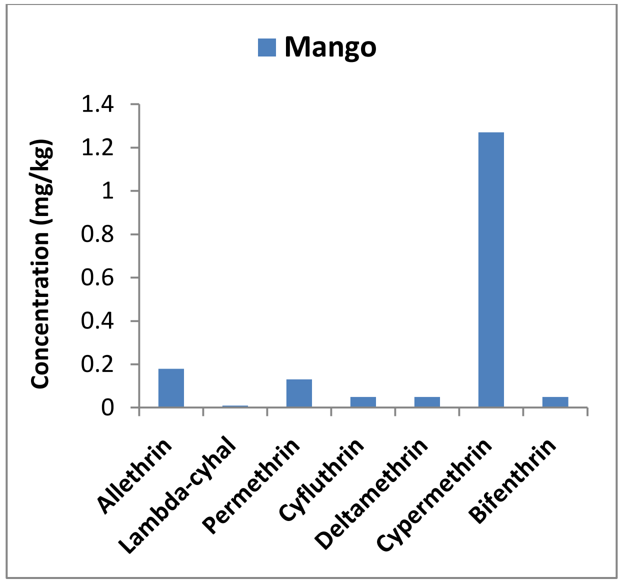


Fig 4.15j: Mean concentration levels of synthetic pyrethroids in mango from all the sampling areas.

4.16: Occurrence and distribution of organochlorine in samples from the Greater Accra Region

The values in table 4.16 indicates the mean, standard deviation and the range of values obtained from the analysis done on all samples from the Greater Accra Region. A total of seven organochlorine pesticides were detected in the samples analyzed. Delta –HCH, gamma HCH, gamma-chlordane, alpha-endosulfan, dieldrin, endrin, p,p'-DDT, methoxychlor were all not detected in any of the samples from the Greater Accra Region. The seven pesticides which were detected were beta-HCH, gamma- HCH, heptachlor, p,p'-DDE, beta-endosulfan and endosulfan sulfate.

The highest mean concentration of 0.16 mg/kg was obtained for gamma HCH, in lettuce followed by a concentration of 0.12 mg/kg for endosulfan s and gamma HCH in pineapple and lettuce respectively. The concentration of the organochlorines in the fruits and vegetables did not vary significantly (statiscally, $p > 0.05$ or $p = 0.606$, appendix a).

Also it can a be observed that gamma HCH (lindane) was found in all the four samples with relatively higher mean concentrations levels of 0.16 mg/kg in lettuce, 0.12 mg/kg in garden eggs, 0.07 mg/kg in pineapple, and 0.08 mg/kg in mango respectively. These values were however higher than the mean concentrations of 0.01 mg/kg in tomato and 0.04 mg/kg in pawpaw detected by Bempah and Donkor, 2010 from some market sites in Accra.. Also comparing the results from the present study with a similar one carried out by Beena Kumari in India where gamma-HCH range from not -detected to 0.02 mg/kg in okro, then the market fruits and vegetables analyzed were highly contaminated.

This occurrence predicts the extensive use of lindane by farmers who supply foodstuffs to Accra market centers. This high concentrations and wide distribution of lindane confirms earlier findings made by Bempah and Donkor, that lindane is widely used by farmers in Ghana (Bempah and Donkor, 2010). The other two isomers (beta-HCH and delta HCH) which are not insecticidal, only beta-HCH recorded mean concentrations of 0.03 mg/kg and 0.02 mg/kg in pineapple and mango respectively**.** Though p,p' -DDT was not detected in any of the samples, the degradation product p,p'-DDE was found in lettuce and pineapple with mean concentrations of 0.08 mg/kg and 0.05 mg/kg respectively. Since p,p' –DDT itself was not detected, the detection of p,p'-DDE in lettuce and pineapple may be due to previous use of p,p' –DDT rather than current use. In the environment, DDT can be broken down to its metabolites such as DDE. This may occur as result of dehydrohalogenation (loss of HCl) of DDT. Thus p,p' –DDT can be found in the environment as the parent p,p' –DDT or its metabolites such as DDE and DDD. While DDT may persist in the environment for about twelve years before breaking down, its metabolites DDE can persist for a much longer period **(**Cooke and Stinger, 1982; Botwe *et al*, 2007)

Table 4.16 Concentrations (mg/kg) of organochlorine pesticide residue detected in samples from the Greater Accra Region.

Pesticide	Lettuce			Garden eggs			Pineapple			Mango		
	Mean	*SD*	*Range*	*Mean*	*SD*	*Range*	*Mean*	*SD*	*Range*	*Mean*	*SD*	*Range*
***Beta*-HCH**	ND	-	-	ND	-	-	0.03	0.01	0-0.03	0.02	-	0-0.02
***Gamma*- HCH**	0.16	0.06	0.10-0.26	0.12	0.06	0-0.17	0.07	0.04	0-0.1	0.08	0.01	0-0.03
***Delta*- HCH**	ND	-	-	ND	-	-	ND	-		ND	-	-
Heptachlor	0.02	-	0-0.02	0.02	-	-	0.02	-	0-0.02	0.02	-	0-0.02
Aldrin	0.01	-	0-0.01	ND	-	-	0.04	-	0-0.04	0.04	0.01	0-0.06
***G*-chlordane**	ND	-	-	ND	-	-	ND	-	-	ND	-	-
A-endosulfan	ND	-	-	ND	-	-	ND	-	-	ND	-	-
P,p'-DDE	0.08	0.01	0--0.08	ND	-	-	0.05	0.03	0.-0.08	ND	-	-
Dieldrin	ND	-	-	ND	-	-	ND	-	-	ND	-	-
Endrin	ND	-	-	ND	-	-	ND	-	-	ND	-	-
***B*-endosulfan**	0.01	-	0--0.01	<0.01	-	-	0.01	-	0-0.01	<0.01	-	-
P,p'-DDT	ND	-	-	ND	-	-	ND	-	0	ND	-	-
Endosulfan S	0.04	0.01	0-0.04	ND	-	-	0.12	-	0-0.12	0.01	-	0-0.01
Methoxychlor	ND	-	-	ND	-	-	ND	-	-	ND	-	0

Limit of detection for all pesticides = 0.01 mg/kg, ND=not detected, SD =standard deviation

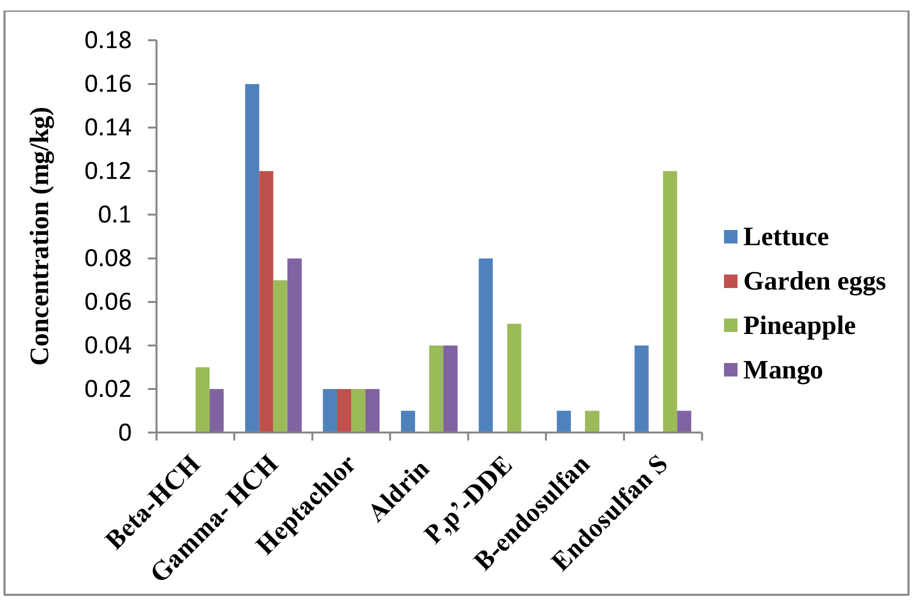


Fig 4.16a: Mean concentration levels of organochlorine pesticides in fruits and vegetables from the Greater Accra Region.

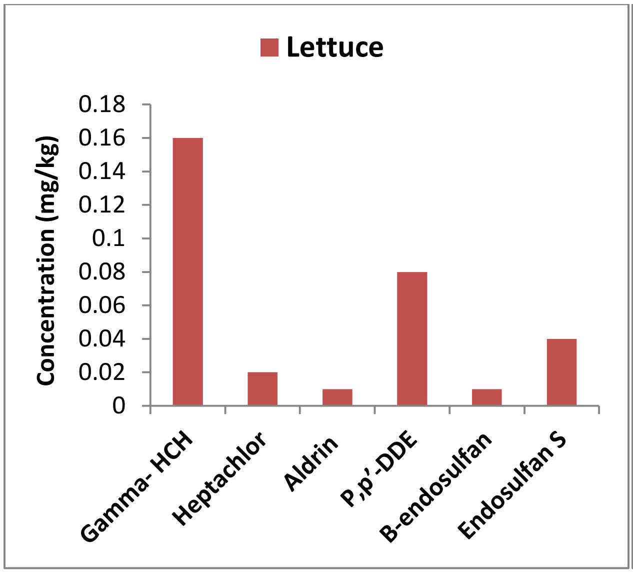


Fig 4.16b: Mean concentration levels of Organochlorine pesticides in lettuce from the Greater Accra Region.

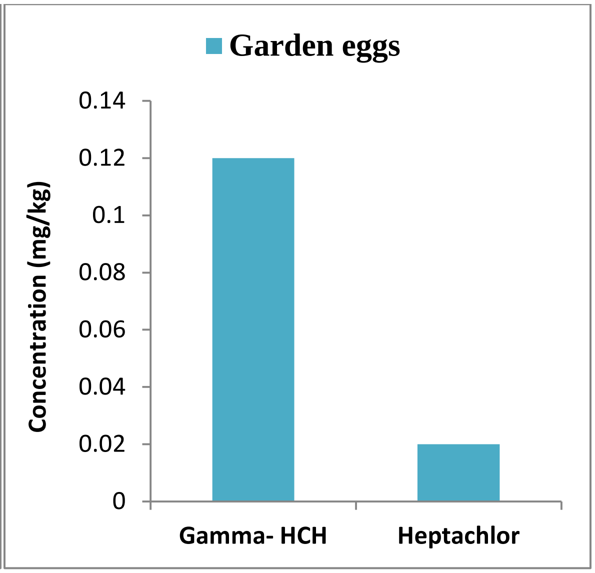


Fig 4.16c: Mean concentration levels of organochlorine pesticides in garden egg from the Greater Accra Region.

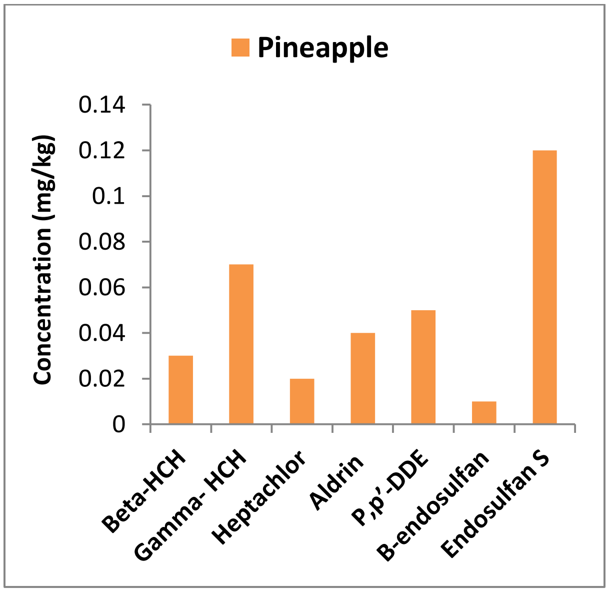


Fig 4.16d: Mean concentration levels of Organochlorine pesticides in pineapple from the Greater Accra Region.

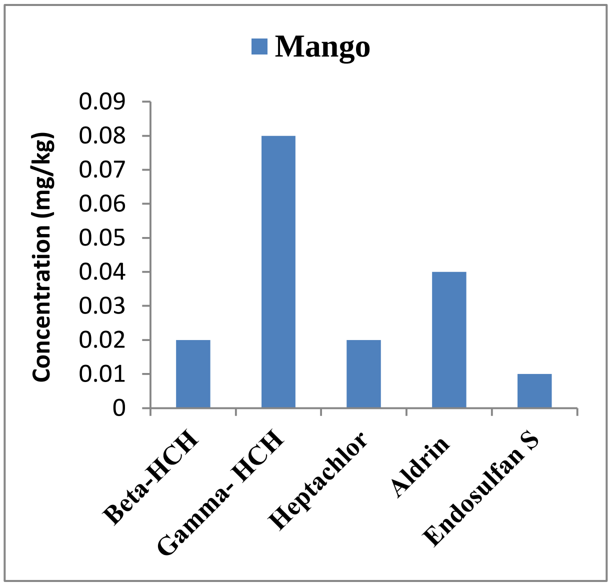


Fig 4.16e: Mean concentration levels of organochlorine pesticides in mango from the Greater Accra Region.

4.1.7: Occurrence and distribution of Organochlorine in samples from the Central Region

Table 4.17 and Fig 4.17a-4.17e show the various mean concentration of organochlorine pesticide residues detected in samples from the Central Region. In all, a total of eleven organochlorine pesticides were detected and they include beta-HCH, gamma- HCH, heptachlor, aldrin, alpha-endosulfan, p,p'-DDE, dieldrin, beta-endosulfan , p,p'-DDT and endosulfan sulfate. Delta-HCH**,** endrin and methoxychlor were not detected in any of the samples. DDT was absent in all samples except in pineapple which recorded a mean concentration of 0.02 mg/kg. It is interesting to note that in Central Region, the sample which recorded a greater no of organochlorine pesticides residues was lettuce followed by garden eggs with pineapple and mango recording fewer number of organochlorine pesticides residues.

Heptachlor was detected in lettuce and garden eggs but was absent in pineapple and mango with mean concentrations of 0.05 mg/kg and 0.02 mg/kg in lettuce and garden eggs respectively. The highest aldrin mean concentration of 0.31 mg/kg was obtained in pineapple while the lowest was obtained in mango with concentration of 0.01 mg/kg. Alpha endosulfan ranged from 0-0.09 mg/kg in lettuce, 0-0.02 mg/kg in garden eggs, 0-0.06 mg/kg in mango. The alpha endosulfan mean concentration values in lettuce and garden eggs were 0.09 mg/kg and 0.21 mg/kg respectively. Interestingly, these values are not different from its isomer endosulfan sulfate which recorded a mean of 0.09 mg/kg in lettuce and 0.03 mg/kg in garden eggs. The difference in concentration of organochlorines in the samples of lettuce, garden eggs, pineapple and mango was not significant (statistically, $p>0.05$ or $p= 0.148$, appendix b).

Out of the total samples analyzed, only one sample showed the presence of p,p-DDT. The absence of p,p-DDT in most of the samples analyzed is not surprising since DDT has been banned and no more in use. The highest concentration of p,p-DDT was detected in pineapple with a mean concentration of 0.02 mg/kg but its metabolite p,p-DDE recorded no detection in pineaple suggesting current pesticide use contamination and not from previous use. Again even though p,p-DDT was not detected in lettuce and mango, its degradation product p,p-DDE was detected in lettuce and mango with mean concentrations of 0.04 mg/kg and 0.05 mg/kg respectively. This finding is an indication of the rate of degradation of the original p,p-DDT to its metabolite p,p-DDE.

.Just as gamma- HCH recorded the highest mean concentration in lettuce in greater Accra so did gamma- HCH record the highest in Central Region samples with concentration of 0.16 mg/kg in lettuce. The high level of gamma- HCH detected in samples from the Central Region suggests that farmers in those regions use lindane in vegetable and fruit production

Table 4.17: **Concentrations (mg/kg) of oganochlorine pesticide residue detected in samples from the Central Region**

Pesticide	**Lettuce**			**Garden eggs**			**Pineapple**			**Mango**		
	Mean	***SD***	***Range***	***Mean***	***SD***	***Range***	***Mean***	***SD***	***Range***	***Mean***	***SD***	***Range***
***Beta*-HCH**	0.13	-	0-0.13	ND	-	-	ND	-	-	ND	-	-
***Gamma*- HCH**	0.53	-	0-0.53	ND	-	-	0.07	-	-	0.09	0.04	0-0.09
***Delta*- HCH**	ND	-		ND	-	-	ND	-	-	ND	-	-
Heptachlor	0.05	-	0-0.05	0.02	-	0-0.02	ND	-	-	ND	-	-
Aldrin	0.06	0.05	0.01-0.13	0.02	0.01	0..01-0.03	0.31	-	-	0.01	-	0-0.01
***G*-chlordane**	ND	-	-	0.01	-	0-0.01	ND	-	-	ND	-	-
A-endosulfan	0.09	-	0-0.09	0.02	-	0-0.02	ND	-	-	0.04	0.03	0-0.06
P,p'-DDE	0.04	-	0-0.04	0.01	-	0-0.01	ND	-	--	0.05	-	0-0.05
Dieldrin	0.01	-	0-0.01	0.01	-	0-0.01	ND	-	--	ND	-	-
Endrin	ND	-	-	ND	-	-	ND	-		ND	-	-
***B*-endosulfan**	0.01	-	0-0.01	ND	-	-	ND	-	-	ND	-	-
P,p'-DDT	ND	-	-	ND	-	-	0.02	-	-	ND	-	-
Endosulfan S	0.09	-	0-0.09	0.03	0.01	0-0.04	ND	-	-	ND	-	-
Methoxychlor	ND	-	-	ND	-	-	ND	-	-	ND	-	-

Limit of detection for all pesticides = 0.01 mg/kg, ND=not detected, SD =standard deviation

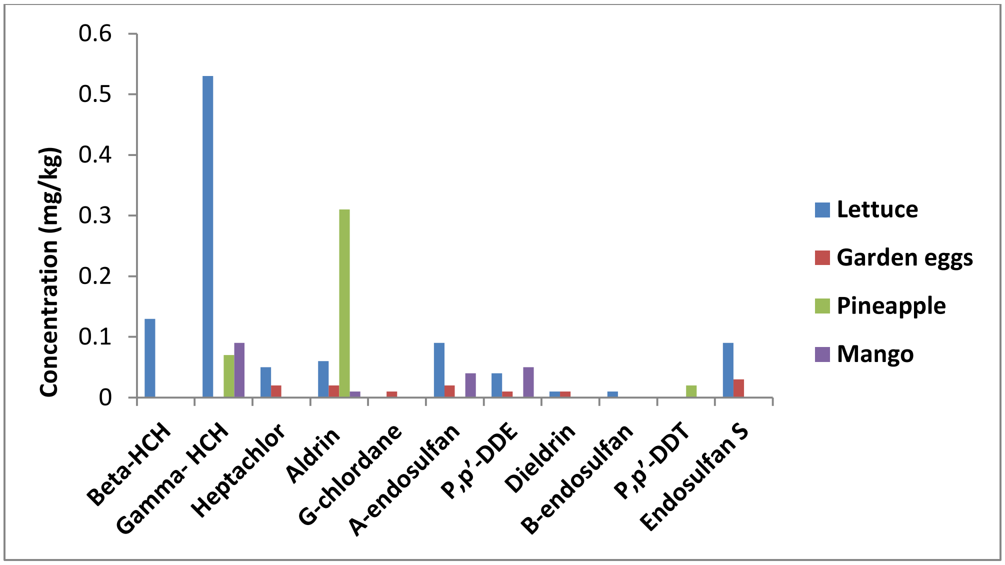


Fig 4.17a: Mean concentration levels of organochlorine pesticides in fruits and vegetables from the Central Region.

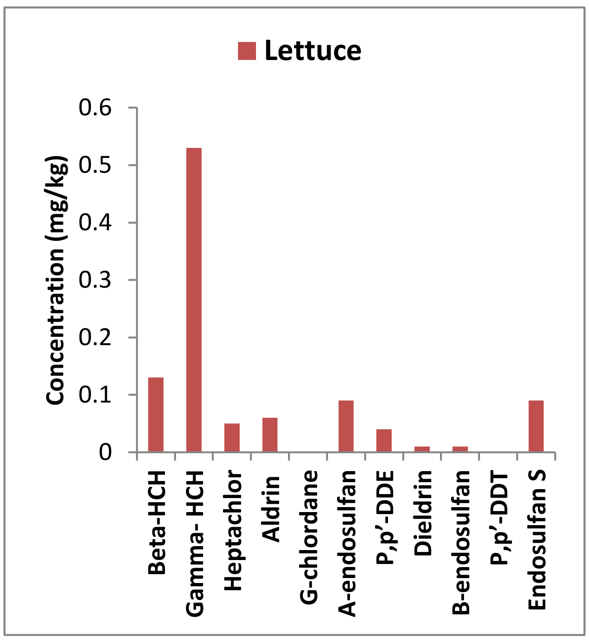


Fig 4.17b: Mean concentration levels of Organochlorine pesticides in lettuce from the Central Region.

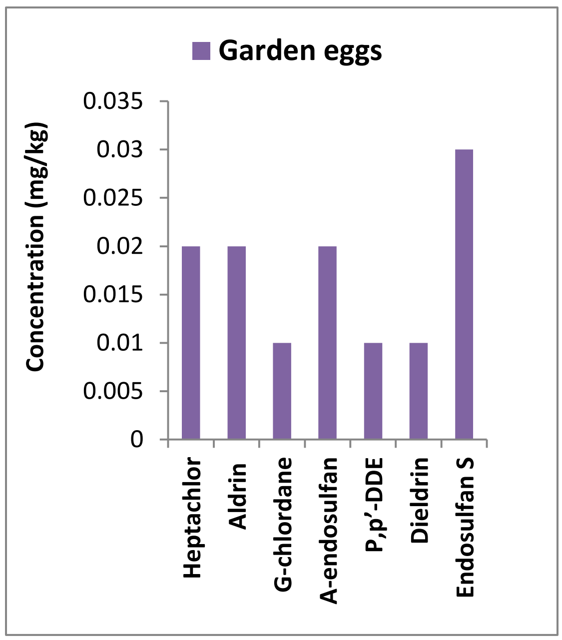


Fig 4.17c: Mean concentration levels of organochlorine pesticides in garden egg from the the Central Region.

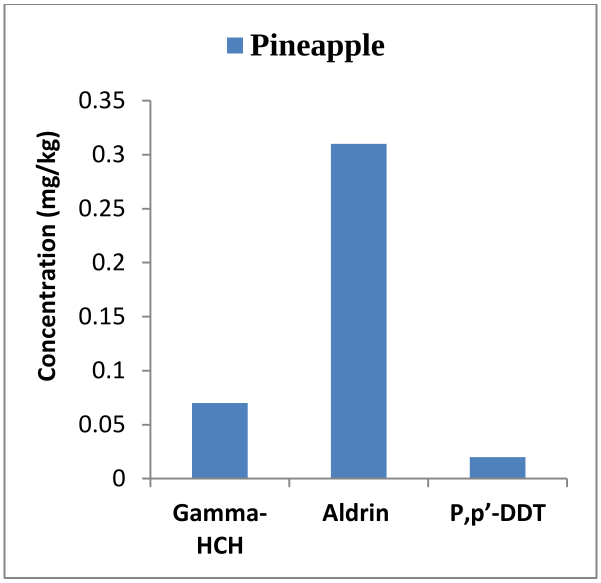


Fig 4.17d: Mean concentration levels of Organochlorine pesticides in pineapple from the Central Region.

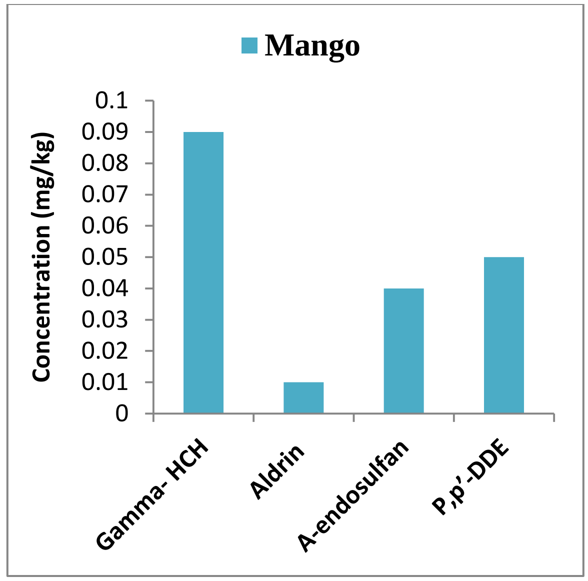


Fig 4.17e: Mean concentration levels of organochlorine pesticides in mango from the Central Region.

4.1.8: Occurrence and distribution of Organochlorine pesticides in samples from the Eastern Region.

In the Eastern Region, a total of twelve different organochlorine pesticides residues were detected in the four samples being the region with highest number of detected organochlorine pesticide residues. Like the other two regions, delta-HCH and methoxychlor were not detected in any of the samples analyzed. Mango recorded the highest number of OCPs followed by lettuce, pineapple and garden eggs. One major mango production area in the Eastern Region which supplies mango to many parts of the region is Somanya. Interestingly mango sampled from this area recorded higher mean concentrations of organochlorine pesticides residues. This occurrence suggests that farmers in this part of the region use a lot of pesticides to control pests which might contain banned pesticides like DDT or have used DDT previously in mango plantations. It is therefore not surprising to detect high levels of organochlorine pesticides in mango samples from these areas. DDT which has been banned in Ghana was recorded in all the different samples of vegetables and fruits except in garden eggs with mean concentrations of 0.02 mg/kg, 0.03 mg/kg and 0.15 mg/kg in lettuce, pineapple and mango respectively. Comparing with the other two regions, Eastern Region recorded the highest mean concentration of DDT but the difference was not significant ($p = 0.07$). The difference in concentration of organochlorines in the samples of lettuce, garden eggs, pineapple and mango from this region was not significant (statistically, $p > 0.05$ or $p = 0.342$, appendix c).

Fig 4.18a shows the mean concentration levels of organochlorine pesticides in fruits and vegetables from the Eastern Region. From the graph it can be observed that highest mean organochlorine pesticides concentration was obtained for gamma- HCH in lettuce with highest mean concentration of 0.22 mg/kg .The mean concentrations of gamma- HCH were 0.22 mg/kg in lettuce , 0.03 mg/kg in garden eggs, 0.05 mg/kg in pineapple and 0.06 mg/kg in mango. The high concentrations of gamma- HCH in these samples suggest that famers in these areas also use lindane in vegetable and fruit production.

Gamma-chlordane and alpha-endosulfan were absent in all samples except in mango recording a mean concentration of 0.05 mg/kg and 0.08 mg/kg for gamma-chlordane and alpha-endosulfan respectively. Beta-endosulfan and endosulfan sulfate mean concentrations in mango did not vary significantly, with mean concentration of 0.05 mg/kg and 0.04 mg/kg respectively. Dieldrin also recorded the highest mean concentration of 0.17 mg/kg in lettuce followed by a concentration of 0.04 mg/kg in mango. Mean endrin concentrations ranged from (0-0.08) mg/kg in lettuce, (0-0.02) mg/kg in garden eggs, (0-0.24) mg/kg in pineapple and no detection in mango.

The lack of significant difference ($p>0.05$) which existed in some of the organochlorine residues detected in the samples collected in Eastern Region suggest that the contamination of samples might have been contributed by similar factors.

Table 4.18: Concentrations (mg/kg) of oganochlorine pesticide residue detected in samples from the Eastern Region

Pesticide	Lettuce			Garden eggs			Pineapple			Mango		
	Mean	*SD*	*Range*	*Mean*	*SD*	*Range*	*Mean*	*SD*	*Range*	*Mean*	*SD*	*Range*
***Beta*-HCH**	0.07	0.03	0-0.09	ND	-	-	ND	-	-	ND	-	-
***Gamma*- HCH**	0.22	0.11	0.05-0.33	0.03	0.02	0-0.04	0.05	0.01	0-0.06	0.06	0.05	0-0.13
***Delta*- HCH**	ND	-	-	ND	-	-	ND	-	-	ND	-	-
Heptachlor	0.05	0.04	0-0.08	0.02	-	0-0.02	0.13	0.11	0-0.24	ND	-	-
Aldrin	0.02	0.01	0-0.03	0.05	-	0-0.05	0.03	0.02	0-0.05	0.01	0.01	0.01-0.02
***G*-chlordane**	ND	-	-	ND	-	-	ND	-	-	0.05	-	0-0.05
A-endosulfan	ND	-	-	ND	--	-	ND	-	-	0.08	0.06	0-0.13
P,p'-DDE	ND	-	-	ND	-	-	ND	-	-	0.07	0.04	0-0.13
Dieldrin	0.17	-	0-0.17	0.01	-	0-0.01	ND	-	-	0.04	0.03	0-0.06
Endrin	0.07	0.04	0-0.11	ND	-	-	ND	-	-	0.05	-	0-0.05
***Beta*-endosulfan**	ND	-	-	ND	-	-	0.02	-	0-0.02	0.05	0.02	0-0.08
P,p'-DDT	0.02	-	0-0.02	ND	-	-	0.03	-	0-0.03	0.15	0.10	0-0.28
Endosulfan S	0.04	0.02	0-0.06	ND	-	-	ND	-	-	0.04	0.03	0-0.09
Methoxychlor	ND	-	-	ND	-	-	ND	-	-	ND	-	-

Limit of detection for all pesticides = 0.01 mg/kg , ND=not detected , SD =standard deviation

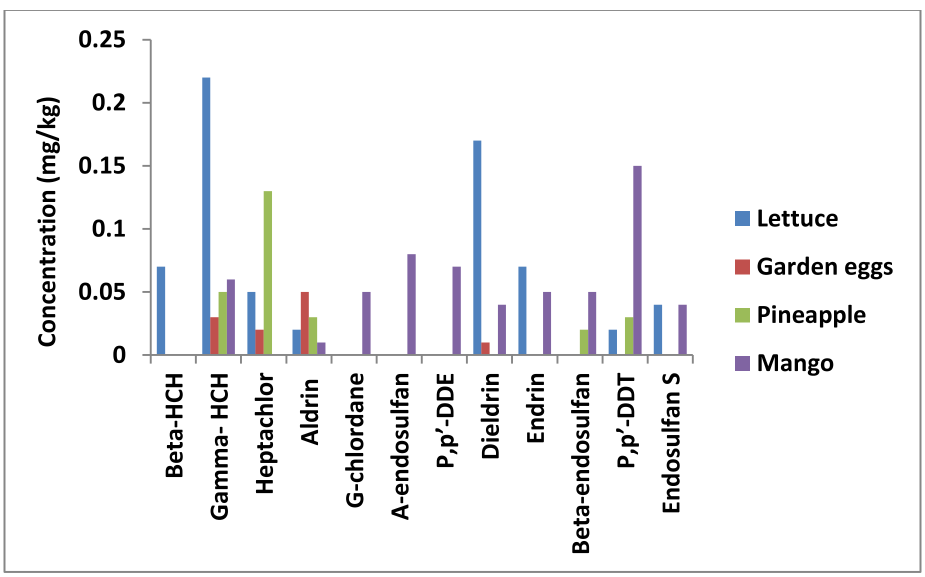
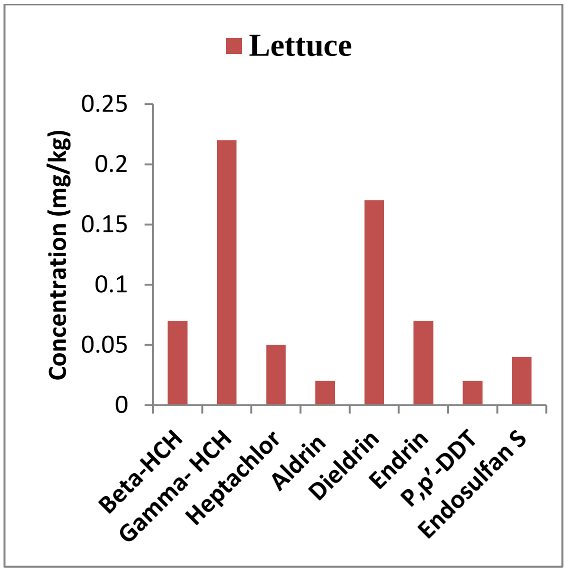


Fig 4.18a: Mean concentration levels of organochlorine pesticides in fruits and vegetables from the Eastern Region.



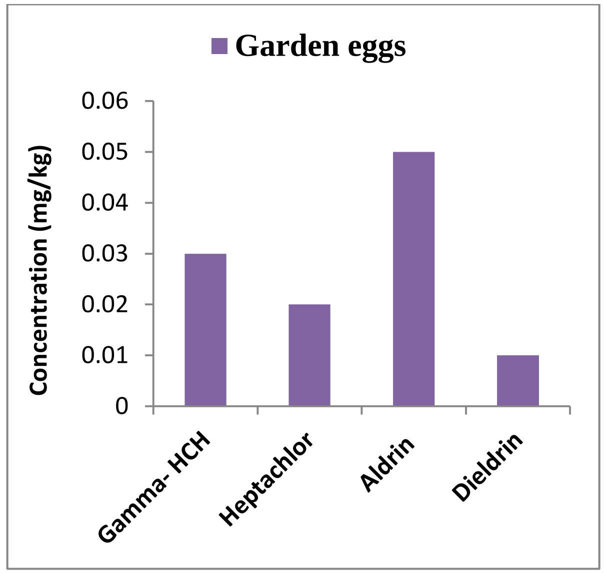
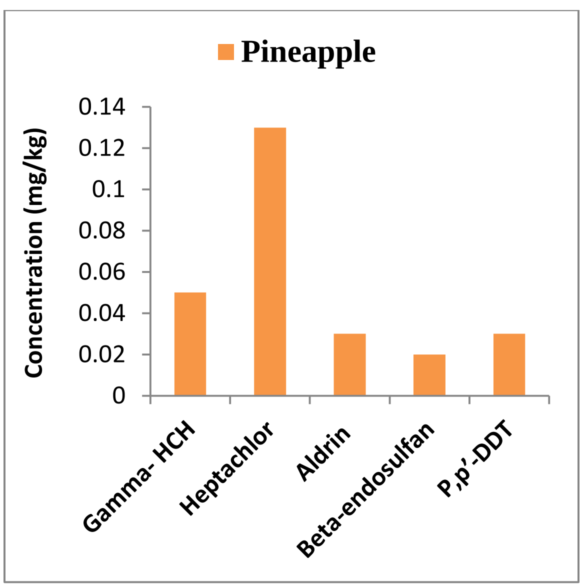


Fig 4.18b: Mean concentration levels of Organochlorine pesticides in lettuce from the Eastern Region.

Fig 4.18c: Mean concentration levels of organochlorine pesticides in garden egg from the the Eastern Region.



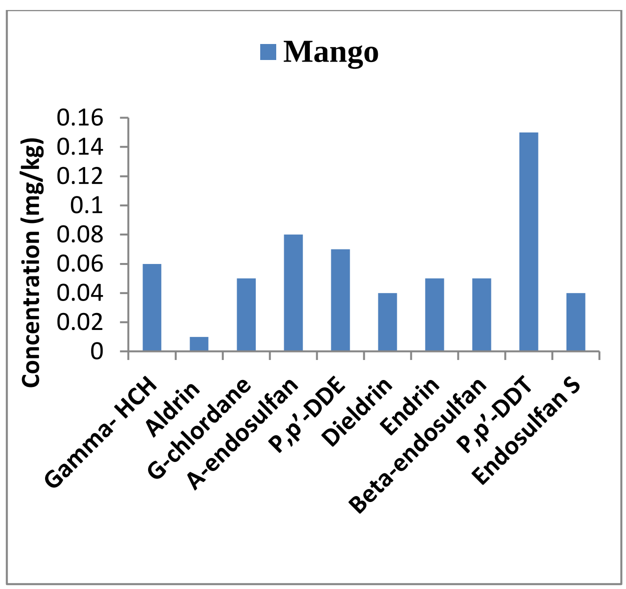


Fig 4.18d: Mean concentration levels of Organochlorine pesticides in pineapple from the Eastern Region.

Fig 4.18e: Mean concentration levels of organochlorine pesticides in mango from the the Eastern Region.

4.1.9: Occurrence and distribution of organochlorine pesticides in samples from all the sampling areas

Fig 4.19a-4.19e show the distribution of the various OCPs levels detected in lettuce, garden eggs, pineapple and mango from the various sampling areas. Table 4.19 also shows the mean concentration levels of oganochlorine pesticide residues in lettuce, garden eggs, pineapple, and mango from all the sampling areas.

Out of a total of fourteen organochlorine pesticide residues, eleven were detected in lettuce, seven in garden eggs, ten in pineapple and twelve in mango. None of the samples recorded any concentration of delta HCH and methoxychlor in all the samples analyzed. Methoxychlor is an analogue of DDT. Half-lives in soil may depend on soil conditions as it can be less than 30 days in anaerobic soils and greater 100 days in aerobic soils (Fogel *et al*, 1982; Muir *et al*, 1984). It has also been observed that 42% of methoxychlor may remain only six months after application (Polyakova *et al*, 1984). Again several studies of the effect of methoxychlor in soil microflora showed that it is moderately persistent, with persistence between thirty days and a year (Howard, 1991; Botwe, 2007). Thus methoxychlor is not as persistent as DDT and this may be the reason why it was not detected in the samples of lettuce, garden eggs, pineapple and mango.

Also pesticide concentrations range from (0-0.55) mg/kg, (0-0.17) mg/kg, (0-0.31) mg/kg and (0-0.28) mg/kg in lettuce, garden eggs, pineapple and mango respectively. The mean beta-HCH concentrations observed in all samples were 0.09 mg/kg, 0.03 mg/kg and 0.03 mg/kg in lettuce, pineapple and mango respectively. The mean residue levels were relatively higher for gamma-HCH (lindane) and aldrin with aldrin recording mean concentrations of 0.45 mg/kg in lettuce, 0.02 mg/kg in garden eggs, 0.13 mg/kg in pineapple and 0.02 mg/kg in mango. Gamma -HCH mean concentrations were 0.29 mg/kg in lettuce, 0.08 mg/kg in garden eggs, 0.09 mg/kg in pineapple and 0.05 mg/kg in mango. Total endosulfan (alpha endosulfan +endosulfan sulfate) concentrations range from (0-0.09) mg/kg, (0-0.24) mg/kg, (0-0.12) mg/kg and (0-0.28) mg/kg in lettuce, garden eggs, pineapple and mango respectively. The difference in concentration of organochlorine pesticides in the samples from all the sampling areas was not significant (statistically, $p>0.05$ or $p= 0.429$, appendix d).

Total DDT concentrations were 0.02 mg/kg in lettuce, 0.03 mg/kg in pineapple and 0.15 mg/kg in mango. DDT was not detected in garden gardens eggs. Interestingly, these values are not different from those obtained from the various regions. DDE/DDT ratios are often used as indicators of recent DDT input into the environment. Low ratios (less than one) indicates recent input and vice versa. DDE/DDT ratios for lettuce, garden eggs, pineapple and mango were calculated as 3.0, 2.0, 3.33, and 0.03 respectively. Generally, the high ratio of DDE to DDT mean values support the assumptions that current DDT exposure levels primarily originates from previous contamination as well as environmental persistence and not from current use (Ntow, 2005;Bempah and Donkor, 2010).

Additionally, this finding is an indication of the rate of degradation and isomerisation of the original organochlorine compounds to their metabolites and isomers, examples DDT to DDE in the terrestrial environment under the hot, dry climatic conditions which is characteristic of tropical climate (Jiries *et al*, 2002). DDT has been banned from agricultural use but has restricted use for public health purposes under the Stockholm convention in which Ghana is a signatory. The present investigation therefore gives a strong indication on the restricted use of DDT for agricultural and vector control purposes in Ghana. However long term persistence in the environment of this pesticide has been reported in various publications (Schfer and Kegley, 2002; Fattore *et al*, 2002)

The total heptachlor mean concentrations were 0.05 mg/kg in lettuce, 0.02 mg/kg in garden eggs, 0.07 mg/kg in pineapple and 0.02 mg/kg in mango. Statiscally, the difference was significant (p=0.02). These values were however higher than the mean concentration detected in aquatic foods and aquatic food products (0.002 mg/kg) in China (Pingping *et al,* 2007).

Generally, it was observed that there were differences in the levels of pesticide residues (especially organophosphates) in fruits and vegetables analyzed from the different sampling areas. This was in accordance with a finding of the Global Environment Monitoring System Project on pesticides in food in 'Global pollution and health' that the concentrations of various residues in foods can vary substantially from one specific food item to another even within the same food group and within the same country. The differences in the levels of pesticides in the vegetables and fruits observed may be attributed to a number of reasons.

The first has to do with different agricultural practices adopted by farmers and also accessibility of the pesticides. For instance higher quantities of pesticides may be applied in areas of massive pest attack and the frequency of pesticide application may be influenced by climatic conditions such as temperature and rainfall. Another reason why variation in pesticide concentration may occur is as a result of some farmers mixing cocktails of various pesticides to increase their efficacy or potency (Ntow *et al* 2005, Drechel *et al* 2002). This practice may also alter both the type and the concentrations of pesticide residues in the fruits and vegetables.

Again within the same field, crops may receive varying amounts of pesticides due to wind drift and also due to non-uniform spraying. The last but not the least is the fact that plants and for that matter fruits and vegetables may exhibit different abilities to take up pesticide residues upon exposure. This is because different plants have different biochemical mechanisms of dealing with foreign chemicals.

Table 4.19: Concentrations (mg/kg) of organochlorine pesticide residues detected in samples from all the sampling areas.

Pesticide	Lettuce			Garden eggs			Pineapple			Mango		
	Mean	***SD***	***Range***	***Mean***	***SD***	***Range***	***Mean***	***SD***	***Range***	***Mean***	***SD***	***Range***
***Beta*-HCH**	0.09	0.04	0-0.13	ND	-	-	0.03	0.01	0-0.03	0.03	0.01	0-0.05
***Gamma*- HCH**	0.29	0.15	0.1-0.55	0.08	0.06	0-0.17	0.09	0.06	0-0.21	0.05	0.04	0-0.13
***Delta*- HCH**	ND	-	-	ND	-	-	ND	-	-	ND	-	-
Heptachlor	0.05	0.03	0-0.08	0.02	-	0-0.02	0.07	0.01	0-0.24	0.02	-	0-0.02
Aldrin	0.45	0.04	0-0.13	0.02	0.01	0-0.03	0.13	0.12	0-0.31	0.02	0.01	0-0.02
***G*-chlordane**	ND	-	-	ND	-	-	0.01	-	0-0.01	0.05	-	0-0.05
A-endosulfan	0.08	0.03	0-0.09	0.02	-	0-0.02	0.03	-	0-0.03	0.07	0.05	0-0.13
P,p'-DDE	0.06	0.02	0-0.08	0.01	-	0-0.01	0.1	0.03	0-0.09	0.05	0.04	0-0.13
Dieldrin	0.08	0.04	0-0.17	0.01	-	0-0.01	ND	-	-	0.04	0.02	0-0.06
Endrin	0.07	0.04	0-0.11	ND	-	-	ND	-	-	0.05	-	0-0.05
***B*-endosulfan**	0.01	-	0-0.01	ND	-	-	0.02	0.01	0-0.02	0.05	0.02	0-0.08
P,p'-DDT	0.02	-	0-0.02	ND	-	-	0.03	0.01	0-0.03	0.15	0.10	0-0.28
Endosulfan S	0.05	0.01	0-0.06	0.03	0.01	0-0.04	0.12	-	0-0.12	0.04	0.04	0-0.09
Methoxychlor	ND	-	-	ND	-	-	ND	-	-	ND	ND	-

Limit of detection for all pesticides = 0.01 mg/kg, ND=not detected, SD =standard deviation

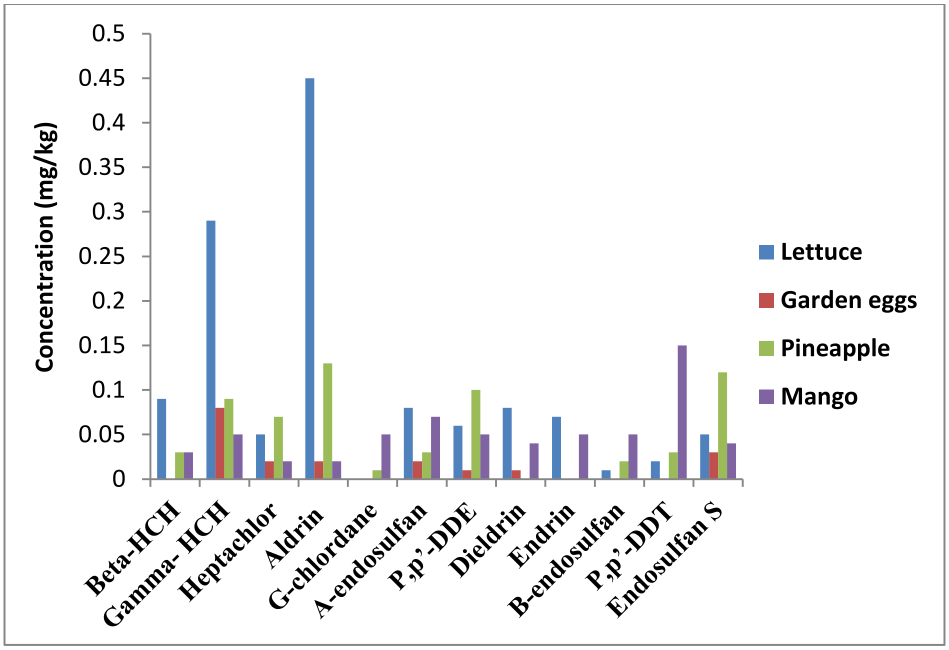


Fig 4.19a: Mean concentration levels of organochlorine pesticides in fruits and vegetables from all sampling areas.

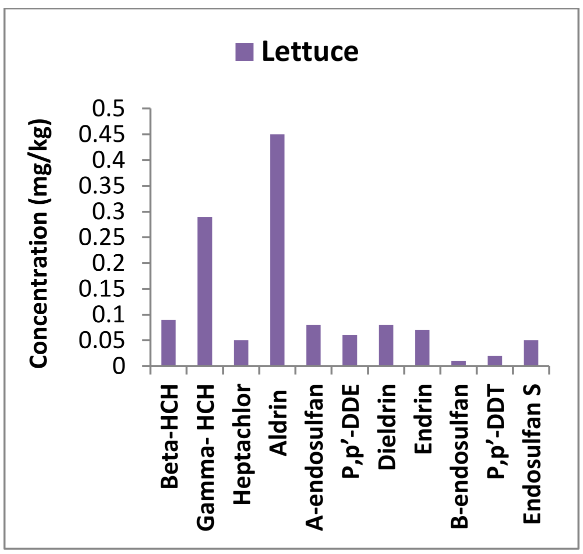


Fig 4.19b: Mean concentration levels of Organochlorine pesticides in lettuce from all the sampling areas.

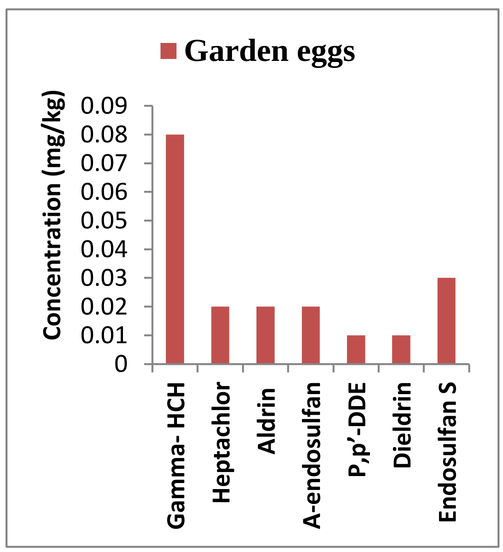


Fig 4.19c: Mean concentration levels of organochlorine pesticides in garden eggs from all the sampling areas.

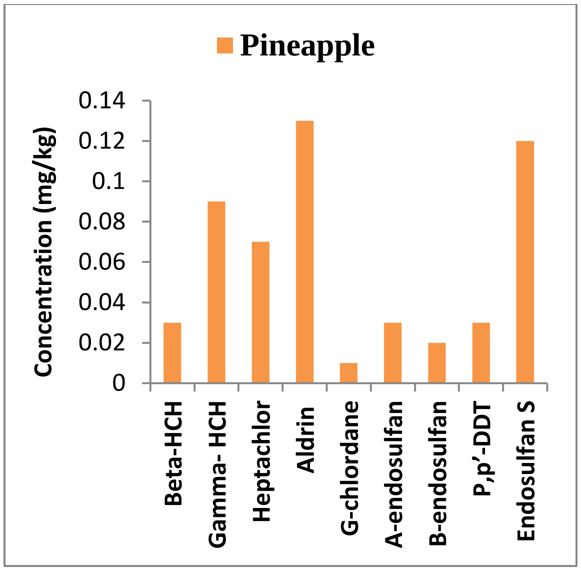


Fig 4.19d: Mean concentration levels of Organochlorine pesticides in pineapple from all the sampling areas.

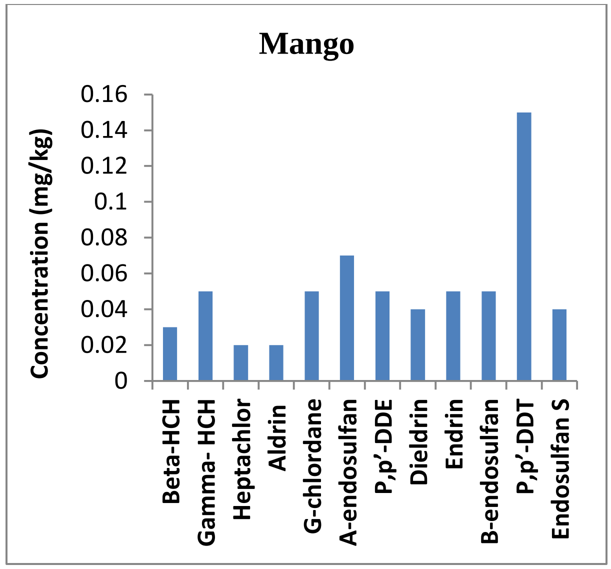


Fig 4.19e: Mean concentration levels of organochlorine pesticides in mango from all the sampling areas.

4.2: Tolerance limits

The concentration of organochlorine pesticides in various fruits and vegetables sampled from the selected sampling areas were compared with maximum residue limits (MRLs) set forth by the FAO/WHO Codex Alimentarius Commission (table below).

Table 4.20: Highest organochlorine pesticide residue concentration found in lettuce, garden eggs, pineapple, mango from the selected sampling areas compared with FAO/WHO maximum residue limits (mg/kg).

Pesticides	Highest amounts found				Maximum residue limit			
	Lettuce	Garden eggs	Pineapple	Mango	Lettuce	Garden eggs	Pineapple	Mango
***Beta*-HCH**	0.13	ND	0.03	0.05	0.1	0.1	0.1	0.1
***G*- HCH**	0.55	0.17	0.21	0.13	0.1	0.1	0.1	0.1
***Delta*- HCH**	ND	ND	ND	ND	0.1	0.1	0.1	0.1
Heptachlor	0.08	0.02	0.24	0.02	0.01	0.01	0.01	0.01
Aldrin	0.13	0.03	0.31	0.02	0.05	0.05	0.05	0.05
***G* -chlordane**	ND	ND	0.01	0.05	0.02	0.02	0.02	0.02
A-endosulfan	0.09	0.02	0.03	0.13	0.1	0.1	0.5	0.5
P,p'-DDE	0.08	0.01	0.06	0.13	0.05	0.05	0.05	0.05
Dieldrin	0.08	0.01	ND	0.06	0.05	0.05	0.05	0.05
Endrin	0.11	ND	ND	0.08	0.05	0.05	0.05	0.05
***β*-endosulfan**	0.01	ND	0.02	0.28	0.1	0.1	0.5	0.5
P,p'-DDT	0.02	ND	0.03	0.28	0.05	0.05	0.05	0.05
Endosulfan S	0.06	0.04	0.12	0.09	0.1	0.1	0.5	0.5
Methoxychlor	ND	ND	ND	ND	0.01	0.01	0.01	0.01

Limit of detection for all pesticides = 0.01 mg/kg , ND=not detected , SD =standard deviation

From table 4.20**,** it can be observed that the highest concentration of gamma- HCH (lindane) recorded in lettuce (0.55 mg/kg), garden eggs (0.17 mg/kg), pineapple (0.21 mg/kg) and mango (0.13 mg/kg) were all higher than the maximum residue limits (MRLs) set forth by the FAO/WHO Codex Alimentarius Commision. Also the highest concentration of *Beta*-HCH in all samples except lettuce were all lower than the maximum residue limits (MRLs) set forth by the FAO/WHO Codex Alimentarius Commission while no concentrations of Delta-HCH and methoxychlor were recorded in any of the samples.

Heptachlor concentrations in all samples were above the MRLs values. In addition, highest endosulfan levels (alpha-endosulfan and beta-endosulfan) in lettuce, garden eggs, pineapple and mango were all lower than the maximum residue limits (MRLs) set forth by the FAO/WHO Codex Alimentarius Commision.

The concentration of DDT in mango was above the maximum residue limits (MRLs) but was lower than the MRLs in lettuce, garden eggs and pineapple. The highest DDE values were all above the MRLs except in garden eggs which recorded a concentration of 0.01 mg/kg. Gamma-chlordane values were all lower than the maximum residue limits (MRLs) set forth by the FAO/WHO Codex Alimentarius Commision except in mango which recorded highest value of 0.05 mg/kg. Also highest aldrin concentrations in lettuce and pineapple were higher than the MRLs. However its concentrations in garden eggs and mango were all below the MRLs.

It is interesting to note that both diedrin and endrin highest concentration in lettuce and mango were all above the MRLs while their highest concentration in garden eggs, pineapple were all below the MRLs.

Generally, it can be deduced from the data that some fruit and vegetable samples analyzed contain residues of the monitored organochlorines above the accepted maximum residue limits

(MRLs) adopted by the FAO/WHO Codex Alimentarius Commision. Since fruits and vegetables consumption by humans is an indispensable part of our daily life, this makes the safety of market fruits and vegetables an important health issue and therefore underscores the importance of the potential health risks of organochlorine pesticides in fruits and vegetables.

4.2.1: Health Risk Assessment

In view of the potential toxicity associated with organochlorine pesticides than the other types of pesticides, it was prudent to conduct a health risk assessment on organochlorine pesticides in order to help consumers make informed choices when buying fruits and vegetables since food consumption is an important route of human exposure to organochlorine pesticides residues (Jiang *et al*, 2005).

In estimating the potential health risk associated with each organochlorine pesticide, the following assumptions were made based on the United States Environmental Protection Agency's guidelines (USEPA, 1996). The first is that a hypothetical body weight of 70 kg for adults and 10 kg for children and the second is that there is maximum absorption rate of 100% and bioavailability rate of 100%. In Ghana, food consumption rate for fruits and vegetables is found to be 0.064 mg/kg (Bempah, 2008). Therefore for each type of exposure, the estimated lifetime exposure dose (mg/kg) was obtained by multiplying the residual pesticide concentration (mg/kg) in the food of interest by the food consumption rate (mg/kg) and dividing the product by the body weight (kg). The hazard indices for adults and children were computed as ratios between estimated pesticides exposure doses and the reference doses which are considered to be safe levels of exposure over the lifetime.

Tables 4.21, 4.22, 4.23 and 4.24 show the reference dose, the estimated dose and the corresponding hazard index for each organochlorine pesticide in lettuce, garden eggs, pineapple and mango respectively. The data analysis indicates that organochlorine pesticides such as beta-HCH, gamma-HCH, alpha endosulfan, beta endosulfan, p,p-DDE and DDT do not pose a direct hazard to human even though residual concentration were detected in all the four different samples. Heptachlor, aldrin, dieldrin gamma chlordane however had their hazard indexes more than unity in the samples in one or more of the samples indicating a potential systemic toxicity especially in children.

The results further indicate that heptachlor in particular may be of public concern since its concentration levels exceeded the reference dose in all the four different types of samples analyzed indicating a great potential for systemic toxicity to consumers in Ghana.

Table 4.21: Health risk estimates for systemic effects associated with pesticide residues in Lettuce

Pesticide	Reference dose (mg/kg/day)	Estimated dose (mg/kg/day)	hazard index	health risk
Beta -HCH	0.003	8.23 $x10^{-5}$ [adult]	0.027	no
		5.76 $x10^{-4}$[children]	0.192	no
Gamma- HCH	0.003	2.65 $x10^{-4}$[adult]	0.088	no
		1.86 $x10^{-3}$[children]	0.619	no
Heptachlor	0.0001	4.57 $x10^{-5}$[adult]	0.457	no
		3.20 $x10^{-4}$[children]	3.200	yes
Aldrin	0.0002	4.57 $x10^{-5}$[adult]	0.229	no
		3.20 $x10^{-4}$[children]	1.600	yes
Alpha-endosulfan	0.006	7.31 $x10^{-5}$ [adult]	0.012	no
		5.12 $x10^{-4}$[children]	0.085	no
Beta -endosulfan	0.006	9.14 $x10^{-6}$[adult]	0.002	no
		6.40 $x10^{-5}$ [children]	0.011	no
P,p'-DDE	0.02	5.49 $x10^{-5}$ [adult]	0.003	no
		3.84 $x10^{-5}$ [children]	0.019	no
Dieldrin	0.0002	7.31 $x10^{-5}$ [adult]	0.366	no
		5.12 $x10^{-4}$ [children]	2.560	yes
Endrin	0.0002	6.40 $x10^{-5}$ [adult]	0.320	no
		4.48 $x10^{-4}$ [children]	2.240	yes
P,p'-DDT	0.02	1.83 $x10^{-5}$ [adult]	0.001	no
		1.28 $x10^{-5}$ [children]	0.0064	no

Table 4.22: Health risk estimates for systemic effects associated with pesticide residues in garden eggs

Pesticide	Reference dose (mg/kg/day)	Estimated dose (mg/kg/day)	Hazard index	Health risk
Gamma- HCH	0.003	7.31×10^{-5}[adult]	0.024	no
		5.12×10^{-4}[children]	0.171	no
Heptachlor	0.0001	1.83×10^{-5}[adult]	0.183	no
		1.28×10^{-4}[children]	1.280	yes
Aldrin	0.0002	1.83×10^{-5}[adult]	0.091	no
		1.28×10^{-4}[children]	0.640	no
Alpha-endosulfan	0.006	1.83×10^{-5}[adult]	0.003	no
		1.28×10^{-4}[children]	0.021	no
P,p'-DDE	0.02	9.14×10^{-6}[adult]	0.000	no
		6.4×10^{-5}[children]	0.003	no

Table 4.23: Health risk estimates for systemic effects associated with pesticide residues in pineapple

Pesticide	Reference dose (mg/kg/day)	Estimated dose (mg/kg/day)	Hazard index	Health risk
Beta -HCH	0.003	2.74×10^{-5}[adult]	0.009	no
		1.92×10^{-4} [children]	0.064	no
Gamma- HCH	0.003	8.23×10^{-5}[adult]	0.027	no
		5.76×10^{-4} [children]	0.192	no
Heptachlor	0.0001	6.40×10^{-5}[adult]	0.640	no
		4.48×10^{-4}[children]	4.480	yes
Aldrin	0.0002	1.19×10^{-4}[adult]	0.594	no
		8.32×10^{-4} [children]	4.160	yes
Gamma chlordane	0.0001	9.14×10^{-6}[adult]	0.091	no
		6.40×10^{-5} [children]	0.640	no
Alpha-endosulfan	0.006	2.74×10^{-5}[adult]	0.005	no
		1.92×10^{-4}[children]	0.032	no
Beta -endosulfan	0.006	1.83×10^{-5}[adult]	0.003	no
		1.28×10^{-4} [children]	0.021	no
P,p'-DDE	0.02	5.49×10^{-5}[adult]	0.003	no
		6.40×10^{-4}[children]	0.032	no
P,p'-DDT	0.02	2.74×10^{-5}[adult]	0.001	no
		1.92×10^{-4} [children]	0.010	no

Table 4.24: Health risk estimates for systemic effects associated with pesticide residues in Mango

Pesticide	Reference dose (mg/kg/day)	Estimated dose (mg/kg/day)	Hazard index	Health risk
Beta -HCH	0.003	2.74 x10^{-5}[adult] 1.92 x10^{-4} [children]	0.009 0.064	no no
Gama- HCH	0.003	4.57 x10^{-5}[adult] 3.20 x10^{-4}[children]	0.015 0.107	no no
Heptachlor	0.0001	1.83 x10^{-5}[adult] 1.28 x10^{-4} [children]	0.183 1.280	no yes
Aldrin	0.0002	1.83 x10^{-5} [adult] 1.28 x10^{-4}[children]	0.091 0.640	no no
Gamma chlordane	0.0001	4.57 x10^{-5} [adult] 3.20 x10^{-4}[children]	0.457 3.200	no yes
Alpha-endosulfan	0.006	6.40 x10^{-5} [adult] 4.48 x10^{-4}[children]	0.011 0.075	no no
Beta -endosulfan	0.006	4.57 x10^{-5} [adult] 3.20 x10^{-4}[children]	0.008 0.053	no no
P,p'-DDE	0.02	4.57 x10^{-5} [adult] 3.20 x10^{-4}[children]	0.002 0.016	no no
Deldrin	0.0002	3.66 x10^{-5} [adult] 2.56 x10^{-4}[children]	0.183 1.280	no yes
Endrin	0.0002	4.57 x10^{-5} [adult] 3.20 x10^{-4}[children]	0.229 1.600	no yes
P,p'-DDT	0.02	1.37 x10^{-4} [adult] 9.60 x10^{-4}[children]	0.007 0.048	no no

CHAPTER FIVE

5.0 CONCLUSION AND RECOMMENDATIONS

5.1 Conclusions

- The results of this study indicate that some Ghanaian market vegetables and fruits are contaminated with different types of pesticides of which organophosphates and synthetic pyrethroids are the most common. Chlorpyrifos and cypermethrin were the most frequent pesticides among the organophosphates and synthetic pyrethroids respectively with higher concentration levels.
- Twelve organochlorine pesticides were detected of which seven are among the banned pesticides of the environmental protection agency (EPA) of Ghana. These banned organochlorine pesticides are: heptachlor, aldrin, dieldrin, lindane (gamma-HCH), endrin, gamma chlordane and DDT (Afful *et al*,2010)). The occurrence of organochlorine pesticide residues in the vegetables and fruits could be due to its illegal use or due to historic use since these chemicals are prohibited from agricultural use. Lindane was the most common organochlorine pesticide while lettuce was the most frequently contaminated sample. .
- There were no significant variations in the levels of pesticides in the four samples as well as the sampling areas ($p>0.05$) even though there were differences in residual concentrations of pesticides. The differences in residual concentrations of pesticides could be due to different agricultural practices adopted by farmers and also accessibility of the pesticides.
- The concentrations of organochlorine pesticide residues were generally low. However, the concentration of OCPs in some fruits and vegetables exceeded the maximum

tolerable limits or maximum residue limits (MRLs) adopted by the FAO/WHO Codex Alimentarius Commission.

- Health risk analysis Indicates that heptachlor in particular may be of public concern since its concentration levels exceeded the reference dose in all the four different types of samples analyzed indicating a great potential for systemic toxicity to consumers in Ghana.

5.2 Recommendations.

- Future monitoring programs are recommended to acquire adequate information regarding the levels of pesticides especially organochlorines in vegetables and fruits.
- The ministry of agriculture and the environmental protection agency need to check and enforce regulations on the use of banned pesticides in Ghana.
- There is the need to conduct a dietary survey for the entire population of Ghana to generate a food consumption database so that a more complete health risk assessment could be done in the future.
- Farmer education on safe pesticide use should be intensified to limit the levels of pesticides residues in fruits and vegetables.

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Appendix A

ANOVA ANALYSIS

GREATER ACCRA REGION

Organophosphates

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.0262	3	0.008733	0.764565	0.525063	3.008787
Within Groups	0.274143	24	0.011423			
Total	0.300343	27				

Synthetic pyrethroids

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.183443	6	0.030574	5.492301	0.00149	2.572712
Within Groups	0.1169	21	0.005567			
Total	0.300343	27				

Organochlorines

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.002406	3	0.000802	0.618847	0.606207	2.798061
Within Groups	0.0622	48	0.001296			
Total	0.064606	51				

Appendix B

ANOVA ANALYSIS

CENTRAL REGION

Organophosphates

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.06905	7	0.009864	3.4561	0.010589	2.422629
Within Groups	0.0685	24	0.002854			
Total	0.13755	31				

Synthetic pyrethroids

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.04675	3	0.015583	0.035038	0.990934	3.098391
Within Groups	8.8951	20	0.444755			
Total	8.94185	23				

Organochlorines

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.123621	13	0.009509	1.527021	0.147869	1.961218
Within Groups	0.26155	42	0.006227			
Total	0.385171	55				

Appendix C

ANOVA ANALYSIS

EASTERN REGION

Organophosphates

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.064555	3	0.021518	4.04408	0.013314	2.838745
Within Groups	0.212836	40	0.005321			
Total	0.277391	43				

Synthetic pyrethroids

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.107233	3	0.035744	0.134847	0.938108	3.098391
Within Groups	5.3015	20	0.265075			
Total	5.408733	23				

Organochlorines

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.03118	13	0.002398	1.156894	0.342848	1.961218
Within Groups	0.087075	42	0.002073			
Total	0.118255	55				

Appendix D

ANOVA ANALYSIS

OVERALL

Organophoshates
ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	0.05733	3	0.019112	3.052833	0.039358	2.838745
Within Groups	0.250418	40	0.00626			
Total	0.307755	43				

Synthetic pyrethroids
ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	0.008754	3	0.002918	0.020159	0.996005	3.008787
Within Groups	3.473857	24	0.144744			
Total	3.482611	27				

Organochlorines
ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	196.0909	3	65.36362	0.938813	0.429288	2.798061
Within Groups	3341.939	48	69.62372			
Total	3538.029	51				

Appendix E

Table 6.1: Mean concentration levels (mg/kg) of organophosphate and synthetic pyrethroids pesticide residues detected in samples from Mallam Atta market.

Pesticide	Lettuce	Garden eggs	Pineapple	Mango
Dimethoate	0.02	0.05	ND	0.03
Pirimiphos-methy	ND	ND	<0.01	ND
Malathion	ND	ND	0.03	ND
Fenitrothion	0.13	ND	ND	ND
Parathion ethyl	ND	ND	0.14	ND
Chlorfenvinphos	0.04	ND	ND	ND
Profenofos	<0.01	0.02	ND	ND
Methamidophos	ND	0.04	ND	ND
Chlorpyrifos	0.02	1.36	ND	0.02
Allethrin [a]	ND	0.08	<0.01	ND
Lambda-cyhalothrin [a]	0.13	0.03	ND	ND
Permethrin [a]	0.02	ND	ND	ND
Cyfluthrin [a]	0.02	0.03	0.15	0.07
Deltamethrin [a]	<0.01	0.04	ND	ND
Cypermethrin [a]	<0.01	0.63	0.21	0.36
Bifenthrin [a]	ND	0.13	ND	ND

[a] - Synthetic Pyrethroids , Limit of detection for all pesticides = 0.01 mg/kg, ND=not detected, SD= standard deviation

Appendix F

Table 6.2: Mean concentration levels (mg/kg) of organophosphate and synthetic pyrethroids pesticide residues detected in samples from Agbobloshie market.

Pesticide	Lettuce	Garden eggs	Pineapple	Mango
Dimethoate	ND	ND	ND	0.03
Pirimiphos-methyl	ND	<0.01	ND	0.56
Malathion	0.26	0.13	0.17	0.12
Parathion ethyl	0.08	0.02	0.05	0.02
Chlorfenvinphos	ND	0.19	0.02	0.02
Profenofos	0.02	ND	<0.01	0.02
Phorate	ND	ND	0.02	ND
Methamidophos	ND	0.02	ND	ND
Ethoprophos	ND	0.02	ND	ND
Chlorpyrifos	ND	0.19	ND	ND
Allethrin [a]	ND	0.06	ND	ND
Lambda-cyhalothrin [a]	0.03	ND	ND	ND
Permethrin [a]	ND	0.08	<0.01	ND
Cyfluthrin [a]	0.06	0.24	ND	0.02
Cypermethrin [a]	0.04	0.19	ND	ND

[a] - Synthetic Pyrethroids , Limit of detection for all pesticides = 0.01 mg/kg, ND=not detected, SD=standard deviation

Appendix G

Table 6.3: Mean concentration levels (mg/kg) of organophosphate and synthetic pyrethroids pesticide residues detected in samples from Madina market.

Pesticide	Lettuce	Garden eggs	Pineapple	Mango
Fonofos	0.02	ND	ND	ND
Dimethoate	ND	0.05	<0.01	0.03
Pirimiphos-methyl	ND	ND	ND	0.56
Malathion	ND	ND	ND	0.12
Fenitrothion	0.02	0.12	0.02	ND
Parathion ethyl	ND	ND	ND	0.02
Chlorfenvinphos	ND	ND	ND	0.02
Profenofos	ND	ND	ND	0.02
Phorate	0.03	ND	<0.01	0.02
Methamidophos	0.08	ND	ND	ND
Chlorpyrifos	0.01	0.09	0.04	ND
Allethrin [a]	<0.01	0.02	ND	ND

[a] - Synthetic Pyrethroid , Limit of detection for all pesticides = 0.01 mg/kg, ND=not detected, SD =standard deviation

Appendix H

Table 16: Mean concentration levels (mg/kg) of organophosphate pesticide residues detected in samples from Kaneshie market.

Pesticide	Lettuce	Garden eggs	Pineapple	Mango
Fonofos	ND	ND	0.01	ND
Dimethoate	ND	<0.01	0.05	ND
Pirimiphos-methy	0.09	ND	0.05	ND
Malathion	ND	ND	<0.01	ND
Fenitrothion	ND	ND	0.05	0.05
Parathion ethyl	ND	0.12	ND	ND
Chlorfenvinphos	0.02	ND	ND	ND
Profenofos	ND	ND	0.03	ND
Methamidophos	0.02	<0.01	0.06	0.78
Chlorpyrifos	<0.01	0.16	0.09	ND

Limit of detection for all pesticides: 0.01mg/kg ND-not detected

Appendix I

Table 17: Mean concentration levels (mg/kg) of organophosphate and synthetic pyrethroids pesticide residues detected in samples from capecoast market.

Pesticide	Lettuce	Garden eggs	Pineapple	Mango
Dimethoate	0.04	0.01	0.01	ND
Fenitrothion	0.02	ND	ND	ND
Chlorfenvinphos	0.03	0.01	0.01	0.01
Profenofos	0.03	ND	ND	ND
Phorate	<0.01	ND	ND	0.01
Methamidophos	0.05	0.11	0.11	0.06
Ethoprophos	<0.01	ND	ND	ND
Chlorpyrifos	0.02	0.07	0.07	ND
Lambda-cyhalothrin [a]	0.71	ND	ND	<0.01
Permethrin [a]	0.06	0.05	ND	ND
Cyfluthrin [a]	0.26	0.08	ND	ND
Fenvalerate [a]	ND	ND	0.03	ND
Cypermethri [a] **n**	1.75	1.63	1.46	1.41
Bifenthrin [a]	<0.01	ND	ND	ND

[a] - Synthetic Pyrethroids , Limit of detection for all pesticides = 0.01 mg/kg, ND=not detected, SD =standard deviation

Appendix J

Table 18: Mean concentration levels (mg/kg) of organophosphate and synthetic pyrethroids pesticide residues detected in samples from Mankessim market.

Pesticide	Lettuce	Garden eggs	Pineapple	Mango
Dimethoate	0.06	ND	ND	<0.01
Parathion ethyl	ND	<0.01	ND	ND
Chlorfenvinphos	ND	ND	<0.01	ND
Profenofos	ND	ND	ND	0.04
Phorate	ND	0.02	ND	<0.01
Methamidophos	0.07	0.07	ND	ND
Chlorpyrifos	ND	0.27	0.02	0.34
Allethrin [a]	0.06	0.04	ND	ND
Lambda-cyhalothrin [a]	0.17	0.27	0.01	ND
Permethrin [a]	0.07	0.04	0.01	ND
Cyfluthrin [a]	ND	<0.01	ND	ND
Cypermethrin [a]	1.16	2.41	1.91	ND

[a] - Synthetic Pyrethroids , Limit of detection for all pesticides = 0.01 mg/kg, ND=not detected, SD =standard deviation

Appendix K

Table 19: Mean concentration levels (mg/kg) of organophosphate and synthetic pyrethroids pesticide residues detected in samples from Kasoa market.

Pesticide	Lettuce	Garden eggs	Pineapple	Mango
Parathion ethyl	ND	<0.01	ND	ND
Chlorfenvinphos	ND	ND	ND	0.08
Phorate	ND	ND	ND	0.06
Chlorpyrifos	ND	ND	0.02	0.11
Allethrin [a]	0.04	ND	ND	ND
Lambda-cyhalothrin [a]	0.35	0.06	ND	0.01
Permethrin [a]	0.05	0.02	0.03	ND
Cyfluthrin [a]	0.21	ND	ND	ND
Deltamethrin [a]	ND	ND	ND	0.03
Cypermethrin [a]	0.92	1.34	1.19	3.39

[a] - Synthetic Pyrethroids , Limit of detection for all pesticides = 0.01 mg/kg, ND=not detected, SD =standard deviation

Appendix L

Table 20: Mean concentration levels (mg/kg) of organophosphate and synthetic pyrethroids pesticide residues detected in samples from swedru market.

Pesticide	Lettuce	Garden eggs	Pineapple	Mango
Dimethoate	ND	0.01	ND	ND
Chlorfenvinphos	ND	ND	ND	0.02
Phorate	ND	ND	<0.01	0.02
Methamidophos	0.043	0.03	ND	ND
Ethoprophos	0.02	<0.01	ND	ND
Chlorpyrifos	0.06	ND	ND	ND
Allethrin [a]	0.03	0.01	ND	ND
Lambda-cyhalothrin [a]	1.17	ND	ND	ND
Permethrin [a]	0.25	0.09	0.16	0.13
Cyfluthrin [a]	0.41	0.07	ND	0.03
Deltamethrin [a]	ND	ND	0.10	0.06
Cypermethrin [a]	1.53	1.41	1.50	1.54

[a] - Synthetic Pyrethroids , Limit of detection for all pesticides = 0.01 mg/kg, ND=not detected, SD =standard deviation

Appendix M

Table 21: Mean concentration levels (mg/kg) of organophosphate and synthetic pyrethroids pesticide residues detected in samples from koforidua market.

Pesticide	Lettuce	Garden eggs	Pineapple	Mango
Dimethoate	ND	0.02	ND	0.10
Pirimiphos-methy	ND	ND	ND	0.15
Malathion	ND	ND	ND	0.23
Fenitrothion	ND	0.02	ND	0.07
Parathion ethyl	ND	ND	ND	0.08
Chlorfenvinphos	0.02	ND	ND	0.42
Profenofos	ND	0.02	ND	0.23
Phorate	ND	0.04	0.01	ND
Methamidophos	ND	0.04	0.04	0.06
Ethoprophos	<0.01	ND	<0.01	0.35
Chlorpyrifos	0.42	0.02	0.05	0.56
Allethrin [a]	0.01	ND	ND	0.24
Lambda-cyhalothrin [a]	0.07	ND	ND	ND
Permethrin [a]	0.07	ND	0.30	ND
Cyfluthrin [a]	0.05	0.02	0.01	ND
Deltamethrin [a]	ND	ND	0.04	0.01
Cypermethrin [a]	0.89	0.17	1.18	1.21

[a] - Synthetic Pyrethroids , Limit of detection for all pesticides = 0.01 mg/kg, ND=not detected, SD =standard deviation

Appendix N

Table 22: Mean concentration levels (mg/kg) of organophosphate and synthetic pyrethroids pesticide residues detected in samples from Somanya market.

Pesticide	Lettuce	Garden eggs	Pineapple	Mango
Dimethoate	0.02	ND	ND	0.06
Pirimiphos-methy	ND	ND	ND	0.03
Malathion	ND	ND	0.20	ND
Fenitrothion	0.03	ND	ND	ND
Parathion ethyl	ND	ND	0.06	0.02
Chlorfenvinphos	0.02	ND	ND	0.04
Profenofos	ND	ND	0.09	ND
Phorate	<0.01	ND	ND	ND
Methamidophos	0.04	ND	ND	0.05
Ethoprophos	ND	ND	ND	0.26
Chlorpyrifos	0.14	0.16	0.13	0.30
Lambda-cyhalothrin [a]	0.07	<0.01	ND	ND
Permethrin [a]	0.08	0.13	ND	ND
Cyfluthrin [a]	0.18	0.05	ND	ND
Deltamethrin [a]	ND	<0.01	ND	0.08
Cypermethrin [a]	1.21	0.32	ND	1.61
Bifenthrin [a]	ND	ND	ND	0.05

[a] - Synthetic Pyrethroids , Limit of detection for all pesticides = 0.01 mg/kg, ND=not detected, SD =standard deviation

Appendix O

Table 23: Mean concentration levels (mg/kg) of organophosphate and synthetic pyrethroids pesticide residues detected in samples from Asamankese market.

Pesticide	Lettuce	Garden eggs	Pineapple	Mango
Dimethoate	ND	0.02	0.01	ND
Pirimiphos-methyl	0.04	ND	ND	ND
Malathion	ND	0.13	ND	ND
Fenitrothion	ND	ND	0.02	ND
Parathion ethyl	0.02	0.04	ND	ND
Chlorfenvinphos	0.01	ND	0.03	ND
Profenofos	0.06	0.06	ND	0.03
Methamidophos	<0.01	ND	ND	ND
Ethoprophos	ND	ND	0.08	ND
Chlorpyrifos	0.04	0.12	0.04	ND
Allethrin [a]	ND	0.03	<0.01	ND
Lambda-cyhalothrin [a]	0.01	ND	ND	ND
Permethrin [a]	ND	ND	0.16	0.11
Cyfluthrin [a]	ND	0.05	ND	ND
Deltamethri [a]	ND	ND	ND	0.01
Cypermethrin [a]	ND	0.06	1.86	ND

[a] - Synthetic Pyrethroids , Limit of detection for all pesticides = 0.01 mg/kg, ND=not detected, SD =standard deviation

Appendix P

Table 24: Mean concentration levels (mg/kg) of organophosphate and synthetic pyrethroids pesticide residues detected in samples from Nsawam market.

Pesticide	Lettuce	Garden eggs	Pineapple	Mango
Dimethoate	0.01	0.05	ND	<0.01
Pirimiphos-methyl	ND	<0.01	ND	ND
Fenitrothion	0.05	ND	ND	<0.01
Parathion ethyl	ND	ND	0.01	ND
Chlorfenvinphos	0.05	ND	<0.01	0.02
Profenofos	0.04	0.02	ND	ND
Phorate	0.02	0.02	ND	0.01
Methamidophos	ND	0.04	0.01	0.04
Ethoprophos	0.07	0.02	ND	<0.01
Chlorpyrifos	0.16	0.24	0.11	0.03
Allethrin [a]	0.12	0.02	ND	0.12
Permethrin [a]	0.37	0.04	ND	0.15
Cyfluthrin [a]	0.22	0.35	ND	0.08
Deltamethrin [a]	ND	0.04	ND	0.04
Cypermethrin [a]	2.56	2.12	ND	1.24

[a] - Synthetic Pyrethroids , Limit of detection for all pesticides = 0.01 mg/kg, ND=not detected, SD =standard deviation