KWAME NKRUMAH UNIVERSITY OF SCIENCE AND TECHNOLOGY, KUMASI

COLLEGE OF ENGINEERING

DEPARTMENT OF MATERIALS ENGINEERING

ORGANOCHLORINE PESTICIDES RESIDUE LEVELS IN CABBAGE, SOIL AND IRRIGATION WATER IN SOME FARMING COMMUNITIES IN ACCRA

By

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(BSc. Mineral Engineering)

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A thesis submitted to the Department of Materials Engineering of the College of Engineering, in partial fulfilment of the requirements for the degree of Master of Science, in Environmental Resources Management.

DECLARATION

"I hereby declare that this submission is my own work and that, to the best of my knowledge and belief, it contains no material previously published or written by another person (except where explicitly defined in the acknowledgements), nor material which to a substantial extent has been submitted for the award of any other degree or diploma of a university or other institution of higher learning.

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ABSTRACT

Indiscriminate use of pesticides in controlling pests of agricultural crops has been of great concern. This study investigated the residue levels of Organochlorine (OC) in cabbage, soil, irrigation water and waterbed sediments of the Oyansia stream passing through Dzorwulu and Opeibea in Accra, Ghana using gas chromatography. A questionnaire was administered to farmers along the stream to gather information on the level of understanding of the causes and effects of OC pollution. Results showed that with the exception of P,P-DDT that occurred at 0.18 µg/*I* (0.03 µg/*I* less than the WHO guideline value) in upstream soil, levels of all other pesticide components were higher at downstream than upstream and were statistically significant ($p < 0.001$) for HCB, Lindane, P,P'-DDD, Chlorpyrifos-ethyl, γ - endosulfan, and Endosulfan sulphate but not for P-P'-DDE, P,P'-DDT, Chlorpyrifos-ethyl, HCH and β- endosulfan . The survey revealed that farmers relied heavily on synthetic insecticides for insect pest control. These insecticides were applied in various concoctions, at different application rates and at short intervals disregarding the prescribed pre-harvest intervals. Most farmers believed that the oral route of exposure was the most dangerous and needed to be avoided at all cost but not the contact and inhalation routes and therefore did not take adequate precautions against their occurrence. Intensified health education program that takes into account farmers' beliefs and perceptions about insecticides and also aims at promoting greater understanding of the use of OC and the causes and effects of pollution associated with its abuse is very much needed.

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LIST OF ACRONYMS

AMA	Accra Metropolitan Assembly
ASE	Accelerated Solvent Extraction
ATSDR	Agency for Toxic Substances and Disease Registry
DBM	Diamond Back Moth
DDD	Dichloro Diphenyl Dichloroethane
DDE	Dichloro Diphenyl Dichloroethylene
DDT	Dichloro Diphenyl Trichloroethane
EPA	Environmental Protection Agency/Authority
FAO	Food and Agriculture Organization
FDA	Food and Drugs Authority
GIPC	Ghana Investment Promotion Centre
HCB	Hexachlorobenzene
HCH	Hexachlorocyclohexane
IAEA	International Atomic Energy Agency
IARC	International Agency for Research on Cancer
LD	Lethal Dose
MRL	Maximum Residue Limit/Level
NRI	Natural Resource Institute
OC	Organochlorine
OSHA	Occupational Safety and Health Administration
PAH	Polycyclic Aromatic Hydrocarbons

PAN Pesticides Action Network

PCB Polychlorinated Biphenyls

POP Persistent Organic Pollutants

PSE Pressurized Solvent Extraction

SPE Solid Phase Extraction

UNEP United Nations Environmental Programme

UVR Ultra Violet Radiation

WHO World Health Organization

CHAPTER ONE

INTRODUCTION

1.2 Background of the Study

Pesticides are chemical substances defined as poisons and used in certain circumstances to kill specifically targeted pests (Wassemann, 1972). Pesticides have been used in the public health sector for disease vector control and in agriculture to control and eradicate crop pests for the past several decades in Ghana (Clarke, *et al.,* 1997). Some pesticides contain Organochlorine (OC) compounds.

An OC is an organic compound containing at least one covalently bonded chlorine atom (Gribble, 1994). They are a wide group of chemicals, many of which persist in the environment. OC pesticides are pesticides composed primarily of carbon, hydrogen, and chlorine. They are widely used by farmers to control pests because of their effectiveness and their broad-spectrum activity. Most of these OCs are agricultural pesticides or industrial compounds that also double as environmental pollutants. OCs are difficult to degrade under environmental conditions and are also toxic. They mostly have half-life of more than ten years because of their persistent nature and are therefore classified as Persistent Organic Pollutants (POPs). Their chemical structure corresponds to that of aromatic chlorinated hydrocarbons, although some of them contain other elements, such as oxygen and sulphur.

Cabbage (*Brassica oleracea* var *capitata*), an important exotic vegetable is grown in Ghana on both large and small scales. It has high nutritive value and it is used in the preparation of various kinds of dishes. It is used in stews, eaten raw in salads or boiled and eaten (Norman, 1992).

Again, it provides a source of livelihood to individuals who are engaged in cabbage production from its cultivation till it gets to the final consumer (Sinnadurai, 1992). Its cultivation provides an excellent source of employment for both rural and urban dwellers as it is grown in many rural areas through truck farming and in the outskirts of towns and cities as market gardening and backyard gardening to supply fresh vegetables to urban markets. Furthermore, middlemen who purchase the vegetable from the farms and send to the urban centres as well as transport operators who convey the heads to the market centres, all obtain their source of livelihood from the crop.

In spite of the enormous benefits of cabbage to the growth and development of humans and the nation as a whole, production of the crop is beset with a lot of problems. Prominent among these problems in Ghana is insect pest attack and crop diseases which decrease yield (Ntow *et al*., 2006). For instance, the diamondback moth *Plutella xylostella* L. (Lepidoptera: Plutellidae), voraciously feeds on the leaves of cabbage, scratching off the tissues and can completely defoliate the crop (Obeng-Ofori, 2007). The activities of these insect pests and diseases render crops unattractive and are therefore rejected by consumers (Afun *et al*., 1992). Farmers, in a desperate attempt to protect their crops and investments spray them with hazardous insecticides including OCs and at different application rates and frequency of application (Brempong-Yeboah, 1992).

OCs are highly toxic, persistent, bioaccumulating, carcinogenic, mutagenic and teratogenic. Runoff of these toxic OCs may contaminate water bodies to exert their toxicological effect. They may pose serious health problems to human and animals that drink from them, or may contaminate soils (Ntow *et al*., 2006). Chemical residues may also concentrate in crops which can pose health hazards to consumers if the maximum residue limit (MRL) set by the FAO/WHO is exceeded (Ntow, 2001). Non-target flora and fauna concentrate these residues in their tissues and pass them on along the food chain (Koomson, 2012). Studies done by several researchers in Ghana such as Ninsin (1997), Biney (2002), Aboagye (2002), Odhiambo (2005) and Koomson (2012) revealed high residues of OCs in vegetable and fruit crops. Mufiol-de-Toro *et. al.*, (2006) observed that there is much evidence to show OCs interaction with the endocrine system, resulting in numerous biological effects on humans and animals.

1.2 Problem Statement

Vegetable production in Ghana typically occurs in intensely managed smallholder farms or irrigation schemes with relatively high inputs of agrochemicals. Recorded vegetable crops (cabbage, tomato, pepper, okra, eggplants (or garden eggs), and onion) cover approximately 0.4% of the cultivated land of Ghana, equating to 58,270 ha in 1998 (Gerken *et al.,* 2001) with an estimated average agrochemical application rate of 0.08 liters ai/ha to these vegetables. Intensively managed vegetable farms are also characterized by an extensive network of drainage systems where surplus water may flow into local streams and rivers. Consequently, the aquatic ecosystems located downstream of vegetable farmlands are potential recipients and are therefore vulnerable to agrochemical accumulation due to intensive agrochemical use and highprecipitation rates typical of tropical areas where vegetable production occurs.

Farmers in Opeibea and Dzorwulu farming areas spray excess doses of agrochemicals on their crops and also spray at 2-3 days intervals ignoring most often, the pre-harvest spraying timeinterval. They also dispose agrochemical wastes, washouts, and empty containers on the farmlands. This could lead to build-up of pesticide residues in the soils and hence the crops and also contaminate water bodies through run-offs.

1.3 Justification

The food and agricultural industry plays a major role in Ghana's economy, according to GIPC, 2001, from 1990 to 1999, the agricultural sector contributed an average of 41.3% to gross domestic product and 12.2% of national tax revenue. In 1999 alone, it recorded total foreign exchange earnings of $2.1 billion and employed 54.3% of the total workforce. These show that the livelihood of the average Ghanaian depends either on agriculture or agriculture-related business for his or her livelihood. But the activities of insects, pests and diseases which render crops both in the pre- and post-harvest stages unattractive and obnoxious restrict the productivity of the agricultural sector necessitating the application of pesticides including organochlorine pesticides to control this menace.

Cabbage, one of the most consumed vegetables is also one of the crops that are mostly cultivated by the Opeibea and Dzorwulu farming communities in Accra but without adherence to human and environmental safety regulations. This may lead to accumulation of high levels of organochlorine pesticides and since these chemicals are toxic to living organisms, increased accumulation in the food chain may pose serious health hazards to the general populace. In order to avert any human and environmental health hazard associated with organochlorine pesticides residue in such a highly consumed crop, it is essential to assess the residue levels in the crop as well as the soil and irrigation water bodies for its cultivation in order to prescribe the appropriate remedial action.

1.4 Aim

The aim of this study was to determine the wholesomeness of cabbage cultivated with irrigation in terms of organochlorine pesticides contamination in some farming communities in Accra, Ghana.

1.5 Objectives

The objectives of this project were:

- To determine the residue levels of organochlorine in cultivated cabbage in the Oyansia stream at Dzorwulu and Opeibea.

- To determine the residue levels of organochlorine in the soils of cabbage farms along the Oyansia stream at Dzorwulu and Opeibea.
- To determine the residue levels of organochlorine in irrigation water and water sediment of the Oyansia stream at Dzorwulu and Opeibea.
- To assess the level of understanding of the causes and effects of organochlorine pollution of cabbage farmers along the Oyansia stream at Dzorwulu and Opeibea.

CHAPTER TWO

LITERATURE REVIEW

2.1 Origin and Importance of Cabbage

Cabbage (*Brassica olerecea var*.capitata) is an important global vegetable cultivated and consumed by most people. It is a biennial crop and a member of the family Cruciferae (Purseglove, 1969; Rice *et al.*, 1993). The “head” which is the edible part of the cabbage plant is made up of series of overlapping expanded leaves which cover a small terminal bud (Purseglove, 1969; Sinnadurai, 1992; Rice *et al.*, 1993).

The crop is of ancient cultivation and has been grown in Europe since at least 2500B.C. It was introduced by the Romans into England and is now grown all over the world (purseglove, 1969). The information on the introduction of the crop into Ghana is not well documented but it is believed that it was introduced by the British into the country and was grown on a small scale (Sinnadurai, 1992). Cabbage has gained popularity in Ghana and its consumption has increased especially among Ghanaians living in the urban centres. This is due to the nutritional value of the vegetable (Table 2.1). This has therefore increased the demand for cabbage as it is served in many homes, restaurants and other fast food outlets.

Table 2.1: Nutritional value of cabbage leaves, nutrient per 100g of edible portion

NUTRIENT	**CONTENT/**(100g)
Water	90.0
Calories	23.0
Protein	1.5
Fat	1.0
Carbohydrate	24.0
Fibre	28.0
Calcium	0.5
Phosphorous	0.1
Iron	0.5
Thiamine	0.1
Riboflavin	0.7
Niacin	0.7
Ascorbic Acid	40.0
B-Carotene	0.3

Source: (Rice *et al*., 1993)

2.2 Insect Pests of Cabbage

In spite of the enormous benefits of cabbage to the growth and development of humans and the nation as a whole, production of the crop is beset with a lot of problems (Sinnadurai, 2002). Unavailability of land and water, marketing problems and insect pest infestation which happens to be a global problem is some of the constraining factors. These pests include aphids (*Brevicoryne brassicae*), Bagrada bug (*Bagrada hilaris*), flea beetles (*Phyllotreta sp*.), diamondback moth (*Plutella xylostella*) and cutworm (*Agrotis sp*.) (De Lannoy, 2001). The most devastating pest that causes severe damage in cabbage production is the diamondback moth (DBM) (Kwarteng and Towler, 1994).

However, the insect is resistant to many conventional pesticides and so spraying DBM-infested cabbage often has little effect on the pest; thus farmers may be tempted to carry out extensive spraying and eventually give up cabbage protection (Youdeowei, 2002). Furthermore, there is a growing concern about the pollution of the environment and its resultant effects on the health of humans and animals arising from the continuous use of these pesticides. An effective and environmentally friendly approach in managing this menace is thus required (Youdeowei, 2002).

2.3 Pesticides

Pesticides are chemical substances defined as poisons and used in certain circumstances to kill specifically targeted pests (Wassemann, 1972). They refer to chemical substances that are biologically active and interfere with the normal biological processes of organisms deemed to be pests whether noxious plants or weeds, insects, mould or fungi. Pesticides can be broadly classified according to their intended target pest; i.e. herbicide for weeds, insecticide for insects, fungicides for plant diseases and fungi.

The three routes of exposure are oral ingestion, dermal absorption and inhalation. Pesticides can be tracked into home on clothing and in vehicles, exposing family members as well. Pesticides used in pet flea collars, in treatments for scabies and lice and for home infestations of wasps, cockroaches, ants and agricultural pesticides used on farms and greenhouses were ingested by food products. These highly stable compounds can last for years and decades before breaking down. According to William (2000), they circulate globally, and persistent pesticides released in one part of the world can be transported through a repeated process of evaporation and deposit through the atmosphere to regions far away from the original source. Pesticides used domestically or in agriculture run off into ground and surface water exposing entire populations. The higher doses are linked to greater potential effects.

Pesticides are toxic in nature and do not differentiate between targeted and non-targeted species, hence should essentially be subject to safe and judicious use. Due to injudicious and indiscriminate use of pesticides, many accidents have occurred and the presence of pesticides in foods, fruits, vegetables and environment and even in mothers' milk is a matter of grave concern (FAO/WHO, 2005). Of all the pesticides released into the environment every year by human activity, persistent pesticides are among the most dangerous. They are highly toxic, causing an array of adverse effects, notably death, diseases and birth defects among human and animals. Specific effect can include cancer, allergies and hypersensitivity, damage to the central and peripheral nervous systems, reproductive disorders, and disruption of the immune system. (Strict, 1981; Maroni, 1990)

2.4 Organochlorine Pesticides

An organochloride, organochlorine, chlorocarbon, chlorinated hydrocarbon, or chlorinated solvent is an organic compound containing at least one covalently bonded chlorine atom. Their wide structural variety and divergent chemical properties lead to a broad range of applications. Many derivatives are controversial because of the effects of these compounds on the environment (Gribble, 1998). Organochlorine pesticides are insecticides composed primarily of carbon, hydrogen, and chlorine. They break down slowly and can remain in the environment long after application and in organisms long after exposure. Organochlorine pesticides contamination of estuarine and marine waters is closely linked to anthropogenic activities. Organochlorine pesticides mainly enter the aquatic environment through agricultural and domestic application. Unlike metals, there are no known natural sources of some organochlorine compounds such as Polychlorinated Biphenyls (PCBs) and synthetic pesticides (e.g., DDT). Their occurrence in the environment is therefore entirely the consequence of their production and use by man, principally on land. Some organic contaminants do, however, have natural sources. For example, certain Polycyclic Aromatic Hydrocarbons (PAHs) can be produced during combustion (e.g. in forest fires). Organic contaminants such as PCBs are highly stable and degrade only very slowly in the environment. Their widespread occurrence coupled with their persistence has led to concern over the possibility that these compounds may accumulate in more vulnerable compartments of the marine environment, as in marine mammals, including seals.

2.4.1 Chemical, Physical, and Toxicological Properties

Chloride substituents modify the physical properties of organic compounds in several ways. They are typically denser than water due to the presence of high atomic weight of chlorine. Chloride substituents induce stronger intermolecular interactions than hydrogen substituents. The effect is illustrated by trends in boiling points; methane (-161.6°C), methyl chloride (-24.2°C), dichloromethane (40°C), chloroform (61.2°C), and carbon tetrachloride (76.72°C). The increased intermolecular interactions are attributed to the effects of both van der Waals and polarity. Organochlorine pesticides are generally stable in the environment and undergo limited decomposition or degradation. Organochlorine pesticides are not particularly volatile, but because they tend to persist in the environment, they can cycle among air, water, soil, vegetation, and animals.

Organochlorine pesticides are fairly non-polar molecules so they tend to dissolve readily in hydrocarbon-like environments, such as the fatty material in living matter. They are only slightly soluble in water. Although organochlorine pesticides can evaporate into the air, they adhere strongly to soils or sediments, where their concentrations can build up, often exceeding those of surrounding water by orders of magnitude. Organochlorine pesticides in water and sediments tend to bioaccumulate in living tissues, particularly in fish and other aquatic organisms. They also bioaccumulate in plants, birds, terrestrial animals, agricultural livestock, and domestic animals, where their concentrations increase by orders of magnitude as they rise through the food web, particularly as they reach higher organisms.

At low concentrations, organochlorine pesticides exhibit relatively low acute toxicity to humans; however, they may mimic human hormones like estrogen, or have other properties that cause long term health effects. At higher levels, organochlorine pesticides can be very harmful, causing a range of problems including mood change, headache, nausea, vomiting, dizziness, convulsions, muscle tremors, liver damage, and death (Merck 1983). As a result of observed effects on animals and plants in the environment, and potential harmful effects to humans, many uses of organochlorine pesticides have been banned in the U.S. (EIP Associates, 1997).

Table 2.2: Pesticides used in Ghana

Pesticide Product	**Active Ingredient**	**WHO Toxicity Class**	**Status**
Actellic	Pirimiphos-methyl	III	PCL
Cydim super	Cypermethrin + Dimethoate (PY + OP)	II + II	PCL
Cymbush	Cypermethrin (PY)	II	PCL
Cypercal	Cypermethrin (PY)	II	FRE
Dimethoate	Dimethoate (OP)	II	FRE
DDT	DDT(OC)	II	**Banned**
Dursban	Chlorpyrifos (OP)	II	FRE
Furadan	Carbofuran (CARB)	Ib	FRE
Gammalin 20	Lindane (OC)	II	**Restricted**
Karate/PAWA	Lambda-Cyhalothrin (PY)	II	FRE
Pyrinex	Chlorpyrifos (OP)	II	FRE
Topsin	Thiophanate-methyl (OP)	III	PCL

FRE: Fully registered for use in Ghana (valid for maximum of three years)
PCL: Provisional clearance in Ghana (valid for maximum of one year)
OC: organochlorine OP: Organophosphate PY: Pyrenoid CARB: carbonate WHO Toxicity Class:
Ib- highly hazardous; II- moderately hazardous; III- slightly hazardous

Table 2.3 Types of agrochemicals used in horticulture production in Ghana

Agrochemical type (% of total No. in use)	Active Ingredient and concentration	WHO/FAO Hazard Class
Insecticides	Lambda cyhalothrin 2.5%	II
	Fipronil 25g/l	II
	Dimethoate 400g/l	II
	Cypermethrin 10g/l	II
	Azadirachtin	U
	Bacillus thuringiensis 2.86%	IV
	Deltamethrin 25.5g/l	II
	Fenvalerate 20%	II
	Chlorpyrifos-ethyl 480g/l	
	Acetamiprid 25g/l	IV
Fungicides	Copper hydroxide 77%	II
	Mancozeb 800g/kg	III
	Maneb800g/kg	III
	Metalaxyl-M, (6%) + Cuprous oxide (60%)	III
	Carbendazim500g/l	III
Herbicide	Pendimethalin 400g/I	III
	Glyphosate 41%	III
	Paraquat 200g/l	II
	2, 4-D Amine Salts 720g/l	II
	Atrazine 80g/kg	III
	Atrazine 500g/l	III
	Diuron 56%	II
	Bromacil24%	II

2.5 Some Organochlorine Pesticides and their Effects

Organochlorine insecticides may be divided into four distinct groups including Dichlorodiphenyl Trichloroethane (DDT), Cyclodienes (Aldrin, Endrin, Heptachlor, Dieldrin, Chlordane, Endosulfan, Chlordecone), Hexachlorocyclohexane (Lindane) and related compounds.

2.5.1 Dichlorodiphenyltrichloroethanes (DDT)

DDT, $C_{14}H_9Cl_5$ is a white, crystalline solid with no odour or taste. DDT is a pesticide once widely used to control insects in agriculture and insects that carry diseases such as malaria. The use of DDT increased enormously on a worldwide basis after World War II, primarily because of its effectiveness against the mosquito that spreads malaria and lice that carry typhus. The World Health Organization estimates that during the period of its use approximately 25 million lives were saved. DDT seemed to be the ideal insecticide; it is cheap and of relatively low toxicity to mammals (oral LD50 is 300 to 500 mg/kg). However, problems related to extensive use of DDT began to appear in the late 1940s. Many species of insects developed resistance to DDT, and DDT was also discovered to have a high toxicity toward fish.

The chemical stability of DDT and its fat solubility compounded the problem. DDT is not metabolized very rapidly by animals; instead, it is deposited and stored in the fatty tissues. The biological half-life of DDT is about eight years; that is, it takes about eight years for an animal to metabolize half of the amount it assimilates. If ingestion continues at a steady rate, DDT builds up within the animal over time (Harrison, 1997).

2.5.2 Aldrin and Dieldrin

Aldrin, $C_{12}H_8Cl_6$ and Dieldrin, $C_{12}H_8Cl_6O$ are insecticides with similar chemical structures. Aldrin quickly breaks down to dieldrin in the body and in the environment. Pure aldrin and dieldrin are white powders with a mild chemical odor. The less pure commercial powders have a tan color. Neither of these substances occurs naturally in the environment. Sunlight and bacteria change aldrin to dieldrin so that we mostly find dieldrin in the environment. They bind tightly to soil and slowly evaporate to the air. Dieldrin in soil and water breaks down very slowly. Plants take in and store aldrin and dieldrin from the soil. Aldrin rapidly changes to dieldrin in plants and animals. Dieldrin is stored in the fat and leaves the body very slowly (ASTDR, 2002).

2.5.3 Chlordane

Chlordane, $C_{10}H_6Cl_8$ is a broad spectrum contact insecticide that has been used on agricultural crops including vegetables, small grains, maize, other oilseeds, potatoes, sugarcane, sugar beets, fruits, nuts, cotton and jute. It has also been used extensively in the control of termites. Chlordane is highly insoluble in water, and is soluble in organic solvents. It is semi-volatile and can be expected to partition into the atmosphere as a result. It binds readily to aquatic sediments and bioconcentrates in the fat of organisms as a result of its high partition coefficient. The half-life of chlordane in soil has been reported to be approximately one year. This persistence, combined with a high partition coefficient, provides the necessary conditions for chlordane to bioconcentrate in organisms. The chemical properties of chlordane (low water solubility, high stability, and semi-volatility) favour its long range transport, and chlordane has been detected in arctic air, water and organisms.

Chlordane exposure may occur through food but, due to its highly restricted uses, this route does not appear to be a major pathway of exposure. Chlordane has been detected in indoor air of residences of both Japan and the US. Exposure to chlordane in the air may be an important source of exposure to the US population.

2.5.4 Endosulfan

Endosulfan, $C_9H_6Cl_6O_3S$, is an organochlorine insecticide and acaricide, and acts as a contact poison in a wide variety of insects and mites. Endosulfan is effective against a wide range of insects and certain mites on cereals, coffee, cotton, fruit, oilseeds, potato, tea, vegetable and other crops (Ghadiri *et al*., 1994). It can also be used as a wood preservative. Endosulfan is sold as a mixture of two different forms of the same chemical (alpha- and beta-endosulfan). Its colour is cream to brown and it smells like turpentine (ATSDR, 1995).

Endosulfan is a highly toxic substance. The World Health Organisation (WHO) classifies endosulfan in Category II (moderately hazardous). The US Environmental Protection Agency (US EPA) classifies it as a Category 1b (highly hazardous) pesticide (PANAP, 1996). Short-term toxicity is high, and influenced by the solvents and emulsifiers used to dissolve it (EXTOXNET, 1992). Endosulfan is easily absorbed by the stomach, by the lungs and through the skin, meaning that all routes of exposure can pose a hazard. Exposure to endosulfan may result from, for example; breathing air near where it has been sprayed, drinking water contaminated with it, eating contaminated food; touching contaminated soil, smoking cigarettes made from tobacco with endosulfan residues, or working in an industry where endosulfan is used (ATSDR,1995). Proper protective clothing (safety goggles, gloves, long sleeves, long pants, and respirator) is needed to prevent poisoning when handling endosulfan.

Acute toxicity Stimulation of the Central Nervous System is the main characteristic of endosulfan poisoning. Symptoms of acute exposure include hyperactivity, tremors, decreased respiration, salivation, anaemia, and also unco-ordination and a loss of ability to stand (EXTOXNET, 1992). Other signs of poisoning include gagging, vomiting, diarrhoea, agitation, convulsions and loss of consciousness. Blindness has been observed in cows, sheep and pigs which have grazed in fields sprayed with the compound. People with diets low in protein may be more sensitive to the effects of this pesticide (PANAP, 1996).

The half-life of endosulfan in water and in most fruits and vegetables is reported to be three to seven days. However, half-life in sandy loam is reported to be between 60 and 800 days. The degradation rate is dependent on the pH of the soil: alkaline conditions favour degradation, whereas acidic conditions slow down the process. Adding endosulfan to soil appears to reduce the degradation rate of other organochlorine pesticides already present in the soil, either because endosulfan reduces the populations of micro-organisms, or because of reduction of the activity of micro-organisms responsible for degradation of the other organochlorines (Ghadiri, 1995).

2.5.5 Endrin

Endrin, $C_{12}H_8OCl_6$, is a highly toxic chlorinated hydrocarbon. It is a solid, white, almost odourless substance that was used as a pesticide to control insects, rodents, and birds. Endrin does not dissolve very well in water. It has been found in groundwater and surface water, but only at very low levels. It is more likely to cling to the bottom sediments of rivers, lakes, and other bodies of water. It is generally not found in the air except when it was applied to fields during agricultural applications. The persistence of endrin in the environment depends highly on local conditions. Some estimates indicate that endrin can stay in soil for over 10 years. Endrin may also be broken down by exposure to high temperatures or light to form primarily endrin ketone and endrin aldehyde (ATSDR, 1996).

2.5.6 Heptachlor

Heptachlor, $C_{10}H_5Cl_{17}$ is a non-systemic stomach and contact insecticide, used primarily against soil insects and termites. It has also been used against cotton insects, grasshoppers, some crop pests and to combat malaria. Heptachlor is highly insoluble in water, and is soluble in organic solvents. It is quite volatile and can be expected to partition into the atmosphere as a result. It binds readily to aquatic sediments and bioconcentrates in the fat of living organisms. Heptachlor is metabolised in animals to heptachlor epoxide, whose toxicity is similar to that of heptachlor, and which may also be stored in animal fat. The use of heptachlor has been banned and restricted in some parts of the world.

There is no information on accidental or suicidal intoxication by heptachlor in humans. Symptoms in animals include tremors and convulsions. A study of workers from a plant involved in the production of heptachlor and endrin found a significant increase in bladder cancer. This result was unexpected as no known bladder carcinogens were used at the plant, however, the small number of deaths (3) makes interpretation of these findings difficult. No deaths from liver or biliary tract cancer were observed, although mortality from cerebrovascular disease was higher than expected. There is limited evidence that cyclodienes such as heptachlor may affect immune responses.

The half life of heptachlor in temperate soil is up to 2 years. This persistence, combined with a high partition coefficient (KOW = 4.4-5.5), provides the necessary conditions for heptachlor to bioconcentrate in organisms. The chemical properties of heptachlor (low water solubility, high stability, and semi-volatility) favour its long range transport, and heptachlor and its epoxide have been detected in arctic air, water and organisms.

WHO suggests that food is the major source of exposure of heptachlor to the general population. Heptachlor has been detected in the blood of cattle from both the US and Australia. Heptachlor was detected in 30 of 241 samples in American cattle, and violations of the Maximum Residue Level, MRL for heptachlor were detected in 0.02 % of Australian cattle. In both instances, heptachlor was among the most frequently detected organochlorine. A daily intake of 0.25 µg/person/day (for heptachlor and heptachlor epoxide combined, based on a 60 kg person) was estimated for Vietnam, and of 0.07 µg/person/day (for heptachlor alone) for India.

2.5.7 Hexachlorobenzene

Hexachlorobenzene (HCB), C_6Cl_6 is a fungicide that was first introduced in 1945 for seed treatment, especially for control of bunt of wheat. HCB is also a by-product of the manufacture of industrial chemicals including carbon tetrachloride, perchlorethylene, trichloroethylene and pentachlorbenzene. It is a known impurity in several pesticide formulations, including pentachlorophenol and dicloram and may be present as an impurity in others. HCB is highly insoluble in water, and is soluble in organic solvents. It is quite volatile and can be expected to partition into the atmosphere. It is very resistant to breakdown and has a high partition coefficient (KOW=3.03-6.42), and is known to bioconcentrate in the fat of living organisms. IARC has concluded that while there is inadequate evidence for the carcinogenicity of HCB in humans, there is sufficient evidence in experimental animals. IARC has classified HCB as a possible human carcinogen.

HCB is very persistent. Estimated half lives in soil from aerobic and anaerobic degradation range from 2.7 to 22.9 years. This persistence, combined with a high partition coefficient (log KOW = 3.03-6.42), provides the necessary conditions for HCB to bioconcentrate in organisms. The chemical properties of HCB (low water solubility, high stability, and semi-volatility) favour its long range transport, and HCB has been detected in arctic air, water and organisms. HCB is ubiquitous in the environment, and has been measured in foods of all types. HCB was one of two organochlorines detected in all samples of Spanish meat and meat products surveyed with mean levels ranging from 8 ppb (fat weight) in pork products (cured ham) to 49 ppb in lamb, with a maximum level of 178 ppb in lamb. HCB was detected in 13 of 241 serum samples from Colorado beef cattle in a monitoring program, with an average concentration of 3.1 ppb. A survey of US pasteurized milk detected HCB in 8 of 806 composite milk samples. A survey of foods from India found average concentrations of HCB ranging from 1.5 ng/g (fat weight) in both oils and milk to 9.1 ng/g in fish and prawns, with a maximum concentration of 28 ng/g in fish and prawns and an estimated daily intake of 0.13 µg/person. Average HCB residues in foods from Vietnam ranged from 0.28 ng/g (fat weight) in pulses to 27 ng/g in caviar, with an estimated daily intake of 0.10 µg/person.

2.5.8 Polychlorinated Biphenyls

Polychlorinated biphenyls (PCBs) are mixtures of chlorinated hydrocarbons that have been used extensively since 1930 in a variety of industrial uses, including dielectrics in transformers and large capacitors, as heat exchange fluids, as paint additives, in carbonless copy paper and in plastics. The value of PCBs for industrial applications is related to their chemical inertness, resistance to heat, non-flammability, and low vapour pressure and high dielectric constant. There are 209 possible PCBs, from three monochlorinated isomers to the fully chlorinated decachlorobiphenyl isomer. Generally, the water solubility and vapour pressure decrease as the degree of substitution increases, and the lipid solubility increases with increasing chlorine substitution. PCBs in the environment may be expected to associate with the organic components of soils, sediments, and biological tissues or with dissolved organic carbon in aquatic systems, rather than being in solution in water. PCBs volatilize from water surfaces in spite of their low vapour pressure, and partly as a result of their hydrophobicity; atmospheric transport may therefore be a significant pathway for the distribution of PCBs in the environment.

The toxicology of PCBs is affected by the number and position of the chlorine atoms, as substitution in the *ortho* position hinders the rotation of the rings. PCBs without *ortho* substitution are generally referred to as coplanar and all others as non-coplanar. Coplanar PCBs, like dioxins and furans, bind to the AL-receptor and may exert, thus, dioxin-like effects, in addition to AL-receptor independent effects which they share with non-coplanar PCBs (e.g. tumor promoter). Association between elevated exposure to PCB mixtures and alterations in liver enzymes, hepatomegaly, and dermatological effects such as rashes and acne has been reported. Adverse effects are predominantly associated with higher blood concentrations.

Contamination of rice oil by PCBs in Japan (1968) and Taiwan (1979) has resulted in the exposure of a large number of people to PCBs and their contaminants PCDFs. Signs and symptoms of exposure from these incidents include enlargement and hyper secretion of the Meibomian glands of the eyes, swelling of the eyelids, and pigmentation of the nails and mucous membranes, occasionally associated with fatigue, nausea and vomiting. This was followed by hyperkeratosis and darkening of the skin with follicular enlargement and acne form eruptions, often with a secondary staphylococcal infection. Children born up to 7 years after maternal exposure in the Taiwan incident had hyper-pigmentation, deformed nails and natal teeth, intrauterine growth delay, poorer cognitive development up to 7 years of age, behavioural problems and higher activity levels. The affected children appeared to "catch up" to controls at 12 years of age. Children born seven to twelve years after maternal exposure experienced mildly delayed development, but no differences in behaviour. Effects observed in these children are likely to be a result of the persistence of PCBs in the human body, resulting in prenatal exposure long after the exposure took place. These effects are consistent with the observations of poorer short term memory functioning in early childhood, in children exposed prenatally by mothers who had high consumption of Lake Michigan sports fish containing PCBs, amongst other POPs.

PCBs have a low acute toxicity to laboratory animals, with acute oral LD50 values in rats in the range of 2 to 10 g/kg body weight. Effects are manifested primarily through chronic exposure. Effects on the liver, skin, immune system, reproductive system, gastrointestinal tract and thyroid gland have been observed associated with exposure to PCB mixtures or individual congeners. Adverse reproductive effects observed in several studies on monkeys exposed to PCBs include low birth weights, skin hyper-pigmentation, behavioural disturbances, atrophy of the thymus and lymph nodes, bone marrow hypoplasia and hyperplasia of the gastric mucosa.

The degradation of PCBs in the environment depends largely on the degree of chlorination of the biphenyl, with persistence increasing as the degree of chlorination increases. Half-lives for PCBs undergoing photo-degradation range from approximately 10 days for a monochlorobiphenyl to 1.5 years for a heptachlorobiphenyl. The persistence of PCBs combined with the high partition coefficients of various isomers (log KOW ranging from 4.3 to 8.26) provide the necessary conditions for PCBs to bioaccumulate in organisms. Concentration factors in fish exposed to PCBs in their diet were lower than those for fish exposed to PCBs in water, suggesting that PCBs are bioconcentrated (taken up directly from the water) as opposed to being bioaccumulated (taken up by water and in food). The chemical properties of PCBs (low water solubility, high stability, and semi-volatility) favour their long range transport, and PCBs have been detected in arctic air, water and organisms.

The main source of PCB exposure to the general population is through food, especially fish. PCB residues were detected in 8.5% of samples, with a maximum of 0.30 mg/kg fat, taken during a survey of the fat of domestic farm animals in Ontario, Canada between 1986 and 1988. In a survey of foods in Vietnam, the highest levels of PCBs were detected in fish and shellfish, with levels of 760 and 1,400 mg/g fat. The main source of PCBs in the Vietnamese diets is cereals (including rice) and vegetables, and the daily intake of 3.7 µg/person/day is comparable to those of some industrialized countries. A survey of foods in India also found that the highest levels of PCBs were in fish, with an average of 330 ng/g fat. Again, the main source of PCB dietary intake (0.86 µg/person/day) was cereal and vegetable oil.

2.5.9 Hexachlorocyclohexanes

Hexachlorocyclohexane (HCH) is a manufactured chemical that exists in eight chemical forms called isomers. One of these forms, gamma-HCH (or γ-HCH, commonly called lindane) is produced and used as an insecticide on fruist, vegetables, and forest crops. It is a white solid that may evaporate into the air as a colourless vapour with a slightly musty odour. It is also available as a prescription (lotion, cream, or shampoo) to treat head and body lice, and scabies. Lindane has not been produced in the United States since 1976, but is imported for insecticide use. Technical-grade HCH was used as an insecticide in the United States and typically contained 10-15% γ-HCH as well as the alpha (α), beta (β), delta (δ), and epsilon (ε) forms of HCH. Virtually all the insecticidal properties resided in γ-HCH. Technical-grade HCH has not been produced or used in the United States in over 20 years.

The components of technical-grade HCH have been found in soil and surface waters near hazardous waste sites. In the air, the different forms of HCH can exist as a vapour or attached to small particles such as soil and dust. The particles may be removed from the air by rain or degraded by other compounds in the atmosphere. HCH can remain in the air for long periods of time and travel great distances. In soil, sediments, and water, HCH is broken down to less toxic substances by algae, fungi, and bacteria, but this process can take a long time. HCH can accumulate in the fatty tissue of fish (ATSDR, 2005).

2.5.10 Lindane

Lindane is a white crystalline powder, $C_6H_6Cl_6$, used chiefly as an agricultural pesticide. Lindane is an organochlorine insecticide and fumigant which has been used on a wide range of soil-dwelling and plant-eating (phytophagous) insects. It is commonly used on a wide variety of crops, in warehouses, in public health to control insect-borne diseases, and (with fungicides) as a seed treatment. Lindane is also presently used in lotions, creams, and shampoos for the control of lice and mites (scabies) in humans. Technical lindane is comprised of the gamma-isomer of, HCH. Five other isomers (molecules with a unique structural arrangement, but identical chemical formulas) of HCH are commonly found in technical lindane, but the gamma-isomer is the predominant one, comprising at least 99% of the mixture of isomers. Data presented in this profile are for the technical product unless otherwise stated; lindane, HCH, or BHC refer to technical lindane, i.e., Gamma-hexachlorocyclohexane. Gamma-HCH has been shown to be the insecticidally effective isomer. Lindane may also be found in formulations with a host of fungicides and insecticides. It is available as a suspension, emulsifiable concentrate, fumigant, seed treatment, wettable and dustable powder, and ultra low volume (ULV) liquid.

2.5.11 Mirex

Mirex is a white crystalline, odourless solid with a melting point of 485°C. It is soluble in several organic solvents including tetrahydrofuran (30%), carbon disulfide (18%), chloroform (17%), and benzene (12%), but is practically insoluble in water. It has a vapour pressure of 3 ×

10-7mmHg at 25°C. Mirex is considered to be extremely stable. It does not react with sulfuric, nitric, hydrochloric, or other common acids and is unreactive with bases, chlorine, or ozone. Despite its stability, reductive dechlorination of mirex can be brought about by reaction with reduced iron porphyrin or more effectively by vitamin B_{12}. Slow partial decomposition will also result from exposure to ultraviolet radiation (UVR) in hydrocarbon solvents or to gamma rays. Photomirex (8-monohydro-mirex) is the major product of dechlorination by UVR, and may represent the fate of most of the mirex in the environment.

2.5.12 2, 4, 5-Trichlorophenol and 2, 4, 6-Trichlorophenol

They are used as an insecticide, fungicide, herbicide, bactericide, germicide, wood and glue preservative, anti-mildew agent for textiles, defoliant. It is used as a chemical intermediate for the synthesis of other pesticides.

2.6 Uses of Organochlorine Pesticides

Organochlorine (OC) pesticides are mostly used as insecticides. Specific uses take a wide range of forms, from pellet application in field crops to sprays for seed coating and grain storage. Some OCs are applied to surfaces to kill the insects. An example of this strategy is the spraying of interior home walls with DDT to control mosquitoes and the malaria they carry. This is the way DDT is usually applied in countries still using the pesticide for malaria control. Other OCs such as chlordane, heptachlor and pentachlorophenol are used to treat wood to prevent pest damage.

Some organochlorine pesticides are used on a wide array of crops. Endosulfan, for example, was first registered as an insecticide and miticide in the U.S. in 1954. It is still in widespread use in the U.S. to control pests in vegetables, fruits, cereal grains, and cotton, as well as ornamental shrubs, trees, vines, and ornamental plants. Internationally, its use in African cotton production is common, and it is applied to control pests on cashew plantations in India.

Lindane is another organochlorine with a range of uses. In the U.S., lindane has been used to protect crop seeds from insects, for pest control in forests, on livestock and household pets for control of ticks and other pests, and in homes to control ants and other household pests. It is also the active ingredient in many medicated shampoos and soaps to control head lice and scabies. Lindane is now restricted to seed coating uses for a handful of grain crops, and continues to be used to control lice and scabies (except in California, where these uses were recently banned). Internationally, lindane is banned or severely restricted in 40 countries.

2.7 Routes of Exposure

Organochlorine pesticides can travel long distances via wind and deposit on soil and water, so they can be found hundreds or thousands of miles from their point of use. They can also be transported on foods and other products treated with them. Organochlorine pesticides can enter the environment after pesticide applications, disposal of contaminated wastes into landfills, and releases from manufacturing plants that produce these chemicals. Some organochlorines are volatile, and some can adhere to soil or particles in the air. In aquatic systems, sediments adsorb organochlorines, which can then bioaccumulate in fish and other aquatic mammals. These chemicals are fat soluble, so they are found at higher concentrations in fatty foods. In the general population, diet is the main source of exposure, primarily through the ingestion of fatty foods such as dairy products and fish. Usage restrictions have been associated with a general decrease in serum organochlorine levels in the U.S. population and other developed countries (Hagmar *et. al*., 2006; Kutz *et al*., 1991).

Contaminated drinking water and air are usually minor exposure sources. Infants can be exposed through breast milk, and the fetus can be exposed *in utero* via the placenta. Workers can be exposed to organochlorines in the manufacture, formulation, or application of these chemicals. The FDA, U.S. EPA, and OSHA have developed standards for allowable levels of certain organochlorines in foods, the environment, and the workplace, respectively. Attributing human health effects to specific organochlorine chemicals is difficult because exposure to multiple organochlorine chemicals occurs often, and these chemicals may have similar actions. Organochlorines are some of the chemicals found most often in the hundreds of tests of human body tissue, that is, blood, adipose tissue, breast milk in studies conducted around the world. Because of their chemical structure, organochlorines break down slowly, build up in fatty tissues, and remain in our bodies for a long time.

Pesticide residues on food are a major source of organochlorine exposure. In a recent analysis of organochlorine residues in the U.S. food supply, Pesticide Action Network found that even those chemicals that have been banned for decades are showing up consistently in food samples tested by the U.S. Food and Drug Administration. This can be explained in part by the long life of many organochlorines in the environment (dieldrin and the breakdown products of DDT, for example, can remain in soil for decades), and in part from the transport on wind and water currents - as well as food imports - of pesticides that continue to be used in other countries. Inhalation and dermal contact are additional routes of exposure for individuals working directly with the pesticides (farm workers, seed treatment facility workers, etc.) as well as children who are exposed to pharmaceutical products containing the pesticide lindane. Infants also take in organochlorines in breastmilk, where the chemicals accumulate over a mother's lifetime in her fatty tissue. The benefits of breastfeeding outweigh potential health risks of this exposure, but it is a tragic cost-benefit equation to be forced to consider.

2.8 Effects of Organochlorine Pesticide on Human Health

Organochlorine pesticides contribute to many acute and chronic illnesses. Symptoms of acute poisoning can include tremors, headache, dermal irritation, respiratory problems, dizziness, nausea, and seizures. Also Organochlorine pesticides have strong potential to cross placental barriers even in minute concentration and cause serious neonatal damage (Saxena *et al.*, 1981).

Amr *et al.,* (1993) reported an increase in the incidence of bone marrow aplasia due to organophosphate and organochlorine pesticides. Several studies investigated the association between pesticide exposure and the risk of brain, breast, lung, kidney, pancreatic cancers and non hodgkin's lymphoma (Efir *et al.,* 2003; Buzio *et al.,* 2002; Hu and White, 2002). These effects were seen most consistently for longer duration of exposure and were found in the cases of children whose parents were occupationally exposed to pesticides (Carsor, 2002). Persons exposed to pesticides may be manifested by a significant increase in the total chromosomal aberrations in the form of breaks, isobreaks, gaps and deletions (Amr *et al.*, 1994). The chronic effect of pesticides have been positively associated with certain reproductive and developmental manifested effects such as the increased incidence of mutagenicity, teratogenicity, embryotoxicity, infertility reduced sperm count, early pregnant loss, spontaneous abortion, fetal death, certain birth defects and altered growth (Garcia,1998; Pryor *et al.,* 2000). Studies done in the United States had shown that farmers were more likely to contract certain kinds of cancer than non-farmers. The fifty five cancer-causing pesticides had been identified as those leaving the organochlorine such as BHC, DDT, aldrin have long term residual effects than other pesticides (Giri, 1998).

Many organochlorines are known or suspected hormone disruptors, and recent studies show that extremely low levels of exposure in the womb can cause irreversible damage to the reproductive and immune systems of the developing featus. Organochlorine pesticides have been associated with endocrine disrupting ability by interfering with the rate of synthesis or metabolic breakdown of hormones (Go *et al.*, 1999); European Commission, (2000).

2.9 Effects of Organochlorine Pesticide on the Environment

Pesticides, especially the organochlorine and organophosphate tend to persist in the environment, causing several types of damages including lowering of biodiversity, soil contamination, and water contamination. Once released into the environment, pesticides tend to build up in the fatty tissues of living organisms, causing serious harm to the health of species and a potential loss of bio-diversity. Excessive use of persisting pesticides in the fields has caused surface and underground water contaminations. This has been illustrated by records of some international studies. Methyl bromide one of the mostly used pesticides for soil fumigation in many countries have also been identified as the major contributor of ozone depletion (Giri, 1998).

They usually reach aquatic ecosystems through erosion and runoff from agricultural and contaminated land, atmospheric deposition, and discharging of effluents from factories and sewage (Beitz *et al*., 1994). Their lipophillic nature causes them to concentrate in the tissue of exposed organisms (Smith and Gangolli, 2002). Equally important, factors like low solubility and high soil adsorption coefficients cause OCPs to persist in the environment for years after their initial entry (Barbash *et al*., 1996; PAN, 2008).

According to a study by Gilliom (2007), pesticides were detected 90% of the year in NAWQA streams that had developed watersheds. They were found in the fish and sediment of most of the streams investigated. It was concluded that despite bans, most of the nation's rivers and streams are contaminated with pesticides. Mirex is one of the most stable and environmentally persistent pesticides in use today. It is not biodegraded by microorganisms, except occasionally under aerobic conditions, and hydrolysis is very slow. Although general environmental levels are low, it is widespread in the biotic and abiotic environment. Mirex is both accumulated and biomagnified. It is strongly adsorbed on sediments and has low water solubility.

The delayed onset of toxic effects and mortality is typical of mirex poisoning. The long-term toxicity of mirex is uniformly high. It is toxic for a range of aquatic organisms, crustacea being particularly sensitive. Mirex induces pervasive long-term physiological and biological disorders in vertebrates. Although no field data are available, the adverse effects of long-term exposure to low levels of mirex, combined with its persistence, suggest that the use of mirex presents a long-term environmental risk.

2.10 Methods of Extraction

There are various methods for the extraction of organic solvents. Samples can be extracted using pressurized solvent extraction and the soxhlet extraction methods.

2.10.1 Automated Soxhlet Extraction

Franz von Soxhlet in 1879 invented the Soxhlet extractor, a piece of laboratory apparatus (Jensen, 2007). It was originally designed for the extraction of a lipid from a solid material.

However, a Soxhlet extractor is not limited to the extraction of lipids. Soxhlet extraction is only required where the desired compound has a limited solubility in a solvent, and the impurity is insoluble in that solvent. If the desired compound has a significant solubility in a solvent then a simple filtration can be used to separate the compound from the insoluble substance. The sample, mostly, a solid material is placed inside a thimble made from thick filter paper, is loaded into the main chamber of the Soxhlet extractor. The Soxhlet extractor is placed onto a flask containing the extraction solvent. The Soxhlet is then equipped with a condenser. The solvent is heated to reflux. The solvent vapour travels up a distillation arm, and floods into the chamber housing the thimble of solid. The condenser ensures that any solvent vapour cools, and drips back down into the chamber housing the solid material.

The chamber containing the solid material slowly fills with warm solvent. Some of the desired compound will then dissolve in the warm solvent. When the Soxhlet chamber is almost full, the chamber is automatically emptied by a siphon side arm, with the solvent running back down to the distillation flask. This cycle may be allowed to repeat many times, over hours or days. During each cycle, a portion of the non-volatile compound dissolves in the solvent. After many cycles the desired compound is concentrated in the distillation flask. The advantage of this system is that instead of many portions of warm solvent being passed through the sample, just one batch of solvent is recycled.

After extraction the solvent is removed, typically by means of a rotary evaporator, yielding the extracted compound. The non-soluble portion of the extracted solid remains in the thimble, and is usually discarded.

Plate 2.1: A Soxhlet Extractor

2.10.2 Pressurized Solvent Extraction

Pressurized solvent extraction (PSE) is a new technique used for extracting organic compounds from samples. This method reduces solvent consumption and sample preparation time. Solvent is pumped into an extraction vessel containing the sample and is heated and pressurized. The pressurized solvent at high temperature accelerates the extraction process by increasing the solubility of the analyte in the solvent and also increasing the kinetic rate of desorption of the analyte from the sample matrix.

The fast PSE is an automated system which processes six samples simultaneously. The parallel processing technology of the fast PSE considerably increases sample throughput compared to Soxhlet and pressurized solvent extraction systems that employ serial processing. In addition to rapid extraction times, significant reduction in solvent consumption is achieved. Pressurized solvent extraction can be used to replace Soxhlet and sonication techniques and is approved for use (EPA Method 3545A). This application describes the rapid pressurized solvent extraction of organochlorine pesticide residues from dry and wet food products.

2.10.3 Accelerated Solvent Extraction

Residue analysis in crops and food is routinely performed in regulatory and industrial laboratories around the world. Many of the traditional procedures used to perform these extractions are time consuming and solvent-intensive. Accelerated Solvent Extraction (ASE) is an extraction technique that speeds the extraction process and reduces the total amount of solvent used. The system uses conventional liquid solvents at elevated temperatures and pressures, which results in increased extraction kinetics. Extraction of samples ranging from 1-30g typically requires 12-17min and 15-50ml of solvent.

In the environmental industry, ASE has been compared extensively to traditional preparation techniques and has been found to generate similar extracts in a more efficient manner. ASE is now widely used in environmental applications to replace time and solvent intensive techniques such as Soxhlet and Sonication. The principles of ASE technology are based on conventional liquid extraction theory, so the transfer of existing solvent-based extraction processes to ASE is simple. In addition, the ability to extract up to 24 samples unattended can result in a dramatic increase in laboratory efficiency.

2.11 Analytical Methods

2.11.1 Chromatography

Chromatography is a separative technique which consists of a diverse and important group of methods that permit the separation of closely related compounds of complex mixtures. The sample is dissolved in a mobile phase, that is, liquid or gas. The mobile phase is then forced through an immiscible stationary phase which is fixed in a column or on a solid surface. The two phases are chosen so that the components of the sample distribute themselves between the mobile and stationary phase to varying degrees. Those components that are strongly retained by the stationary phase move only slowly with the flow of the mobile phase. Components that are weakly held by the stationary phase travel rapidly. Consequently, sample components separate into discrete bands that can be analysed qualitatively or quantitatively.

Chromatographic methods can be classified into:

Column Chromatography

Planar Chromatography

Liquid Chromatography

Gas chromatography

A gas chromatograph is a chemical analysis instrument for separating chemicals in a complex sample. A known volume of gaseous or liquid analyte is injected into the entrance of the column, using a solid phase micro extraction fiber or micro syringe. The carrier gas moves the analyte molecules through the column. This motion is inhibited by the adsorption of the analyte molecules either onto the column walls or onto packing materials in the column. The strength of absorption, type of molecule and the stationary phase of materials affect the rate at which molecules progress along the column. The various components of the analyte mixture are separated as they progress along the column and reach the end of the column at different times. This is as a result of the different rate of progression of each type of molecule. A detector is used to monitor the outlet stream from the column, its retention time and determine the amount of component.

2.12 Research in and outside Ghana

A similar study by Ntow (2000) at Akumadan, a prominent vegetable-farming community in the Ashanti region of Ghana. The study was on the determination of Organochlorine Pesticides in Water, Sediment, Crops, and Human Fluids. The samples were analysed using the gas chromatography technique. Lindane and endosulfan were found in water and sediment collected from nearby streams and rivers, while other OC pesticide residues, such as hexachlorobenzene (HCB), p, p'-DDE, and heptachlor epoxide, were additionally found in sediment. Heptachlor epoxide was the only OC residue detected in appreciable quantity in crops. Of the quantifiable levels of OCs in water, α-endosulfan showed the highest concentration (mean 62.3 ng/L) and was detected in over 60% of all the samples analyzed. Endosulfan sulfate was the most frequently occurring (78%) OC in water with a mean concentration of 30.8 ng/L.

All the OCs found in sediment appeared in at least 88% of all the samples analyzed. The concentration was highest in sediment for lindane (mean 3.2 mg/kg) and least for β-endosulfan (mean 0.13 mg/kg). However, only heptachlor epoxide was present at a quantifiable level in tomato crops (mean 1.65 mg/kg fresh weight) and in about 50% of the samples analyzed. No quantifiable levels of HCB, lindane, p, p'-DDE, or endosulfan were found in crops. Higher concentrations of heptachlor epoxide were found in crops (mean 1.65 mg/kg fresh weight) than in sediment (mean 0.63 mg/kg dry weight). OCP concentrations in the sediment were higher than in the water. This could be due to the accumulation of residues in sediment over a period of time. Amoah, *et al.* (2005) also carried out a study on Pesticide and Pathogen Contamination of Vegetables in Ghana's Urban Markets. The study was to determine and compare the current level of exposure of the Ghanaian urban population to hazardous pesticide and faecal coliform contamination through the consumption of fresh vegetables produced in intensive urban and peri-urban smallholder agriculture with informal wastewater irrigation. Vegetable samples (lettuce, cabbage, and spring onion) were randomly collected under normal purchase conditions from 9 major markets. Chlopyrifos (Dursban) was detected on 78% of the lettuce, lindane (Gamalin 20) on 31%, endosulfan (Thiodan) on 36%, lambdacyhalothrin (Karate) on 11%, and dichloro-diphenyl trichloroethane on 33%. Most of the residues recorded exceeded the maximum residue limit for consumption.

In South Korea, Hong *et al* conducted a study on Organochlorine Pesticides in the Han River. The Han River is the biggest in the South Korea on the basis of the amount of flowing water which starts from the Mt. Taebaek and flows into the Gyonggi Bay. The total organochlorine pesticide concentrations ranged from 0.84 (St. 1) to 10.66 ng/L (St. 6) in August, 2002 and concentrations ranging from 0.54 (St. 1) to 7.22 ng/L (St. 7) in February, 2003. b- and g-HCH were present in all the samples. a-HCH, endosulfan sulfate, p, p'-DDE, p, p'-DDD, and p,p'-DDT were present in most samples. Aldrin and heptachlor were scarcely detected. Most organochlorine pesticides were banned about 30 years ago, but are still detected in the waters of Korea because of their persistence in the environment and can be long-range transported by air.

Tao *et al.* (2005) carried out a study on Organochlorine Pesticides in Agricultural Soil and Vegetables from Tianjin, China. Samples of eight types of vegetables, the rhizosphere soils, and bulk soils were collected from two sites (A and B) in Tianjin, China for the determination of hexachlorocyclohexane isomers (HCHs), metabolites (DDXs) and dichlorodiphenyltrichloroethane and The average concentrations of total HCHs and DDXs in the bulk soils were 3.6 and 80.1 ng/g for site A and 102 and 235 ng/g for site B, respectively. Relative accumulations of HCHs and DDXs in the rhizosphere soil from site A but not site B were demonstrated. The concentrations of total HCHs and DDXs in vegetable roots were 3.6-60 and 4.2-73 ng/g for site A and 15-152 and 7.1-136 ng/g for site B, respectively.

2.13 Pesticides Residues in Food

The establishment of maximum residue levels (MRLs) in foodstuffs is due mainly to the concerns of food safety expressed by people in the developed world. MRLs represent the maximum amount of residues that might be expected in/on a commodity during pesticide use if good agricultural practices are applied. The public concern about food safety in the developed world has led to the establishment of maximum residue levels which restrict level of pesticide residues in foodstuffs. MRLs are established, taking into account the persistence of the particular pesticide in a given crop, the toxicity of the chemical and how much of the final product is typically eaten by the consumer (Chan, 2000).

According to PAN (1998) residues in food can arise from the use on a crop of legally allowed pesticides at a time interval too close to time of harvest, over-use of a legally permitted pesticide, illegal use of pesticide that is not approved for that crop and incorrect use of pesticides for post-harvest treatment. In developing countries such as Ghana farmers are not equipped technically and lack the necessary technology to strictly adhere to MRLs in food crops. Therefore product of food crops in these countries normally contains high level of residues. Analysis of samples of street vendored food in Accra carried out in 1999- 2000 revealed disturbing levels of contamination by heavy metals, pesticides, microorganisms and mycotoxins (NRI, 2001). Chlorpyrifos was detected in six out of eight samples of "waakye" (rice and beans) and one out of eight samples of "fufu" (cassava and plantain dough)(NRI,2001). When MRLs are set, care is taken to ensure that maximum levels do not give rise to toxicological concerns (FAO/WHO, 1993).

CHAPTER THREE

METHODOLOGY

3.1 Description of Study Area

The study was conducted in the Ayawaso West Sub-metro of the Greater Accra Region of Ghana (Figure 3.1). The sub-metro houses the Opeibea and Dzorwulu sections of the Oyansia Stream. The capital of the Republic of Ghana and the Greater Accra Region was founded by the Ga people in the late 1600s. It is the country’s most populous city and serves as the administrative, communications, and economic heart of the country. Over 70% of Ghana’s manufacturing capacity is located within this region. The Accra Metropolitan Assembly has a total land size of 200km^2 and lies within Longitude 0^o.03 and 0^o.25 West and Latitude 5^o.30 and 5^o.53 North. The city lies along the Atlantic coast and stretches north into the interior. It stretches from Botianor to Sakumo, and James Town to Oyarifa. Tema bounds it on the East, on the South by the sea, West by the Weija dam, and North by the Akwapim hills. The metroplolis is made up of eleven sub metros. These are Ablekuma Central, Ablekuma North, Ablekuma South, Ashiedu Keteke, Ayawaso Central, Ayawaso East, Ayawaso West-Wuogon, La, Okaikoi North, Okaikoi South, and Osu Klottey (AMA, 2006). Inhabitants of these submetros consume cabbage cultivated along rivers and streams in the city and sold on the markets.

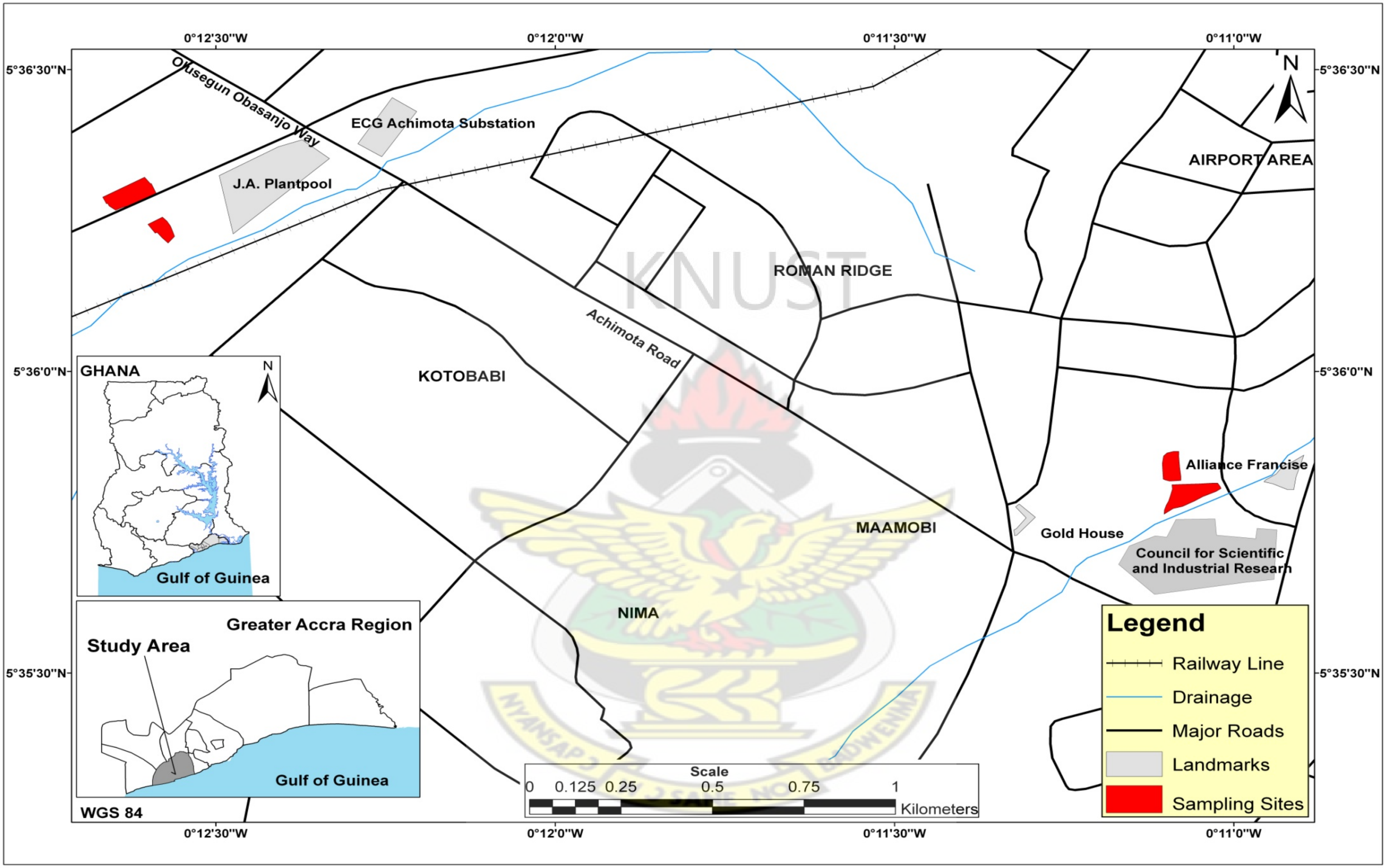

Figure 3.1: Map of Ghana localities in Accra and the study area Ayawaso West Sub-metro of the Greater Accra Region of Ghana (Figure 3.1).

3.1.1 Demographic and Socio-economic Data of the Study Area

The Greater Accra Region is currently the most urbanized region in the country. According to the Ghana Statistical Service (2000), the population of Accra has doubled between 1984 and 2000. The population of Accra has increased from 1,431,099 in March 1984 to 2,903,753 in March 2000. Recent statistics indicate 43.8% urban dwellers in 2000 as against 9% in 1931. Accra alone, according to the 2000 census, represents 25% of the urban dwellers in Ghana, increasing at 4.2% per annum. The population growth rate is estimated at 3.4% per annum in the city itself but up to 10% in its peri-urban districts (Ghana Statistical Service, 2000). The population as at 2010 had increased to 3,963,264.

The occupational structure of the region shows that 42.0% of the economically active population are engaged in sales and services, with professional, technical and their related workers comprising 10.8%. The industrial sector is dominated by wholesale and retail trade (30.4%) and manufacturing made up of 16.7% (Ghana Statistical Service, 2000).

3.1.2 Rainfall

The rainfall of Accra is tropical and falls within the wet sub-equatorial type with two rainy seasons. The first occurs from April to July with peaks in May and June, about 19.8mm rainfall value, and the second from September to November with the peak in October with 6.4mm rainfall value. The yearly rainfall is 75mm, which fall primarily during the two seasons. The coldest time of the year is between June and September, when the main rainfall occurs.

3.1.3 Temperature

There is very little variation in temperature throughout the year. Due to Accra's location adjacent to the ocean, the temperature is fairly stable from 24.7^{o}C in August, which is the coldest to 28°C in March, the hottest with an annual average of 26.8°C. The minimum temperature is about 23°C. The area is warm and comparatively dry. In between the rainy seasons, Accra experiences the harmattan, which is a hot dry desert wind, blowing from the northeast from December to March, lowering the humidity and creating hot days and cool nights in the north.

3.1.4 Topography, Geology and Soil Type

The city is characterized by lowlands and occasional hills with an average altitude of 20m above sea level. The slopes are generally gentle with most slopes below 11 percent, except few places such as MaCarthy hills, the television transmitting station near Abokobi and Kwabenya hills, where slopes are above 22 percent. The water table varies between 4.80m to 70m below the surface at places like Ofankor, Kantamanso and Accra Brewery Limited bottling house in Accra. The geology of Accra consists of Precambrian Dahomeyan schists, granodiorites, granites gneiss and amphibolites to late Precambrian Togo series comprising mainly quartzite, phillites, phylitones and quartz breccias. Other formations found are the palaeozoic accraian sediments, that is, sandstone, shales and interbedded sandstone-shale with gypsum lenses. The coastline of Accra comprises a series of resistant rock outcrops, platforms and sandy beaches near the mouth of the lagoons.

The soils in the metropolitan area can be divided into four main groups: drift materials resulting from deposits by windblown erosion; alluvial and marine motted clays of comparatively recent origin derived from underlying shales; residual clays and gravels derived from weathered quartzites, gneiss and schist rocks, and lateritic sandy clay soils derived from weathered Accraian sandstone bedrock formations. In many low lying poorly drained areas, pockets of alluvial 'black cotton' soils are found. These soils have a heavy organic content, expand, and contract readily causing major problems with foundations and footings. In some areas, lateritic soils are strongly acidic and when saturated are prone to attack concrete foundations causing honeycombing. Near the foothills are the large areas of alluvial laterite gravels and sands. Many of these deposits are being exploited in an uncontrolled manner for constructional purposes (AMA, 2006).

3.1.5 Water Course and Drainage

The area is drained through by natural streams and valley network and artificial drains. Most of the streams like Odaw, Sakumo, Mahahuma, Lador, and Dzorwulu, take their source from the Akwapim range. The artificial drainage is mostly built-up structures that enable quick discharge of waste and storm water.

3.1.6 Land Use and Vegetation

There are three broad vegetation zones in the metropolitan area, namely, shrub land, grassland and coastal lands. The shrub land occurs more commonly in the western outskirts and in the north towards the Aburi hills. It consists of dense clusters of small trees and shrubs, which grow, to an average height of five metres. The grasses are a mixture of species found in the undergrowth of forests. They are short, and rarely grow beyond one metre. Ground herbs are found on the edge of the shrub. They include species, which normally flourish after fire. The coastal zone comprises two vegetation types, wetland and dunes. The coastal wetland zone is highly productive and an important habitat for marine and terrestrial, mainly bird life. Mangroves, comprising two dominant species, are found in the tidal zone of all estuaries sand lagoons. Salt tolerant grass species cover substantial low-lying areas surrounding the lagoons. These grasslands have an important primary production role in providing nutrients for prawns and juvenile fish in the lagoon systems. In recent times, wetlands are however being encroached upon. Protection of the coastal wetland zone is very important to the long-term sustainability of the fish industry, which the Ga population of Accra depend upon.

The dune lands have been formed by a combination of wave action and wind. They are most unstable but stretch back several hundred metres in places. There are several shrub and grassland species, which grow and play an important role in stabilising dunes. Coconuts and palms which are economic crops grow well in this zone. Most of the coconuts were planted in the 1920s but it is estimated that over 80% of those plantations have disappeared as a result of felling, disease and coastal erosion. The loss of these trees is one of the principal reasons for the severity of erosion in some areas. In addition to the natural vegetation zones, a number of introduced trees and shrubs thrive in the metropolitan area. Neems, mangoes, cassias, avocados, and palms are prominent trees on the Accra landscape. Introduced shrubs like bouganvilia are also very prominent. These are being damaged by residential encroachment, bush fire, sand collection and illegal tree felling.

Most of the farm lands in Accra are used for the cultivation of food crops like corn, okro, tomatoes, cabbage and other vegetables. Fertilizers and insecticides are used in these areas.

Constant felling of trees, bad farming practices and indiscriminate burning has altered the vegetation and greatly depleted the fertility of the soil.

Plate 3.1.1: A Section of the Oyansia Stream at Opeibea

Plate 3.1.2: A Section of the Oyansia Stream at Dzorwulu

There is evidence that the vegetation of the metropolitan areas has been altered in the past decades by climatic and other factors. Much of the metropolitan area was believed to have been covered by dense forest of which only a few remnant trees survive (AMA, 2006).

3.2 Selection of Farms

All the farms selected for the study was based on the fact that the farmers were active pesticide handlers and harvesters. They mixed and loaded pesticides and applied them to their cabbage farms. Selection of farmers was done randomly. The Oyansia stream also known as the Nima creek which takes its source from the Akwapim mountains and flows through the Opeibea House area, behind the Water Research Institute, Plant Pool area, through Dzorwulu and ends up joining the Odaw river was selected for the study. The selection was based on the fact that as many as sixty-eight (68) vegetable farms are located along the stream from the Opeibea House area down to Dzorwulu before it joins the Odaw River.

Plate 3.2.2: A Cabbage Farm along the Oyansia Stream at Opeibea

Plate 3.2.3: A cabbage farm at Dzorwulu being sprayed with pesticides

3.3 Samples for Laboratory Analysis

Samples of cabbage, soil and water were collected for analysis of OC's. Soil and water samples were collected into sampling bottles while samples of cabbage were collected in aluminium foil. All the sampling bottles were rigorously scrubbed with a brush in hot water and detergent. The bottles were rinsed five times with tap water and twice with distilled water. They were again rinsed with acetone followed by hexane. The bottles were placed overnight in an oven at 300°C and stored in dust-free cabinets. When not in use the bottles were sealed tightly with pre-cleaned aluminium foil as described by (UNEP *et al*., 1987). In most cases the bottles were cleaned immediately before use.

3.3.1 Cabbage samples

Forty cabbage leaves were obtained from the farms by cutting with knife for assessment of pesticides residues. They were collected in aluminium foil and transported to the laboratory for analysis. Normally the crops are not treated with pesticides 14 days before harvesting. However, depending on the demand they may be harvested even a day after treatment.

Plate 3.3.1: Cabbage crop being sprayed

Plate 3.3.2: Harvested cabbage fruit

3.3.2 Soil samples

Soil samples were collected from a depth of 0-15cm from the spots where cabbage samples were harvested into bottles wrapped with aluminium foil, labelled and transported to the laboratory. One end of the PVC pipe was place in the soil and a wooden block placed on top. Using a hammer, the block was carefully pounded to drive the pipe into the soil. The pipe was grabbed and gently twirled in a circle to loosen it up. With the soil still inside, it was then pulled out carefully with a dowel. The soils were collected into bottles wrapped with aluminium foil, labelled and transported to the laboratory. They were hot air-dried at $40^{o}C$ for 72 hours and ground in a mortar to make it fine and sieved with a 1mm sieve. The samples were mixed homogenously for analysis.

3.3.3 Water samples

Water samples were collected at forty (40) points (at 10 m intervals) in the Oyansia Stream to determine the presence of pesticide contamination. The stream passes through areas of intense cabbage farming. The samples were collected in 1-L glass bottles and corked. After collection, the water samples were taken to the laboratory for analysis.

3.3.4 Water-Bed Sediments samples

Forty (40) core samples of water-bed sediment were collected at points where water samples were taken in the Oyansia Stream where cabbage farming occurred. Twenty (20) samples were located upstream (the area between the Opeibea House and Kawukudi junction) and another twenty (20) downstream is the area between the Plant pool and Dzorwulu. They were kept in glass beakers in the upstream and another 20 samples were collected in the downstream. The samples were wrapped with aluminum foil, stored on ice and transported to the laboratory for analysis of OC concentrations.

3.4 Analyses of Laboratory Samples

Initially, the various sample types were spiked with a solution containing a mixture of the OC standards. Each spiked sample was homogenized (for even distribution) and stored (for equilibrium) before extraction, clean-up, concentration, and analysis as described below. The recovery percentages were determined by subtraction of the peak heights on the chromatograms of samples with and without the pesticide standards.

Plate 3.4.1: Laboratory analyses of sampled sediments, cabbage and soil for organochlorine concentrations.

3.4.1 Organocholrine (OC) Standards

The following standards obtained from the International Atomic Energy Agency (IAEA) in sealed ampules. were used for the analyses: 2, 4, 5-TCB; aldrin; dieldrin; endrin; HCB; lindane; p,p'-DDE; p,p'-DDD, p,p'-DDT; heptachlor epoxide; endosulfan (α and β); endosulfan sulfate and chlorpyrifos-ethyl 480g/l (97.5% purity). They were diluted with insecticide grade hexane.

3.4.2 Analysis of Cabbage for OC Concentration

Procedures described in FAO/IAEA (1997) were adopted for this analysis. From each of the batch of harvested cabbage, 10 g (fresh weight) of cabbage fruits was homogenized in a mortar and transferred to a pre-cleaned extraction thimble. This was extracted with 200 ml methanol for 8 hours in a soxhlet apparatus cycling 4-5 times per hour. The extract was passed through a preconditioned SPE column and treated in the same way as described above for water sediments. The quantification limits were set to 0.1 µg/kg fresh weight for HCB, p,p'-DDE, heptachlor epoxide, 0.01 µg/kg fresh weight for β-endosulfan and endosulfan sulfate; 0.05 µg/kg fresh weight for α-endosulfan; and 2.5 µg/kg fresh weight for lindane. In all 40 samples of the cabbage were analyzed.

3.4.3 Analysis of Water for OC Concentration

A Soil Phase Extraction SPE column was preconditioned by passing two 10-ml volumes of methanol, followed by two 10-ml volumes of 30% (v/v) methanol in water through the column. One liter of each water sample was passed through the preconditioned column at a flow rate of 2 ml/min. The column was then washed with 1 ml of 30% (v/v) methanol in water followed by 1 ml of distilled water and air-dried under vacuum for 15 min. The analytes trapped in the column were eluted with 1.5 ml hexane into a glass vial. The eluate is made up to 2 ml with more hexane and then analyzed by gas chromatography in accordance with Analytichem International (1987), FAO/IAEA (1997) and Osafo-Acquaah (1997). The average recoveries for all compounds varied from 85–94%. Repeated analysis also gave a standard error of about 11%. The quantification limits were set to 100 ng/L for HCB, p, p9-DDE, and heptachlor epoxide; 2,500 ng/L for lindane; 50 ng/L for α- endosulfan; and 10 ng/L for β-endosulfan and endosulfan sulfate.

3.4.4 Analysis of Soil for OC Concentration

Residues extraction from soils was done using the method of Singh *et al*. (1999) with slight modification. Hot-air dried soil (10g) were put in a 100ml conical flask and mixed with 25ml hexane and ethyl acetate solution in the ratio of 9:1. These were then stirred on a magnetic stirrer for 12 hrs and the organic phase decanted into a 100ml flask. The process was repeated with fresh solvents. The two fractions were pooled together and centrifuged for 5 mins at 3000 rpm using Gallenkamp bench centrifuge (radius of rotor = 6.1 cm). The supernatant was transferred into a clean 100ml flask. Duplicate extraction was performed for each sample.

Methanol, ethyl acetate and hexane were used as eluting solvents to clean-up the extracts through C-18 solid phase extraction (SPE) columns. The C-18 cartridge SPE columns were pre-conditioned with 2ml of methanol. The extracts were applied to the top of the tube using a pipette. Two millilitres of eluting solvents in the order, ethyl acetate and hexane were passed through the columns to elute the sample. The effluents were collected into pre-weighed 5ml vials and evaporated to dryness under a stream of nitrogen gas. The weight of the fractions recovered after the clean-up was determined and the extract was reconstituted in appropriate volume of solvent to obtain a 10mg/ml stock solution from which 1mg/ml solutions were prepared for GC analysis.

3.4.5 Analysis of Water-bed Sediment for OC Concentration

The water layer over the sediment was decanted and discarded. The sediments were stirred with a stirrer to obtain a homogenous sample and then transferred to a pan to air-dry at ambient temperature. Five grams (dry weight) of each of the 20 samples upstream and 20 samples downstream were weighed into an extraction thimble and extracted with 200 ml methanol for 8 hours in a soxhlet apparatus cycling 4-5 times per hour. Five-milliliter aliquot of the extract was evaporated to dryness over water bath. The residue was dissolved in 1 ml methanol and diluted with 2.5 ml water as described by FAO/IAEA (1997). The water-diluted extract was passed through a preconditioned SPE column for analysis by gas chromatography.

Analyses were performed with a Perkin-Elmer Auto-System gas chromatograph equipped with a 63Ni electron capture detector. Separations were on a 30 m x 0.32 mm i.d. capillary column with 0.25µm methyl phenyl phase (Perkin-Elmer Elite-225). Gas flow (helium) was set to 16ml/min through the column and at 30 ml/min makeup (N) through the detector. About 1µl of each sample was injected in a split mode at 250°C, and the oven temperature was programmed as follows: 100°C for 1min, increased to 150°C (10°C/min), 250°C (5°C/min), then at 30°C/min to 300°C for 10 min. The detector temperature was set at 350°C. The average recoveries for all compounds varied from 80-110%. Repeated analysis gave a standard error of about 10%. The quantification limits were set to 0.1 µg/kg dry weight for HCB, p,p'-DDE and heptachlor epoxide; 0.01 µg/kg dry weight for β-endosulfan and endosulfan sulfate; 0.05 µg/kg dry weight for α-endosulfan; and 2.5 µg/kg dry weight for lindane.

3.5 Gas Chromatographic Analysis

A gas chromatograph (Hewlett Packard 5890 series II) equipped with a 63Ni electron capture detector and an integrator (Hewlett Packard 3396A) was used for the analysis. A capillary column (length 30 m, ID 0.53 mm, film thickness 1.5 mm) coated with DB-5 was used for the OC pesticides. Working conditions were: oven 150°C (2 min) to 275°C at 10°C/min, injector 180°C, detector 310°C, and carrier gas flow 15 ml N2/min. Sample peaks were identified by their retention times compared to the corresponding retention times of the pesticide standards. No independent method of confirmation was applied.

3.6 Calculation of Residue Levels

Residue levels (mg/l) were calculated using the equation (NRI, 1994) below:

time interval, use of protective clothing, calibration of spraying equipments and years of farming. Comparison was made between the activities and practices that lead to occupational exposure to insecticides; possible insecticide impact on health for different age categories (i.e younger < 45 years and older >45 years) of farmers, the current use patterns and practices of insecticides in horticulture production (types and quantities used for selected horticultural farming systems), the educational level and insecticides management practices.

3.8.1 Statistical Analysis

All data generated from the field survey (questionnaire) were analyzed using descriptive statistics (percentages). Chi-square (χ^2) test was used to identify the possible associations (Ntow *et al*., 2006), the independence of method of insecticide application and farm size was also assessed by the χ^2 test and the relationship between farmers' perception of insecticide hazards and insecticides perceived effectiveness against pests.

CHAPTER FOUR

RESULTS

This chapter presents the results of the laboratory analysis of organochlorine pesticides residues in irrigation water, sediment, soils and harvested cabbage from farms along the Oyansia stream at Dzorwulu and Opeibea. The responses of farmers pertaining to their level of understanding of issues relating to the causes and effects of organochlorine pollution are also represented graphically.

4.1.1 Demographic Information

A total of forty male farmers were identified and interviewed for the survey on pesticide use pattern. The results showed that about 60% of the farmers were married while 40% of them were single. Majority (45%) of the farmers were between the ages of 18 - 35 years while 35% of them were between of 36- 45 years and the remaining 20% above 45 years. Majority (32.5%) of the farmers had farming experience of 15 years and above with 25% between 6-10 years while 22.5% between 1-5 years and 20% of the farmers between 11-15 years (Figure. 4.1).

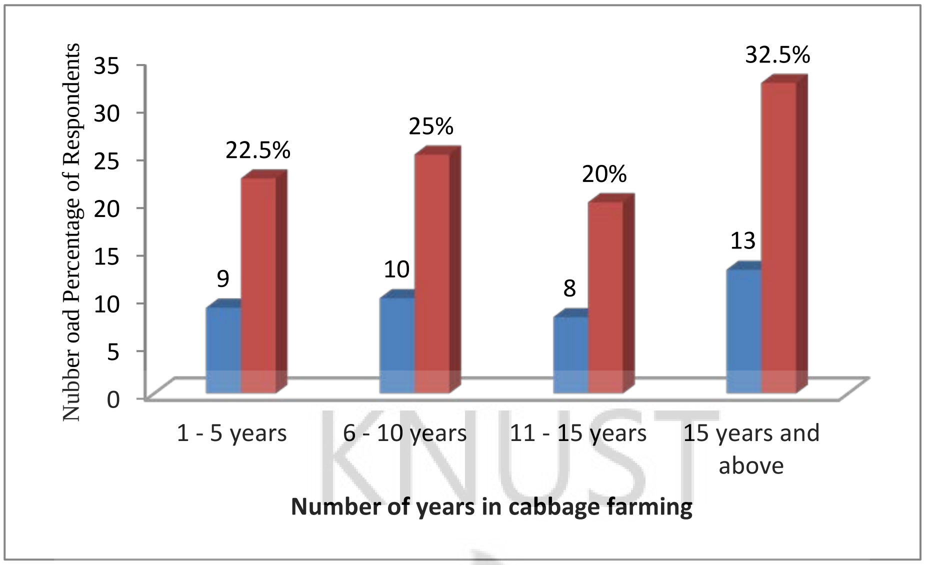

Figure 4.1 Distribution of farming experience of cabbage farmers along the Oyansia Stream

Half (50%) of the farmers interviewed had basic form of education while 45% of them did not attend any formal school. A relatively small number (5%) of the respondents have attained secondary level of education (Figure 4.2). All the farmers interviewed were small scale farmers. The cabbage farm land ownership scheme in the area was mainly of the leasehold type and farmers sometimes cultivate cabbage with other vegetables depending on which vegetable was patronized most at a particular time.

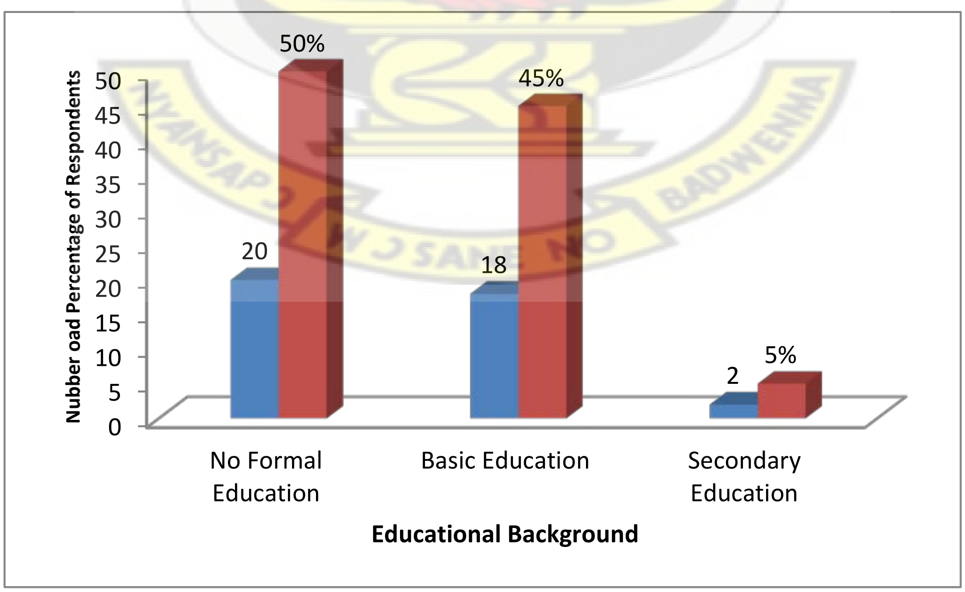

Figure 4.2 Distribution of Educational Level of Cabbage Farmers

4.1.2 Pest Problems and Choice of Pesticides

All the farmers interviewed reported that they encounter problems with insect pests. Chemical insecticides like Deltamethrin and Imidacloprid and fungicides like Mancozeb and Maneb were the main pesticides used in controlling the pests in the cabbage farms. Farmers also used herbicides to control the growth of unwanted weeds in the farms. The reason for choosing these insecticides was due to the fact that most farmers thought that they were effective in controlling the pests. Farmers purchased insecticides at the beginning of each growing season and after the appearance of pests. Pesticides are purchased from chemical retail shops and are normally stored in the farm before use.

4.1.3 Insecticide Application and Protective Clothing Used

Nursery application of insecticides was done by all the farmers interviewed. They generally use knapsack during application. However, few of the respondents use brooms, cups during nursery application of pesticides. On the other hand, almost all the farmers in the survey use knapsack when applying pesticides in the field. Majority (67.50%) of the farmers applied pesticides without considering the direction of the wind while 32.50% applied pesticides in the direction of the wind.

Results showed that 25% of the respondents do not observe any health and safety measures whiles the remaining 75% observe health and safety measures by wearing protective clothing. Type of protective clothing used by farmers during pesticide application include gloves (40%), wellington boots (30%), respirator (0%), nose masks (26%) and majority of the farmers used long sleeve shirts (80%) and (52%) long trousers (Table 4.1).

Table 4.1 Protective clothing used during pesticide application

Protective Clothing	Percentage of Respondents
Long Sleeve Shirt	80
Long Trousers	52
Wellington Boot	30
Gloves	40
Respirator	0
Nose Mask	26

Most (57.5%) of the farmers obtain information on pesticide application from pesticide dealers or retailers with 37.5% of them following instruction on pesticide labels and 5% of them obtain information from fellow farmers (Figure 4.3).

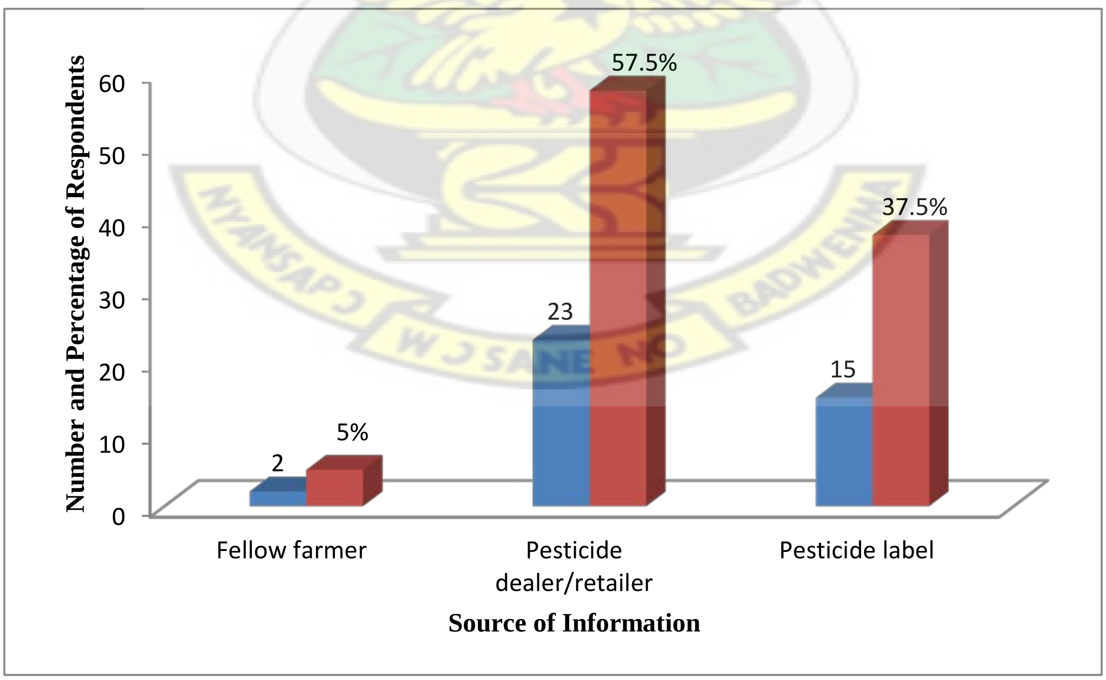

Figure 4.3 Distribution of Farmers' Source of Information on Pesticide Application

52.5% of the respondents indicated that they dispose of empty chemical containers by throwing them away on farm and burn them when it is enough to. 32.5% of the farmers burn them soon after using them whiles 15% of the farmers re-use these empty containers.

Majority (85%) of the farmers use water from stream to irrigate crops whiles 15% of the farmers depend on waste water from nearby factories to irrigate crops. All the respondents washed their spraying equipment after use with 52.5% of them disposing it on crops and weeds whiles 47.5% pour the wash water on the field. 35% of the farmers calibrate their equipment while 65% do not calibrate them. Majority (80%) of the farmers apply pesticides themselves with 15% of the farmers said application is sometimes done by their sons, labourers or themselves. 5% of them said their sons do the application for them. 75% of the farmers had no knowledge in pollution due to improper disposal of pesticide containers (Plate 5) whiles 25% of them had knowledge in pollution.

Plate 4.1: Improperly disposed pesticide containers on the cabbage farm along the Oyansia Stream

About ninety three percent of farmers observed a pre-harvest interval, after the last insecticide application normally of 1-2 weeks interval. However, 7.5% of the farmers in the study did not observe pre-harvest interval. Majority of the farmers interviewed do not keep farm records on insecticide use.

4.2 Insecticides Residue Levels in Water sediments, Cabbage, Soil and water

The results of water sediment, soil and cabbage, soil and water analyses are presented in Tables 4.2 to and 4.4.

Table 4.2: Insecticide residues in water sediments in the Oyansia Stream.

Insecticide components	**WHO Guideline**	**Upstream Mean ± SD µg/kg (DW)**	**% Diff**	**Downstream Mean ± SD µg/kg (DW)**	**% Diff**
HCB	-	0.68 ± 0.01[a]	-	0.73 ± 0.01[b]	-
Lindane	0.04	0.23 ± 0.03[a]	475	0.43 ± 0.02[b]	970
P,P'-DDE	0.04	0.35 ± 0.02[a]	775	0.32 ± 0.02[a]	700
P,P'-DDD	0.05	0.18 ± 0.01[a]	260	0.22 ± 0.01[b]	340
P,P'-DDT	0.05	0.11 ± 0.02[a]	120	0.14 ± 0.01[a]	180
Chlorpyrifos-ethy	-	l0.77 ± 0.01[a]	-	0.69 ± 0.01[b]	-
α –HCH	-	0.05 ± 0.02[a]	-	0.07 ± 0.01[a]	-
β –HCH	-	0.08 ± 0.01[a]	-	0.10 ± 0.01[a]	
γ –HCH	-	0.04 ± 0.01[a]	-	0.03 ± 0.01[a]	-
α –endosulfan	0.05	0.46 ± 0.04[a]	820	0.40 ± 0.02[a]	700
β –endosulfan	0.04	0.41 ± 0.06[a]	720	0.45 ± 0.06[a]	1025
γ –endosulfan	-	0.50 ± 0.02[a]	-	0.58 ± 0.02[b]	-
Endosulfan sulphate	0.04	0.46 ± 0.01[a]	1050	0.51 ± 0.02[b]	1175

Number of samples = 40. Means of samples on the same row followed by different letters are significantly different at ($P < 0.001$), LSD

NB: Units of concs. of insecticide component are µg/*I* for soil and water and µg/g for cabbage.

Sediment samples showed the highest number of insecticide compounds (Table 4.2). All the insecticides found in sediment appeared in at least 88% of all the upstream and downstream samples analyzed. The concentration was highest in the sediments for chlorpyrifos-ethyl (mean 0.77 ± 0.01µg/kg for the upstream and 0.62± 0.01µg/kg for the downstream) and least for α-HCH (mean 0.04± 0.01µg/kg for upstream and 0.07± 0.01µg/kg for the downstream). P, P'-DDE and Endosulfan sulfate were the only insecticides that were present in all the samples. There were significant differences in concentrations of HCB, lindane, P, P'-DDD, Chlorpyrifos-ethyl, γ -endosulfan and endosulfan sulfate in the upstream and downstream sediments. The chromatographic peaks showing the abundance of the various insecticides in the sediments can be found in Figure 4.4. The peaks showed that chlorpyrifos-ethyl is the most abundant and γ-HCH is the least abundant insecticide in the samples respectively.

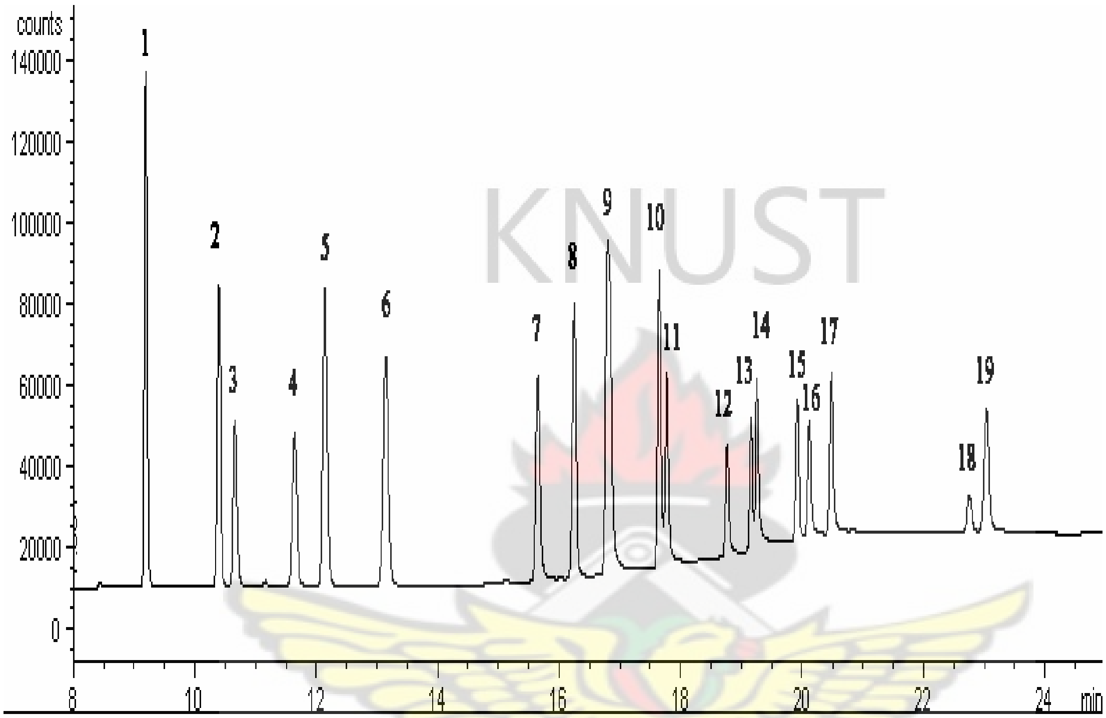

Figure 4.4: Chromatograms of Organochlorine Insecticide in Waterbed Sediments

(1) α-HCH; (2) γ-HCH; (3) β-HCH; (4) no target compound; (5) δ-HCH; (6) aldrin; (7) heptachlor epoxide; (8) endosulfan I; (9) 4,4-DDE; (10) dieldrin; (11) no target compound; (12) endrin; (13) 4,4-DDD; (14) endosulfan II; (15) 4,4-DDT; (16) endrin aldehyde; (17) endosulfan sulfate; (18) methoxychlor; (19) endrin ketone.

Table 4.3: Mean Insecticide residue levels in soil and cabbage in mg/kg (FW) ±SD

Insecticide component	**Soil sample**	**WHO Guideline. for soil**	**% diff**	**Cabbage sample**	**WHO Guideline for cabbage**	**% diff**
HCB	$<0.01^{a}$			$<0.01^{a}$		
Lindane	0.02 ± 0.01^{b}	0·04	-50	0.02 ± 0.01^{b}	0.01	100
P,P'-DDE	0.22 ± 0.01^{c}	0.04	450	0.23 ± 0.01^{c}	0.07	229
P,P'-DDD	0.18 ± 0.02^{c}	0.05	260	0.20 ± 0.02^{c}	0.09	122
P,P'-DDT	0.18 ± 0.02^{b}	0.05	260	0.21 ± 0.02^{b}	0.21	-
Chlorpyrifos-ethyl	0.02 ± 0.01^{a}	-		0.49 ± 0.12^{b}	0.01	480
HCH	0.02 ± 0.01^{a}	-		0.02 ± 0.01^{a}	0.01	100
α –endosulfan	0.29 ± 0.03^{d}	0.05	480	0.31 ± 0.03^{d}	0.05	520
β –endosulfan	0.19 ± 0.01^{c}	0.04	375	0.20 ± 0.01^{c}	0.05	300

ɣ-endosulfan	0.23 ± 0.11^{c}	-	0.21 ± 0.11^{c}	-

Number of samples = 40. Means of samples on the same row followed by different letters are significantly different at ($P < 0.001$), LSD

It can be deduced from table 4.3 that the levels of detectable insecticides were generally lower in the samples. Residues of chlorpyrifos-ethyl were the highest in all the samples taken. There were no significant differences in residue levels of HCH among all the samples whiles residue levels of α-endosulfan was significantly different among the samples analyzed. The chromatographic peaks of the various insecticides showing the abundance of the various insecticides in the samples can be found in Figures 4.4 and 4.5.

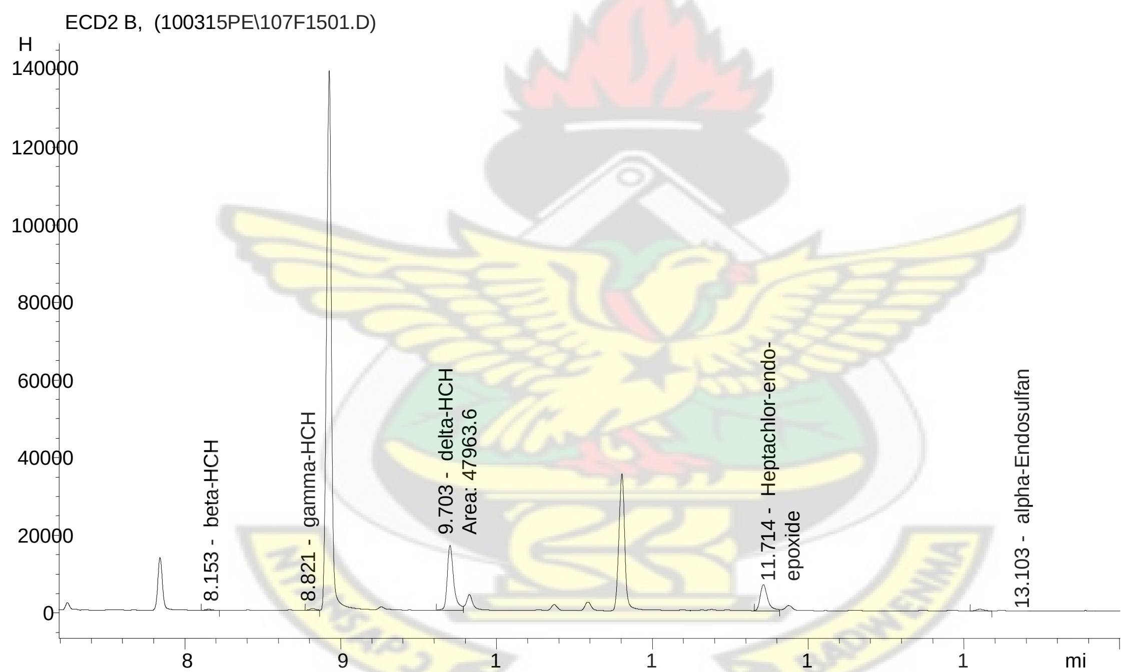

Figure 4.5: Chromatograms of Organochlorine Insecticides in Cabbage Samples from Farms

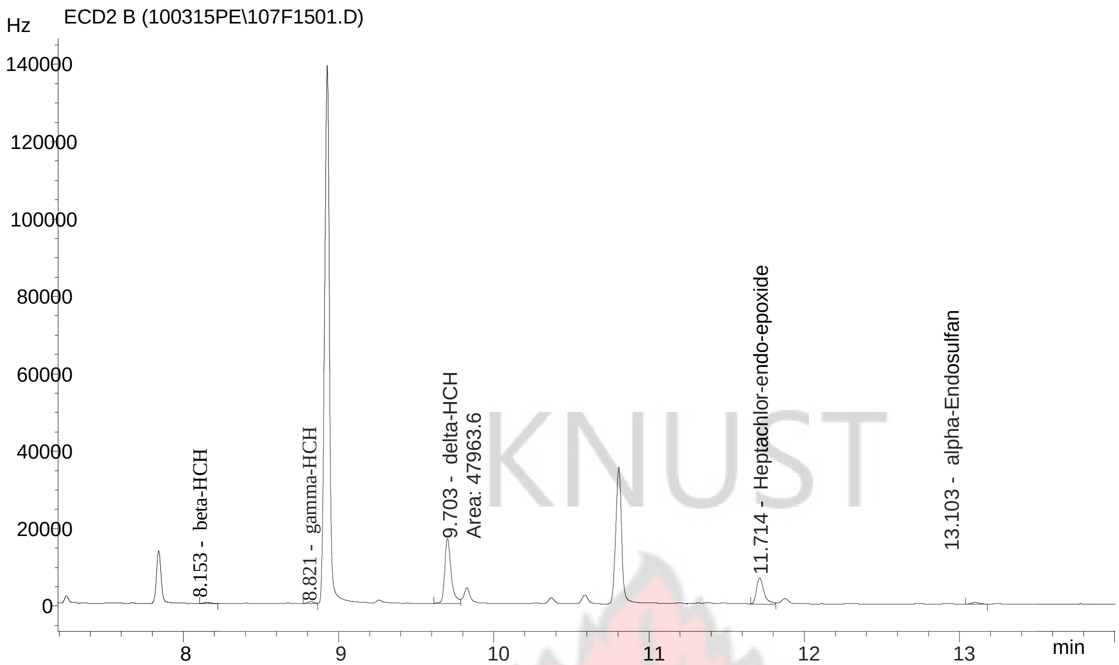

Figure 4.6: Chromatograms of Organochlorine Insecticides in Soil Samples from the Farms

4.3 Residue levels of organochlorine pesticides in water

There were no levels of organochlorines recorded in the water samples from the Oyansia stream. This is because organochlorine is soluble in water; therefore, all residues of organochlorine will leach into the water sediments.

Table 4.4: FAO/WHO guidelines for Organochlorine Pesticides

Organochlorine Pesticides	**Soil (µg/L)**	**Water (µg/L)**	**Cabbage**
HCB	-	-	-
Lindane	0.04	0.04	0.01
p,p'-DDE	0.04	0.04	0.074
p,p'-DDD	0.05	0.10	0.09
p,p'-DDT	0.05	0.10	0.214
Chlorpyrifos-ethyl	-	-	0.01
HCH	-	-	0.01
α –endosulfan	0.05	0.04	0.05
β –endosulfan	0.04	0.04	0.05
γ -endosulfan	-	-	-

Endosulfan Sulfate	0.04	0.04	0.05

CHAPTER FIVE

DISCUSSIONS

5.1.1 General concentrations of insecticide residues

According to Cope (2000), biological organisms, by the process of bioaccumulation, accumulate contaminants from their surroundings by several routes of exposure including oral intake through diet, direct contact with their outer protective coverings (membranes, skin, feathers, fur, etc.). Insecticide components in soil samples were generally higher than the FAO/WHO Standard Values. With the exception of lindane that recorded a value less than fifty percent of the FAO/WHO level, each of the other components showed more than 260 % of its recommended concentration. Meanwhile, the concentration of α-endosulfan was highest and about 480% above the FAO/WHO Standard Value. The trend of high levels of the various components was also observed in cabbage samples. Although, the percentage increases of some components were not as high as those in soil samples, none of them was less than 120%. Even lindane and α -endosulfan concentrations which were -50% (i. e. lower) and 480% in soil sample increased by 100% and 520% respectively in the cabbage sample. These observations could therefore be due to the persistent nature of the OC insecticide residues in the soil and cabbage samples and their bioaccumulation abilities.

5.1.2 Concentrations of insecticide residues in cabbage, soil and water-bed sediments

For all the components of insecticide residues that were recorded, the concentrations in the sediments were the highest and above the FAO/WHO standard values (Tables 4.4). This was followed by cabbage (Table 4.3) and finally water samples (Tables 4.2). Ntow (2001) has also noted that, sediment also serves as a major sink for chemicals applied to crops. These insecticide residues could have accumulated in the sediment over a long period of time. There is also the possibility of further accumulation if the current practices such as importation of banned pesticides, misapplication and improper disposal of insecticide containers that bring about the liberation of these insecticide residues are not controlled.

Both lindane and endosulfan persist in all sections of the environment. Persistence patterns vary from climate to climate and also depend on the chemical nature of the pesticide and type of substrate (Zaranyika and Mugari, 1995). Other organochlorine pesticide residues, such as HCB, DDE, and HCH, were detected in the sediment, although these chemicals were not mentioned as being used continuously in agriculture in the area. HCB, DDE and HCH are among the most persistent insecticides and their presence in sediment may be due to previous agricultural, industrial, or health uses.

The differences in the concentrations of lindane and endosulfan in the samples may be due to the fact that the chemicals have different degradation rates. In the study area, different pesticides were applied on crops at different times of the year. In this study, chlorpyrifos-ethyl and endosulfan were the only insecticide residues detected in appreciable quantities in cabbage. Several researchers including Ninsin (1997), Biney (2001), Aboagye (2003), Odhiambo (2005) and Ntow (2006) have studied the occurrence of insecticide residues in tomatoes, pineapples and cabbages. Residue levels of insecticides found in cabbage samples in this study was slightly higher than those found in samples analysed by Ninsin (1997) and Ntow (2006) suggesting an appreciable increase and possible mis-use of insecticides on horticultural crops.

5.1.3 Upstream and downstream levels of organochlorine pesticides

Downstream concentrations of pesticide residues in sediment were generally higher than upstream concentrations (Table 4.2). Agrochemicals may have negative downstream impacts and that there is a hydrological connection between upstream and downstream concentrations which is of major importance in order to understand the impacts of water resources development on uplands and downstream users. Downstream, are marked by higher vulnerability to extreme agro-ecosystem and meteorological events than upstream communities (Ploeg *et al*. 2010). Although the intensity of farming as observed in the study was high at both upstream and downstream, the downward direction of flow of the stream could explain this observation. Runoff might have washed the pesticides applied on the various farms into the stream. As the river flows, they settle in the bottom sediments along the stream course. At downstream, pesticide residues from both upstream and downstream may settle to cause higher build-up of pesticide residues. The occurrence of contaminant is more pronounced in lentic water than lotic waters probably due to the relative longer resident time which encourage contaminant build-up. In the case of lotic waters downstream communities are at greater risk of pollution than upstream communities.

Although lindane and endosulfan are not supposed to be used in horticultural production in Ghana since they have been banned by the EPA since 1992, they appeared in cabbage, soil and water-bed sediments samples (Tables 4.2 and 4.3). Apart from the existence of banned lindane and endosulfan on the market, their concentrations in cabbage, sediments and soil recorded in this study were above the WHO standards for organochlorine pesticide residues.

aside the attitudes of offenders, those enforcement agencies may be confronted with other external factors that have marked effect on the efficient enforcement of environmental regulations. These can properly be related to all the usual problems facing administrative and bureaucratic systems. Also Gurivitch (1996) suggested that there is often a set of pattern of enforcement which is adopted by enforcement agencies to underpin the cooperational approach. Again, according to Kobieh (1997), the major factors hampering the development, management and maintenance of sound environmental sanitation are the fragmentation of the responsibility for environmental sanitation among several ministries and agencies causing disjointed and uncoordinated planning, management of programmes and services. In addition to this possibility there could be wrongly labelled insecticides on the market or those that contain active ingredients of the banned chemicals.

The entry of the banned pesticides into the country as displayed on the market may be attributed to lack of vigilance and strict enforcement of laws governing importation of chemicals into the country currently. This situation might have enabled the banned chemicals to find their ways through illegal routes into the country. However, the USEPA (2000) noted that it is required to take into account the economic, social and environmental costs and benefits of the use of any pesticide, as well as human dietary risk from residues that result from the use of any pesticides in or on any food in accordance with standards. Also Tobey (1924) stated that the actions of public health authorities must be conducted in a strictly legal manner, with due guarantee of the constitutional right of individual citizens and the people as a whole. This therefore suggests that address of the factors that militated against the effective enforcement of the laws is long overdue and therefore an immediate call for the necessary steps to halt the practice is an appropriate and timely one.

5.2 Assessment of the level of farmers' understanding of the causes and effects of organochlorine pollution

Majority (55%) of the farmers have had formal education. This consists of basic education (50%) and secondary education (5%) (Figure 4.2). These generally suggest that there is the likelihood of efficient farming and is supported by. Again, Weir (1999) noted that education may enhance productivity by improving quality of labour, increase ability to adjust to disequilibrium and propensity to successfully adopt innovations.

Contrary to this observation, majority (67.50%) of farmers applied pesticides without considering the direction of the wind. The use of knapsack during application of insecticides instead of brooms and cups poses a health danger to farmers. These observations may be attributed to disregard for the application in their operations.

In the cabbage ecosystem, the insects that the farmers attributed the destruction of their crop to were the larvae of *Plutella xylostella* and *Spodoptera littoralis*. Other insects implicated in the study were *Brevicoryne brassicae* and *Zonocerus variegatus*. Brempong-Yeboah (1992) and Ninsin (1997) observed that *P. xylostella* was a pest of cabbage in the Accra plains of Ghana.

The growers conceded that the diamondback moth could be so damaging that they completely destroy their crops. The damaging stage of this insect is the larvae (Hill, 1993). It causes damage by feeding on the underside of the leaves, making holes right through them (Hill, 1993). The damage caused by *B. brassicae* was not quite obvious on the farms despite the presence of aphids on the cabbage crop. Growers also remarked that the pest status of aphids was next to that of the diamondback moth. Ninsin (1997) also observed that aphids cause stunted growth and isolated wilting of cabbage plants. These aphids have been implicated as vector of 23 viral diseases in Crucifers (Hill and Waller, 1994). The larvae of *S. littoralis*, also cause extensive damage to cabbage leaves. Z. *variegatus* a sporadic sever pest of many crops (Hill and Waller, 1994) chewed cabbage leaves, leaving characteristic ragged edges or completely defoliated plant.

These insect pests and diseases pose big problems in horticultural production. The damage caused by them has led to farmers using insecticides (Ntow *et al*., 2006). Dinham (2003) estimates that 87% of farmers in Ghana use chemical pesticides to control pests and diseases in crops. All respondents in the survey sprayed their crops with insecticides to control insect pests. In fact chemicals are used extensively on horticultural farms, small or large and farmers use a wide range of herbicides, fungicides and insecticides. In the survey the main method of weed control were identified as manual weeding with hoe and cutlass, and the use of herbicides. Farmers perceived that herbicides are able to suppress weeds for a longer time and over a wider area than manual weeding with hoe and cutlass.

Farmers in the survey sprayed the same wide range of insecticides on all their crops. For instance, cabbage farmers sprayed their crops with insecticides such as Acetamiprid 20g/l

(Cocoprid 20 SL). This information has serious public health implications because the product Cocoprid 20SL is registered by the EPA as an insecticide for the control of caspid bugs in cocoa due to its toxicity and persistence. Insecticides are readily available in agricultural retail shops, and those responsible for retailing them have adopted the extensive practice of measuring out the quantities of the pesticides from a larger container. Majority of the farmers especially cabbage farmers come from poorer sections of the community and as insecticides are expensive for them, they purchase less expensive products even if they are
less suited to the pest(s) requiring control.

Furthermore, insecticides are usually sprayed in combinations and the efficacy of one may musk the inefficacy of others in the mixture. Mixing of insecticides is encouraged by the farmers desire to have a rapid knockdown of pests and this practice may have contributed to the increase in incidence of insect pest resistance and infestation of horticultural crops (Metcalf, 1980 and Biney, 2002). The commonest way of disposing of sprayer washes and empty insecticides containers was by throwing them on the farm, majority of which are scattered on the edges of the farm. Where the farms are close to waterways as in the case of cabbage farms in the survey area (along the Oyansia stream), the disposal of unwanted insecticide solutions and empty containers on the farms presents a potential pollution problem for aquatic systems which are sources of livelihood for human communities and support varied plant and animal life.

CHAPTER SIX

CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

The activities of pests and diseases render horticultural crops unattractive and obnoxious and are therefore rejected by consumers in Ghana. To protect their investments, farmers have resorted to the use of insecticides even if they have no training in the choice of insecticides to use. The study revealed that cabbage farmers in communities along the Oyansia Stream of Accra, Ghana do not take adequate protection from insecticides. Their perceptions and beliefs on insecticides have obscured the importance of preventive and precautive measures for protecting themselves from health hazards associated with insecticides and their wrongful handling and abuse of insecticides.

The presence of persistent, bioaccumulative and toxic organochlorine insecticides in cabbage and the environment at levels generally above the FAO/WHO guideline values that raise public health concerns were also revealed. These residues originated from the use of insecticides for agricultural activities including cabbage cultivation in the area. Because of their persistent and lipophillic nature, these residues have bioaccumulative behaviour. If the current practice is not controlled, an appreciable build-up of residues with time in cabbage crops cultivated in the communities along the Oyansia stream is likely to occur with its environmental and human health problems.

6.2 Recommendations

In view of the above, it is recommended that:

Intensification of health educational programmes to promote greater awareness among farmers and labourers about insecticides is highly needed. This awareness should be undertaken by the EPA Ghana, Extension Education Division and the Plant Protection and Regulatory Services Directorate of the Ministry of Agriculture and the Ghana Standards Authority and should tap the belief system. It should include relevant information that explicitly takes into account farmers' beliefs and perceptions about insecticides and specific details of the risk and mode of entry into the body and precautions for exposure reduction**.** The governments should provide logistics to the above mentioned key institutions to promote effectiveness in the discharge of their mandates.

A pesticides use/management bill to promote human health and the environment should be passed by the Parliament of Ghana. This would empower the EPA and other regulatory bodies to regulate the production and importation of pesticides.

There should be stricter enforcement of environmental laws. Enforcements of such laws should include observation of an established 100 m buffer zone between rivers/streams and farm lands to prevent the contamination of river/stream ecosystems.

Further studies on simple, rapid on-the-spot analytical techniques for insecticide residue analysis for effective monitoring and surveillance of insecticides residues programme on food and water should be undertaken.

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APPENDICES

APPENDIX A: SURVEY QUESTIONNAIRE

ASSESSMENT OF PESTICIDE USE PATTERN AMONG CABBAGE FARMERS IN SOME FARMING COMMUNITIES IN ACCRA

Personal Information

i. Name of Respondent..

ii. Age of Respondents...

iii. Gender Male ( ) Female ( )

iv. Date of Interview...

v. Period of Farming

- ☐ 1-5 yrs
- ☐ 6-10yrs
- ☐ 11-15yrs
- ☐ 15 yrs and above

vi. Level of Education

- ☐ No formal education
- ☐ Basic education
- ☐ Secondary education
- ☐ Tertiary education

Incidence of Pests/ Choice and Source of Pesticides

vii. Do you encounter pest(s) problems? Yes ☐ No ☐

viii. Do you apply pesticides on your crops? Yes ☐ No ☐

ix. If yes, what kind of pesticides?

- [ ] Insecticides
- [ ] Herbicides
- [ ] Fungicides
- [ ] Others

x. What factors inform your choice of pesticide?

- [ ] Efficacy
- [ ] Availability
- [ ] Persistency
- [ ] Safety

Pesticide Application / Safety

xi. At what stage of crop growth do you apply pesticides?

- [ ] ence of pests
- [ ] Degree of pest infestation
- [ ] Date of transplanting
- [ ] Early stage
- [ ] At maturity
- [ ] Before harvest

xii. In what direction do you spray pesticide?

- [ ] In the wind direction
- [ ] Against the wind

☐ Perpendicular

☐ Do not consider wind direction

xiii. Do you observe any health safety measures? ☐ Yes ☐ No

xiv. If yes which?

☐ No protective cover

☐ Partial protective cover

☐ Full protective cover

☐ Others

xv. If not what are your reasons?

☐ Discomfort

☐ Sweat

Knowledge of Pesticide Use

xvi. Do you have of knowledge in pesticides application rates? ☐ Yes ☐ No

xvii. How do you estimate application dose?

☐ Use of pesticide container lids

☐ Empty tomato /milk tins

☐ Measuring cup

☐ No idea

xviii. If yes what are your sources of knowledge?

☐ Pesticide label

☐

Agricultural Extension Officer

☐ Adverts (radio, TV, Newspaper)

☐ Pesticide dealer/ retailer

☐ Fellow farmer

xix. How do you dispose of pesticide containers?

☐ Reuse ☐ Sell

☐ Throw away on farm ☐ Burn on farm

☐ Triple rinse and punch

xx. Do you use water from stream to irrigate crops? ☐ Yes ☐ No

xxi. What type of sprayers do you use?

☐ Manual knapsack sprayer ☐ Motorized sprayer

☐ Hand operated (brush, broom)

xxii. Do you wash sprayers after use? ☐ Yes ☐ No

xxiii. Do you calibrate spraying equipment? ☐ Yes ☐ No

xxiv. How do you dispose of the waste water (after washing)?

☐ In irrigation canal ☐ On field

☐ In nearby stream ☐ On crops and weeds

xxv. Who applies pesticides?

☐ Farmers ☐ Sons of farmers

☐ Labourers ☐ All of the above

xxvi. Do you have of knowledge in pollution due to improper disposal of pesticides containers?

Y☐ No☐

xxvii. If yes could you please explain...

....

xxviii. Do you observe pre-harvest interval? ☐ Yes ☐ No

xxix. If yes, what is your pre-harvest interval? ....

....

....