KWAME NKRUMAH UNIVERSITY OF SCIENCE AND TECHNOLOGY,

KUMASI

COLLEGE OF SCIENCE

LEVELS OF ORGANOCHLORINE PESTICIDE RESIDUES IN VEGETABLES, SOIL, AND WATER FROM SELECTED AGRICULTURAL FIELDS IN KUMASI

BY

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MASTER OF PHILOSOPHY (MPHIL) IN ANALYTICAL CHEMISTRY

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DECLARATION

I hereby declare that this thesis is my own work towards the M.Phil. in Analytical Chemistry deg

ree and that, to the best of my knowledge, it contains no material previously published by another person nor material which has been accepted for the award of any other degree of the University, except where due acknowledgement has been made in the text.

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DEDICATION

I dedicate this work to my parents, Mr. and Mrs. Kumah, for their love and support towards my education.

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ABSTRACT

The levels of organochlorine pesticides residue in cabbage, lettuce, onion, soil around cabbage, soil around lettuce, soil around onion, and irrigation water from five farms at Ayigya, Nsenie, Gyenyase, Kentinkrono were determined to assess the potential health risk associated with exposure to the pesticide residues from vegetables consumption. Sample collection and preparation were conducted using standard procedures. The concentrations of organochlorine pesticide (OCP) residues in the samples were determined using gas chromatograph (Varian CP-3800) equipped with electron capture detector (ECD). A total of fifteen different OCP residues were detected. The residue concentration in vegetables, soil, and irrigation water ranged from <0.01 to 184.10±12.11 µg/kg, <0.01 to 165.20±31.11 µg/kg, and <0.01 to 8.87±0.34 µg/L respectively. Methoxychlor recorded the highest mean concentration of 184.10±12.11 µg/kg in cabbage from Ayigya and beta-HCH recorded the lowest mean concentration of 0.20±0.00 µg/kg also in cabbage from Ayigya. Most of the organochlorine residues detected were below the maximum residue limits (MRLs). Bioconcentration in the fatty tissues of consumers could result in chronic health effects. The differences in residual concentrations of pesticides could be due to different agricultural practices adopted by farmers and also accessibility of the pesticides. Health risk estimation revealed that aldrin in lettuce could pose potential toxicity to the children. The combined risk index showed significant health risk to children. The overall risk index for combined pesticides due to consumption of all the vegetables was higher than 1, which signifies potential health risk to consumers. The carcinogenic risk of the OCP residues in vegetables was of little concern since their carcinogenic rates were below the acceptable risk level.

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LIST OF ABBREVIATIONS

ADHD	-	Attention deficit hyperactivity disorder
ADI	-	Accepted daily intake
ATSDR	-	Agency for Toxic Substances and Disease Registry in the United States
CARDIA	-	Coronary Artery Risk Development in Young Adults
DDD	-	Dichlorodiphenyldichloroethane
DDE	-	Dichlorodiphenyldichloroethylene
DDT	-	Dichlorodiphenyltrichloroethane
Dw	-	Dry weight
DNA	-	Deoxyribonucleic acid
EC	-	European Commission
ECD	-	Electron capture detector
EDB	-	Ethylenedibromide
EDs	-	Endocrine disrupting chemicals
EU	-	European Union
FAO	-	Food and Agriculture Organisation
GAEC	-	Ghana Atomic Energy Commission
GC-ECD	-	Gas Chromatography Electron Capture Detector
HCB	-	Hexachlorocyclobenzene
HCH	-	Hexachlorocyclohexane
mg/L	-	Milligram per liter
MRL	-	Maximum Reside Level
o, p-isomer	-	ortho, para-isomer

OC	-	Organochlorine
OCPs	-	Organochlorine pesticides
PCB	-	Polychlorinatedbiphenyl
PD	-	Parkinson‘s disease
POP	-	Persistent Organic Pollutants
PVC	-	Polyvinylchloride
SPE	-	Solid Phase Extraction
UN	-	United Nations
UK	-	United Kingdom
WHO	-	World Health Organization
µg/kg	-	Microgram per kilogram
µg/L	-	Microgram per liter
cm	-	Centimeter
ppb	-	Part per billion
ng/mL	-	Nanogram per milli liter

CHAPTER ONE

1.0 INTRODUCTION

1.1 Background of study

Pesticides are extensively used for control of agricultural pests and vector borne diseases. Various pesticides including organochlorine, organophosphate, and synthetic pyrethroid insecticides are commonly used for pest control in agriculture (Bhupander *et al.*, 2011).

Environmental pollution by pesticides is a matter of great concern because of their prolonged persistence lipophilic nature and tendency to accumulate in animal and plant tissues. Pesticides are among the hazardous contaminants and can persist in soil and sediments for decades even after ban (Bhupander *et al.*, 2011). They have wide range of acute and chronic health effects, including cancer, neurological damage, reproductive disorder, immune suppression, birth defects, and stress and also suspected endocrine disruptors (Cervera *et al*., 2012).

Barriada-Pereira *et al.*, (2010) indicated that pesticides vary in their mode of action, uptake by the body, metabolism and removal from the body and toxicity potential. In a research paper by Akan *et al*., (2014), it is reported that loamy sands with low pH tend to have high pesticide dissipation rates and warm moist soil containing high organic matter generally accelerate the decomposition process. These climatic elements effect pesticide persistence in soil; air temperature, light intensity, rainfall and wind direction.

Although the production and use of many OCPs such as dichlorodiphenyltrichloroethane (DDT), hexachlocyclohexane (HCH) and hexachlorobenzene (HCB) have been banned

(Jeyakumar *et al.*, 2014) in most countries since the 1970s, their residues in the environmental reservoirs may still continue to be sources of current atmospheric contamination (Jiang *et al.*, 2014).

Fresh vegetables containing residue concentration above the prescribed maximum residue level (MRL) may pose health hazard to consumers (Cervera *et al*., 2012). This study aims to determine the residual levels of OCPs in vegetables widely consumed in Kumasi, the soil used for their cultivation and the water used for irrigation. It is also to generate data on OCPs for the study area.

1.2 Problem Statement

OCPs, due to their effectiveness in the control of pests and disease vectors were widely used in agriculture globally. The production and uses of OCPs have been restricted or even banned in many countries. However, they are still found widespread in the environment because of their extreme stability thus persisting as a result of their indiscriminate use historically and allowed limited use of them in disease control.

OCPs are extensively used by farmers in Ghana due to their efficiency and their broadly action. Gamma-HCH is usually used on cocoa plantations, vegetable farms, and for the control of stem borers in maize. Gerken et al., (2001) reported the use of organochlorine pesticides on agricultural crops.

The accumulation of pesticide residues in agricultural products is of great concern because plants act as intermediates in the transport of these contaminants. Therefore the monitoring of pesticide residues in vegetables may show the degree of contamination of pesticides that may pose a potential risk to human health.

1.3 Objectives of the Study

1.3.1 Main Objectives

In view of the fact that people of Kumasi consume large amounts of vegetables, the current study seeks to determine the levels of OCP residues in vegetables and assess the human health risk associated with the consumption of these vegetables.

1.3.2 Specific Objectives

- To identify various organochlorine pesticide residues in vegetable, soil and water samples
- To determine the concentrations of organochlorine pesticide residues in the vegetable, soil and water samples.
- To determine human health risk on consumption of the vegetables.

1.4 Justification

Environmental pollution by pesticides is a matter of great concern because of their prolonged persistence, lipophilic nature and tendency to accumulate in animal and plant tissues. Improper use of pesticides in agriculture is a major source of environmental pollution (Darko *et al.*, 2008). In order to effectively control environmental pollution, there is the need to come out with very good, effective and enforce laws and guideline. However, this step will only be possible when the residual levels of pesticides in the environment have been established.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 Occurrence of Organochlorine Pesticides in Humans and the Environment

OCPs have been used in Ghana for many decades. Different researches have been piloted on the agricultural and mining communities and on human fluids to evaluate the environmental contamination status and the level of accumulation in humans (Asante and Ntow, 2009).

Daou and Dahchour, (2014) assessed the degree of contamination by organochlorine pesticides (OCP) in Loukkos area in the northwest of Morocco. The research showed that a substantial contamination by OCPs in the drained Loukkos area.

Akan *et al*., (2014) conducted a study on soil and five vegetables namely spinach, tomato, onion lettuce, and cabbage for the analysis of selected organochlorine pesticide residues. They reported that the maximum residue concentration was p,p'-DDD while the lowest concentration was p,p'-DDT. In general, higher concentrations of the residues were recorded.

2.2 Organochlorine Compounds

Organic pesticides can 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.

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 pesticides and chlorinated synthetics. 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, DDE and methoxychlor. Examples of cyclodienes include dieldrin, endrin, aldrin, endosulfan, chlordane and heptachlor. The chlorinated benzenes or cyclohexanes also include lindane, and mirex. In general, many organochlorines and their metabolites have the tendency to bioaccumulate owing to their low water solubility and high chemical stability (Rathore and Nollet, 2012).

2.2.1 Dichlorodiphenyltrichloroethane

The active ingredient is p,p- DDT (65 % to 80 %). DDT compounds can be degraded to DDD under anaerobic conditions while it can be degraded to DDE. In areas where DDT exposure is recent, the ratio of DDE / DDT is low, while in areas where considerable time has passed since its use DDE connection / DDT is larger (Rathore and Nollet, 2012). Figure 2.1a and 2.1b below are chemical structures of o,p-DDE and p,p- DDE respectively.

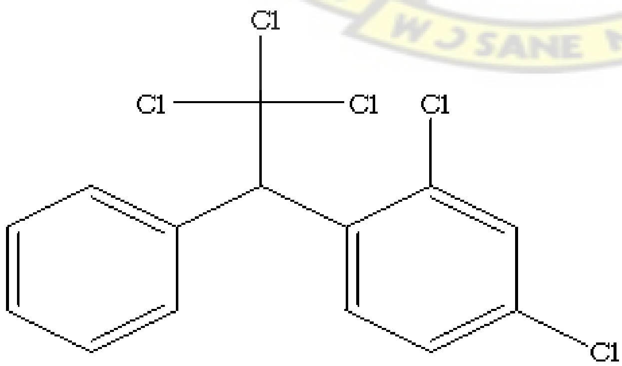

Figure 2.1a: Chemical Structure of o,p-DDE

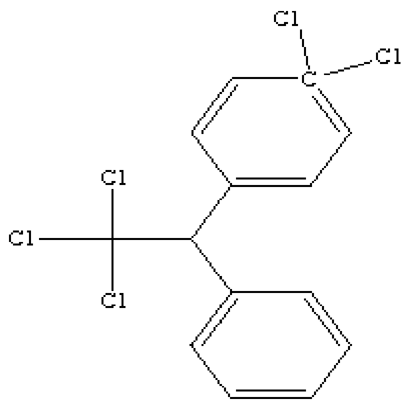

Figure 2.1b: Chemical Structure of p,p- DDE

2.2.2 Endrin

Endrin is an odorless, white crystal. It is slightly soluble in alcohol and insoluble in water. It is an insecticide used on field crop such as maize, cotton, sugar cane, rice, cereals and ornamentals. Endrin has also been used for grasshoppers on non-crop lands and to control voles and mice in orchid (Udeh, 2004). Endrin released to soils will persist for up to 14 years or more. It is persistent in treated soils and accumulates in sediments and terrestrial biota but known to be broken down by sunlight. It has a high potential to accumulate in fish and shell fish. The chemical is known to cause damage to liver, kidney and heart of laboratory animals.

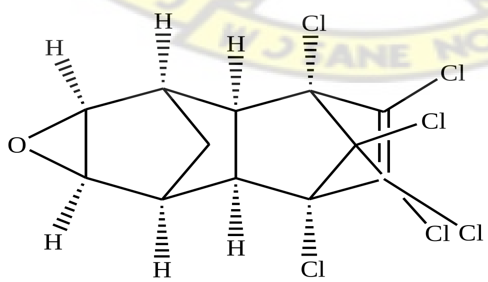

Figure 2.2: Chemical Structure of endrin

2.2.3 Aldrin

Until the 1970s, aldrin was extensively used to treat seeds and soil. Aldrin is synthesized by combination of hexachlorocyclopentadiene and norbornadiene in a Diels-Alder reaction. The figure below is the chemical structure of aldrin.

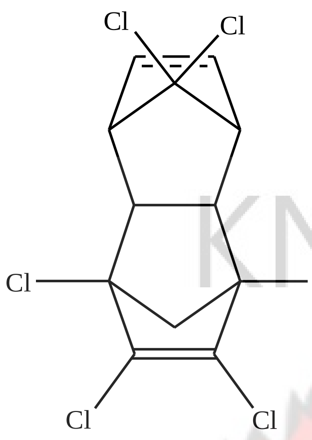

Figure 2.3: Chemical Structure of aldrin

2.2.4 Dieldrin

Dieldrin has a ring structure based on naphthalene. It is rapidly synthesized with the aid of sunlight and bacteria from aldrin to dieldrin in plants, animals and the environment. It has been associated to health problems including breast cancer, nervous system damage, and reproduction. Soto *et al*., (1994) reported that it has estrogenic properties. The figure below is the chemical structure of dieldrin.

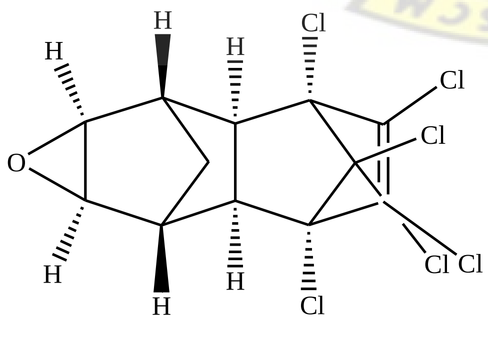

Figure 2.4: Chemical Structure of dieldrin

2.2.5 Hexachlorocyclohexane (HCH)

HCH exists in eight isomeric forms. One is, gamma-HCH which is produced and used as pesticides on agricultural products. Gamma – HCH may be converted to other isomers in the environment and also micro – organisms and plants may convert gamma – HCH into alpha, beta or delta schemes. Bioisomerism does not appear to be a significant path way in mammals. In mammals, metabolism of alpha- HCH generally leads to less chlorinated unsaturated metabolites. Gamma HCH undergoes dechlorination in alkalis with DT50 values (22°C) of 91 days (pH 7) and 11 hours pH 9 (Roberts *et al.*, 1999). The figure below is the chemical structure of hexachlorocychlohexane.

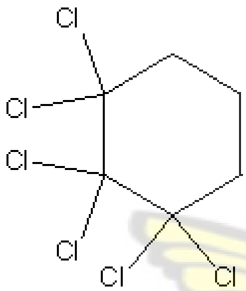

Figure 2.5: Chemical Structure of HCH

2.2.6 Chlordane

Chlordane is viscous, amber to coloured liquid with slight chlorine-like odour. It is a mixture of steroeisomers and other chlorinated analogs including heptachlor. It enters the environment primarily for its application as an insecticide and is not very mobile in soils. Though chlordane adheres to the soil, its presence in ground water indicates its tendency to leach into the groundwater (Udeh, 2004). Rathore and Nollet, (2012) indicated that chlordane has been found to be in soils after twenty (20) years its initial application. The figure below is the chemical structure of chlordane.

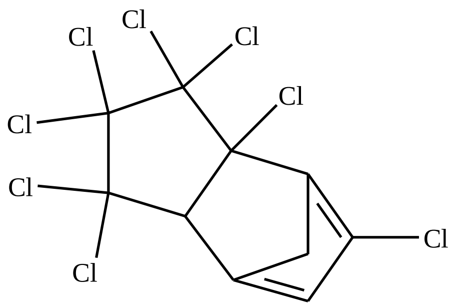

Figure 2.6: Chemical Structure of chlordane

2.2.7 Heptachlor

Heptachlor is an organochlorine cyclodiene, it is also applied as seed treatment, soil treatment or direct foliage. Metabolic processes by which it undergoes transformation are epoxidation, hydrolysis and dechlorination. It is not readily dehydrochlorinated but it is most susceptible to epoxidation. It is hydrolysed in water to 1-hydroxychlordene. It is transformed into a variety of products which differ from one another only in stereoechemical features while retaining the carbon skeleton (Roberts *et al*., 1999). Heptachlor is known to cause cancer in laboratory animals investigated and may increase cancer risk in humans who are open to it for long periods (Udeh, 2004). The figure below is the chemical structure of heptachlor.

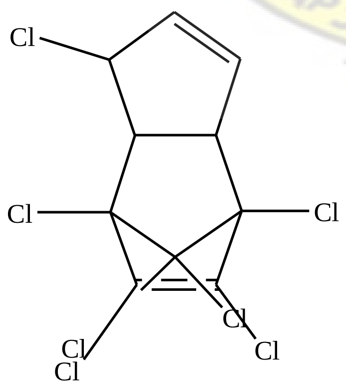

Figure 2.7: Chemical Structure of heptachlor

2.2.8 Endosulfan

Endosulfan is an organochlorine pesticide which belongs to the cyclodiene group. Endosulfan sulphate is the key metabolite of endosulfan. Endosulfan sulphate is considered to be similarly toxic in relation with the parent isomers (USEPA, 2007).

2.2.9 Methoxychlor

Methoxychlor is degraded slowly in air, water and soil by sunlight and microscopic organisms (ATSDR, 2002). Methoxychlor half-life is greater than six months in soil. The figure below is the chemical structure of methoxychlor.

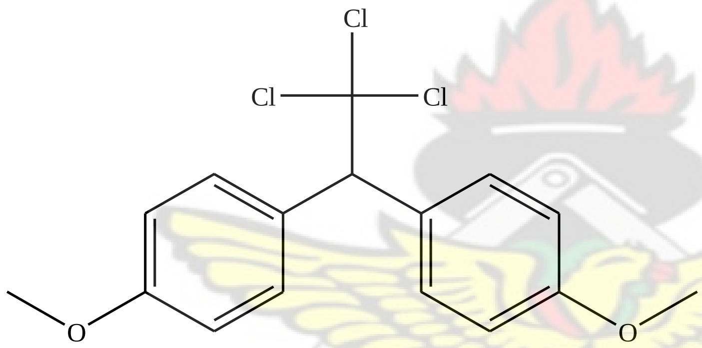

Figure 2.8: Chemical Structure of methoxychlor

2.3 Health Effects of organochlorine on Humans

The existence of contaminants in the human body does not mean they cause negative effects on health. However, the introduction of environmental chemicals affects human health. The dose and duration of exposure have a substantial impact on the performance of any potential health. Health effects of exposure to organochlorine pesticides depend on the particular pesticide, the level of exposure, the exposure time and the individual (Xavier et al., 2004) .

Kannan *et al*., (1997) report indicated that organochlorines are endocrine disrupters. Studies have associated a decrease in sperm counts with exposure to organochlorine insecticides.

2.3.1 Diabetes

Montgomery et al., (2008) reported that exposure to certain toxic substances in the environment may be associated with increased risk of developing diabetes. They found seven specific pesticides chances of diabetes incidence increased by ever use and cumulative days of use.

Recent epidemiological studies have revealed strong association between organochlorine pesticides and type 2 diabetes. Lee et al. (2006) showed a very strong correlation between levels of POPs in serum.

2.3.2 Cytotoxic defects

Ündeğer and Basaran, (2002) conducted research on pesticides residues and revealed DNA damage in peripheral lymphocytes among workers employed. In their research, the metabolite of malathion (malaoxon) was found to be more toxic than the parental compound. Malaoxon has potential to cause harm to DNA. Blasiak and Stańkowska, (2001) reported that malaoxon can methylate DNA bases.

2.3.3 Cancer

Høyer *et al*., (1998) conducted studies on exposure and risk of breast cancer and reported that dieldrin was linked to a significantly increased dose-related risk cancer. Alavanja *et al*., (2003) studied the association between pesticides and prostate cancer incidence. It was reported that of OCPs among applicators over 50 years of age and the use of methyl bromide were significantly associated with risk of prostate cancer.

2.3.4 Immune system dysfunction

Studies shows that many pesticides extensively use globally are immunosuppressive. Organochlorine pesticides that are known to alter the immune system are DDT, chlordane, aldrin, lindane, hexachlorobenzene, mirex, and arochlor (a PCB).

Persistent exposure to toxins, causing some detoxification, to be inefficient, resulting in the accumulation of toxins and dead cells of microorganisms grow in the blood. To combat these foreign particles, the immune system will produce large-inflammatory chemicals. During the hyper - excited state, the immune system produces autoantibodies. This can cause symptoms of immune dysfunction, including recurrent infections, inflammatory diseases, allergies, swollen glands, autoimmune diseases, and chronic fatigue syndrome (Desi al, 1978 ;. Glick, 1974; Giurgea et al, 1978 ;. Streets and Sharma, 1975 ; Latchoumycandane and Mathur, 2002).

2.3.5 Childhood developmental disorders

Research by Bourcher *et al*., (2013) results suggested that prenatal exposure to chlordecone is associated with specific impairments in fine motor function in boys, and add more evidence that exposure to organochlorine pesticides early in life reduces the child's development. A study in India (Kuruganti, 2005) evaluated the effect of pesticide exposure on children's ability to accomplish the tasks of development. It was found that over 80 percent of children tested performed much worse than less prone children.

CHAPTER THREE

3.0 MATERIALS AND METHODS

3.1 Reagent

Standards of the fifteen OCPs were acquired from Supelco (PA, USA). Analytical grade acetone, sodium sulphate, ethyl acetate and sodium hydrogencarbonate were bought from a local chemical shop (Fregeosco Co. Ltd) in Accra who also obtained their supplies from CDH group in India. The n-hexane was Super Purity Solvents from Romil (Cambridge, UK).

3.1.1 Cleaning of glassware

Prior to the analysis, all glassware used for the analysis were washed with a detergent with hot water, rinsed with tap water and then distilled water. All glassware were further rinsed with acetone and then placed over night in an oven at about 40 ºC.

3.1.2 List of apparatus

The following lists of apparatus were used for laboratory analysis: Gas chromatograph (Varian CP-3800) with ECD, Rotary evaporator (BÜCHI Rotavapor R-200), grab water sampler (Cole-Palmers, India), ultrasonic bath (Branson 220, Branson Ultrasonic Cleaner, USA) Pasteur pipettes, Weighing balance-meter, Round bottom flasks (250ml), aluminum foils, oven, auto sampler vials (2ml) ,and chromatographic columns.

3.2 Description of study area

Kumasi is capital of the Ashanti region. It is the second largest city and one of the fastest growing metropolitan areas in Ghana, with an estimated population of 2,035,064 and an annual growth rate of 5.47% (Ghana Statistical Service, 2010). It covers a total area of 57sq.m and topography of the region varies from gently undulating hilly and mountainous clear (Taylor and Georghiou, 1982). The region has two main seasons, the rainy and dry seasons. The rainy season is characterized by heavy rains during the period from March to July, and light rain between September and November, with an annual rainfall of about 1300 mm. Relative humidity varies between 1270-1410 mm, and the mean daily sunshine duration between 2-7 hours, and the daily minimum and maximum temperatures 21.20 °C and 35.50 ° C, respectively (Department of Meteorological Services, Kumasi Airport Weather Station, 2002). Kumasi unique position and the availability of infrastructure in conjunction with the main markets have made it a center of trade in the Ashanti region. Kumasi Central Market is one of the largest markets in Africa. Other markets include Asafo market, which is the second largest in the region. The study was conducted on selected vegetable production fields in Kumasi.

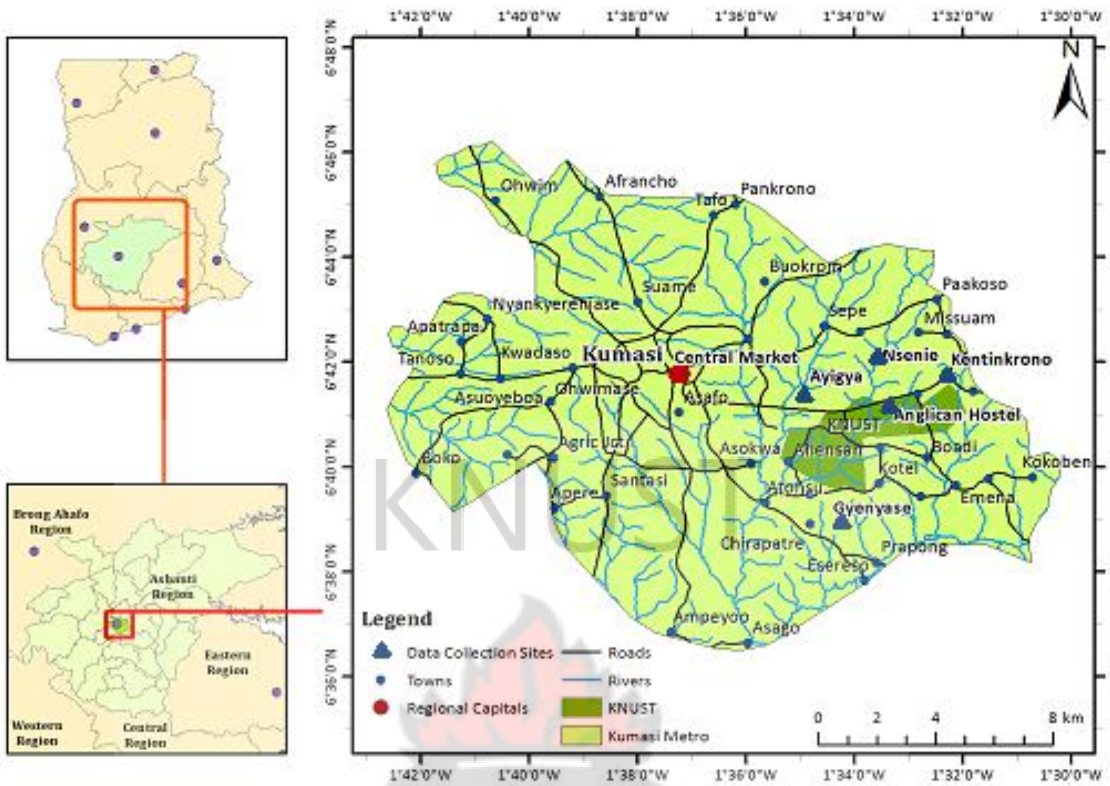

Figure 3.1: A map showing the study areas in Kumasi, Ashanti Region, Ghana

3.2.1 Sampling of vegetables

At each sampling site, three vegetables specifically, cabbage, lettuce, and onion were bought from five farms in Kumasi (Kentinkrono, Ayigya, Nsenie, Gyenyase, and the Anglican Hostel) within the month of September, 2014. The vegetables were bought directly from the farmers during harvest. Samples were immediately wrapped in aluminium foil that had already been cleaned with acetone. They were then placed in zip lock bags and appropriately labeled. The labeled samples were then placed in ice chest containing ice and transported to the Nuclear and Environmental Centre Laboratory, Ghana Atomic Energy Commission (GAEC) within 5 hours after sampling. They were then frozen at about -20 ºC prior to analysis. A total of 15 samples of vegetable composites were sampled for analysis of the organochlorine pesticide residue levels using gas chromatography.

3.2.2 Sampling of soil

Soil samples were collected from five farms within Kumasi (Kentinkrono, Ayigya, Nsenie, Gyenyase, and the Anglican Hostel). In each farm, samples were collected at various depths (0-30 cm), using spiral auger. Samples were immediately wrapped in aluminium foil that had already been cleaned with acetone. They were then placed in zip lock bags and appropriately labeled. The labeled samples were then placed in ice chest containing ice and transported to the Nuclear and Environmental Centre laboratory, Ghana Atomic Energy Commission (GAEC) within 5 hours after sampling. A total of 15 samples of soil composite were collected for analysis of the organochlorine pesticide residue levels using gas chromatography.

3.2.3 Sampling of water

Water samples were collected using grab water sampler (Cole-Palmers, India) and drained directly into a pre-rinsed 1L amber glass bottle. The samples were kept at 4 ^{0}C until extraction. A total of 5 samples composites were sampled for analysis of the organochlorine pesticide residue levels using gas chromatography.

3.3 Analysis for organochlorine pesticide residues

Analysis of individual organochlorine pesticides (OCPs) was done by first extracting the OCP residues from the samples followed by cleanup of extracts and finally qualitative and quantitative determination by the GC-ECD.

3.3.1 Extraction of organochlorine pesticides from water samples

Liquid-liquid extraction using hexane adopted by Afful *et al.*, (2013) was used. 20 mL portion of the water sample was shaken with 20 mL of hexane in 100 mL separating funnel. The hexane extract was then separated from the aqueous layer. Extraction was repeated three times and the organic layers put together. The combined organic layer was dried over anhydrous sodium sulphate. Extract was then concentrated on rotary evaporator (BÜCHI Rotavapor R-200 rotary evaporator) to about 5 ml and then subjected to clean up to remove co-extractives.

3.3.2 Extraction of organochlorine pesticides from soil samples

OCPs in the soil samples was extracted with 50 mL of 3:1 hexane/acetone solvent system (Afful *et al.*, 2013) by sonicating 2.5 g of the sample on an ultrasonic bath (Branson 220, Branson Ultrasonic Cleaner, USA) for 1 hour at 40 ^{o}C. The extracts were filtered with whatman No. 42 filter paper. The extract was then dried over anhydrous sodium sulphate and concentrated to about 5 mL using rotary evaporator (BÜCHI Rotavapor R-200 rotary evaporator). Extracts were then subjected to clean up.

3.3.3 Extraction of organochlorine pesticides from vegetables

A 10 g of the vegetable was homogenized in glass blender and transferred into 250mL conical flask. 50 mL of 1:1 acetone/ethyl acetate solvent system was then added. Earlier portion of part of the 50 mL of the solvent system was used to rinse the glass blender and this was added to the sample in the conical flask. Extraction was performed by sonicating 10 g of the homogenate on an ultrasonic bath (Branson 220, Branson Ultrasonic Cleaner, USA) for 1 hour at 40 ^{o}C. Extracts were filtered with whatman No. 42 filter paper. The extracts were then dried over anhydrous sodium sulphate and concentrated to about 5 mL. Extracts were then subjected to clean up.

3.3.4 Combined florisil-silica clean-up of extracts

The clean-up procedure was carried out according to the method used by Kuranchie-Mensah *et al.,* (2011). A combined florisil-silica solid phase extraction columns was prepared by packing 1.5 g and 0.5 g pre-activated florisil and silica adsorbent material respectively with 1.0 g anhydrous sodium sulphate packed on top of the adsorbents in glass column. The packed columns was then conditioned with 10 ml of hexane prior to clean up after which the extract was passed through the columns and the eluate collected into 50 ml conical flask. The column was further eluted first with 15 ml hexane followed by 5 ml of 2:1 hexane/diethyl ether. The eluate was concentrated almost to dryness on rotary evaporator (BÜCHI Rotavapor R-200 rotary evaporator) and eluate picked up in 1.5 ml ethyl acetate. The extract was finally transferred into 2 ml glass vial using Pasteur pipette for GC - ECD analysis.

3.3.5 Quantification

Quantification of the residues in sample extracts was performed by running a standard mixture of known concentration of the pesticide and detector response for each compound was found. The area of the corresponding peak in the sample compared with the standard. All assays were performed in triplicate, and the average concentrations are calculated accordingly.

3.4 Gas chromatography analysis

The GC equipped with Electron Capture Detectors was used for analysis. The Gas Chromatograph was Varian CP-3800 equipped with an auto sampler. A volume of 1.00 µL of the extracts was injected. The operating conditions were;

Capillary column: VF-5ms, 30 m x 0.25 mm x 0.25 µm

Temperature programme: 70°C (2min) to 180°C (1min) 25°C/min to 300°C 5°C/min

Injection temperature: 270°C

Detector temperature: 300°C

Carrier gas: Nitrogen at 1.0mL/min

Make up gas: Nitrogen at 29ml/min.

A 0.5 ppm mixed standard solution of organochlorine pesticides were analyzed in a similar manner for identification. Peak identification was conducted by comparing the retention time of authentic standards and those obtained from the extracts and quantified by external standard method. Concentrations were calculated using a four point calibration curve.

3.5 Analytical quality assurance

The efficiency of the method of analysis (extraction and cleaning methods) was determined by recovery of an external standard. Moreover, a sample from each batch analysis enriched with a 0.5 ppm external standard and extracted under the same conditions as the analytes. To check for cross contamination and interferences, a blank sample was analysed in each batch of analysis.

3.6 Recovery Test

Loss of target compounds can occur during treatment, extraction and analysis of sample. The extent of analyte loss in particular during extraction was determined by performing a recovery. A recovery test was carried out and executed by spiking the samples with 1.0 ml of the standard organic mix. Spiked samples and blanks were subjected to extraction, SPE clean-up, GC - analysis and quantification (Bempah and Donkoh, 2011).

The concentration of pesticides recovered in the extracts were calculated by the formula

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

3.7.0 Exposure Assessment

3.7.1 Estimation of daily intakes (EDI)

To estimate the potential health risk linked to each organochlorine pesticide, some assumptions were made based on the United States Environmental Protection Agency's guidelines (USEPA, 2000). The first assumption made was that, a hypothetical body weight of 10 kg for children and 60 kg for adult and the additional is that there is maximum absorption rate of 100 % and bioavailability rate of 100 %. According to Bempah, *et al*., (2012), food consumption rate for vegetable is estimated to be 0.137 µg/kg/day in Ghana. Consequently for each type of organochlorine pesticides exposure, the estimated daily intake (µg/kg) was gotten by multiplying the mean residual pesticide concentration (µg/kg) in the vegetable of concern by the vegetable consumption rate (µg/kg/day) and dividing the product by the body weight (kg).

$$\text{EDI} = \frac{\text{C} \times \text{CR}}{\text{BW}}$$

Where EDI is the estimated daily intake, C is the concentration of the pesticide residue (µg/kg), CR is the consumption rate (kg/day) and BW is the average body weight (kg) of Ghanaian children and adult.

3.7.2 Risk Characterization

The potential public health risk significance of OCP residues to human through daily food intakes were characterized based on the guidelines suggested by the US EPA

(2000). In the case of non-carcinogenic effects, the hazard indices (HI) for human were computed as ratios between estimated daily intake (EDI) and the acceptable daily intake (ADI) which are considered to be harmless levels of exposure over the lifetime. When HI is greater than 1, it indicates that lifetime consumption of vegetable containing the measured level of OCP residues could pose health risks (Wang *et al.*, 2011). The HI was calculated as:

$$HI = \frac{EDI}{ADI}$$

3.7.3 Combined risk of multiple OCP pollutants

Akoto *et al*., (2015) and Reffstrup *et al*., (2010) reported that the effect of two or more pollutants can lead to additive and / or interactive effects. The proposed method US EPA hazard index was used to assess the risk of collection of pesticides acting as a general mechanism or toxicological (US EPA 2000, Reffstrup *et al*, 2010). Hazard Index combination (HI), was evaluated using the equation recommended by Reffstrup al. (2010).

$$\mathrm{HI} = \frac{B_1}{L_1} + \frac{B_2}{L_2} + \cdots + \frac{B_n}{L_n} = \sum_{i=1}^{n} \frac{B_i}{L}$$

Where B_1, E_2, B_n and B_i are the levels of exposure of each discrete pesticide (i) in a mixture of n pesticides. L_1, L_2, L_n and L_i are the maximum acceptable levels (ADIs) for every pesticide (US EPA 2000). If the indices of danger go above 1, the mixture has exceeded the maximum permissible level, and may be a potential risk to consumers.

3.7.4 Overall health risk effect of pesticide residue in vegetables

The method used by the US EPA (1986) was used to measure the total potential risk of noncarcinogenic effects in the context of a particular combination of ways. It was calculated as the sum of the combined effects of all OCP residues present in vegetables used for the preparation of the diet (Akoto al., 2015).

3.7.5 Carcinogenic risk

Screening for potential health effects associated with cancer because of exposure to residues of OCP, cancer risk was calculated. Test concentration of carcinogenic effects were obtained using US EPA oral slope factor. The risk assessment was carried out on the basis of concentration of OCPs residues in vegetables. Hazard ratios (HRs) was calculated by dividing the estimated daily intake (EDI) by the benchmark concentrations (BC) for cancer (Dougherty et al., 2000). Hazard ratio of greater than one indicates that the average daily consumption exceeds the benchmark concentrations (Dougherty et al., 2000).

$$HR = \frac{EDI}{BC}$$

$$\text{BC} = \frac{\text{Risk} \times \text{Body weight}}{\text{Vegetable consumption rate} \times \text{Slope factor}}$$

Where risk is the probability of lifetime cancer risk, and slope factor is cancer slope factor. The benchmark concentration is derived by setting the cancer risk to one in one million due to lifetime exposure (Han *et al*., 1998).

CHAPTER FOUR

4.0 RESULT & DISCUSSION

The concentrations of fifteen (15) OCP residues were measured in seven different samples namely, cabbage, lettuce, onion, soil around cabbage, soil around lettuce, soil around onion, and water used for irrigation from the selected farms. Analysis of the samples discovered varying concentrations of pesticide residues.

Tables 4.1- 4.8 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 (cabbage, lettuce, onion, soil around cabbage, soil around lettuce, soil around onion, and irrigation water) as well as the different areas (Ayigya, Gyenyase, Nsenie, Kentinkrono, and Anglican Hostel) from which they were sampled. All tests were regarded as statistically significant when $p<0.05$. Also, the results of the pesticide residues were compared with the maximum residue limit (MRL) set forth by the United Kingdom/European Commission (UK/EC) for vegetables. Health risk estimation for carcinogenic and non-carcinogenic was calculated for each organochlorine pesticide residue and is presented in Tables 4.9- Tables 4.14 and the results discussed.

Table 4.1 Concentrations (µg/kg) of organochlorines in cabbage samples

Pesticide	Cabbage Ayigya Mean±SD	Gyenyase Mean±SD	Nsenie Mean±SD	Kentinkrono Mean±SD	Anglican Hostel Mean±SD	UK/EC MRL,2013
Gamma-HCH	1.40±0.41	<0.01	<0.01	<0.01	<0.01	10
Beta-HCH	0.20±0.01	<0.01	<0.01	35.20±0.35	14.76±3.57	10
Heptachlor	<0.01	<0.01	<0.01	<0.01	<0.01	10
Delta-HCH	1.50±1.81	12.41±0.14	<0.01	9.53±0.28	7.91±0.02	10
Aldrin	<0.01	<0.01	<0.01	<0.01	<0.01	10
Gamma-chlord	<0.01	<0.01	<0.01	<0.01	<0.01	10
A-endosulfan	<0.01	<0.01	<0.01	<0.01	<0.01	10
p,p'-DDE	<0.01	<0.01	<0.01	<0.01	<0.01	50
Dieldrin	<0.01	<0.01	<0.01	<0.01	<0.01	10
Endrin	<0.01	<0.01	<0.01	<0.01	<0.01	10
p,p'-DDD	<0.01	<0.01	<0.01	<0.01	<0.01	50
B-endosulfan	<0.01	<0.01	<0.01	<0.01	<0.01	10
p,p'-DDT	5.67±0.44	0.34±0.02	<0.01	31.73±0.07	10.29±0.07	50
Endosulfan s	28.47±2.68	<0.01	<0.01	<0.01	<0.01	10
Methoxychlor	184.10±12.11	<0.01	<0.01	<0.01	9.02±0.65	10

Limit of detection = 0.01 µg/kg, SD =standard deviation

4.1 Occurrence of organochlorine pesticide residues in cabbage

The levels of OCP residues in cabbage collected from the farms are shown in Table 4.1. The detected levels ranged from 0.20±0.01 µg/kg to 184.10±12.11 µg/kg. In general, nine OCP residues were detected in cabbage from all the five farms. Most of the residues were below their United Kingdom/European Commission Maximum Residue Limit (UK/EC MRL). Comparing sampling areas with regard to mean concentrations on cabbage, samples from Ayigya farm recorded the highest mean concentration level of OCP residues followed by Kentinkrono, Anglican hostel, Gyenyase and Nsenie in that order. Methoxychlor was recorded as OCP residue with the highest mean concentration and beta-HCH recorded least mean concentration with concentrations 184.10±12.11 µg/kg and 0.20±0.01 µg/kg respectively. The recorded mean concentrations, 35.20±0.35 for beta-HCH in the cabbage from Kentinkrono, 184.10±12.11 µg/kg for methoxychlor in the cabbage from Ayigya and 31.73±0.07 µg/kg for p,p'-DDT in the cabbage from Kentinkrono were all higher than mean residue concentration of 30 µg/kg reported by Bempah and Donkor, (2011). However, the rest of the OC residues were lower than the 30 µg/kg.

Beta-HCH levels ranged from 0.20±0.01 µg/kg to 35.20±0.35 µg/kg which is higher than residue mean ranged of ND to 20 µg/kg reported by Kumari *et al*., (2001) in India. This high concentration of beta-HCH confirms earlier findings made by Bempah and Donkor, (2011) that beta-HCH is widely used by farmers in Ghana. The concentration of Delta-HCH on the other hand, ranged from 1.50±1.81 µg/kg to 12.41±0.14 µg/kg which is higher than MRL of UK/EC of 10 µg/kg.

Endosulfan sulfate was not detected in all cabbage samples except sample from Ayigya with mean concentration of 28.47±2.68 µg/kg which is above the UK/EC MRL of 10 µg/kg.

Table 4.2 Concentrations (µg/kg) of organochlorines in lettuce samples

Pesticide	Lettuce Ayigya Mean±SD	Gyenyase Mean±SD	Nsenie Mean±SD	Kentinkrono Mean±SD	Anglican Hostel Mean±SD	UK/EC MRL,2013
Gamma-HCH	9.54±0.02	5.19±0.00	<0.01	7.16±0.14	<0.01	10
Beta-HCH	<0.01	2.10±1.84	12.00±1.70	<0.01	<0.01	10
Heptachlor	2.29±0.14	2.30±0.14	0.20±0.00	1.08±0.14	<0.01	10
Delta-HCH	<0.01	<0.01	<0.01	<0.01	<0.01	10
Aldrin	22.66±0.15	15.58±0.28	21.50±0.42	23.92±0.28	<0.01	10
Gamma-chlord	<0.01	<0.01	<0.01	<0.01	<0.01	10
A-endosulfan	0.60±0.28	1.30±0.42	4.10±0.14	<0.01	<0.01	10
p,p'-DDE	<0.01	<0.01	<0.01	<0.01	<0.01	50
Dieldrin	1.49±0.14	<0.01	<0.01	4.22±1.25	<0.01	10
Endrin	1.69±0.42	3.60±0.00	6.10±0.42	1.47±0.14	<0.01	10
p,p'-DDD	<0.01	<0.01	<0.01	<0.01	<0.01	50
B-endosulfan	<0.01	<0.01	<0.01	<0.01	<0.01	10
p,p'-DDT	9.34±0.22	5.09±3.53	11.50±4.38	4.51±0.83	2.20±0.02	50
Endosulfan s	<0.01	<0.01	<0.01	<0.01	<0.01	10
Methoxychlor	165.21±12.65	25.57±0.34	38.10±6.38	57.75±25.93	<0.01	10

Limit of detection = 0.01 µg/kg, SD =standard deviation

4.2 Occurrence of organochlorine pesticide residues in lettuce

The residue levels of OC pesticides in lettuce collected from the farms are shown in Table 4.2. The detected levels ranged from 0.20±0.00 µg/kg to 165.21±12.65 µg/kg. In general, nine OCP residues were detected in lettuce from all the five farms. However, not all of them were detected in the various sampling areas. All the residues were however, below UK/EC MRL except beta-HCH, aldrin and methoxychlor. Comparing sampling areas with regard to mean concentrations pesticide on lettuce, samples from Ayigya recorded the highest residues levels followed by Kentinkrono, Nsenie, Gyenyase and Anglican Hostel on the other hand recorded the least residue concentration. Delta-HCH, gamma-chlordane, p,p'-DDE, p,p'-DDD, B-endosulfan, Endosulfan sulfate were all below the detection limit of the instrument. It is interesting to note that methoxychlor recorded the overall highest mean concentration in the lettuce samples which was similar to the trend observed for cabbage. Also the highest mean concentration in the lettuce was recorded in the samples from Ayigya. Mean concentrations of methoxychlor in all the samplesexceeded UK/EC MRL except that recorded in the Anglican Hostel samples. Beta-HCH recorded mean concentration of 12.00±1.70 µg/kg in Nsenie which exceeded UK/EC MRL. Aldrin detected levels ranged from 15.58±0.28 µg/kg to 23.92±0.28 µg/kg. The mean concentrations of Aldrin exceeded the MRL set forth by UK/EC except in Anglican Hostel which was detected below the detection limit of the instrument.

Table 4.3 Concentrations (µg/kg) of organochlorines in onion samples

Pesticide	Ayigya	Gyenyase	Onion Nsenie	Kentinkrono	Anglican Hostel	UK/EC MRL,2013
	Mean±SD	Mean±SD	Mean±SD	Mean±SD	Mean±SD	
Gamma-HCH	<0.01	<0.01	<0.01	<0.01	16.82±4.80	10
Beta-HCH	<0.01	11.15±0.27	48.35±5.09	4.07±2.67	<0.01	10
Heptachlor	<0.01	<0.01	0.90±0.14	<0.01	<0.01	10
Delta-HCH	0.78±0.23	<0.01	<0.01	<0.01	5.23±0.09	10
Aldrin	<0.01	7.88±0.27	5.49±0.14	<0.01	21.78±1.19	10
Gamma-chlord	<0.01	<0.01	<0.01	<0.01	<0.01	10
A-endosulfan	<0.01	1.54±0.00	<0.01	<0.01	<0.01	10
p,p'-DDE	<0.01	<0.01	<0.01	<0.01	<0.01	50
Dieldrin	<0.01	<0.01	<0.01	<0.01	0.19±0.13	10
Endrin	<0.01	6.73±0.05	<0.01	<0.01	1.21±0.10	10
p,p'-DDD	<0.01	<0.01	<0.01	<0.01	<0.01	50
B-endosulfan	<0.01	<0.01	<0.01	<0.01	<0.01	10
p,p'-DDT	<0.01	4.42±0.54	<0.01	<0.01	4.49±1.45	50
Endosulfan s	<0.01	<0.01	2.80±0.28	2.18±3.20	<0.01	10
Methoxychlor	<0.01	160.96±12.24	<0.01	88.29±9.02	40.19±2.38	10

Limit of detection = 0.01 µg/kg, SD =standard deviation

4.3 Occurrence of organochlorine pesticide residues in onion

The residue levels of OC pesticides in onion collected from the farms are shown in Table 4.3. The detected levels ranged from 0.19±0.13 µg/kg to 160.96±12.24 µg/kg. Eleven OCP residues were detected in samples from the various sampling areas out of fifteen residues considered in this work. Gamma-chlordane, p,p'-DDE, p,p'-DDD, and B-endosulfan were all below the detection limit of the instrument. Methoxychlor recorded the highest mean value of 160.96±12.24 µg/kg in Gyenyase samples followed by Kentinkrono samples with mean value of 88.29±9.02 µg/kg and Anglican Hostel samples with mean value of 40.19±2.38 µg/kg all exceeded the UK/EC MRL.

Gamma-HCH exceeded the UK/EC MRL in onion samples from Anglican Hostel with mean concentration of 16.82±4.80 µg/kg but the rest were below UK/EC MRL. The mean concentration values for Beta-HCH exceeded the UK/EC MRL in samples from Gyenyase and Nsenie with mean concentration of 11.15±0.27 µg/kg and 48.35±5.09 µg/kg respectively. Aldrin recorded mean concentration of 21.78±1.19 µg/kg in samples from Anglican Hostel which is higher than UK/EC MRL. The remaining residues were below UK/EC MRL.

Table 4.4 Concentrations (µg/kg) of organochlorines in soil around cabbage samples

Pesticide	Soil around cabbage				
	Ayigya	Gyenyase	Nsenie	Kentinkrono	Anglican Hostel
	Mean±SD	Mean±SD	Mean±SD	Mean±SD	Mean±SD
Gamma-HCH	<0.01	<0.01	<0.01	<0.01	<0.01
Beta-HCH	<0.01	36.00±1.13	1.60±0.02	49.00±1.69	16.80±3.27
Heptachlor	<0.01	<0.01	<0.01	<0.01	<0.01
Delta-HCH	<0.01	<0.01	<0.01	<0.01	<0.01
Aldrin	<0.01	<0.01	<0.01	6.77±1.60	<0.01
Gamma-chlord	<0.01	<0.01	<0.01	<0.01	<0.01
A-endosulfan	<0.01	<0.01	<0.01	<0.01	<0.01
p,p'-DDE	<0.01	<0.01	<0.01	<0.01	<0.01
Dieldrin	<0.01	<0.01	<0.01	<0.01	<0.01
Endrin	<0.01	<0.01	<0.01	<0.01	<0.01
p,p'-DDD	<0.01	<0.01	<0.01	<0.01	<0.01
B-endosulfan	<0.01	<0.01	<0.01	<0.01	<0.01
p,p'-DDT	97.60±27.15	28.00±2.02	<0.01	54.98±2.33	<0.01
Endosulfan s	<0.01	<0.01	<0.01	<0.01	<0.01
Methoxychlor	39.31±3.95	<0.01	<0.01	<0.01	165.20±31.11

Limit of detection = 0.01 µg/kg, SD =standard deviation

4.4 Occurrence of organochlorine pesticide residues in soil around cabbage

OC pesticide residues in soil samples collected around the cabbage are shown in Table 4.4. The detected levels ranged from 1.60±0.02 µg/kg to 165.20±31.11 µg/kg. Beta-HCH recorded mean concentration which were high in all the sampling areas except Ayigya and Nsenie with mean concentrations of 36.00±1.13 µg/kg for Gyenyase samples, 49.00±1.69 µg/kg for Kentinkrono samples and 16.80±3.27 µg/kg for Anglican Hostel. Methoxychlor was detected in soil around cabbage from Ayigya and Anglican Hostel samples with mean concentrations of 39.31±3.95 µg/kg and 165.20±31.11 µg/kg respectively. p,p'-DDE and p,p'-DDD were not detected in all the samples. This confirms no previous application of the residue but the presence of high concentrations of p,p'-DDT with mean concentrations of 97.60±27.15 µg/kg, 28.00±2.02 µg/kg and 54.98±2.33 µg/kg respectively for Ayigya, Gyenyase and Kentinkrono samples indicates recent application of p,p'-DDT. This result favorably agrees with the findings of Ntow (2001). He reported that the residues of some pesticides are present in areas of highly intensive agricultural activity. The high concentration of p,p'-DDT in soils around the cabbage samples also agrees with that of Amoah *et al*., (2006). Darko and Acquaah., (2007) reported evidence of OC pesticides continued used in many developing countries such as Ghana because of inadequate regulations and supervision in the field of production, trade and use of these chemicals .

Table 4.5 Concentrations (µg/kg) of organochlorines in soil around lettuce samples

Pesticide	Soil around lettuce Ayigya Mean±SD	Gyenyase Mean±SD	Nsenie Mean±SD	Kentinkrono Mean±SD	Anglican Hostel Mean±SD
Gamma-HCH	<0.01	<0.01	<0.01	<0.01	<0.01
Beta-HCH	11.20±1.83	<0.01	<0.01	<0.01	<0.01
Heptachlor	<0.01	3.20±0.39	<0.01	<0.01	<0.01
Delta-HCH	<0.01	<0.01	<0.01	<0.01	<0.01
Aldrin	2.80±0.57	6.54±0.51	0.27±0.03	8.00±2.02	<0.01
Gamma-chlord	<0.01	<0.01	<0.01	<0.01	<0.01
A-endosulfan	<0.01	<0.01	<0.01	<0.01	<0.01
p,p'-DDE	<0.01	<0.01	<0.01	<0.01	<0.01
Dieldrin	<0.01	<0.01	<0.01	<0.01	<0.01
Endrin	<0.01	<0.01	<0.01	<0.01	<0.01
p,p'-DDD	<0.01	<0.01	18.80±1.70	<0.01	<0.01
B-endosulfan	<0.01	<0.01	<0.01	<0.01	<0.01
p,p'-DDT	39.60±2.24	<0.01	12.04±0.31	<0.01	17.60±0.43
Endosulfan s	<0.01	<0.01	<0.01	<0.01	<0.01
Methoxychlor	6.90±2.00	3.24±0.21	7.83±0.00	2.96±0.01	<0.01

Limit of detection = 0.01 µg/kg, SD =standard deviation

4.5 Occurrence of organochlorine pesticide residues in soil around lettuce

The OCP residues concentration in soils around the lettuce samples are shown in Table 4.5. The detected levels ranged from 0.27±0.03 µg/kg to 39.60±2.24 µg/kg. Beta-HCH recorded mean concentration of 11.20±1.83 µg/kg for Ayigya samples but it was not detected in the rest of the soil samples around lettuce. It is interesting to note that p,p'-DDD which is metabolite of p,p'-DDT was only detected in the soil around lettuce at Nsenie with mean concentration of 18.80±1.70 µg/kg. p,p'-DDT recorded a mean concentration of 39.60±2.24 µg/kg , 12.04±0.31 µg/kg and 17.60±0.43 µg/kg respectively for the Ayigya Nsenie and Aglican Hostel samples.

Table 4.6 Concentrations (µg/kg) of organochlorines in soil around onion samples

Pesticide	Soil around onion Ayigya Mean±SD	Gyenyase Mean±SD	Nsenie Mean±SD	Kentinkrono Mean±SD	Anglican Hostel Mean±SD
Gamma-HCH	<0.01	<0.01	<0.01	<0.01	0.27±0.01
Beta-HCH	<0.01	<0.01	<0.01	<0.01	<0.01
Heptachlor	<0.01	<0.01	<0.01	<0.01	<0.01
Delta-HCH	<0.01	<0.01	<0.01	<0.01	<0.01
Aldrin	0.80±0.01	4.80±0.05	<0.01	1.60±0.02	<0.01
Gamma-chlord	<0.01	<0.01	<0.01	<0.01	<0.01
A-endosulfan	<0.01	<0.01	<0.01	<0.01	<0.01
p,p'-DDE	<0.01	<0.01	<0.01	<0.01	<0.01
Dieldrin	<0.01	<0.01	<0.01	<0.01	<0.01
Endrin	<0.01	<0.01	<0.01	<0.01	<0.01
p,p'-DDD	<0.01	<0.01	<0.01	<0.01	<0.01
B-endosulfan	<0.01	<0.01	<0.01	<0.01	<0.01
p,p'-DDT	13.55±0.31	53.60±2.90	<0.01	48.80±0.00	148.21±6.91
Endosulfan s	<0.01	<0.01	<0.01	<0.01	<0.01
Methoxychlor	<0.01	22.8±4.22	<0.01	7.26±0.81	9.71±0.05

Limit of detection = 0.01 µg/kg, SD =standard deviation

4.6 Occurrence of organochlorine pesticide residues in soil around onion

OC pesticide residues in soil samples around onion are shown in Table 4.6. The detected levels ranged from 0.80±0.01 µg/kg to 148.21±6.91 µg/kg. p,p'-DDT was detected in all the soil around onion samples except samples from Nsenie with mean concentration of 13.55±0.31 µg/kg, 53.60±2.90 µg/kg, 48.80±0.00 µg/kg, and 148.21±6.91 µg/kg in Ayigya, Gyenyase, Kentinkrono and Anglican Hostel respectively. It was observed that the residual levels in samples from Gyenyase and Anglican Hostel were high and it is a public health concern.

Table 4.7 Concentrations (µg/L) of organochlorines in water

Pesticide	Water Ayigya Mean±SD	Gyenyase Mean±SD	Nsenie Mean±SD	Anglican Hostel Mean±SD	Kentinkrono Mean±SD	(WHO, 2013)
gamma-HCH	<0.01	<0.01	<0.01	<0.01	<0.01	2.00
beta-HCH	<0.01	1.63±0.00	<0.01	0.50±0.00	1.03±0.01	2.00
Heptachlor	<0.01	<0.01	<0.01	<0.01	<0.01	-
delta-HCH	<0.01	<0.01	<0.01	<0.01	<0.01	2.00
Aldrin	1.00±0.18	0.35±0.07	3.57±0.09	<0.01	<0.01	0.03
gamma-chlord	<0.01	<0.01	<0.01	<0.01	<0.01	0.02
A-endosulfan	<0.01	<0.01	<0.01	<0.01	<0.01	-
p,p'-DDE	<0.01	<0.01	<0.01	<0.01	<0.01	2.00
Dieldrin	<0.01	<0.01	<0.01	<0.01	<0.01	0.03
Endrin	<0.01	<0.01	<0.01	<0.01	<0.01	-
p,p'-DDD	<0.01	<0.01	<0.01	<0.01	<0.01	-
B-endosulfan	<0.01	<0.01	<0.01	<0.01	<0.01	-
p,p'-DDT	2.80±1.93	3.63±0.02	<0.01	3.82±0.02	2.07±0.03	2.00
Endosulfan s	<0.01	<0.01	<0.01	<0.01	<0.01	-
Methoxychlor	<0.01	<0.01	8.87±0.34	<0.01	1.53±0.00	20.00

4.7 Occurrence of organochlorines in water

Mean concentrations of organochlorine pesticide residues in water samples from all the study areas are presented in Table 4.7. The identified levels ranged from 0.50±0.00 µg/L to 8.87±0.34 µg/L. Gamma-HCH, heptachlordane, delta-HCH, gamma-chlordane, alpha-endosulfan, p,p'-DDE, dieldrin, endrin, p,p'-DDD, beta-endosulfan, and endosulfan sulfate were below the detection limit of the instrument. Organochlorine pesticides whose concentrations were detected above detection limit of the instrument were beta-HCH, aldrin, p,p'-DDT, and methoxychlor. Beta-HCH was detected with mean concentration of 1.63±0.00 µg/L in Gyenyase samples, 0.50±0.00 µg/L in Anglican Hostel samples, and 1.03±0.01 µg/L in Kentinkrono samples. Aldrin was detected with mean concentration of 1.00±0.18 µg/L in Ayigya samples, 0.35±0.07 µg/L in Gyenyase samples, and 3.57±0.09 µg/L in Nsenie samples. p,p'-DDT was detected with highest mean concentration of 3.82±0.02 µg/L in Anglican Hostel samples, followed by 3.63±0.02 µg/L in Gyenyase samples, 2.80±1.93 µg/L in Ayigya samples and lowest

2.07±0.03 µg/L in Kentinkrono samples. Methoxychlor recorded the highest mean concentration of 8.87±0.34 µg/L in Nsenie samples followed by 1.53±0.00 µg/L in Kentinkrono samples. Analysis of variance showed that the differences in the mean concentrations of the residues in the water samples was statistically insignificant, $p > 0.05$ as shown in Appendix O.The p,p'-DDT identified levels ranged from 2.07±0.03 µg/L to 3.82 µg/L which is higher than level reported by Afful *et al.,* (2013) in water samples from Lake Bosomtwe. In their work, they reported mean level of DDTs ranged <0.02 µg/L to 0.25 µg/L. The concentrations of beta-HCH in Gyenyase and Kentinkrono samples exceeded the MRL set forth by Australia. Also the mean concentrations of methoxychlor in Nsenie and Kentinkrono samples exceeded the MRL set forth by Australia. This is in agreement with Ntow, (2005) who reported that the Volta Lake was also found to be mildly contaminated with lindane, p,p'-DDT, p,p'-DDD and endosulfan. Jeyakumar *et al.,* (2014) reported OCPs concentration ranged of 0.00568 µg/L to 0.02512 µg/L in surface water from selected agricultural sectors of Kanyakumari District, India which is lower than the ranged reported by this work.

Table 4.8 Comparison of concentration (µg/kg) of OC pesticide residues on vegetables to that of their corresponding soil samples

Pesticide	Vegetable			Soil around		
	Cabbage Mean±SD	Lettuce Mean±SD	Onion Mean±SD	Cabbage Mean±SD	Lettuce Mean±SD	Onion Mean±SD
Gamma-HCH	1.40±0.41	7.30±0.08	16.82±4.80	<0.01	<0.01	0.27±0.01
Beta-HCH	16.72±1.31	7.05±1.77	21.19±2.68	25.85±1.53	11.20±1.83	<0.01
Heptachlor	<0.01	1.47±0.14	0.90±0.14	<0.01	3.20±0.39	<0.01
Delta-HCH	7.84±0.56	<0.01	3.01±0.16	<0.01	<0.01	<0.01
Aldrin	<0.01	20.92±0.28	11.72±0.53	6.77±1.60	4.40±0.78	2.40±0.03
Gamma-chlord	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
A-endosulfan	<0.01	2.00±0.28	1.54±0.00	<0.01	<0.01	<0.01
p,p'-DDE	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Dieldrin	<0.01	2.85±0.69	0.19±0.13	<0.01	<0.01	<0.01
Endrin	<0.01	3.21±0.33	3.97±0.08	<0.01	<0.01	<0.01
p,p'-DDD	<0.01	<0.01	<0.01	<0.01	18.80±1.78	<0.01
B-endosulfan	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
p,p'-DDT	12.00±0.15	6.53±1.80	4.46±1.00	60.19±10.50	23.08±0.99	66.04±3.37
Endosulfan s	28.47±2.68	<0.01	2.49±1.74	<0.01	<0.01	<0.01
Methoxychlor	96.56±6.38	71.67±11.33	96.48±7.88	102.26±17.53	<0.01	13.26±1.69

Limit of detection = 0.01 µg/kg, SD =standard deviation

4.8 Occurrence of concentration of OC pesticide residues on vegetables to that of their corresponding soil samples

Table 4.8 shows fifteen organochlorine pesticide residues that were investigated in vegetable and soil samples from the study areas. The identified levels ranged from 0.27±0.01 µg/kg to 102.26±17.53 µg/kg. Analysis of variance showed that the differences in the mean concentrations of the residues in the soil and corresponding vegetable samples was statistically insignificant ($p > 0.05$). Generally, gamma-chlordane, beta-endosulfan, and p,p'-DDE were detected below the detection limit of the instrument in each of the samples analysed. p,p'-DDT was detected in all samples analysed with mean concentration of 66.04±3.37 µg/kg, 60.19±10.50 µg/kg, 23.08±0.99 µg/kg, 12.00±0.15 µg/kg, 6.53±1.80 µg/kg, and 4.46±1.00 µg/kg in soil around onion, soil around cabbage, soil around lettuce, cabbage, lettuce, and onion respectively. Methoxychlor recorded the overall highest mean of 102.26±17.53 µg/kg in soil around cabbage followed by 96.56±6.38 µg/kg in cabbage and its least mean value of 13.26±1.69 µg/kg was recorded in onion. It is observed that vegetable samples recorded relatively higher residues values than their corresponding soil samples. In cabbage and soil around cabbage, five residues; heptachlor, dieldrin, endrin A-endosulfan and p,p'-DDD were detected below the detection limit of the instrument. Also Beta-HCH and methoxychlor were not detected in the samples analysed. Gamma-HCH, delta-HCH and endosulfan sulfate were detected in cabbage but were below detection limit in soil around cabbage; however aldrin was detected in soil around cabbage but below detection limit in cabbage.

Delta-HCH was detected below detection limit of the instrument in both the lettuce and the soil around lettuce; however beta-HCH, heptachlor and aldrin were present in both samples. Gamma-HCH, dieldrin, and endrin were detected in lettuce but were below detection limit in the soil around lettuce. A-endosulfan was not detected in soil around lettuce but was present in lettuce. P,p'-DDE was detected in lettuce soil but was below detection limit in lettuce. Methoxychlor was detected in lettuce but not detected in soil around lettuce.

P,p'-DDD was below detection limit in both onion and soil around onion samples analysed. Aldrin was detected in both samples. Gamma-HCH, beta-HCH, Delta-HCH, heptachlord, dieldrin, endrin, and A-endosulfan were detected in onion but were below detection limit in soil around onion. Endosulfan sulfate and methoxychlor were detected in onion but were not detected in soil around onion.

Studies in Ghana (Glover-Amengor *et al*., 2008; Darko and Acquaah, 2007) have reported the detection of different kinds of pesticides especially organochlorines in soil and sediment in different parts of Ghana.

From Table 4.8, it can be observed that p,p'-DDT was detected in all samples with mean concentration ranging from of 4.46±1.00 µg/kg to 66.04±3.37 µg/kg. p,p'-DDT was detected in soil around cabbage with mean concentration of 60.19±10.50 µg/kg. Beta-HCH and methoxychlor were both detected in cabbage and soil around cabbage. Beta-HCH with mean concentration of 16.72±1.31 µg/kg in cabbage and 25.85±1.53 µg/kg in soil around cabbage. Methoxychlor had mean concentration of 96.56±6.38 µg/kg and 102.26±17.53 µg/kg in cabbage and in soil around cabbage respectively. This can pose possible health risk because their concentrations exceeded UK/EC MRL.

Beta-HCH had mean concentration of 11.20±1.83 µg/kg in soil around lettuce and aldrin 20.92±0.28 µg/kg in lettuce which are above MRL. Gamma-HCH (lindane), beta-HCH and aldrin had mean concentration of 16.82±4.80 µg/kg, 21.19±2.68 µg/kg and 11.72±0.53 µg/kg all in onion respectively.

Table 4.9 Combined health risks of multiple residues of organochlorine pesticide

Farms	Hazard Index					
	Cabbage		Lettuce		Onion	
	Adult	Children	Adult	Children	Adult	Children
Ayigya	4.31×10^{-1}	2.59×10^{1}	4.31×10^{-1}	2.59×10^{1}	5.94×10^{-4}	3.56×10^{-3}
Gyenyase	9.48×10^{-3}	5.69×10^{-2}	2.90×10^{-1}	1.74×10^{1}	2.50×10^{-1}	1.50×10^{1}
Nsenie	-	-	3.49×10^{-1}	2.09×10^{1}	1.21×10^{-1}	7.27×10^{-1}
Kentinkrono	3.77×10^{-2}	2.26×10^{-1}	3.95×10^{-1}	2.37×10^{1}	4.42×10^{-2}	2.65×10^{-1}
Anglican Hostel	2.25×10^{-2}	1.35×10^{-1}	2.51×10^{-4}	1.51×10^{-3}	3.00×10^{-1}	1.80×10^{1}

4.9 Combined health risks of multiple residues of organochlorine pesticide

Combined health risk estimated by the discrete OCP residues detected in the vegetable samples is represented in Table 4.9. Calculation of the health risks shows that aldrin in lettuce samples from Ayigya, Gyenyase, Kentinkrono, and onion sample from Anglican Hostel could pose potential toxicity to the children (summarized in Table 4.9). The combined health risks for adults due to OCP residues in Ayigya, Gyenyase, Nsenie, Kentinkrono and Anglican Hostel samples were 8.63×10^{-1}, 5.49×10^{-1}, 4.70×10^{-1}, 4.77×10^{-1} and 3.23×10^{-1}, respectively, signifying that Adult in Kumasi have little risk to the consumption of these vegetables, all calculated values were less than 1. However, combined health risks due to the consumption of these vegetables by children in Ayigya, Gyenyase, Nsenie, Kentinkrono and Anglican Hostel samples were 5.18×10^{0}, 3.29×10^{0}, 2.82×10^{0}, 2.86×10^{0} and 1.94×10^{0}, respectively.

Total potential health risks for noncarcinogenic effects through eating a diet from these vegetables are 2.68×10^{0} and 1.61×10^{1} for adult and children respectively, signifying that consumers of Kumasi and its nearby towns may experience adverse health effects. These values were achieved by adding all the combined health risks of discrete OCP residues in vegetables as described Saha and Zaman, (2012).

Table 4.10 Carcinogenic risk estimation for the OCP residues detected in the vegetables from Ayigya

Vegetable	Pesticide	OSF	Adult EDI	Children EDI	Adult CBC	Children CBC	Adult HR	Children HR
Cabbage	Gamma-HCH	1.30×10^{3}	3.20×10^{-3}	1.92×10^{-2}	3.37×10^{5}	5.61×10^{4}	9.49×10^{-9}	3.42×10^{-7}
	Beta-HCH	1.30×10^{3}	4.57×10^{-4}	2.74×10^{-3}	3.37×10^{5}	5.61×10^{4}	1.36×10^{-9}	4.88×10^{-8}
	Delta-HCH	1.30×10^{3}	3.43×10^{-3}	2.06×10^{-2}	3.37×10^{5}	5.61×10^{4}	1.02×10^{-8}	3.66×10^{-7}
	p,p'-DDT	3.40×10^{2}	1.29×10^{-2}	7.77×10^{-2}	1.29×10^{6}	2.15×10^{5}	1.01×10^{-8}	3.62×10^{-7}
Lettuce	Gamma-HCH	1.30×10^{3}	2.18×10^{-2}	1.31×10^{-1}	3.37×10^{5}	5.61×10^{4}	6.47×10^{-8}	2.33×10^{-6}
	Heptachlor	4.50×10^{3}	5.23×10^{-3}	3.14×10^{-2}	9.73×10^{4}	1.62×10^{4}	5.37×10^{-8}	1.93×10^{-6}
	Aldrin	1.70×10^{4}	5.17×10^{-2}	3.10×10^{-1}	2.58×10^{4}	4.29×10^{3}	2.01×10^{-6}	7.23×10^{-5}
	Dieldrin	1.60×10^{4}	3.40×10^{-3}	2.04×10^{-2}	2.74×10^{4}	4.56×10^{3}	1.24×10^{-7}	4.47×10^{-6}
	p,p'-DDT	3.40×10^{2}	2.13×10^{-2}	1.28×10^{-1}	1.29×10^{6}	2.15×10^{5}	1.66×10^{-8}	5.96×10^{-7}
Onion	Delta-HCH	1.30×10^{3}	1.78×10^{-3}	1.07×10^{-2}	3.37×10^{5}	5.61×10^{4}	5.29×10^{-9}	1.90×10^{-7}

Table 4.11 Carcinogenic risk estimation for the OCP residues detected in the vegetables from Gyenyase

Vegetable	Pesticide	OSF	Adult EDI	Children EDI	Adult CBC	Children CBC	Adult HR	Children HR
Cabbage	Delta-HCH	1.30×10^{3}	2.83×10^{-2}	1.70×10^{-1}	3.37×10^{5}	5.61×10^{4}	8.41×10^{-8}	3.03×10^{-6}
	p,p'-DDT	3.40×10^{2}	7.76×10^{-4}	4.66×10^{-3}	1.29×10^{6}	2.15×10^{5}	6.03×10^{-10}	2.17×10^{-8}
Lettuce	Gamma-HCH	1.30×10^{3}	1.19×10^{-2}	7.11×10^{-2}	3.37×10^{5}	5.61×10^{4}	3.52×10^{-8}	1.27×10^{-6}
	Beta-HCH	1.30×10^{3}	4.80×10^{-3}	2.88×10^{-2}	3.37×10^{5}	5.61×10^{4}	1.42×10^{-8}	5.12×10^{-7}
	Heptachlor	4.50×10^{3}	5.25×10^{-3}	3.15×10^{-2}	9.73×10^{4}	1.62×10^{4}	5.40×10^{-8}	1.94×10^{-6}
	Aldrin	1.70×10^{4}	3.56×10^{-2}	2.13×10^{-1}	2.58×10^{4}	4.29×10^{3}	1.38×10^{-6}	4.97×10^{-5}
	p,p'-DDT	3.40×10^{2}	1.16×10^{-2}	6.97×10^{-2}	1.29×10^{6}	2.15×10^{5}	9.02×10^{-9}	3.25×10^{-7}
Onion	Beta-HCH	1.30×10^{3}	2.55×10^{-2}	1.53×10^{-1}	3.37×10^{5}	5.61×10^{4}	7.56×10^{-8}	2.72×10^{-6}
	Aldrin	1.70×10^{4}	1.80×10^{-2}	1.08×10^{-1}	2.58×10^{4}	4.29×10^{3}	6.98×10^{-7}	2.51×10^{-5}
	p,p'-DDT	3.40×10^{2}	1.01×10^{-2}	6.06×10^{-2}	1.29×10^{6}	2.15×10^{5}	7.84×10^{-9}	2.82×10^{-7}

Table 4.12 Carcinogenic risk estimation for the OCP residues detected in the vegetables from Nsenie

Vegetable	Pesticide	OSF	Adult EDI	Children EDI	Adult CBC	Children CBC	Adult HR	Children HR
Lettuce	Beta-HCH	1.30×10^{3}	2.74×10^{-2}	1.64×10^{-1}	3.37×10^{5}	5.61×10^{4}	8.13×10^{-8}	2.93×10^{-6}
	Heptachlor	4.50×10^{3}	4.57×10^{-4}	2.74×10^{-3}	9.73×10^{4}	1.62×10^{4}	4.69×10^{-9}	1.69×10^{-7}
	Aldrin	1.70×10^{4}	4.91×10^{-2}	2.95×10^{-1}	2.58×10^{4}	4.29×10^{3}	1.91×10^{-6}	6.86×10^{-5}
	p,p'-DDT	3.40×10^{2}	2.63×10^{-2}	1.58×10^{-1}	1.29×10^{6}	2.15×10^{5}	2.04×10^{-8}	7.34×10^{-7}
Onion	Beta-HCH	1.30×10^{3}	1.10×10^{-1}	6.62×10^{-1}	3.37×10^{5}	5.61×10^{4}	3.28×10^{-7}	1.18×10^{-5}
	Heptachlor	4.50×10^{3}	2.06×10^{-3}	1.23×10^{-2}	9.73×10^{4}	1.62×10^{4}	2.11×10^{-8}	7.60×10^{-7}
	Aldrin	1.70×10^{4}	1.25×10^{-2}	7.52×10^{-2}	2.58×10^{4}	4.29×10^{3}	4.87×10^{-7}	1.75×10^{-5}

Table4.13 Carcinogenic risk estimation for the OCP residues detected in the vegetables from Kentinkrono

Vegetable	Pesticide	OSF	Adult EDI	Children EDI	Adult CBC	Children CBC	Adult HR	Children HR
Cabbage	Beta-HCH	1.30×10^{3}	8.04×10^{-2}	4.82×10^{-1}	3.37×10^{5}	5.61×10^{4}	2.39×10^{-7}	8.59×10^{-6}
	Delta-HCH	1.30×10^{3}	2.18×10^{-2}	1.31×10^{-1}	3.37×10^{5}	5.61×10^{4}	6.46×10^{-8}	2.33×10^{-6}
	p,p'-DDT	3.40×10^{2}	7.25×10^{-2}	4.35×10^{-1}	1.29×10^{6}	2.15×10^{5}	5.62×10^{-8}	2.02×10^{-6}
Lettuce	Gamma-HCH	1.30×10^{3}	1.63×10^{-2}	9.81×10^{-2}	3.37×10^{5}	5.61×10^{4}	4.85×10^{-8}	1.75×10^{-6}
	Heptachlor	4.50×10^{3}	2.47×10^{-3}	1.48×10^{-2}	9.73×10^{4}	1.62×10^{4}	2.53×10^{-8}	9.12×10^{-7}
	Aldrin	1.70×10^{4}	5.46×10^{-2}	3.28×10^{-1}	2.58×10^{4}	4.29×10^{3}	2.12×10^{-6}	7.63×10^{-5}
	Dieldrin	1.60×10^{4}	9.64×10^{-3}	5.78×10^{-2}	2.74×10^{4}	4.56×10^{3}	3.52×10^{-7}	1.27×10^{-5}
	p,p'-DDT	3.40×10^{2}	1.03×10^{-2}	6.18×10^{-2}	1.29×10^{6}	2.15×10^{5}	7.99×10^{-9}	2.88×10^{-7}
Onion	Beta-HCH	1.30×10^{3}	9.29×10^{-3}	5.58×10^{-2}	3.37×10^{5}	5.61×10^{4}	2.76×10^{-8}	9.93×10^{-7}

Table 4.14 Carcinogenic risk estimation for the OCP residues detected in the vegetables from Anglican Hostel

Vegetable	Pesticide	OSF	Adult EDI	Children EDI	Adult CBC	Children CBC	Adult HR	Children HR
Cabbage	Beta-HCH	1.30×10^{3}	3.37×10^{-2}	2.02×10^{-1}	3.37×10^{5}	5.61×10^{4}	1.00×10^{-7}	3.60×10^{-6}
	Delta-HCH	1.30×10^{3}	1.81×10^{-2}	1.08×10^{-1}	3.37×10^{5}	5.61×10^{4}	5.36×10^{-8}	1.93×10^{-6}
	p,p'-DDT	3.40×10^{2}	2.35×10^{-2}	1.41×10^{-1}	1.29×10^{6}	2.15×10^{5}	1.82×10^{-8}	6.57×10^{-7}
Lettuce	p,p'-DDT	3.40×10^{2}	5.02×10^{-3}	3.01×10^{-2}	1.29×10^{6}	2.15×10^{5}	3.90×10^{-9}	1.40×10^{-7}
Onion	Gamma-HCH	1.30×10^{3}	3.84×10^{-2}	2.30×10^{-1}	3.37×10^{5}	5.61×10^{4}	1.14×10^{-7}	4.10×10^{-6}
	Delta-HCH	1.30×10^{3}	1.19×10^{-2}	7.17×10^{-2}	3.37×10^{5}	5.61×10^{4}	3.54×10^{-8}	1.28×10^{-6}
	Aldrin	1.70×10^{4}	4.97×10^{-2}	2.98×10^{-1}	2.58×10^{4}	4.29×10^{3}	1.93×10^{-8}	6.95×10^{-7}
	Dieldrin	1.60×10^{4}	4.34×10^{-4}	2.60×10^{-3}	2.74×10^{4}	4.56×10^{3}	1.58×10^{-8}	5.71×10^{-7}
	p,p'-DDT	3.40×10^{2}	1.03×10^{-2}	6.15×10^{-2}	1.29×10^{6}	2.15×10^{5}	7.96×10^{-9}	2.87×10^{-7}

4.10 Carcinogenic risk estimation for the OCP residues detected in the vegetables from the farms

The carcinogenic risk of the OCP residues in vegetables from Ayigya is presented in Table 4.10. The cancer risk of the OCP residues in vegetables is irrelevant, since their carcinogenic rates were below the acceptable level of risk (Table 4.10). The probabilities of lifetime cancer hazard risks posed by gamma-HCH, beta-HCH, delta-HCH and p,p'-DDT through the consumption of cabbage from Ayigya were 9.49×10^{-9}, 1.36×10^{-9}, 1.02×10^{-8}, and 1.01×10^{-8} respectively for adult and 3.42×10^{-7} ,4.88×10^{-8} , 3.66×10^{-7} and , 3.62×10^{-7} respectively for children. The probabilities of cancer risks for lifetime

posed by gamma-HCH, heptachlor, aldrin, diedrin and p,p'-DDT through the consumption of lettuce from Ayigya were 6.47×10^{-8}, 5.37×10^{-8}, 2.01×10^{-6}, 1.24×10^{-7} and 1.66×10^{-8} respectively for adult and 2.33×10^{-6}, 1.93×10^{-6}, 7.23×10^{-5}, 4.47×10^{-6} and , 5.96×10^{-7} respectively for children. The probabilities of cancer risks for lifetime posed by delta-HCH through the consumption of onion from Ayigya were 5.29×10^{-9} and 1.90×10^{-7} respectively for adult and children. It is interesting to note that the trend in Ayigya is similar to those of Gyenyase, Nsenie, Kintinkrono and Anglican Hostel as presented in Table 4.11, Table 4.12 Table 4.13 and Table 4.14 respectively. These values are less than 1 and therefore raise no concern for carcinogenic risk in the consumption of the vegetables. This result favorably agrees with the findings of Akoto *et al*., (2015). They reported carcinogenic risk in okra below the acceptable risk level.

Table 4.15 Highest organochlorine pesticide residue concentration found in cabbage, lettuce, and onion from the sampling areas compared with UK/EC MRLs (µg/kg).

Pesticide	Highest amounts found			Maximum residue limit		
	Cabbage Mean±SD	Lettuce Mean±SD	Onion Mean±SD	Cabbage Mean±SD	Lettuce Mean±SD	Onion Mean±SD
gamma-HCH	1.40±0.41	9.54±0.02	16.82±4.80	10	10	10
beta-HCH	35.20±0.35	12.00±1.70	48.35±5.09	10	10	10
Heptachlor	<0.01	2.29±0.14	0.90±0.14	10	10	10
delta-HCH	12.41±0.14	<0.01	5.23±0.09	10	10	10
Aldrin	<0.01	23.92±0.28	21.78±1.19	10	10	10
gamma-chlordane	<0.01	<0.01	<0.01	10	10	10
A-endosulfan	<0.01	4.10±0.14	1.54±0.00	10	10	10
p,p'-DDE	<0.01	<0.01	<0.01	50	50	50
Dieldrin	<0.01	4.22±1.25	0.19±0.13	10	10	10
Endrin	<0.01	6.10±0.42	6.73±0.05	10	10	10
p,p'-DDD	<0.01	<0.01	<0.01	50	50	50
B-endosulfan	<0.01	<0.01	<0.01	10	10	10
p,p'-DDT	31.73±0.07	11.50±4.38	4.49±1.45	50	50	50
Endosulfan s	28.47±2.68	<0.01	2.8±0.28	10	10	10
Methoxychlor	184.10±12.11	165.21±12.65	160.96±12.24	10	10	10

Limit of detection = 0.01 µg/kg

4.11 Tolerance limit

The concentration of organochlorine pesticides in various vegetables sampled from the selected study areas were compared with maximum residue limits (MRLs) set forth by the UK/EC in Table 4.15. Beta-HCH and methoxychlor had mean values higher than MRL set by the UK/EC in all the samples analysed. Gamma-HCH recorded mean concentration of 16.82±4.80 µg/kg in onion which is higher than the MRL set forth by the UK/EC. Endosulfan sulfate recorded mean value of 28.47±2.68 µg/kg in cabbage which is higher than the MRL set forth by the UK/EC. Aldrin had mean concentration of 23.92±0.28 µg/kg in lettuce and 21.78±1.19 µg/kg in onion. Delta-HCH recorded mean value of 12.41±0.14 µg/kg in cabbage which is higher than the MRL set forth by the UK/EC. Heptachlor, A-endosulfan, Dieldrin, Endrin, and p,p'-DDT recorded values less than the MRL set forth by the UK/EC. Gamma-chlordane, p,p'-DDE, p,p'-DDD, and B-endosulfan recorded mean concentrations below detection limit of the instrument.

It can be observed from Table 4.15 that the mean concentration of gamma-HCH (lindane) recorded in cabbage (1.40±0.41 µg/kg), lettuce (9.54±0.02 µg/kg) were all lower than MRL except in onion with mean concentration of 16.82±4.80 µg/kg. Also the highest mean concentrations of beta-HCH were all higher than MRL. Heptachlor, gamma-chlord, α -endosulfan, p,p'-DDE, dieldrin, endrin, p,p'-DDD, β -endosulfan, p,p'-DDT and endosulfan sulfate in all samples recorded concentration lower than the MRL. Delta-HCH and endosulfan sulfate had highest mean concentrations in cabbage higher than MRL but it was lower in lettuce and onion.

Generally, it can be inferred from the data that some vegetable samples analyzed contain residues of the monitored organochlorines above the accepted MRL adopted by the UK/EC. Since vegetables consumption by humans is an indispensable part of our daily life, this makes the safety of vegetables an important health issue and therefore underscores the importance of the potential health risks of organochlorine pesticides in vegetables.

CHAPTER FIVE

5.0 CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

The results of this study indicate that some vegetables grown in the study areas are contaminated with different types of OC pesticide. Although the concentrations are generally low, the study shows that the organochlorine pesticides are still being used despite the fact that they have been banned from use in Ghana. Most of the organochlorine residues detected were below the maximum limits set by the UK/EC.

The occurrence of organochlorine pesticide residues in the vegetables could be due to its illegal use or due to historic use since these chemicals are now banned from agricultural use in Ghana. Aldrin 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 seven different samples (cabbage, lettuce, onion, soil around cabbage, soil around lettuce, soil around onion and irrigation water) 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 to the farmers.

Health risk analysis indicates that aldrin in particular may be of public concern since its mean concentration levels were high in all the different types of samples analyzed indicating a potential health risk to consumers in Kumasi and Towns around. The combined risk index revealed significant risk to children. The total risk index for combined pesticides due to consumption of all the vegetables was higher than 1, which shows potential health risk to consumers. The cancer risk of the OCP residues in vegetables was little concern due to their low risk levels.

5.2 Recommendations

The following recommendations are therefore suggested:

- Future monitoring programs are recommended to acquire adequate information regarding the levels of pesticides especially organochlorines in other vegetables.

- The regulatory bodies such as Environmental Protection Agency need to check and enforce regulations on the use of banned OC pesticides in Ghana.

- There is the need to conduct a dietary survey for 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 OCP residues in vegetables.

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APPENDICES

Appendix A

ANOVA ANALYSIS

Mean concentration levels of organochlorines (µg/kg) in vegetables from all the sampling areas

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	12194.273	2.000	6097.136	1.092	0.345	3.220
Within Groups	234405.466	42.000	5581.083			
Total	246599.738	44.000				

Appendix B

Mean Concentration of organochlorines (µg/kg) in vegetable samples from Ayigya

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	9673.342	2.000	4836.671	0.779	0.465	3.220
Within Groups	260779.936	42.000	6209.046			
Total	270453.278	44.000				

Appendix C

Mean Concentration of organochlorines (µg/kg) in vegetable samples from Gyenyase

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	1160.953	2.000	580.477	0.993	0.379	3.220
Within Groups	24558.321	42.000	584.722			
Total	25719.275	44.000				

Appendix D

Mean Concentration of organochlorines (µg/kg) in vegetable samples from Nsenie

ANOVA

Source of Variation	*SS*	*Df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	296.583	2.000	148.291	1.632	0.208	3.220
Within Groups	3817.142	42.000	90.884			
Total	4113.725	44.000				

Appendix E

Mean Concentration of organochlorines (µg/kg) in vegetable samples from Kentinkrono

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	20.383	2.000	10.191	0.034	0.966	3.220
Within Groups	12499.335	42.000	297.603			
Total	12519.718	44.000				

Appendix F

Mean Concentration of organochlorines (µg/kg) in vegetable samples from Aglican Hostel

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	20.383	2.000	10.191	0.034	0.966	3.220
Within Groups	12499.335	42.000	297.603			
Total	12519.718	44.000				

Appendix G

Mean Concentration of organochlorines (µg/kg) in vegetable samples from Central market

ANOVA

Source of Variation	*SS*	*Df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	818.301	2.000	409.151	5.815	0.006	3.220
Within Groups	2955.073	42.000	70.359			
Total	3773.374	44.000				

Appendix H

Mean Concentration of organochlorines (µg/kg) in vegetable samples from all the sampling areas

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	12194.273	2.000	6097.136	1.092	0.345	3.220
Within Groups	234405.466	42.000	5581.083			
Total	246599.738	44.000				

Appendix I

Mean Concentration of organochlorines (µg/kg) in soil samples from Ayigya

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	231.269	2.000	115.635	0.459	0.635	3.220
Within Groups	10571.133	42.000	251.694			
Total	10802.402	44.000				

Appendix J

Mean Concentration of organochlorines (μg/kg) in soil samples from Gyenyase

ANOVA

Source of Variation	*SS*	*Df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	150.556	2.000	75.278	0.705	0.500	3.220
Within Groups	4485.120	42.000	106.789			
Total	4635.676	44.000				

Appendix K

Mean Concentration of organochlorines (μg/kg) in soil samples from Nsenie

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	14.485	2.000	7.243	0.916	0.408	3.220
Within Groups	332.267	42.000	7.911			
Total	346.752	44.000				

Appendix L

Mean Concentration of organochlorines (μg/kg) in soil samples from Kentinkrono

ANOVA

Source of Variation	*SS*	*Df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	409.952	2.000	204.976	1.254	0.296	3.220
Within Groups	6866.585	42.000	163.490			
Total	7276.537	44.000				

Appendix M

Mean Concentration of organochlorines (μg/kg) in soil samples from Anglican Hostel

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	1005.069	2.000	502.534	0.457	0.636	3.220
Within Groups	46155.913	42.000	1098.950			
Total	47160.982	44.000				

Appendix N

Mean Concentration of organochlorines(µg/kg) in soil samples from all the sampling areas

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	1615.085	2.000	807.543	1.043	0.361	3.220
Within Groups	32531.704	42.000	774.564			
Total	34146.789	44.000				

Appendix O

Mean Concentration of organochlorines(µg/L) in water samples from all the sampling areas

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	3.402	4.000	0.851	0.485	0.746	2.503
Within Groups	122.696	70.000	1.753			
Total	126.099	74.000				

Appendix P

Concentration, EDI, and health risk estimation for OCP residues measured in vegetables from Ayigya

Vegetables	Pesticide	Mean	ADI	EDI	HI	HR
Cabbage	Gamma-HCH	1.4	3	3.20×10^{-3} Aldult	1.07×10^{-3}	No
				1.92×10^{-2} Children	6.39×10^{-3}	No
	Beta-HCH	0.2	3	4.57×10^{-4} Adult	1.52×10^{-4}	No
				2.74×10^{-3} Children	9.13×10^{-4}	No
	Delta-HCH	1.5	3	3.43×10^{-3} Adult	1.14×10^{-3}	No
				2.06×10^{-2} Children	6.85×10^{-3}	No
	p,p'-DDT	5.67	20	1.29×10^{-2} Adult	6.47×10^{-4}	No
				7.77×10^{-2} Children	3.88×10^{-3}	No
	Endosulfan s	28.47	6	6.50×10^{-2} Adult	1.08×10^{-2}	No
				3.90×10^{-1} Children	6.50×10^{-2}	No
	Methoxychlor	184.1	5	4.20×10^{-1} Adult	8.41×10^{-2}	No
				2.52×10^{1} Children	5.04×10^{-1}	No
Lettuce	Gamma-HCH	9.54	3	2.18×10^{-2} Adult	7.26×10^{-3}	No
				1.31×10^{-1} Children	4.36×10^{-2}	No
	Heptachlor	2.29	0.1	5.23×10^{-3} Adult	5.23×10^{-2}	No
				3.14×10^{-2} Children	3.14×10^{-1}	No
	Aldrin	22.66	0.2	5.17×10^{-2} Adult	2.59×10^{-1}	No
				3.10×10^{-1} Children	1.55×10^{0}	Yes
	A-endosulfan	0.6	6	1.37×10^{-3} Adult	2.28×10^{-4}	No
				8.22×10^{-3} Children	1.37×10^{-3}	No
	Dieldrin	1.49	0.2	3.40×10^{-3} Adult	1.70×10^{-2}	No
				2.04×10^{-2} Children	1.02×10^{-1}	No
	Endrin	1.69	0.2	3.86×10^{-3} Adult	1.93×10^{-2}	No
				2.32×10^{-2} Children	1.16×10^{-1}	No
	p,p'-DDT	9.34	20	2.13×10^{-2} Adult	1.07×10^{-3}	No
				1.28×10^{-1} Children	6.40×10^{-3}	No
	Methoxychlor	165.21	5	3.77×10^{-1} Adult	7.54×10^{-2}	No
				2.26×10^{1} Children	4.53×10^{-1}	No
Onion	Delta-HCH	0.78	3	1.78×10^{-3} Adult	5.94×10^{-4}	No
				1.07×10^{-2} Children	3.56×10^{-3}	No

Appendix Q

Concentration, EDI, and health risk estimation for OCP residues measured in vegetables from Gyenyase

Vegetables	Pesticide	Mean	ADI	EDI	HI	HR
Cabbage	Delta-HCH	12.41	3	2.83×10^{-2} Adult	9.45×10^{-3}	No
				1.70×10^{-1} Children	5.67×10^{-2}	No
	p,p'-DDT	0.34	20	7.76×10^{-4} Adult	3.88×10^{-5}	No
				4.66×10^{-3} Children	2.33×10^{-4}	No
Lettuce	Gamma-HCH	5.19	3	1.19×10^{-2} Adult	3.95×10^{-3}	No
				7.11×10^{-2} Children	2.37×10^{-2}	No
	Beta-HCH	2.1	3	4.80×10^{-3} Adult	1.60×10^{-3}	No
				2.88×10^{-2} Children	9.59×10^{-3}	No
	Heptachlor	2.3	0.1	5.25×10^{-3} Adult	5.25×10^{-2}	No
				3.15×10^{-2} Children	3.15×10^{-1}	No
	Aldrin	15.58	0.2	3.56×10^{-2} Adult	1.78×10^{-1}	No
				2.13×10^{-1} Children	1.07×10^{0}	Yes
	A-endosulfan	1.3	6	2.97×10^{-3} Adult	4.95×10^{-4}	No
				1.78×10^{-2} Children	2.97×10^{-3}	No
	Endrin	3.6	0.2	8.22×10^{-3} Adult	4.11×10^{-2}	No
				4.93×10^{-2} Children	2.47×10^{-1}	No
	p,p'-DDT	5.09	20	1.16×10^{-2} Adult	5.81×10^{-4}	No
				6.97×10^{-2} Children	3.49×10^{-3}	No
	Methoxychlor	25.57	5	5.84×10^{-2} Adult	1.17×10^{-2}	No
				3.50×10^{-1} Children	7.01×10^{-2}	No
Onion	Beta-HCH	11.15	3	2.55×10^{-2} Adult	8.49×10^{-3}	No
				1.53×10^{-1} Children	5.09×10^{-2}	No
	Aldrin	7.88	0.2	1.80×10^{-2} Adult	9.00×10^{-2}	No
				1.08×10^{-1} Children	5.40×10^{-1}	No
	A-endosulfan	1.54	6	3.52×10^{-3} Adult	5.86×10^{-4}	No
				2.11×10^{-2} Children	3.52×10^{-3}	No
	Endrin	6.73	0.2	1.54×10^{-2} Adult	7.68×10^{-2}	No
				9.22×10^{-2} Children	4.61×10^{-1}	No
	p,p'-DDT	4.42	20	1.01×10^{-2} Adult	5.05×10^{-4}	No
				6.06×10^{-2} Children	3.03×10^{-3}	No
	Methoxychlor	160.96	5	3.68×10^{-1} Adult	7.35×10^{-2}	No
				2.21×10^{1} Children	4.41×10^{-1}	No

Appendix R

Concentration, EDI, and health risk estimation for OCP residues measured in vegetables from Nsenie

Vegetables	Pesticide	Mean	ADI	EDI	HI	HR
Lettuce	Beta-HCH	12	3	2.74×10^{-2} Adult	9.13×10^{-3}	No
				1.64×10^{-1} Children	5.48×10^{-2}	No
	Heptachlor	0.2	0.1	4.57×10^{-4} Adult	4.57×10^{-3}	No
				2.74×10^{-3} Children	2.74×10^{-2}	No
	Aldrin	21.5	0.2	4.91×10^{-2} Adult	2.45×10^{-1}	No
				2.95×10^{-1} Children	1.47×10^{1}	No
	A-endosulfan	4.1	6	9.36×10^{-3} Adult	1.56×10^{-3}	No
				5.62×10^{-2} Children	9.36×10^{-3}	No
	Endrin	6.1	0.2	1.39×10^{-2} Adult	6.96×10^{-2}	No
				8.36×10^{-2} Children	4.18×10^{-1}	No
	p,p'-DDT	11.5	20	2.63×10^{-2} Adult	1.31×10^{-3}	No
				1.58×10^{-1} Children	7.88×10^{-3}	No
	Methoxychlor	38.1	5	8.70×10^{-2} Adult	1.74×10^{-2}	No
				5.22×10^{-1} Children	1.04×10^{-1}	No
Onion	Beta-HCH	48.35	3	1.10×10^{-1} Adult	3.68×10^{-2}	No
				6.62×10^{-1} Children	2.21×10^{-1}	No
	Heptachlor	0.9	0.1	2.06×10^{-3} Adult	2.06×10^{-2}	No
				1.23×10^{-2} Children	1.23×10^{-1}	No
	Aldrin	5.49	0.2	1.25×10^{-2} Adult	6.27×10^{-2}	No
				7.52×10^{-2} Children	3.76×10^{-1}	No
	Endosulfan s	2.8	6	6.39×10^{-3} Adult	1.07×10^{-3}	No
				3.84×10^{-2} Children	6.39×10^{-3}	No

Appendix S

Concentration, EDI, and health risk estimation for OCP residues measured in vegetables from Kentinkrono

Vegetables	Pesticide	Mean	ADI	EDI	HI	HR
Cabbage	Beta-HCH	35.2	3	8.04×10^{-2} Adult	2.68×10^{-2}	No
				4.82×10^{-1} Children	1.61×10^{-1}	No
	Delta-HCH	9.53	3	2.18×10^{-2} Adult	7.25×10^{-3}	No
				1.31×10^{-1} Children	4.35×10^{-2}	No
	p,p'-DDT	31.73	20	7.25×10^{-2} Adult	3.62×10^{-3}	No
				4.35×10^{-1} Children	2.17×10^{-2}	No
Lettuce	Gamma-HCH	7.16	3	1.63×10^{-2} Adult	5.45×10^{-3}	No
				9.81×10^{-2} Children	3.27×10^{-2}	No
	Heptachlor	1.08	0.1	2.47×10^{-3} Adult	2.47×10^{-2}	No
				1.48×10^{-2} Children	1.48×10^{-1}	No
	Aldrin	23.92	0.2	5.46×10^{-2} Adult	2.73×10^{-1}	No
				3.28×10^{-1} Children	1.64×10^{0}	Yes
	Dieldrin	4.22	0.2	9.64×10^{-3} Adult	4.82×10^{-2}	No
				5.78×10^{-2} Children	2.89×10^{-1}	No
	Endrin	1.47	0.2	3.36×10^{-3} Adult	1.68×10^{-2}	No
				2.01×10^{-2} Children	1.01×10^{-1}	No
	p,p'-DDT	4.51	20	1.03×10^{-2} Adult	5.15×10^{-4}	No
				6.18×10^{-2} Children	3.09×10^{-3}	No
	Methoxychlor	57.75	5	1.32×10^{-1} Adult	2.64×10^{-2}	No
				7.91×10^{-1} Children	1.58×10^{-1}	No
Onion	Beta-HCH	4.07	3	9.29×10^{-3} Adult	3.10×10^{-3}	No
				5.58×10^{-2} Children	1.86×10^{-1}	No
	Endosulfan s	2.18	6	4.98×10^{-3} Adult	8.30×10^{-4}	No
				2.99×10^{-2} Children	4.98×10^{-3}	No
	Methoxychlor	88.29	5	2.02×10^{-1} Adult	4.03×10^{-2}	No
				1.21×10^{1} Children	2.42×10^{-1}	No

Appendix T

Concentration, EDI, and health risk estimation for OCP residues measured in vegetables from Anglican Hostel

Vegetables	Pesticide	Mean	ADI	EDI	HI	HR
Cabbage	Beta-HCH	14.8	3	3.37×10^{-2} Adult	1.12×10^{-2}	No
				2.02×10^{-1} Children	6.74×10^{-2}	No
	Delta-HCH	7.91	3	1.81×10^{-2} Adult	6.02×10^{-3}	No
				1.08×10^{-1} Children	3.61×10^{-2}	No
	p,p'-DDT	10.3	20	2.35×10^{-2} Adult	1.17×10^{-3}	No
				1.41×10^{-1} Children	7.05×10^{-3}	No
	Methoxychlor	9.02	5	2.06×10^{-2} Adult	4.12×10^{-3}	No
				1.24×10^{-1} Children	2.47×10^{-2}	No
Lettuce	p,p'-DDT	2.2	20	5.02×10^{-3} Adult	2.51×10^{-4}	No
				3.01×10^{-2} Children	1.51×10^{-3}	No
Onion	Gamma-HCH	16.8	3	3.84×10^{-2} Adult	1.28×10^{-2}	No
				2.30×10^{-1} Children	7.68×10^{-2}	No
	Delta-HCH	5.23	3	1.19×10^{-2} Adult	3.98×10^{-3}	No
				7.17×10^{-2} Children	2.39×10^{-2}	No
	Aldrin	21.8	0.2	4.97×10^{-2} Adult	2.49×10^{-1}	No
				2.98×10^{-1} Children	1.49×10^{0}	Yes
	Dieldrin	0.19	0.2	4.34×10^{-4} Adult	2.17×10^{-3}	No
				2.60×10^{-3} Children	1.30×10^{-2}	No
	Endrin	1.21	0.2	2.76×10^{-3} Adult	1.38×10^{-2}	No
				1.66×10^{-2} Children	8.29×10^{-2}	No
	p,p'-DDT	4.49	20	1.03×10^{-2} Adult	5.13×10^{-4}	No
				6.15×10^{-2} Children	3.08×10^{-3}	No
	Methoxychlor	40.2	5	9.18×10^{-2} Adult	1.84×10^{-2}	No
				5.51×10^{-1} Children	1.10×10^{-1}	No

Appendix U

Pesticide	Mean concentration	% Recovery
Gamma-HCH	0.390	104.00
Beta-HCH	0.336	89.60
Heptachlor	0.394	105.07
Delta-HCH	0.279	74.27
Aldrin	0.420	112.00
Gamma-chlordane	0.412	109.73
A-endosulfan	0.292	77.73
p,p'-DDE	0.304	80.93
Dieldrin	0.289	76.93
Endrin	0.389	103.73
p,p'-DDD	0.331	88.27
B-endosulfan	0.375	99.86
p,p'-DDT	0.376	100.27
Endosulfan s	0.349	92.93
Methoxychlor	0.382	101.73