RESIDUE CONCENTRATIONS OF CHLORPYRIFOS IN FRENCH BEANS AND SOIL AND ASSESSMENT OF DIMETHOATE AND CHLORPYRIFOS RESIDUE LEVELS IN FRENCH BEANS IN NAIROBI, KENYA

BY

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DECLARATION

This thesis is the original work of the author except where due references are made. It has not been submitted partially or wholly for the award of degree to this or any other institution of learning.

KING´OLA ANGELA MANDUU

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This thesis has been submitted with our approval as university supervisors

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DEDICATION

This thesis is dedicated to my dear husband Fredrick, my children Marion and Ryan and all my friends who have supported me in my studies.

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ABSTRACT

Residue concentration of applied chlorpyrifos in soil and French beans was determined in green house experiment, the residue levels of chlorpyrifos and dimethoate in French beans sold in Nairobi County were also determined and a survey to identify the most commonly used pesticides and their safety on farmers in Kiambu County was conducted in this study. Controlled and treated experiments were conducted in a green house on soil obtained from Kiambu County, Kenya. Samples from green house, open air markets and supermarkets were soxhlet extracted using organic solvents. Clean up was done using 8 % deactivated alumina and elution achieved by hexane solvent. Detection and quantification of dimethoate and chlorpyrifos was done by gas chromatograph-mass spectrometer (GC-MS). The survey in Kiambu County was achieved by using structured field questionnaires which were distributed to 64 respondents chosen randomly.

The half life of chlorpyrifos dissipation was calculated using Langmuir-Hinshelwood kinetic model equation and regression curves were drawn to get the rate constant. Results obtained indicated that chlorpyrifos has a dissipation half-life of 3.05 days in French bean and 7.8 days in soil. Chlorpyrifos residue on the pre-harvest day was 0.05 mg/Kg which is the same as both the EU and Codex MRLs. All the samples analyzed from open air market and super market had below detection limit of both chlorpyrifos and dimethoate residue levels.

A survey conducted in Kiambu County showed that fifteen pesticides were identified as commonly used. Out of the fifteen pesticides 7 % are classified as most hazardous according to WHO (2002) classification of pesticides. Farmers identified the following factors which determined the choice of a given pesticide: increased yield, cost effectiveness, suggested by NGOS, suggested by agrochemical dealers, sales agents and suggested by other farmers.

Farmers within this region mostly obtained information on proper handling of chemicals from: government agricultural extension workers, non-governmental organizations (NGOS), radio, Agro- chemical industries and dealers. General knowledge among farmers about chemicals risks, safety, and chronic illnesses was low. Activities that increase environmental awareness and safety of pesticides should be initiated by the agrochemical firms, NGOs and both the local and national government.

There are major pests problems in Kiambu County and therefore an active pest management programme is necessary to secure the harvest in the region. Results obtained from this study indicate that it’s important to monitor and ascertain the residue levels of pesticides in soil and horticultures. This gives information to be used in surveillance programs for pesticide residue levels in Kenya.

ABBREVIATION

ADI	Acceptable Daily intake
CBD	Central Business District
a.i	Active Ingredient
EPZA	Export Processing Zones Authority
FAO	Food and Agriculture Organization
GAP	Good Agricultural Practice
GC-MS	Gas chromatography - Mass Spectrometry
IUPAC	International Union of Pure and Applied Chemistry
KARI	Kenya Agriculture Research Institute
KEPHIS	Kenya Plant Health Inspectorate Service
mg/Kg	Milligrams per Kilogram
MRL	Maximum Residue Limit
PCPB	Pest Control Products Board
PHI	Pre - Harvest Interval
STMR	Supervised Trial Median Residue.
TMDI	Theoretical Maximum Daily Intake

UNEP	United Nations Environment Programme
UNIDO	United Nations Industrial Development Organisation
USDA	United States Department of Agriculture
USEPA	United States Environment Protection Agency
WHO	World Health Organisation

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CHAPTER ONE

INTRODUCTION

1.1 General Background

Agriculture remains the backbone of the Kenyan economy. It is the most important sector in the economy, contributing approximately 25 % of the GDP, and employing 75 % of the national labor force [MTTI, 1999]. The objective of agricultural sector strategy has been to increase agricultural growth. This necessitates integration of technology into agriculture to enhance production and improve food security as well as poverty alleviation. An example of such technology is the use of pesticides in protection of agricultural produce, and this has significant consequences on agricultural production [MTTI, 1999].

Up to 80 % of horticultural production in Kenya is undertaken by small holder's farmers. The sub-sector employs approximately 4.5 million people country wide directly in production, processing and marketing while another 3.5 million benefit indirectly through transport and other activities [Horticultural Crops Development Authority, 2009]. Horticulture contributes an estimated 36 % of the agricultural GDP and is one of the fastest growing sub-sectors clocking growth rates of between 15 % and 20 % per year. The horticultural industry is among the leading foreign exchange earners and contributes enormously to food security and household incomes to a majority of Kenyan producers who carry out one form of horticultural production or another [Kenya Economic Survey, 2012]. French beans and snowpeas provided over Ksh. 6.9 billion [COM TRADE, 2011]. In 2011 Trade of high-value crops from Kenya to European Union, especially French beans and snowpeas provided a lucrative market for small scale growers, giving opportunities for market access to horticultural producers and rural economic development.

Despite all these impressive statistics, food safety and quality standards challenges abound, like non-compliance with market requirements resulting in interception of produce in the international market; emerging issues related to constant change in maximum residue levels (MRLs), new European Union regulations on pesticide and conformity of fruits and vegetables have made it necessary to have in depth analysis of our systems. Kenya is the largest exporter of French beans and snow peas to the European Union [Mwangi, 2013]. Starting 1st January, 2013 European Union imposed a 10% sampling restrictions on all beans and unshelled peas from Kenya, on grounds that there are insufficient guarantees on pesticide maximum residue limit(MRL) from Kenya’s official control systems [Mwangi, 2013]. Green beans have been a representative export product of Kenya's fresh produce trade for many years, mainly to European Union (EU) market [COM TRADE, 2011]. Kenya's beans have a number of food safety and standards to comply with sanitary and phyto-sanitary regulations required to enter in the European Union market. This compliance is part of the successful expansion of green bean production and export from Kenya into the European Union market [COM TRADE, 2011].

Production and export of horticultural produces are increasing rapidly in many developing countries. Demand for these high value commodities is stimulated by income growth, reductions in transport cost and increased market access. Production for export is often encouraged as a means of generating foreign exchange, increasing income to produce and providing employment for the rural poor. Rapid growth in horticultural production has been accompanied by increased application of pesticide. Consumers have grown increasingly concerned about pesticides residues in food. Rapid urbanization has resulted in expansion of urban and semi-urban horticulture, where pesticides use is more evident and its overuse even less acceptable to the public [Musila, 2011].

Public concerns are being translated into more rigorous standards for both domestic and international trade. Major retailers and supermarket Chains have endorsed stricter worker welfare, food safety, traceability and environmental requirements. However weak regulation and management of pesticides continue to undermine efforts to broaden and sustain ecologically based pest management strategies. This is because pesticides are aggressively marketed and therefore often seen as the cheapest and quickest option for pest control.

1.2 Kenyan horticultural sub-sector

The horticultural subsector of agriculture has grown in the last decade to become a major foreign exchange earner, employer and contributor to food needs in the country. Currently the horticulture industry in the country is ranked third in terms of foreign exchange earnings from exports after tourism and tea. Fruits, vegetables and cut flower production are the main aspects of horticultural production in Kenya. Kenya has a living history of growing horticulture crops for both local and exports markets. Kenya's ideal tropical and temperate climate condition makes it favorable for horticultural crops production and development. The climate is highly varied supporting the growth of a wide range of horticultural crops [EPZA, 2005]. Horticulture in Kenya is mainly rain fed with few farms using irrigation. The sub sector is characterized by tremendous diversity in terms of farm size, variety of produce, and geographical areas of production. Farm sizes ranges from large scale estate with substantial investment in irrigation and high level use of inputs, hired labour and skilled management to small scale farms, usually less than one acre.

The subsector generates over US$ 300 million in foreign exchange earnings, the total horticultural production is close to 3 million tonnes making Kenya one of the major producer and exporters of horticultural produce [Horticultural Crops Development Authority, 2009], with the main importing countries being, UK, Germany, France, Switzerland, Belgium, Holland and Italy. Other non European importing countries include Saudi-Arabia and South Africa [Horticultural Crops Development Authority, 2009].

1.3 Pesticide regulation in Kenya

In Kenya, Pest Control Product Board (PCPB) is the statutory body of the government, charged with the task of regulating the importation and exportation, manufacturing, distribution, transportation, sale, disposal and safe use of pest control products and mitigate potential harmful effects to the environment. It was established under an Act of parliament, the Pest Control Product Act, Cap 346, Laws of Kenya of 1982. Through its pesticide registration process, the board ensures that only products that have been assessed for safety, quality, efficacy and economic value are authorized for use in the country. PCPB is also charged with the responsibility of informing the industry, extension agencies and the ministry of agriculture, of the authorized use of crop protection products [PCPB, 2008].

1.4 Pesticides use and distribution in Kenya

The use of pesticides in Kenya has steadily increased since 1986 from Ksh. 580.2 million to Ksh. 4.5 billion 2005/06 [PCPB, 2006]. Out of the 7708 metric tonnes imported only 82 metric tonnes were exported to neighboring countries and involved the active ingredients of pirimiphos methyl, permethrin and chlorfenviphos [PCPB, 2006]

1.5 History of pesticides use in Kenya

Pesticide use in Kenya traces its way back to the colonial era in 1900. Acaricides mainly sodium arsenite was among the first pesticides to be introduced in Kenya between 1912 and 1949 for vector control of serious livestock diseases such as East Coast Fever [Keating, 1983]. Lindane (benzene hexachloride, BHC or hexachlorocyclohexane, and Hexachlorohexane, HCH) was introduced in 1949 and resistance to BHC was first noted in 1954 in *B.decolaratus* [Keating, 1983]. Due to the development of resistance of tick strains to HCH and arsenic led to the increased use of toxaphene, a chlorinated camphene, which was introduced in 1950 [Keating, 1983]. By 1956, toxaphene was the major pesticide in use, due to its stability in dip washes and its prolonged residue effect.

The organochlorine like DDT was introduced in 1956 and Dieldrin was introduced in 1961 but because the tick resistance developed and the organochlorines were accumulating in the body fat and were secreted in milk from dairy animals they were banned in 1976 [Keating, 1983]. Due to the ban and restriction of some organochlorines, there was decline of pesticide imports into the country between 1988 and 1990 [Munga, 1985]. Organophosphates like dioxathion and coumaphos were introduced in 1959 [Keating, 1983]. Other pesticides that were in use during 1950s included dinitrocresol (DNC) and the OP compounds, TEPP (tetraethyl pyrophosphate) and schradan [Keating, 1983]. The most common pesticides imported for the control of pests include glyphosate, Mancozeb, Amitraz, Copper oxychloride, 1, 3-dichloropropene, 2, 4-D, Amine, Sulphur, Dimethoate, Methy bromide, cabaryl, quintiofos, chlorfenviphos, coumaphos, formamidines, chlorpyrifos, malathion, diazinon, the pyrethroids *cis*-permethrin and *trans*-permethrin, the carbamates propoxur, bendiocarb, and *ortho*-phenylphenol.

1.6 French beans growing in Kenya

French beans (*Phaseolus vulgaris*) are the major vegetables exported from Kenya and are a potential income earner to small scale farmers. Small holders grow most of the crop and virtually all is exported to Europe. The major French beans producing areas in Kenya are: Athi-river, Meru and Naivasha [Horticultural Crops Development Authority, 2009]. Picking of French beans begins 9 weeks after sowing and continues for about 3 weeks when the weather is dry [Nderitu *et al.,* 2009]. It requires triable loam soil that is well drained with high levels of organic matter and a pH of 6.5-7.5 [HCDA, 1996]. French beans can be grown between 1000 and 2100m above sea level. Higher productivity is achieved in cooler weather. Dry winds, long rains and long periods of dry weather are harmful. However irrigation is vital to maintain continuous production [Legget, 1992].

1.7 Problem Statement

Horticulture is among the leading foreign exchange earner and employer either directly or indirectly in Kenya. Though pesticide residue trials to provide data for registration of pesticides and the establishment of maximum residue limits are carried out, instances of farm produce having pesticide residues levels above the MRL continue to occur, Study conducted in Nairobi found Dimethoate pesticide in the range of 1.07mg/Kg in tomatoes which is above the EU MRL of 0.02mg/Kg [KOAN, 2006]. The continued occurrence of these residues brings into question the level of application of good agricultural practices (GAP) by farmers. Chloropyrifos and dimethoate are commonly used in Kenya on a variety of crops and with the current challenges at hand; there is dire need to study their fate and asses their residue levels in French beans sold in Kenyan market. This study focuses on French beans grown under local climatic conditions as well as assessment of residues of the same in Nairobi markets.

1.8.1 Main Objective

The main objective was to generate data on the residue concentrations of chlorpyrifos applied to French beans and soil under local conditions.

1.8.2 Specific objectives

1. Identify the commonly used pesticides and their safety on farmers in Kiambu County.
2. Study the dissipation rate of chloropyrifos pesticide in soil and French beans in a green house.
3. Assess the pesticide residue levels of chlorpyrifos and dimethoate in French beans collected from markets within Nairobi County.

1.9 Justification of the study

Use of pesticides to protect vegetation has become indispensable and their effectiveness depends upon their properties. Organophosphate pesticides are more soluble and degrade quite readily in soil. Hence they play a major role in controlling insects and pests in agriculture and their judicious use is improving production in the horticultural subsector in Kenya and subsequently source of foreign earnings.

Residue analysis provides a measure of the nature and level of any chemical contamination within the environment and of its persistence. In order to cope with the contemporary international market, there is dire need to do systematic research in order to determine pesticide residues in fruits and vegetables. That is why the pesticides manufacturers of different fruits and vegetables in many countries may carry out supervision trials. At the moment, pesticides are either imported as finished products or locally formulated from imported active ingredients; hence data in the country of origin is accepted by default. However, the behaviour of pesticides may vary in different environments. In addition local farming practices concerning application of pesticides and subsequent harvest of treated crops have raised concerns over the possibility of excessive residues in farm produce.

Keeping in view the importance of pesticide usage in today’s production system and the problem associated with this essential input, results from this study will therefore assist policy makers in decisions on MRL in agricultural exports from Kenya as well as assisting farmers on executing good agricultural practices.

CHAPTER TWO

LITERATURE REVIEW

2.1 Pesticides

Pesticides are substances used with the intention of preventing, attracting, destroying and controlling pests including unwanted plants or animals [Oudejans, 1991]. Pesticides are chemicals used in agriculture to protect crops against destructive pests both in the field and during storage. They are also used in public health and other areas for the eradication of disease vectors and other pests. When used, pesticides may contaminate the environment and accumulate in the food chain thereby posing hazard to human health. [Blasco *et al.*, 2003; Pesticides Action Network, 2001].

2.2 Classification of Pesticides

Pesticides can be classified into two main groups: organic or inorganic pesticides. Inorganic pesticides are derived from naturally occurring elements and do not contain carbon. They are generally stable, non volatile and soluble in water. Most inorganic pesticides contain arsenic, cyanide, mercury and thallium, but the presence of such metals make pesticides persistent and bioaccumulative [Hassall, 1990]. While organic pesticides are mainly synthetic compounds containing either alphatic or aromatic hydrocan chains. They consist of organochlorines, organophosphorates, orgonosulfates, carbamates and pyrethroids depending on the element(s) bonded to the hydrocarbon system [Wasswa, 2008].

2.3 Organophosphorates Pesticides (OPs)

Organophosphorates Pesticides (OP) are phosphate esters derived from phosphoric acid comprising of a central phosphate atom and three organic side chains (R), two of which are usually ethyl or methyl, whereas one is more specific for a given pesticide. Examples of OPs include; acephate, dichlorvos, dimethoate, ethion, malathion, mevinphos, chlorfenvinphos, parathion, chlorpyrifos and diazinon. OPs are chemically unstable, less-persistent and toxic to man and vertebrate animals. This group of pesticides has virtually replaced the persistent organochlorine compounds [Briggs, 1992].

Organophosphates are highly potent compounds used mainly as insecticides especially in food crops. They are very toxic and more often involved in acute poisoning than other classes of pesticides [Collins, 2006; Mansour, 2004]. Organophosphates exert their toxic activity by inhibiting the enzyme acetyl cholinesterase. This enzyme is responsible for the hydrolysis of acetylcholine a neurotransmitter that conducts nerve impulses across neuromuscular junction in the nervous system of vertebrates as well as insects. Inhibition of this enzyme causes accumulation of Ach leading to generalized cholinergic action and muscles which eventually lead to paralysis, respiratory failure and death [Podolska and Napierska, 2006; Guilermino *et al.*, 2004]. Chronic exposure of humans to low doses of pesticides through air, water and food may lead to chronic toxicity due to accumulation of residues in the body over a long period of time. Possible health problems associated with chronic pesticide toxicity include cancer, congenital malfunction, neurological disorders, infertility, impotence, immunological disorders, liver and kidney damage, skin alterations and worsening of existing health conditions. [Jobling *et al.*, 1995]. Acute and sub acute toxicity may also arise from exposure to high doses among people who are directly involved in the manufacture, formulation, mixing and application of pesticide or in suicide and homicide cases. Human exposure may be through dermal contact, inhalation or accidental ingestion. Symptoms of acute toxicity vary with individual chemical involved but may generally include dizziness, headache, sweating, fatigue, numbness, vomiting neurological effects, liver and kidney damage, coma or death [Turgut, 2007]. Despite their benefits to man, pesticides are poisons and must be properly used to minimize human exposure and reduce health risks. Therefore, government regulation of pesticide use all over the world and analysis of pesticide residues in food is one way of monitoring effectiveness of the set regulatory systems.

2.4 Chlorpyrifos

2.4.1 Physical and Chemical Properties of Chlorpyrifos

Chemical name	Chloroprifos
CAS NO	2921-88-2
Molecular weight	350.62
Empirical formula	$C_9H_{11}Cl_3NO_3PS$
IUPAC name	*0, 0-diethy 0-3, 5, 6- trichloro-2pyridyl phosphorus thioate*
Trade name	Dursban, Lorsban
Use	Insecticide
Chemical class	Organophosphorus

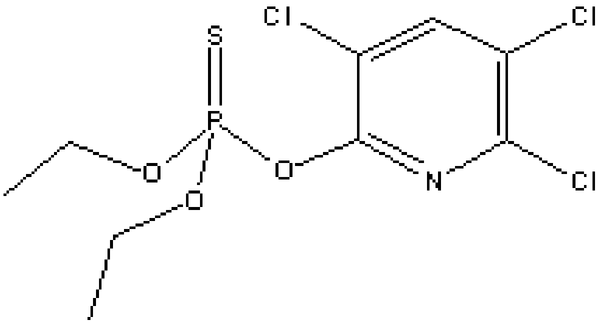

Figure 2. 1: Chemical Structure of Chlorpyrifos

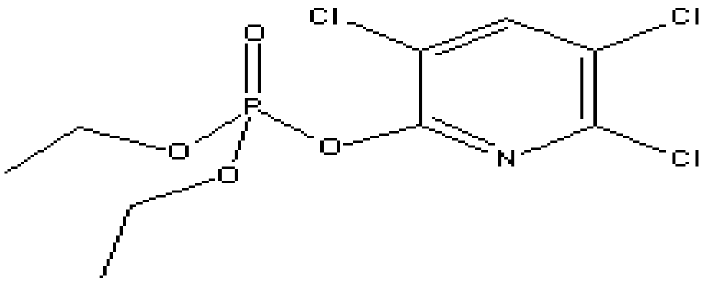

Figure 2. 2: chemical structure of Chlorpyrifos Oxon metabolite

Chlorpyrifos (O O-diethy O-3, 5, 6- trichloro-2pyridyl phosphorus thioate) is an emulsifiable broad-spectrum Organophosphate contact and stomach poison with a long residual action for the control of flies, mosquitoes, cockroaches, bedbugs and ants on a wide variety of crop types [EPA, 1984]. Chlorpyrifos has been registered in the U.S. since 1965 [U.S. EPA, 1984] and is manufactured by DowElanco, formerly the Dow Chemical Company. Common brand names are Dursban (for household products) and Lorsban (for agricultural products) [Racke, 1993].

Chlorpyrifos is the most widely used insecticide in the United States, both in crop production and in nonagricultural applications [Aspelin, 1994]. Its nonagricultural use in the United States is estimated at between 9 and 12 million pounds per year [Aspelin, 1994]. Agricultural use estimates vary.The U.S. Environmental Protection Agency (EPA) estimates that between 10 and 15 million pounds are used annually [Aspelin, 1994]. While the U.S. Department of Agriculture (USDA) estimates agricultural uses at 21 million pounds per year [U.S.E.P.A, 1994]. Chloropyrifos insecticide is an anti-cholinesterase agent with moderate toxicity: acute oral (rat) LD50= 82-155mg /Kg, dermal LD50 = 202 mg/Kg. Studies on this compound shows that the compound does not penetrate either root or leaves but only the metabolite enters the plants and the amount of radioactive compound found inside the plants is 0.5% to 2% of the applied dose [Gennady *et al.*, 2001].

2.4.2 Mode of Action of Chlorpyrifos

Chlorpyrifos is an organophosphate insecticide. Investigations of this family of chemicals began during World War II when chemists studied their use as nerve gases [Cremlyn, 1991]. Chlorpyrifos is directly toxic to the nervous system. In addition, it is transformed inside animals to chlorpyrifos-oxon [Chambers *et al.*, 1993; Sultatos, 1991], which is about 3000 times as potent against the nervous system as chlorpyrifos itself [Chambers *et al.*, 1989]. Like all organophosphates, chlorpyrifos and chlorpyrifos-oxon, inhibits an enzyme, acetylcholinesterase (AChE) that breaks down acetylcholine, a chemical involved in transmitting nerve impulses across the junctions between nerves. Without functioning AChE, acetylcholine accumulates, producing rapid twitching of involuntary muscles, convulsions, paralysis, and ultimately death [Cremlyn, 1991]. Chlorpyrifos exposure has also been shown to inhibit enzymes other than AChE. It impedes respiration (production of energy within a cell) in the livers of laboratory animals. This results from the effect of chlorpyrifos on the activity of ATPase, an enzyme important in cellular respiration [Sakai, 1990]. Chlorpyrifos-oxon inhibits the enzyme Cholesterol ester hydrolase; inhibition of this enzyme in rats eliminates one of their normal reactions to stress [Civen *et al.*, 1977].

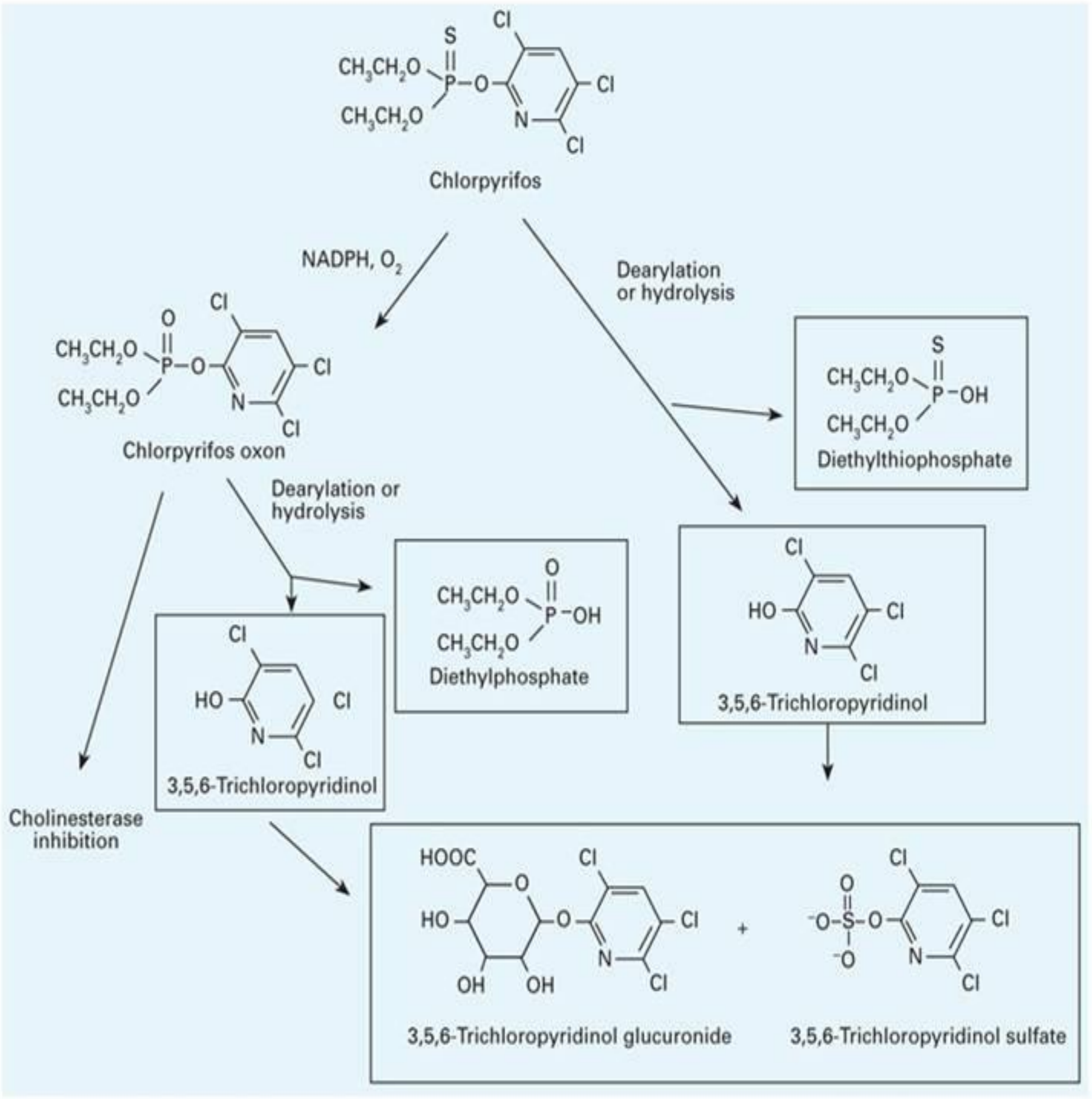

Figure 2. 3: Metabolism of Chlorpyrifos

2.4.3 Health Effects of Chlorpyrifos

Human being can be exposed to chlorpyrifios through direct skin contact with the insecticide, either as a solid or in water, ingestion, breathing of vapors, or contact with chlorpyrifos-treated soil [Racke, 1993]. Two-year study in which rats were fed chlorpyrifos showed some degeneration of the exposed rats' retinas [California Environmental Protection Agency. Dept. of

Pesticide Regulation. Medical Toxicology Branch, 1993]. Effects on eyes were also found in a study that involved injecting chlorpyrifos into rats. Recordings of the electrical activity of the retina found dose-dependent abnormalities up to two days after chlorpyrifos exposure [Yoshikawa *et al.*, 1990]. The two year rat study also found that chronic exposure to chlorpyrifos caused rats to gain less weight than was gained by unexposed rats [California Environmental Protection Agency. Dept. of Pesticide Regulation. Medical Toxicology Branch, 1993]. The inhibition of AChE activity caused by chlorpyrifos is more persistent than that caused by other organophosphates with measurable inhibition two weeks after exposure [Chambers, *et al.*, 1993], one month after exposure in another study [Sakai, 1990], and six weeks in other studies [Pope, 1992; Bushnell *et al.*, 1993]. Researchers believe that this is because chlorpyrifos is lipophilic (attracted to the non-water soluble, fatty, parts of body tissues). This means the chlorpyrifos is stored but then released and transformed to chlorpyrifos-oxon so that effects occur over a long interval [Chambers *et al.*, 1993].

Along with the AChE inhibition, EPA researchers measured behavioral changes, including a reduction in working memory and a slowing of motor activity, 2 to 3 weeks following exposure [Bushnell *et al.*, 1993]. One response was altered for 12 weeks after exposure [Pope, 1992]. Weekly injections of smaller amounts of chlorpyrifos caused similar changes. Ninteen Researchers caution that “subtle, long-term changes in behavior may be induced” by acute exposure to chlorpyrifos [Pope, 1992]. Chlorpyrifos has also caused reproductive problems in laboratory tests. In tests conducted by Dow Chemical, feeding chlorpyrifos at high doses caused pregnant mice to give birth to small pups with an increased incidence of skeletal abnormalities. At a lower dose, the same study found an increase in skull defects that allowed the brain to be exposed [Deacon *et al.*, 1980]. Others tests, also conducted by Dow, showed that chlorpyrifos reduced pup weight and pup survival in studies of pregnant rats [California Environmental Protection Agency. Dept. of Pesticide Regulation. Medical Toxicology Branch, 1993].

Chlorpyrifos-related problems with reproduction made headlines in 1993 in a McCall's article which featured the Burke family from Suffolk County, New York. When their oldest daughter was a toddler, the Burkes began regularly treating their carpets with Dursban to kill Lyme-disease carrying ticks that their dog might have brought in. Their second child was born with cerebral palsy, cataracts, and suffered from seizures. When their third child was born with similar problems, doctors agreed that the children might have been damaged prenatally by the Dursban treatments [Clavin, 1993]. Injection of pregnant female rats with low doses of Dursban (less than 1/1000 of the LD50) caused increased fetal mortality as well as decreased body weight and neurotoxicity in the pups that survived [Muto *et al.*, 1992]. Injection of male rats with Dursban caused death of the cells that make up the semen-producing tubules (small tubes) in the testes [Mikhail *et al.,* 1979]. Dermal exposure of mice to a Dursban -bran mixture resulted in high mortality of parents, particularly females who have a large skin area relative to their weight. Surviving mothers gave birth to fewer litters, smaller litters, and litters with smaller pups. Almost half of the pups died as newborns [Gregory *et al.*, 1993].

EPA has evaluated the carcinogenicity tests submitted in support of chlorpyrifos's registration and classifies them evidence of noncarcinogenicity [U.S. EPA, 1994]. These tests showed that feeding of chlorpyrifos to rats and mice over a two year period resulted in "no increase in the incidence of tumors [EXTOXNET, 1993]. However, xylenes, used as solvents in some chlorpyrifos-containing products [MSDS, 1992] have caused increased rates of leukemia in workers who inhaled xylenes on the job. Xylenes also seem to be cocarcinogenic and increases the number of skin cancers caused by other carcinogens in laboratory animals [U.S. Dept. of

Health and Human Services. Public Health Service. Agency for Toxic Substances and Disease Registry, 1993]. A variety of other tests show that chlorpyrifos, in fact, can cause genetic damage. Tests using cells from human lymph nodes showed that Dursban causes an increase in the frequency of sister chromatid exchanges (SCE; exchange of genetic material within a chromosome pair during cell division) [Sobti *et al.,* 1982]. A test using human white blood cells showed a similar increase in SCEs [Nelson *et al.,* 1990]. Tests with laboratory animals have also shown that chorpyrifos has the potential to cause genetic damage. In spleen cells from mice, chlorpyrifos caused an increase in chromosomal aberrations as well as an increased frequency of SCEs [Amer *et al.,* 1992]. In live mice, injection, ingestion, or skin absorption of Dursban caused an increase in the number of polychromatic (young or degenerating) red blood cells in the bone marrow. Oral and dermal exposure to chlorpyrifos also increased the number of micronuclei in the red blood cells. These are small pieces of genetic material formed when preceding cell divisions have been abnormal [Amer *et al.,* 1982]. Micronuclei were also found after chlorpyrifos exposure in bone marrow cells from Chinese hamsters. These tests were conducted both on live hamsters and on cell cultures [Ni, 1993].

Chlorpyrifos can also cause genetic damage in organisms other than mammals. In fruitflies, an agricultural chlorpyrifos product caused an increase in mutations of the wing primordia cells as well as an increase in the frequency of recessive sex-linked lethal mutations [Patnaik *et al.*, 1992]. Chlorpyrifos has also caused chromosome aberrations in barley pollen mother and root-tip cells [Kaur *et al.,* 1985]. Chromosome aberrations in vetch root-tip cells, [Abdou *et al.*, 1985]. Micronuclei in onion root-tip cells [Rao *et al.,* 1988], and DNA damage in three species of bacteria [Garrett *et al.,* 1986].

Recent research has identified immune system abnormalities in individuals following chlorpyrifos exposure. Higher than usual frequencies of allergies and sensitivities to antibiotics together with a typical abundances of certain types of lymphocytes (decreases in T cells and increases in CD26 cells) were found in patients one to five years following chlorpyrifos exposure. Increased expression of CD26 cells is associated with autoimmunity, where an individual's immune system acts against itself, rather than against infections [Thrasher *et al.*, 1993].

2.5 Dimethoate

2.5.1 Physical and Chemical Properties of Dimethoate

Chemical name:	O, O-dimethyl-(N-methylCarbamoyl) phosphorodithioate
Chemical family	organophosphate
Empirical formula	$C_5H_{12}NO_3PS_2$
Cas Reg number	60-51-5
Molecular weight	229.3
Trade names:	Digon, Duragon, Rebelate, Dimale.

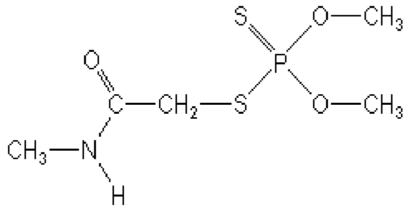

Figure 2. 4: Chemical Structure of Dimethoate

Dimethoate is an organophosphate insecticide and an acaricide used for the control of houseflies, as well as a wide range of insects and mites on a variety of fruit, vegetable, field and forestry crops [Environment Canada/Agriculture Canada, 1986]. Its white crystalline solid with a mercaptan odour and a melting point of 45-48 degrees. It is soluble in water at 250g/L at 21^0C, is highly soluble in chloroform, methyl chloride, benzene, toluene, alcohol, esters and ketones but only slightly soluble in xylenes, and aliphatic hydrocarbons.

The major toxic degradation product of dimethoate is omethoate (O, O-dimethyl S-(N-methyl carbamoylmethyls) phosphorothioate ($C_5H_{12}NO_4PS$). Hydrolytic degradation is the main inactivating pathway of dimethoates in the environment. In moist air it is degraded photo chemically to hydrolytic and oxidation products. The half life of dimethoate in different plants is between 2 and 5 days. Degradation in soil is dependent on the type of soil, temperature and pH levels [IPCS, 1989]. Dimethoate has a vapour pressure of 1.1×10^{-3} Pa at 25°C; its solubility in water at 21°C is 25 g/L [Hayes, 1982]. Reported log octanol-water partition coefficients are 0.78 and 0.79 [Suntio *et al.,* 1988].

Dimethoate released to the environment does not adsorb onto the soil and is subject to considerable leaching. It is also lost from the soil through evaporation and biodegradation. The half-life of dimethoate in soil ranges from four to 16 days [Hazardous Substances Database, 1988].It is relatively stable in aqueous media at pH 2 to 7 [RSC, 1988]. Reported half-lives for dimethoate in raw river water range from 18 hours to eight weeks (Sunti, *et al.,* 1988). Dimethoate is degraded in the environment to another more toxic pesticide, omethoate; the proportion of omethoate in the total residue reaches about 50% after five weeks [FAO/WHO, 1984]. Dimethoate is an organophosphate pesticide used for the control of a wide range of pests [EFSA, 2011].

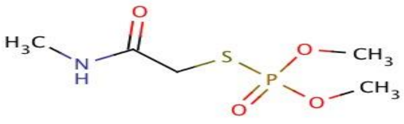

Figure 2. 5: Chemical Structure of the omethoate, a metabolite of dimethoate

2.5.2 Mode of Action of Dimethoate

Like all organophosphates, dimethoate acts by contact and systemic action by inhibiting the enzyme acetylcholinesterase in insects and other animals, including humans. Because of this toxicity to the nervous system, it inhibits an enzyme, acetylcholinesterase (AChE) that breaks down acetylcholine, a chemical involved in transmitting nerve impulses across the junctions between nerves. Without functioning AChE, acetylcholine accumulates, producing rapid twitching of involuntary muscles, convulsions, paralysis, and ultimately death [Cremlyn, 1991]. Its main plant metabolite is the omethoate which has similar biochemical mode of action but has a higher toxicity

2.6 Advantages in the use of pesticides

Pests are ecological problem and therefore the control strategies must be ecologically sound. Basically there are two approaches to pest control: prevention, care or removal of the cause.

Control methods evolve over time as knowledge and techniques improve. These include the development of chemical means of control which becomes very important because of a number of advantages. These advantages in the use of pesticides can be summarized as follow:

2.6.1Cost effectiveness: They require low input and allow large areas to be tested quickly and efficiently. It has been conservatively estimated that for every dollar a farmer spends on pesticides he/she receives $4 returns [Anon, 1990]

2.6.2 Time-line and flexibility: A suitable pesticides is available for most pest problems with variation in activity, selectively and persistence. The best product can be chosen for the situation. This allows more flexibility in management options and better time-lines of pest control.

2.6.3 Quality, Quantity and price of produce: Pesticides ensure a plentiful supply and variety of high quality wholesome food at a reasonable price.

2.6.4 Prevention of problems: Pesticides are frequently used to prevent pest problems from occurring, e.g. preserving weeds in gardens, treatment of export and import produce to prevent the spread of pests.

2.6.5 Protection of the environment: Pesticides have been used to control environmental pests' e.g noxious weeds, feral animals which have led to improved environment. Herbicides have been used to control crop weeds which reduce the need for cultivation thus preventing land degradation.

2.7 Adverse effects of pesticides use

Pesticides uses have lots of adverse effects which can be summarized as follows:

1.4.1 Residues in food

Pesticides continue to be important in controlling pests that carry human disease, but today most pesticides are used to control various pests in our food supply systems. Without pesticides, food production in Kenya would be reduced from 15 to 80 percent, depending on the crop and the pest causing the damage [Musila, 2011]. Despite the tremendous advantage of pesticides use, there is need for scientific evaluation and control of these products. Incidences of produce having high level of pesticide residues have been recorded. Some are known carcinogens and may have long term effects like nervous system disorders and immune suppression. Unpublished reports from KEPHIS on a market basket and farm gate survey on tomatoes conducted in 1994 indicated levels above maximum residues limits (MRLs) for dithiocarbamates (specifically mancozeb).

A new report by the European commission (EC) health and consumer directorial showed that in 2010 alone, there were four cases of suspected contaminated food from Kenya compared to just one case in the previous years. Statistics showed the shipments of fruits and vegetables, nuts and nut products as well as herbs were most affected by the European contamination alert in 2010. In a tough stance to ensure that maximum residues levels (MRIs) are as low as possible, applicants seeking to make shipments to the EU must get approval for the pesticide used by submitting scientific information about the minimum amount of pesticides necessary to protect a crop and the residue level remaining on the crop after such treatment. In 2005, Kenya passion fruits and French beans were intercepted in Sweden and Belgium during monitoring. The passion fruits were found to have dithiocarbamates, chlorothalonil, dimethoate, tebuconazole and omethoate residues [Kephis, 2006].

Pesticides residues in vegetables not only pose problems for international trade but also damage the public health. For example, China's export have suffered due to vegetables safety issues, as food safety standard in developed countries such as Europe, Japan and USA are more strictly enforced [Calvin *et al.*, 2006]. It is reported that substantive application of pesticides may cause pest reduction in food crops, which is especially true for vegetables which among other crops receive the highest application of pesticides but pose a serious health risk [Ngowi *et al.*, 2007].

In Kenya, the use of pesticides has been promoted to expand agricultural production and increase productivity. Kenya imports most pesticides from the developed countries. Though pesticide residue trials to provide data for registration of pesticides and the establishment of maximum residue limits are carried out, instances of farm produce having pesticide residues above the MRL continue to occur. Furthermore these trials are carried out at the country of origin of the pesticide most of which have climatic conditions that are different from the Kenyan one. The continued occurrence of pesticide residues above MRLs brings into question the level of good agricultural practice (GAP) by farmers.

The presence of chemicals in food has been described as a potential risk to human health including the development of chronic diseases [Caldas and Souza, 2006]. In Brazil dithiocarbamates and ten organophosphates; were analysed and found in samples of prepared food collected at a University restaurant. Residues of dithiocarbamates found in sample ranged from levels below 0.10 to 0.24mg/kg CS2, with vegetables being the dominant group with detectable residues. In Kenya, a survey of deltamethrin and lambdacyhalothin in vegetables reported mean residues levels ranging between 0.0130 and 0.3400 mg/kg during the dry seasons and between non-detectable levels and 0.01100 mg/kg during the wet seasons. In the same study, it was found that vegetables consumed in urban areas had higher residues compared to rural areas reaching a maximum of 0.3400 mg/kg in the samples analysed in the areas. In the same study, samples analysed from rural areas had levels between 0.0012 and 0.11 mg/kg. Although the levels were below the MRL, they were however well above the ADI [Njagi, 2005]. A market basket and farm gate survey on tomatoes conducted in 1994 indicated mancozeb levels above MRL at farm gates.

The residues are based on the whole fruits and vegetables presented for sale. In Ireland, a monitoring program was conducted in 2004 for three different food groups for which MRL have been established thus, food of plant origin (including fruits and vegetables), cereals and food of animal origin (meat) by the department of agriculture and food [DAFPCS, 2006]. Of the samples taken, 27 % were of domestic origin, 44 % were imports from EU countries and 29 % were imports from countries outside EU. Samples were analysed for residues of up to 118 pesticides and metabolites. Forty eight percent of the samples analysed contained detectable pesticide residues while the remaining 52 % contained one or more detectable residues in which 3.4 % contained residues in excess of the MRLs. In all residues 53 different pesticides were detected.

In the monitoring program Kenyan produce was found to have residues. In particular avocado was found to contain fludioxinil at 0.02 mg/Kg, while passion fruit samples were found to have propargite residues at 0.15mg/Kg. While there were no MRLS for propargite, the levels exceeded the EU MRL for chlorothalonil (0.01 mg/Kg). Dimethotate was found to be at 0.13mg/Kg which was above the EU MRL of 0.02 mg/Kg. The second was found to contain dimethoate and tebuconazole at 0.12 and 0.05 mg/Kg, respectively and although there is no MRL for tebucanozole, the dimethoate MRL (0.02 mg/Kg) was exceeded. The third sample contained dimethoate and omethoate at 0.22 and 0.1 mg/Kg respectively, but both were below the codex and EU MRL of 1 mg/Kg for mange tout/sugar peas. The fourth sample contained residues of kresoxim methyl at 0.02 mg/Kg which fell below the MRL 0.05 mg/Kg [DAFPCS, 2006].

Foods of animal's origin industry, bovine, ovine, porcine, dairy products, venison, poultry, eggs and honey samples were also analysed in 2004 PRM program. One hundred and twenty seven samples of bovine meat were analysed. Six of these contained detectable pesticides residues and were originating from Ireland. Four of the samples contained DDT as the metabolite p, p'-DDE, one contained HCB and another diazinon [DAFPCS, 2006]. A study carried out on 6391 food samples in USA, found 358 to be containing dimethoate residues. Ninety six percent of the samples had levels at or below 2 mg/kg [IPCS, 1989]. A study on oranges where dimethoate (480 ais/iEC) was applied to orange trees with ground equipment at 4.5g ai was conducted. Oranges and processed commodities were analyzed and the residues found on the unwashed oranges was 1.82 mg/kg dimethoate and 0.17 mg/kg omethoate. A survey by the Australian National Residue Survey reported information on residues in consumed food [Hamilton *et al.*, 1998]. The Australian market basket survey estimated the total dietary intake of certain pesticides for six different sub-populations. Simulated diets for these groups were developed from national Dietary Surveys and each of the foods in the diet was prepared for consumption and analysed for dimethoate and other selected pesticides. Dimethoate was found in nine commodities; apple juice 0.0013 mg/g average, 0.02 mg/kg maximum, green beans 0.0004 mg/kg average, 0.01mg/kg maximum, while cabbage 0.0029 mg/kg average 0.05 mg/kg maximum, peaches 0.0611 mg/kg ,average,0.22 mg/kg. The estimated intake as a percentage of the ADI of 0.02 mg/kg bw/day ranged from 0.1 % for adult males and boys and girls aged 12 years to 0.5 % for toddlers aged two years. Oral doses administered to Leghorn chickens 0.9mg/kg of dimethoate for 7 days revealed presence of the radioactive residue levels in liver, muscles, fat, egg yolk and egg white as 0.64, 0.09, 0.038, 0.34 and 0.15 mg/kg respectively [FAO, 1998].

2.7.2 Water contamination

There are four major routes through which pesticides reach water bodies: they may drift outside of the intended area when sprayed, they may percolate, or leach, through the soil, they may be carried to the water as runoff, they may be spilled, for example accidentally or through neglect, or they may also be carried to water by eroding soil [Barlas, 2002].

Ground waters seem to be at risk chiefly from the normal spraying of pesticides on land. Generally only between 10 % and 40 % of pesticides applied reach their target (pests or weeds) [Neil *et al*. 1993]. A significant proportion remains in the soil, and this is greater for those pesticides aimed at plant roots rather than leaves. Herbicides pose the greatest risks because they are often applied directly onto soil to kill weeds as they emerge, leaving them more prone to being washed away by rain [Neil *et al.*, 1993].

The ignorant or deliberate discharge of pesticides into water courses, via for example, leaky stores, careless disposal of containers and direct spraying is generally characterized as point source pollution [Neil *et al*., 1993]. Concentrations rise rapidly over short periods of time and the source can often be unambiguously assigned. In contrast, diffuse pollution tends to rise from normal agricultural practice as pesticides make their way from their target to surface and ground water over long periods of time and it is difficult, if not impossible to assign this type of contamination to a specific farmer [Neil *et al*., 1993].

Factors that affect a pesticide's ability to contaminate water include its water solubility, the distance from an application site to a body of water, weather, soil type, presence of a growing crop, and the method used to apply the chemical [Barlas, 2002]. Maximum limits of allowable concentrations for individual pesticides in public bodies of water are set by the Environmental Protection Agencies in any country. Similarly, the government of the United Kingdom sets Environmental Quality Standards (EQS), or maximum allowable concentrations of some pesticides in bodies of water above which toxicity may occur. The European Union also regulates maximum concentrations of pesticides in water.

2.7.3 Resistance

Pesticide resistance is the sorting of pest population targeted by a pesticide resulting in decreased susceptibility to that chemical. In other words, pests develop a resistance to a chemical through natural selection, the most resistant organisms are the ones to survive and pass on their genetic traits to their offspring.

2.7.4 Drift of sprays and Vapor

Pesticides can contribute to air pollution. Pesticide drift occurs when pesticides suspended in the air as particles are carried by wind to other areas, potentially contaminating them. Pesticides that are applied to crops can volatilize and may be blown by winds into nearby areas, potentially posing a threat to wildlife. Weather conditions at the time of application as well as temperature and relative humidity change the spread of the pesticide in the air. As wind velocity increases so does the spray drift and exposure. Low relative humidity and high temperature result in more spray evaporating. The amount of inhalable pesticides in the outdoor environment is therefore often dependent on the season. Also, droplets of sprayed pesticides or particles from pesticides applied as dusts may be blown with wind to other areas, or pesticides may adhere to particles that blow in the wind, such as dust particles.

2.8 Health Effects of Pesticides

Humans are exposed to pesticides by direct inhalation of contaminated air or ingestion of contaminated food and water or dermal absorption. Pesticides have been detected in human blood, urine, breast milk, semen, adipose tissues, amniotic fluids, infant meconium and umbilical cord blood [Bouwman *et al.*, 2006]. In the body, pesticides are metabolized, secreted or stored in fatty tissues. Farm and industry workers are at higher risk of occupational exposure.

Already OCs have been implicated in a broad range of adverse human health and environmental effects including reproductive failure and birth defects [Edwards, 1987] immune system dysfunction, endocrine disruption and cancer [world wildlife fund, 1999; Garabrant *et al.*, 1992]. Exposure to pesticides has been shown to have adverse health effects [Landrigan *et al.*, 1999]. Exposure to aldrin, dieldrin, Hexachlorocyclohexane and chlordane are associated with illness and death depending on the level of exposure. The dangerous acute dose of the technical HCH may be about 30 g. The main lethal dose of technical HCH may be about 400 mg/kg that may within 3 days cause toxic effect [Gosselin *et al.*, 1984]. Some acute effects include the development of photosensitive skin lesion, hyper pigmentation, hirsute, colic, severe weakness, porphyrinuria and debilitation. Nursing mothers who ingest these seeds dressed with HCH passed it to their breast feeding babies. Babies born by the pregnant women who consumed the

HCH treated seeds developed a condition called pink sore (pembe yara) and had mortality rate of approximately 95 % [Stober, 2000].

Exposure to p, p'-DDE is associated with testicular germ cell tumors whereas exposure to chlordane compounds and its metabolites have been associated with the risk of seminoma. Research suggests that the development of testicular germ cell tumours in the early stages of life could be associated with the exposure to persistent organic pollutants either during pregnancy or via breast feeding [Katherine *et al.*, 2008]. Other organochlorine pesticides have been shown to affect reproduction of various test animals [Hayes, 1982].

Hormonal disturbance caused by DDE have been associated with thinning of egg shells and feminization of Baltic seals. Chronic exposure to endosulfan has been associated with abnormal behavior in rats. Slowed development and increased mortality of tadpoles were also reported [Bernes and Naylor, 1996]. In humans, OCPs have been associated with birth of premature and underweight babies to mothers whose blood concentration of DDE was above 10ppb and 9.83ppb β-HCH. These pesticides have been found to alter levels of maternal thyroid hormones during pregnancy. Women with hexachlorobenzene concentration that ranged from 7.5-8.41 ppb had altered thyroids hormone levels [Chevrier *et al.*, 2008].

CHAPTER THREE

METHODOLOGY

3.1 Study Area

The study was conducted in two open air market (Wakulima and Kangemi), two supermarkets (Turskys and Nakumatt) and in a green house situated at Chiromo campus University of Nairobi, Nairobi County, Kenya. Nairobi´s geographical coordinates are 1º17´0´´South, 36º49´0´´East. Its altitude is 1661m above sea level. Nairobi has a subtropical highland climate whereby the sunniest and warmest part of the year is from mid-December to mid-March with mean maximum temperature of 24 ^{0}c.There are two rain seasons with the long rains occurring from April to June and shorts rains from October to mid December. Cool rather cloudy dry season occurs from June to mid- September. A green house located at the college of Biological and Physical Sciences within the School of Biological Sciences Chiromo Campus was used. The mean temperature of the green house throughout the study period was recorded. Figure 3.1 shows the map study area.

3.1.1 Nakumatt Supermarket

Nakumatt supermarket is a private company, owned by the Atul Shah family and Hotnet Limited. As of May 2014, Nakumatt had nearly 50 stores in the African Great Lakes countries of Kenya, Uganda, Rwanda and Tanzania. It employed over 5,500 workers and had gross annual revenue in excess of US$450 million. The supermarket sampling was done in one of its branches located in Nairobi central business district (CBD). Commodities from the supermarket were considered for sampling because most the commodities that don’t meet grading requirements for export market are usually dumped in various chain stores in the country.

3.1.2 Kangemi Open Air Market

Kangemi Market is owned and managed by Nairobi City County. The market is located in Kangemi along Waiyaki way. Currently the market accommodates about 10,000 dealers. The choice of Kangemi open air market was to capture farm produce originating from Kiambu County and other parts of rift valley.

3.1.3 Wakulima Open Air Market

Wakulima Market was build in 1966 and is Nairobi’s largest fresh produce market owned and managed by Nairobi City County. The market is located in Muthurwa along Haile Selassie avenue. Currently the market accommodates about 7000 dealers.

3.1.4 Kiambu County

Kiambu county is located in the former Central Province of Kenya. Its capital is Kiambu and its largest town is Thika. The county is adjacent to the northern border of Nairobi County and has a population of 1,623,282 and is predominantly rural. However its urban population is increasing as Nairobi is growing rapidly. The county has twelve constituencies/Sub counties: Githunguri, Kiambaa, Kabete, Limuru, Lari, Gatundu North, Gatundu South, Ruiru, Kikuyu, .Juja, Thika, Kiambu. The major economic activity is agriculture especially in horticulture farming, tea, dairy and poultry farming. The trend however is changing to real estate development since it’s a sub urban of Nairobi city.

3.1.5 Turskys Supermarket

Tuskys owns and operates nearly fifty supermarkets in Kenya and Uganda. Tuskys is the second-largest supermarket chain in the Great Lakes region, behind Nakumatt. Tuskys employs more than 6,000 people in Kenya. The choice of the supermarket was to capture products majorly sold to middle class people who are main clients of the chain stores.

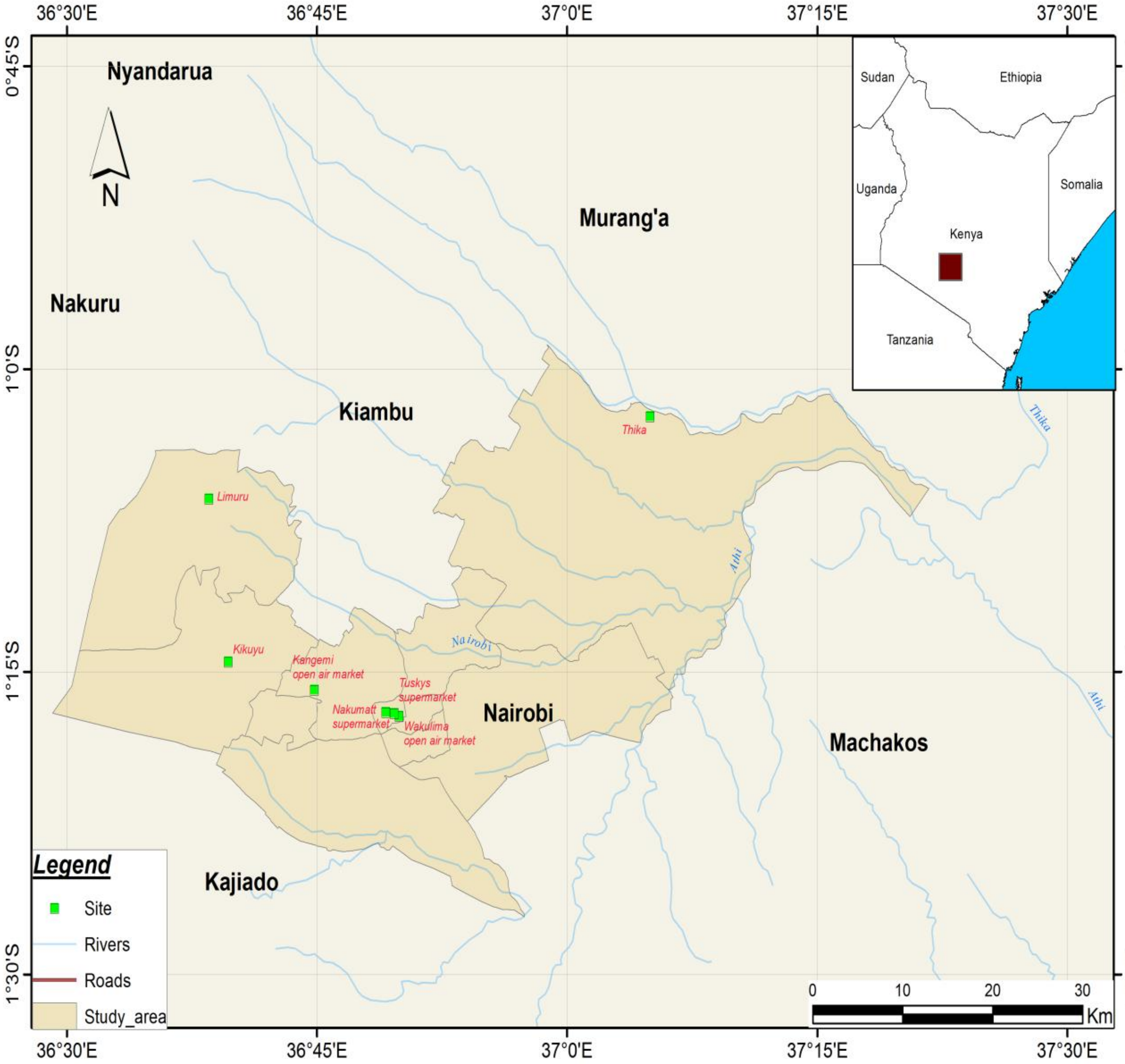

Figure 3. 1: Map of Study Area

3.2 Pesticide Use Survey

Information on pesticides commonly used in Kiambu County was obtained through visits to the area agriculture and livestock extension officers, farmers and agrochemical dealers. The key places where the survey was conducted included Thika, Kikuyu, Limuru and their environs. This was achieved using structured field questionnaires which were distributed to a total of 64 respondents chosen randomly. The questionnaire consisted of both open and closed ended questions. Information was obtained on gender, age, main occupation, and level of education of the respondents. The Respondents were asked questions on pesticide use and safety information, training on the use and formulation, pesticide related accidents and their frequencies, any known effects of pesticides to the users, use of any unlabelled pesticides and their source and any technical assistance from agricultural extension workers. Additional questions were designed to gather more information from the agro-veterinary dealers and the extension workers. The questions touched on awareness on safe handling of pesticides, stock of pesticides within the area as well as emerging issues. A sample questionnaire used is attached in Appendix II

3.3 Chemicals and Reagents Used

General Purpose Grade n-hexane, acetone and HPLC grade iso-octane were purchased from SCIELAB LTD, Nairobi. In the laboratory, General Purpose Grade solvents were triple distilled before use. Analytical grade Aluminium oxide, anhydrous sodium sulphate, copper metal, methanol, hydrochloric acid and activated charcoal were purchased from SCIELAB LTD, Nairobi.

High purity nitrogen (99%) used for reducing samples was bought from Gas labs LTD, Nairobi. High purity helium used for chromatography was purchased from BOC Kenya LTD. High purity pesticide standard was provided by the Institute of Environmental Studies (IVM) through a UNEP-GEF project. Water used to prepare solutions and rinse glassware was distilled at the department of chemistry, University of Nairobi.

3.3 Equipment and Apparatus Used

Sampling of soil was done using stainless steel core samplers. Extraction of soil and French beans (*Phaseolus vulgaris*) samples were done using soxhlet-extraction and LABCONCO rotary evaporator was used for concentrating the sample extracts. Fractional distiller was used for distillation of the solvents. During activation of copper, centrifuge was used to achieve separation of the activated copper and the acid. Scientific pH meter model IQ 150 was used to measure the pH of the water used in the greenhouse. TDS and electron conductivity was measured using scientific Martin instruments model Mi 306. Moisture in soil and French beans was determined by heating the samples in BINDER E28#04-71528 oven whereas all glassware was dried in MAMMOTH oven. All weights were taken using Fisher scientific A-160 weighing balance. Centrifuge was used to activate the copper powder. A lab-line explosion proof refrigerator was used for temporal storage of sample extracts before analysis and deep freezer was used for temporal storage of samples before extraction. HP Agilent GC system 6890N equipped with mass spectrometer detector was used for qualification and quantification of pesticide residues in the sample extracts. One liter polyvinyl pots and watering trays were used in the green house experiment.

3.4 Preparation of Reagents

Aluminium oxide (Al_2O_3) was dried overnight at 200 ^{0}C to make it 100 % active, this was followed by deactivation of the Al_2O_3 with water: Al_2O_3 (8 %w/w) was prepared by adding 8 ml of HPLC grade water to 92 g of activated Al_2O_3 in 250 ml Erlenmeyer flask and shaken by hand until all lumps were eliminated. After deactivation the Aluminium oxide was left overnight to condition.

Anhydrous Sodium Sulphate (Na_2SO_4) was prepared by baking out for 16 hours at 200 ^{0}C to remove all the impurities. Copper powder was activated by shaking with 9 ml of dilute hydrochloric acid solution (3:1 ration for H_2O: HCl). The mixture was centrifuged for 1 minute at 300 rpm and acid solution discarded. The powder was rinsed three times with methanol to eliminate all the hydrochloric acid, and the supernatant discarded. The remaining powder was dried under a gentle stream of nitrogen before use. General purpose grade Acetone, Hexane and dichloromethane were each triple distilled to analytical grade level in a distillation set up.

3.5 Green House Experimental Set up

Thirty three 1 litre poliugal clay pots were filled with approximately 700 g of soil. Eighteen pots for planting French beans and six pots for determining pesticide dissipation in soil. Nine more pots were set aside for setting up control experiments, six pots for untreated French beans and three pots for untreated soil. Each pot had two holes and the total area the pots covered in the green house was approximately ten square metres. Soil and farm manure were obtained from a farm in Kiambu County which is a high potential agricultural zone, while bore hole water available in the green house was used for irrigation. High quality seeds were obtained from KEPHIS (Kenya Plant Health Inspection Services).

Farm manure was applied and six seeds were sown in each pot. The plants started germinating on the sixth day and germination was complete by the ninth day. Thinning of weak plants was carried out on the fourteenth day leaving only three healthy plants per pot. Watering of the plants, pots for soil dissipation, soil control experiments and French beans control experiment was done early in the morning thrice a week. Both plants and soil were sprayed at the fifth day with chlorpyrifos pesticide (600g/ha) at the label application rate by use of a hand sprayer except the nine pots for control experiment. The control pots were sufficiently separated to exclude any contamination from the sprayed pots. The temperature of the green house was monitored throughout the experiment.

The predicted environmental concentration in soil (PECS) in mg/kg following a single application was estimated as follows:

Initial PECS = A x (1- fint) / (100 x depth x bd)

Where:

A = application rate (g/ha)

fint = fraction intercepted by crop canopy

depth = mixing depth (cm)

bd = dry soil bulk density (g/cm3)

3.6 Sampling

3.6.1 Market Sampling

Two open air markets were geo-referenced for sampling, one in the central business district of Nairobi (Wakulima Market) and another one in the suburbs of Nairobi (Kangemi Market). Sampling of French beans was done in the months of January 2013 warm and dry season, March 2013 long rain season and July 2013 dry and cold season. The French beans were sampled by buying from five different sellers around the market and mixed thoroughly on aluminum foil. A representative sample of about 500 g was placed in aluminum foil, packed in a self-sealing bag and labeled, then put in an ice box containing ice for transportation to the laboratory. At the laboratory the samples were kept in a freezer at -20 ^{0}C prior to extraction.

Sampling in the supermarket was done at the same time with open air market sampling. This was done by buying the commodity just like any other customer. Samples comprised of 500 g.

3.6.2 Green house Sampling

3.6.2.1 Green house soil sampling

Sampling of both soil for control and dissipation experiment in the greenhouse was done an hour after spraying soil with the pesticide. This was represented at day zero and thereafter seven, fourteen and twenty one days following pesticide spraying. The soil samples were collected 5 cm deep using pre-cleaned stainless steel core samplers from five different points inside the pot. This was repeated for all the pots and mixed thoroughly on an aluminum foil. A representative sample of about 100 g was placed in aluminum foil, packed in a self-sealing bag and labeled. At the laboratory the soils were kept in a freezer at -20 ^{o}C prior to extraction.

3.6.2.2 Green House French Beans Sampling

Sampling of both plant for control and dissipation experiment was done an hour after spraying of the French beans by sacrificing the whole plant using a pair of stainless steel scissors. The plants were then reduced into smaller size and mixed thoroughly on an aluminum foil, packed in a self-sealing bag and labeled. At the laboratory the French beans were kept in a freezer at -20^{o}C prior to extraction. This was done at day zero, seven, fourteen and day twenty one after spraying.

3.7 Extraction

3.7.1 Soil Extraction

Soil extraction procedure was adopted from UNEP POP Training Manual 2010. Soil samples were removed from the freezer and allowed to thaw for four hours prior to weighing 10 g of the sample in triplicate, mixed with 30 g of Na_2SO_4 then ground using mortar and pestle until homogenous powder was obtained. The samples were then covered with aluminum foil and left overnight to dry. The dry samples were transferred into Soxhlet thimbles and 20 µL of 1ppm PCB 52 solution added as an internal standard.175 ml of hexane: acetone (1:1, v/v) mixture was placed in a round bottomed flask before connecting the Soxhlet setup. Extraction was done for 16 hours. To the extracts 1ml of isooctane was added as keeper then concentrated to 1ml using rotary evaporator after which the extracts were put in vials.

3.7.2 French beans Extraction

French beans extraction procedure was adopted from UNEP POP Training Manual 2010. Samples were removed from the freezer and allowed to thaw for 4 hours, the French beans were then cut into small pieces using a knife prior to weighing 10 g of the sample in triplicate, and mixed with 30 g of Na_2SO_4 then ground using mortar and pestle until homogenous powder was obtained. Samples were then covered with aluminium foil and left overnight to dry. The dry samples were transferred into Soxhlet thimbles and 20 µL of 1ppm PCB 52 solution added as an internal standard.175 ml of hexane: acetone (1:1, v/v) mixture was placed in a round bottomed flask before connecting the Soxhlet setup. Extraction was done for 16 hours. To the extracts 1ml of isooctane was added as keeper then concentrated to 1ml using rotary evaporator after which the extracts were put in vials.

3.8 Sample cleanup

Sample clean up was done using alumina. A chromatographic column 20 cm length and 2cm internal diameter was packed with 1 g of freshly baked anhydrous sodium sulphate, followed by 15 g of deactivated alumina, 1 g of activated charcoal and finally another 1 g layer of anhydrous sodium sulphate. The column was pre-conditioned with 15 ml hexane and discarded. The sample extract was introduced into the column; the vial was rinsed four times with 1ml portions of hexane then eluted with 165 ml of the same. 1 ml of iso-octane was added to each cleaned sample as a keeper then concentrated to 1 ml using a rotary evaporator and transferred to clean vial.

3.9 Sulphur Extraction

Sulphur removal from all soil samples was done by gently adding freshly activated copper powder until no more formation of black coloration of copper sulphide was observed. The extract was then filtered into a clean vial, 1ml of iso-octane was added and concentrated using the rotary evaporator then transferred to a clean auto- vial and concentrated to 0.5 ml under a stream of nitrogen. The samples were ready for GC-MS analysis.

3.10 Measurement of physiochemical parameters of water used for irrigation

The water used for irrigation at the green house experiment was analysed. The pH of water was determined using scientific pH meter. The meter was calibrated using buffers of pH 10.0, 7.0, and 4.0 before use. TDS and electron conductivity was measured using meter. The chlorides was determined using chloride meter, chloride DPD#3 code 6197A-J and DPD #1 code 6903A-J tablets were used during the measurement of chlorides. Carbonates and bicarbonates were measured by titration process. Measurement of sodium, potassium, magnesium and calcium was done at mines and geology department.

3.11 Physicochemical Parameters of Soil

The test soil was analysed for chlorpyrifos and both physical and chemical parameters to obtain baseline information. Soil analysis was carried out using methods described in the physical and chemical methods of soil analysis [MoANAL, 1980]. Soil analysis involved physical and chemical analyses. The physical analyses included texture analysis also called mechanical or particle size analysis by pipette method, complete moisture retention (pF) where undisturbed soil core samples were subjected to negative pressure suction (kaolin box apparatus) and positive external gas pressure (pressure cooker) to remove water, and Bulk density determined according to the core method where the double cylinder core samplers were used, porosity and particle specific density. The double cylinder core samplers used were 5 cm diameter by 5 cm height.

The chemical analysis included pH determined in a 1:1(w/v) soil-water suspension with a pH meter, total organic carbon using the calorimetric method, where all organic carbon in the soil sample was oxidised by a 15 ml mixture of concentrated sulphuric acid and 5 % potassium dichromate in 1:2 ratio v/v at 150 ^{o}C for thirty minutes to ensure complete oxidation. Barium chloride was added to the cool digest, mixed thoroughly and allowed to stand overnight. The amount of organic carbon in sample was determined by concentration of chromic ions (Cr^{3+}) produced after oxidation spectrophotometrically at 600 nm.

Total Nitrogen was also analysed using the Kjeldhal method where organic nitrogen compounds in soil are digested with concentrated sulphuric acid and selenium mixture as a catalyst to convert Nitrogen to ammonium sulphate. The digest was made alkaline with sodium hydroxide and the released ammonia distilled off and collected in boric acid indicator solution and titrated against standard acid.

Other available nutrients like phosphorous, magnesium, manganese, calcium potassium and sodium were analysed using Mehlic 1 (double acid) method. Oven dry soil was extracted in 1:5 ratios (w/v) with a mixture of 0.1 M hydrochloric acid and 0.5 M sulphuric acid; where the acid replaces the bulk exchangeable metal cations and the sulphate anion is exchanged for phosphate. The P, Mg and Mn were determined calorimetrically while Ca, K and Na were determined by flame photometry.

3.12 Moisture content determination

Moisture content in soil and French beans samples was determined by heating 5 g of the sample in pre-cleaned and pre-weighed watch glass in an oven at 105 ^{0}C for 24 hours. The difference in weight between wet and dry sample was taken as the moisture content. Percentage moisture was calculated as:

$$\textbf{\%moisture} = \frac{\text{moisture content}}{\text{Weight of wet sample}} \text{ X } 100$$

3.13 GC-MS Analysis and Quantification of the extract samples

Analysis of the pesticide residues was carried out using the GC-MS 6890 at the Department of Chemistry pesticide laboratory, University of Nairobi. The DB-5 fused silica capillary column of 30m x 0.25µm i.d. x 0.25µm film thickness was coated with cross-linked 5 % phenyl dimethyl polysiloxane. The carrier gas was helium (99.99 % purity) at a flow rate of 1.0ml/min. Oven temperature was maintained initially at 70 ^{0}C for 1min, increased at 15 ^{0}C/min to 175 ^{0}C, then at 2 ^{0}C/min to 215 ^{0}C, at 10 ^{0}C/min to 265 ^{0}C and finally at 20 ^{0}C/min to 290 ^{0}C and held for 8 minutes. Injection volume was 1µL, injected in splitless mode at injection temperature of 250 ^{0}C.

3.14 Quality Assurance and Quality Control

Control pots for dissipation of chlorpyrifos in soil and French beans were set alongside the experimental pots. The control pots were separated to exclude any contamination from the treated pots. Analysis of controls was carried out alongside the samples to ascertain that no artifact in the crop derived from local conditions gave rise to interference in the analysis and to establish the transport and storage stability of any residue. Analysis was done by spiking each matrix with internal standard (PCB52) prior to extraction to check extraction efficiency and recoveries of replicate samples.

3.15 Statistical Data Analysis

The data obtained was analyzed using Statistical Programme for Social Scientists (SPSS) and Microsoft Excel programme. Calculation of half life was done using first and second order rate equations. Calibration standard series used were evaluated for within laboratory reproducibility acceptability. Results are presented as mean of triplicate analysis with standard deviation.

CHAPTER FOUR

RESULT AND DISCUSSION

4.1 Pesticides Use Survey in Kiambu County

4.1.1 Background information on Farming In Kiambu County

The survey was conducted in Kiambu county.The areas visited were: Thika,Limuru Kikuyu and their environs where 64 farmers were interviewed on the use, safety, handling, and environmental awereness of pesticides used. The survey indicated that 59 % of farmers in Kiambu county are men while 41 % of farmers are women, 75 % of the farmers interviewed indicated that they were over 35 years old. The average number of years that the interviewed farmers had been into farming was 15 years and 53 % of the farmers interviewed indicated that they had 15 or more years experience in farming. 33 % of the resipondents had primary education, 38 % had secondary education while 29 % had post secondary education. Most of the farmers practice small scale farming with more than one type of crops grown in their small farm while more than 90 % of the farmers interviewed practise crop rotation. Some of the crops grown include French beans, maize, tomatoes, soghurm, irish potatoes, coffee, tea and carbages. The farmers also practise cattle rearing especially dairy farming,sheep and pig rearing.The most common pests in kiambu County are amphids, ticks, ants, housefly and mealybugs. The most common plants and animal diseases in Kiambu county include rust, root rot, anthracnose and yellow fever in animals. The common market of kiambu county farmers’ produce is Nairobi county. The summary of the field questionairre is attached in Table 3.1 appedix III.

4.1.2 Pesticides used in Kiambu County

The most commonly used pesticides in Kiambu County are organophosphates, carbamates and pyrethroids. All these pesticides are registered in Kenya by the Pest Control Products Board [PCPB, 2004]. Table 4.1 and Figure 4.1 show summary of pesticide available in Kiambu County.

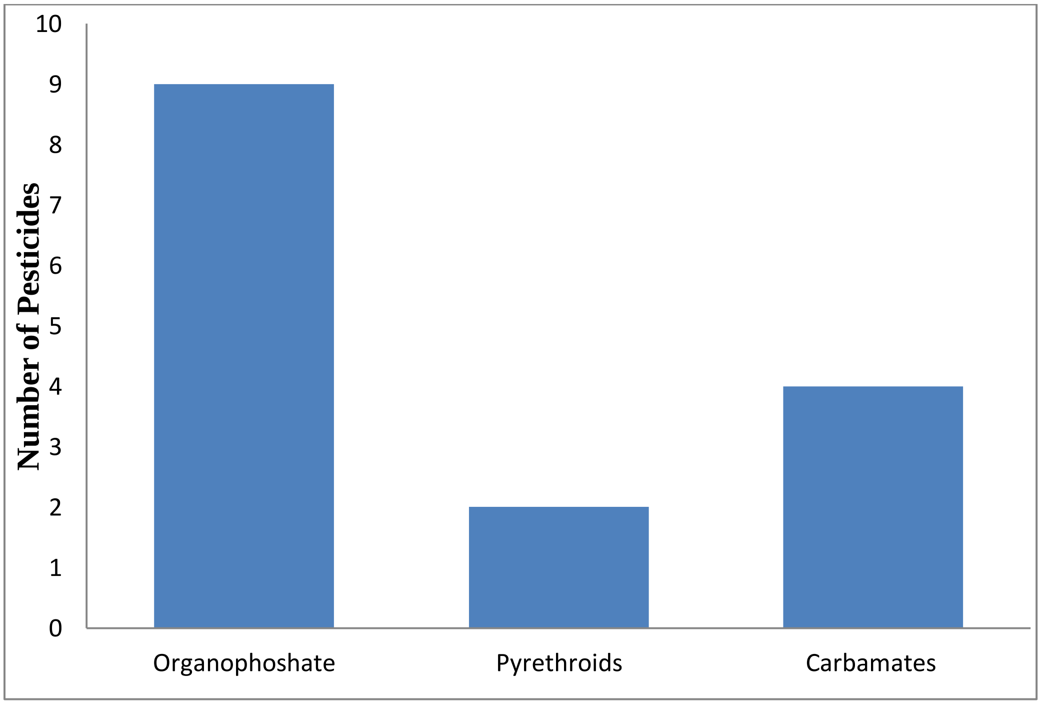

Figure 4. 1: Types of pesticide sold in Kiambu County

Table 4. 1: Pesticides Used in Kiambu County and their Classifications

Pesticides	**Active ingredient (a.i)**	Class	Toxic Classification	Used by % Household	Crops Treated
Karate	λ-cyhalothrin	Sythetic Pyrethroid	WHO II	64	Vegetable, Tomatoes
Milraz	Mancozeb	Sythetic Pyrethroid	WHOIII	78	Tomatoes
Dithane	Mancozeb	Carbamate	WHOIII	54	Tomatoes, vegetables
Dimethoate	Dimethoate	Organo phosphate	WHO II	32	FrenchBeans, Tomatoes, Vegetables
Dursban	Chlorpyrifos	Organo phosphate	WHOII	81	French beans, Beans
Ridomil	Mancozeb	Carbamate	WHOIII	15	Potatoes
Milthane	Mancozeb	Organo phosphate	WHO III	42	Vegetables
Furdan 5G	Carbofuran	carbamate	WHOI	54	Vegetables
Diazinon	OrganoPhosphate	organophosphate	WHOII	92	Animals, Fruits
Antracol	Propinab	Carbamate	WHOIII	39	Potatoes, Vegetables
Round Up	Glyphosate	Organo Phosphate	WHOII	65	Tomatoes, Maize
Sumithin	Fenithrothion	Organo Phosphate	WHO II	11	In door use
Ambush	Cypermethrin	Organo phosphate	WHO III	87	Vegetabes
Tactic	Amitraz	Organo phosphate	WHO III	45	Vegetables
Tixfix	Amitraz	Organo phosphate	WHO III	51	Tomatoes

N/B Pesticide data obtained on 22/ March 2015

WHO (2002): Classification from I to III, with I being the most hazardous

4.1.2 Factors Affecting Choice of Pesticide

The main consideration for use of a particular pesticide by farmers from the survey was whether the pesticide enables the farmer to get good yield as indicated by 39 % of the respondents, followed by cost effectiveness of the pesticide by 36 % of the respondents noting it as an important factor. 8% used a given pesticide because it was suggested by NGO, While 3 % used a given pesticide because it was suggested by the agrochemical dealers and the sales agent of the agrochemical industries. Also 11 % of the respondents said they were suggested by other farmers, while 3 % of the farmers used the pesticide because it was good for the environment. See figure 4.2.

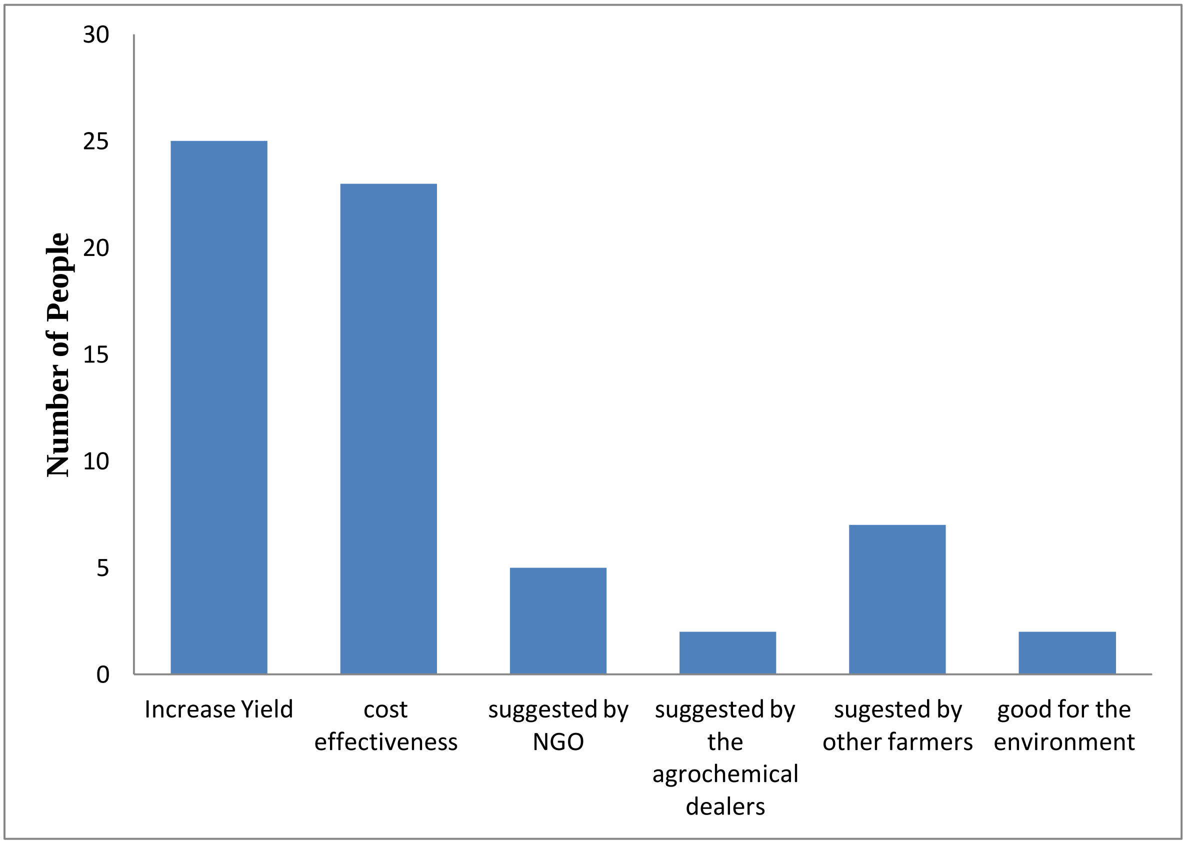

Figure 4. 2: Factors affecting the choice of pesticide by farmers

4.1.3 Pesticide Training and Knowledge by Farmers

All the respondents were aware of the use of pesticides, but 46 % had basic training, 10 % had advanced training and 44 % had no training about the use of pesticides. 51 % of the farmers even those who had training on how to handle and knowledge of the effects of pesticides did not use protective devices when handling pesticides, and complained that the devices were expensive and hence they could not afford them. 72 % of the respondents always read instruction menu on the pesticide before use while 6 % were not aware of the instruction menu and 22 % did not read the instruction menu at all, these was attributed mostly to ignorance. Farmers who had higher level of education past secondary education always read instructions on the pesticide use and formulation, those with secondary education majority will always read the instruction about the use of pesticides but they did not read instructions on the formulation of the pesticide while the respondents who had only primary level of education did not read the instructions at all. As shown in figure 4.3.

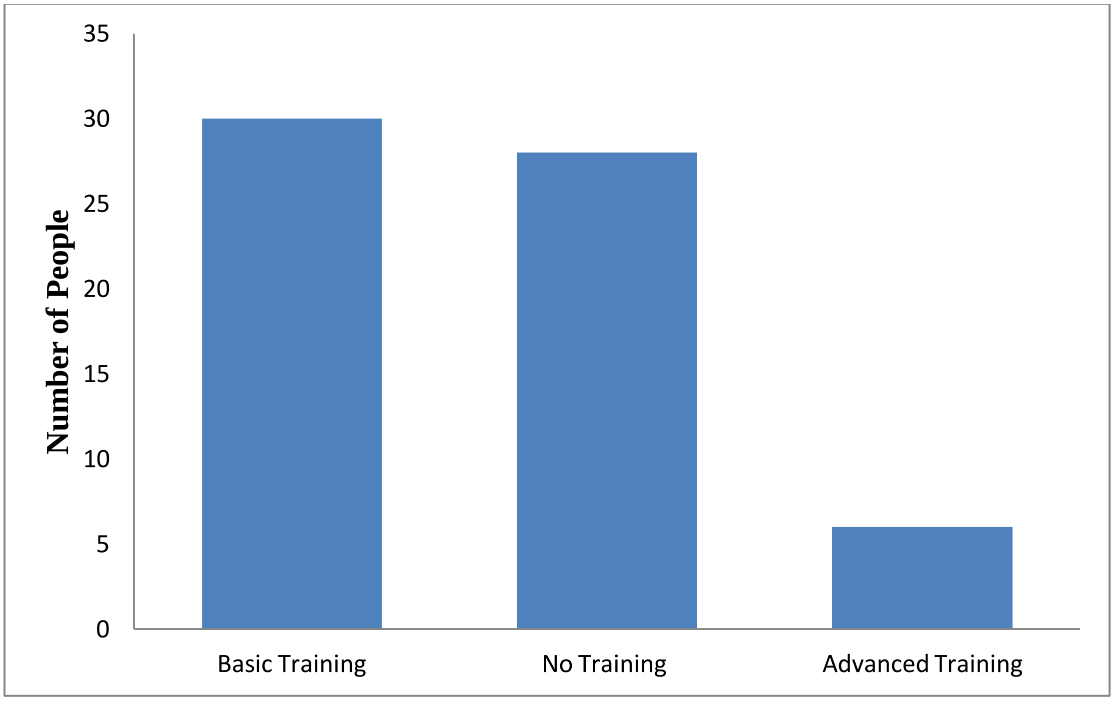

Figure 4. 3: Farmers Training on pesticide use

4.1.4 Farmers Training on pesticides Residue in Food

All the respondents were aware of pesticide residues in food, but 53 % had basic training, 3 % had advanced training and 44 % had no training about pesticide residues in food, as shown in figure 4.4.

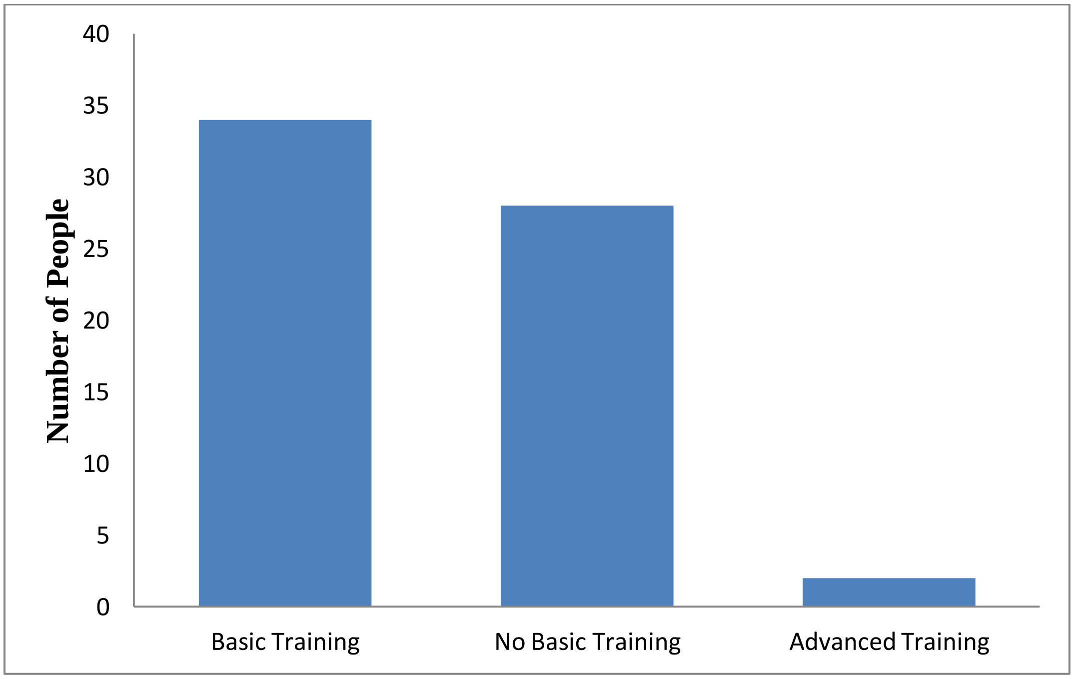

Figure 4. 4: Farmers Training on pesticides Residue in Food

4.1.5 Impacts of Pesticides on the Environment

It was noted that 64 % of the respondents were aware that the use of a number of pesticides has been banned or restricted in Kenya, while 36 % of the respondents had no information on the restrictions or ban of these pesticides. 94 % of the respondents were aware of the effects of pesticides to the environment in case of poisoning the environment with pesticides while 6 % were not aware. There were 5 reported cases of pesticide human poisoning of people in the area. Figure 4.5 shows the farmer's environmental awareness of pesticides.

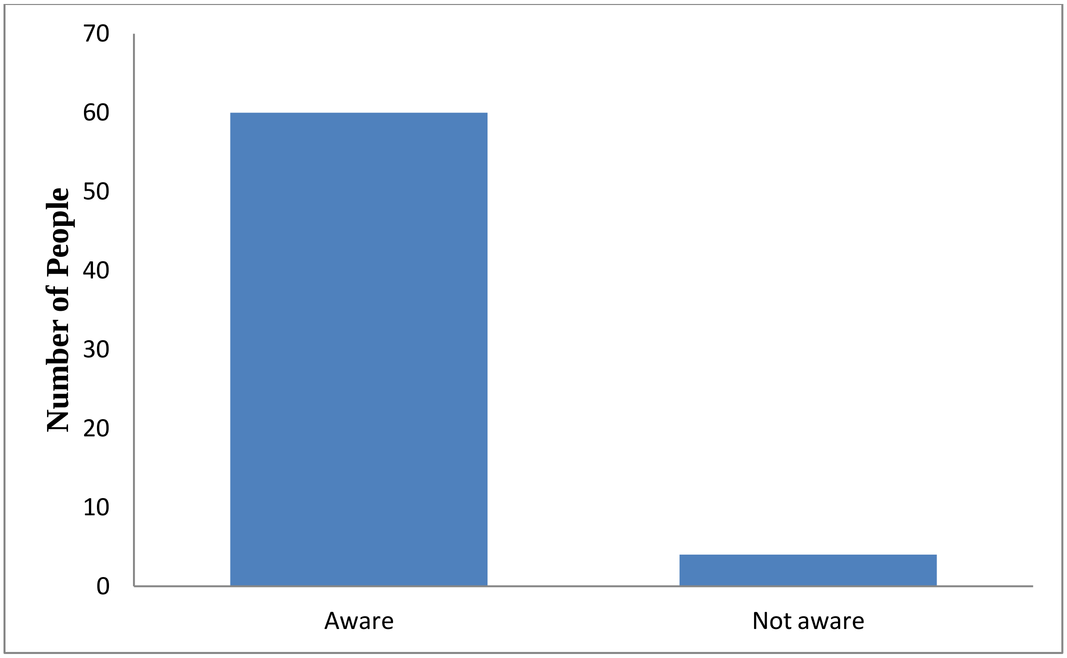

Figure 4. 5: Effects of Pesticides to the Environment

4.1.6 Sources of Information on Pesticide Use

The main information source for the farmers on pesticide use are through the agricultural sector government workers, non-governmental organizations (NGO), Agro- chemical industries, agro-chemical dealers and radio. 41% of the respondents get information from NGOS, while 36 % get information from radio, 10 % get information from agriculture extension officer, 6 % get information from agro- chemical dealers and only 10 % get information from agro- chemical industries as shown in Figure 4.6.

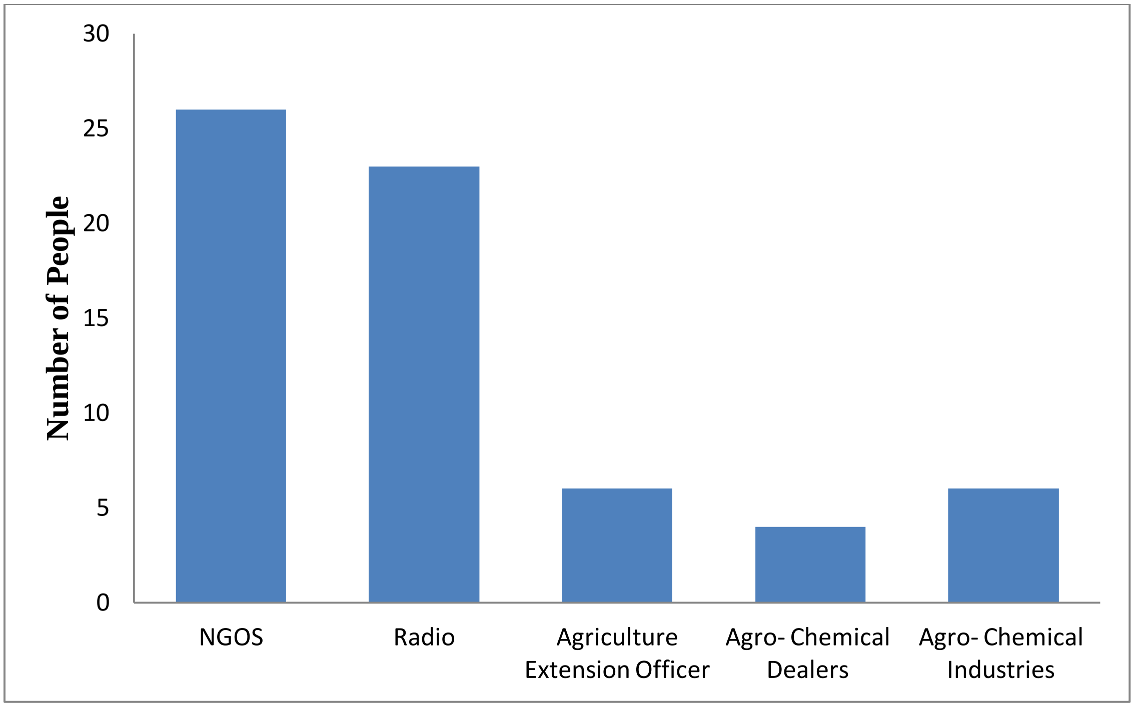

Figure 4. 6: Farmers' sources of information on the use of pesticides

4.2 Physicochemical Parameters of Water Used for Irrigation And Soil

Borehole water was used to irrigate the plants. The water had a pH of 7.9, sodium content of 6.25 m.e per litre, chlorides content of 10.65 m.e per litre, conductivity of 310 µs/cm (micro Siemens per centimeter), TDS of 155 mg/L and a sodium adsorption ratio (SAR) of 14.64 making it a medium salinity-medium sodium water. Contents of other elements were: potassium 0.42 m.e per litre, calcium 0.035 m.e per litre, magnesium 0.01 m.e per litre, bicarbonates 2.73 m.e per litre, sulphates 5.775 m.e per litre and carbonates were not detected. A summary of the chemical characteristics of the water are presented in Table 3.3, Appendix III.

The soil used in this study was ranked to be 75 % clay, 8.1 % sand, and 16.9 % silt. The soil had a bulk density of 0.72 g/cc. It was slightly acidic with a pH of 6.72. The percent total nitrogen was 0.48 while the organic carbon was 4.03 %. All macro elements potassium, calcium, magnesium and sodium were adequate except phosphorous which was low at 29.5 ppm based on the Mehlich double acid method (Mehlich1) whose critical level for phosphorous is 30 ppm. The micro-elements copper, iron and manganese were adequate while zinc was low at 2.98 ppm. A summary of the characteristics of soil is presented in Table 3.4, Appendix III.

4.3 Method Accuracy

Recovery data for pesticide residue analysis method were generated by fortifying blank samples with 20 µl of 1 mg/kg chlorpyrifos stock solution and 20 µl of 1 mg/kg dimethoate stock solution. These were then analysed to establish the recovery of the analyte. The cleanup stage was optimised and gave recovery of 115.15 % for dimethoate and 105.5 % for chlorpyrifos with elution of 200 mls Hexane, 99 % for dimethoate and 103 % for chlorpyrifos with elution of 200 ml of 1:1 mixture of dichloromethane: hexane and 86 % for chlorpyrifos and 92 % for dimethoate with elution of 200 ml of 1:1 mixture of dichloromethane: hexane. 200 ml of hexane was therefore used as eluting solvent for clean up.

Samples of French bean, soil and blank (unhydrous Na_2SO_4) were spiked with 20 µl of 1 mg/kg chlorpyrifos and 20 µl of 1 mg/kg dimethoate and the percentage recoveries calculated. The recoveries of chlorpyrifos and dimethoate ranged between 92 % and 115 % Table 4.2

Table 4. 2: Method Recovery data in % for Dimethoate and Chlorpyrifos Residues

Commodity	Dimethoate	Chlorpyrifos
French beans	92.97±10.3	107.97±5.6
Soil	108.02±2.8	98.86±8.4
Control	115.15±5.4	105.5±1.9

4.4 Multi level Calibration Curves

Quantification was based on calculations from calibration curves in the concentration range of 2.56 mg/L to 136.30 mg/L and 1.22 mg/L to 173.06 mg/L for chlorpyrifos and dimethoate respectively. The calibration curve of the standard was a straight line for the two compounds and the best line of fit drawn from plotting the relative response factor, that is, ratio of instrument response (peak area), against analyte concentration. All analyte lines gave a correlation factor (R^2) above 0.99 indicating a high correlation between instrument response ratio and analytes concentration. Figure 4.7 and 4.8 below shows calibration curve for chlorpyrifos and dimethoate. Sample analytes concentrations were obtained by interpolation from the graphs which applies the equation of the line i.e Y= mX+c

Where Y= Peak area (Instrument response)

X=Analyte concentration,

m=Gradient, and

c= Constant

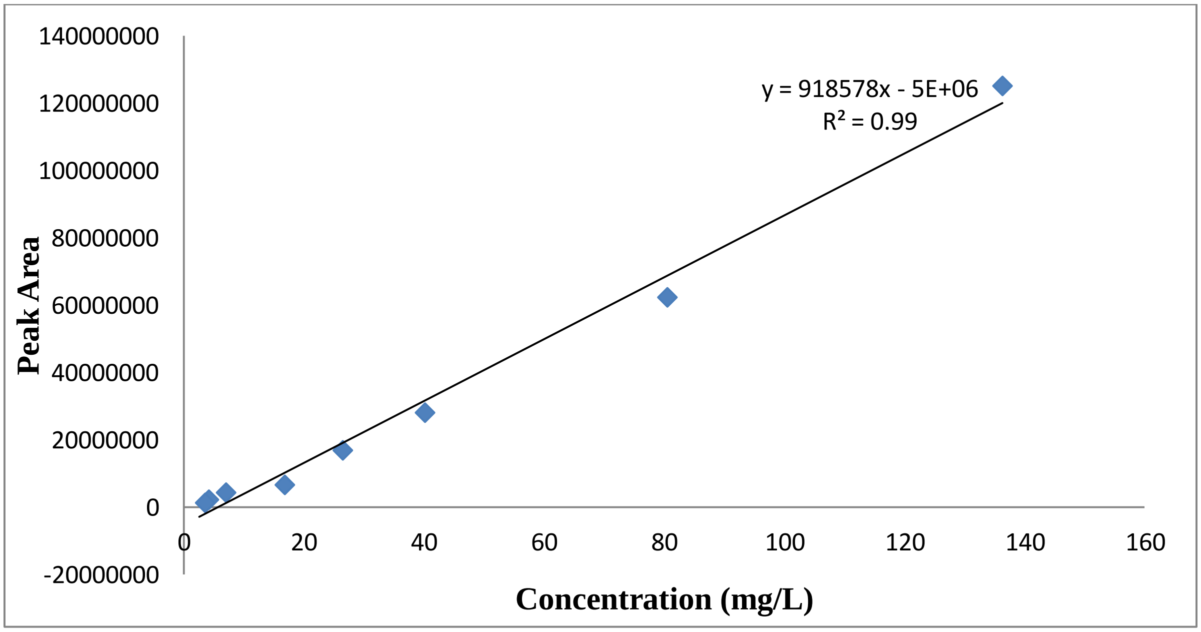

Figure 4. 7: Calibration curve for Chlorpyrifos

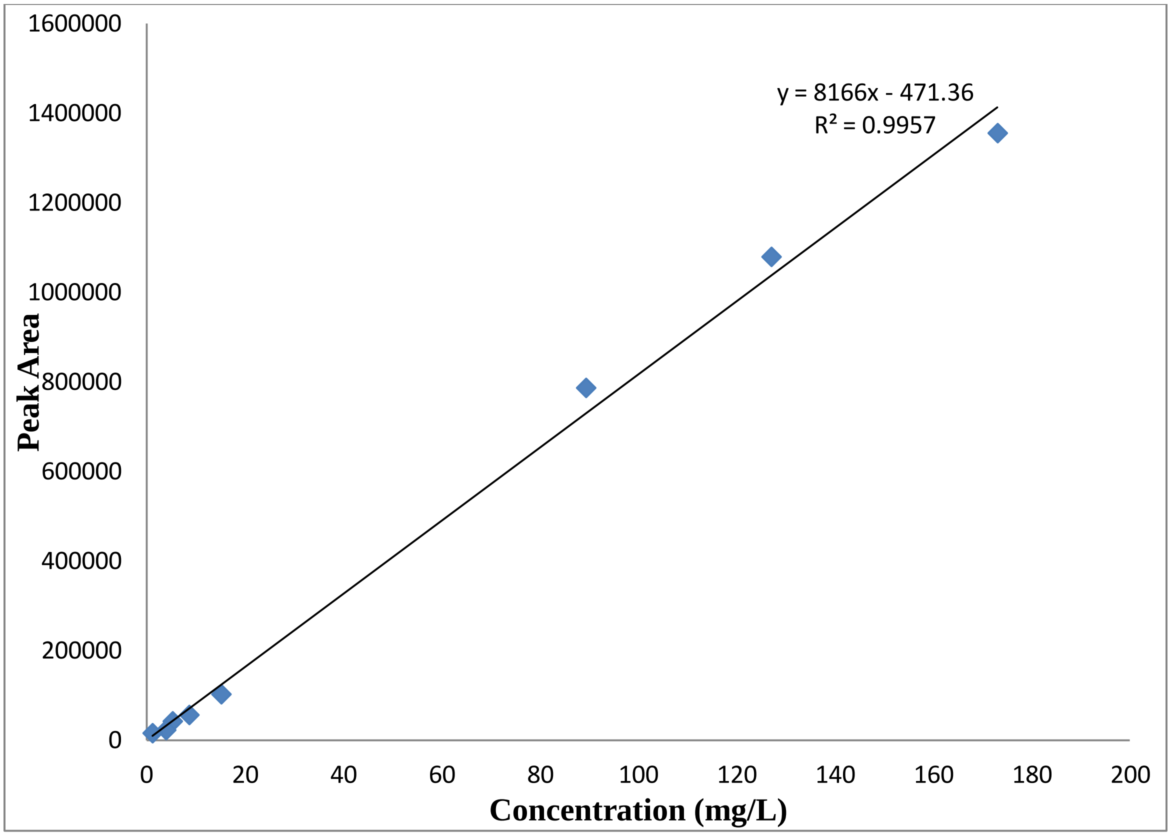

Figure 4. 8: Calibration curve for Dimethoate

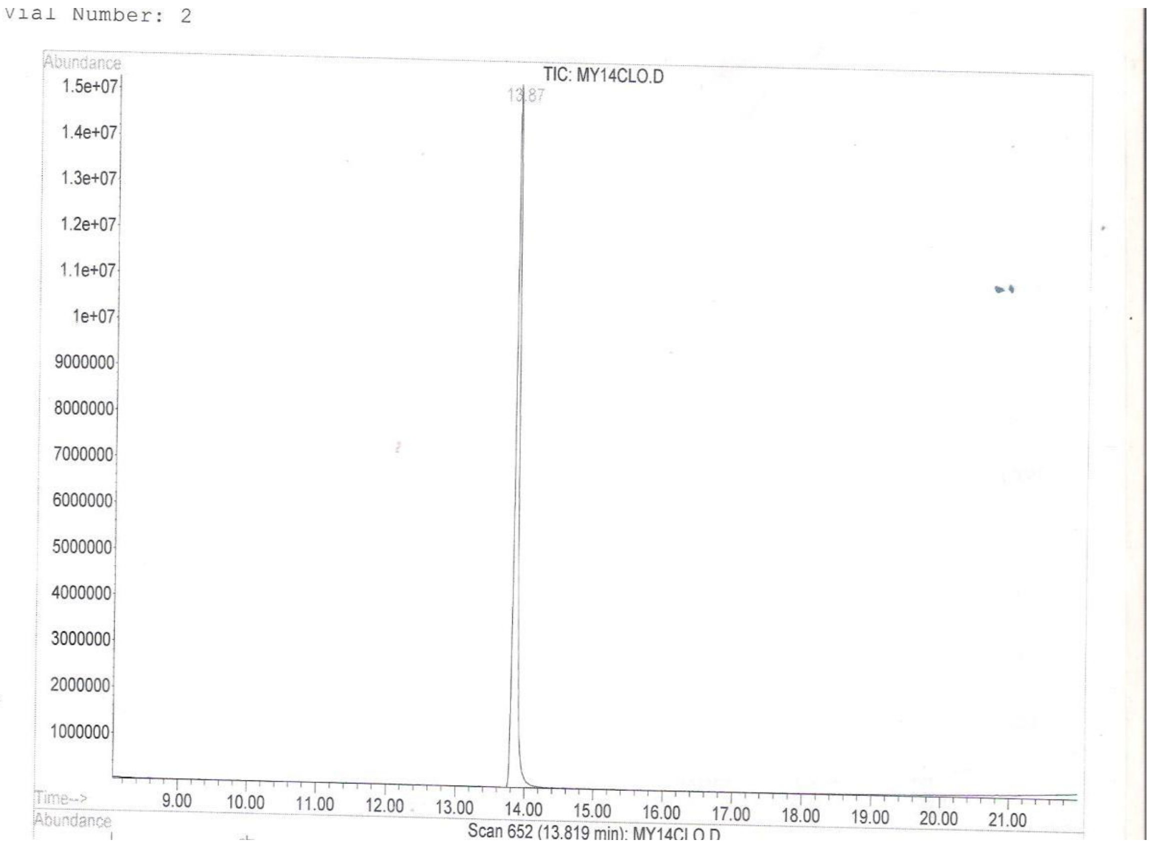

Figure 4. 9: Chromatogram for Chlorpyrifos Standard

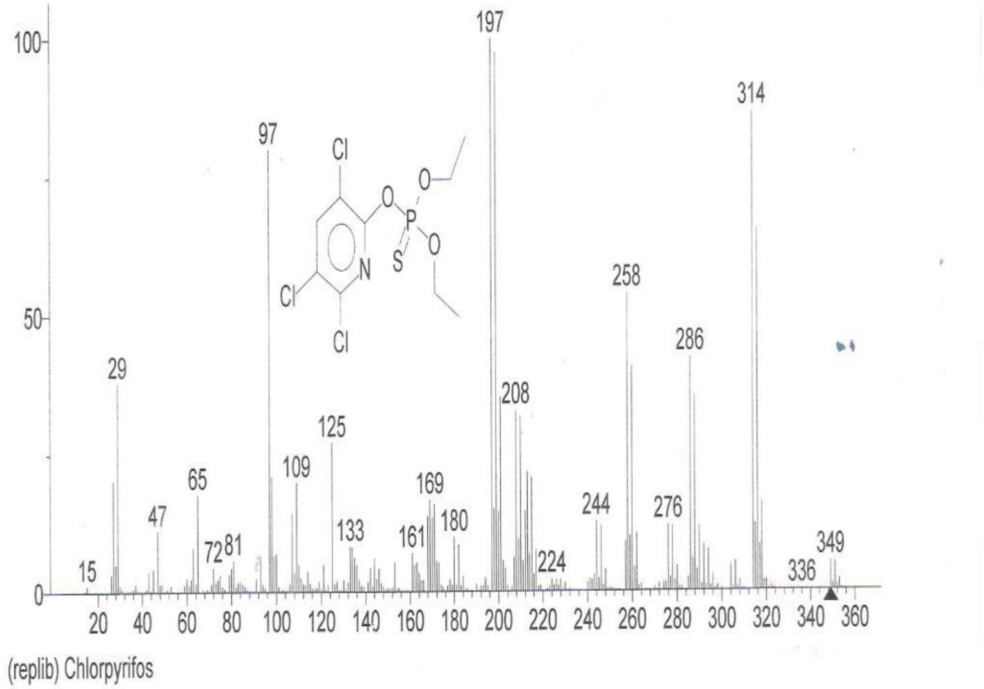

Figure 4. 10: Chemical structure and ionic Mass Spectra for Chlorpyrifos

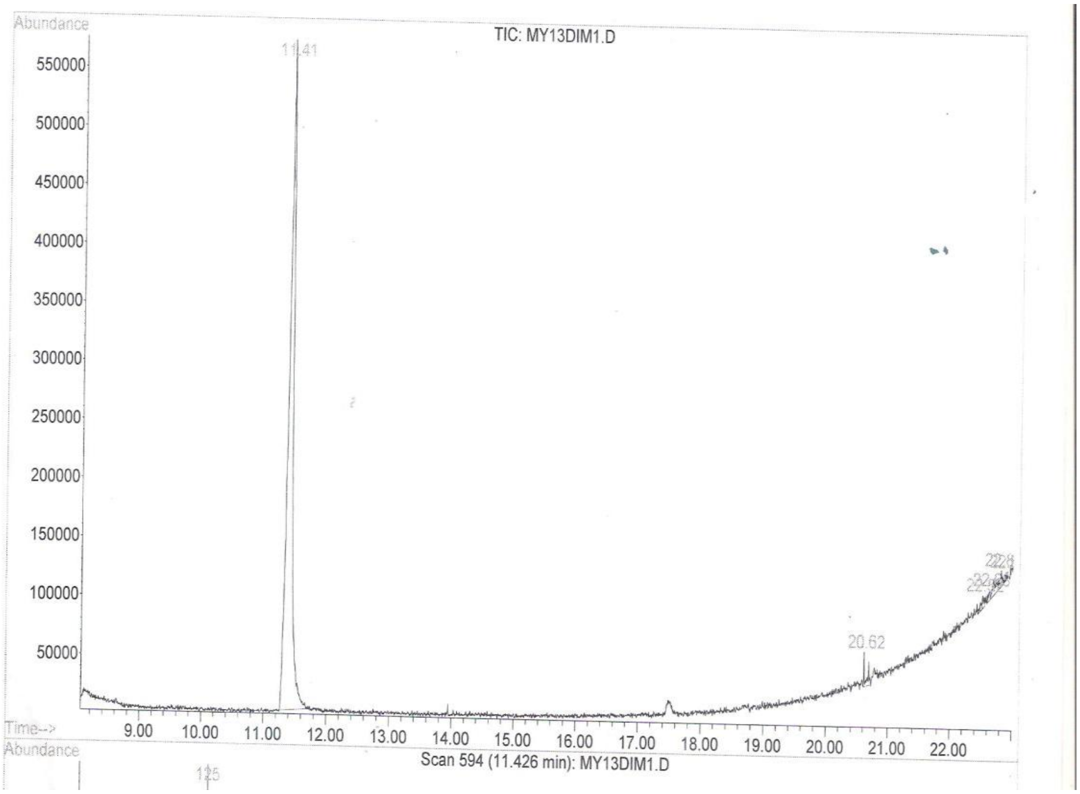

Figure 4. 11: Chromatogram for Dimethoate Standard

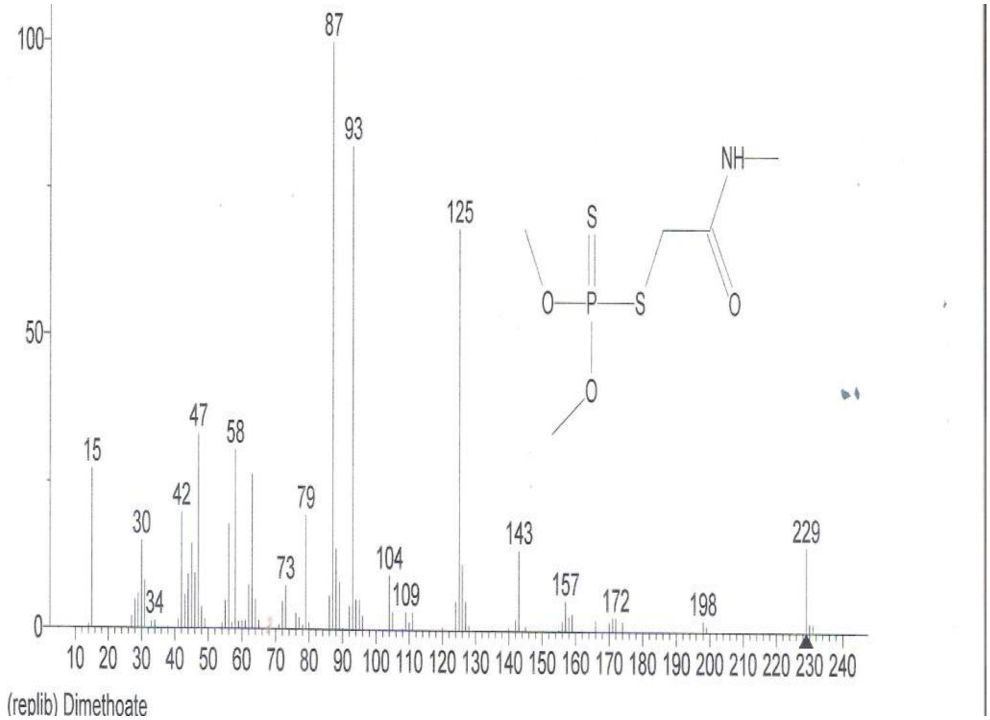

Figure 4. 12: Chemical structure and ionic Mass Spectra for Dimethoate

4.5 Dissiopation of Chlorpyrifos in soil

This study was conducted to establish whether application of chlorpyrifos on crops growing on chlorpyrifos treated soil result in elevated residue. The results based on dry weight for the dissipation of chlorpyrifos in soil are presented in Table 4.3.

Table 4. 3: Results of Chlorpyrifos Dissipation in Soil (mg/Kg, dw)

Time(Day)	Recovery Treated Soil	Untreated Soil (Control)
0	9.31±0.25	<LOD
7	3.36±0.04	<LOD
14	2.31±0.10	<LOD
21	1.34±0.06	<LOD

LOD: Limit of Detection

The trend of dissipation (Figure 4.13) was obtained by plotting determined concentration of Chlorpyrifos versus time in days for sprayed soil.

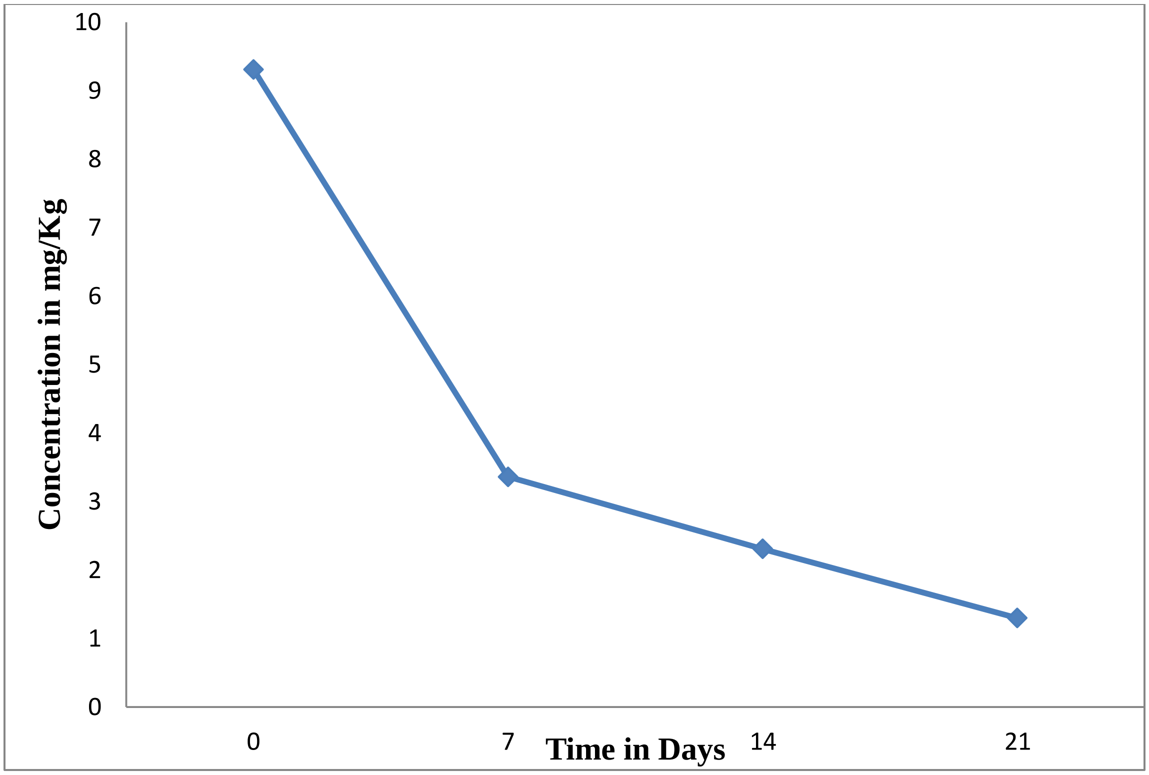

Figure 4. 13: Trends of Chlorpyrifos Dissipation in Soil

The concentration of chlorpyrifos in soil decreased over time (Figure 4.13). The average initial deposition of chlorpyrifos was 9.31± 0.25 mg Kg^{-1} (day 0) and the final residue was 1.34±0.06 mg Kg^{-1} on day 21. After 7 days 36 % of chlorpyrifos remained in the soil while by day 14 after the deposition of chlorpyrifos in the soil, 24 % of the initial deposited pesticide remained in the soil and 13.96 % of the initial deposited chlorpyrifos remained in the soil by day 21. The results showed that there was rapid dissipation of chlorpyrifos in the soils for the first 7 days and that the characteristic two-phase dissipation pattern showing the initial faster dissipation rate followed by lower rate starting after 7 days was seen and which is much consistent with other reports from other soils [Langat, 2011].

The data was fitted into Langmuir-Hinshelwood kinetic model for reaction rate dependence on initial reactant concentration [Kar *et al.*, 2013].

$r= dC/dt = kKC/(1+KC)$--(1)

Where r is the rate of reaction (mol/L.min), C is the equilibrium concentration of reagent (mol/L), t is the time (min), k is the rate constant (1/min), and K is the Langmuir constant (L/mol). When the initial concentration Co is <<<1, the denominator in equation 1 above can be ignored as 1, and the equation can be simplified to an apparent first-order equation:

$dC/dt=kKC$---(2)

$dC/C=kKdt$--(3)

$dC/dt = -Kt$ −−−−−−−−−−−−−−−−−−−−−(4)

Integrating equation 3 and taking boundary conditions of C = Co at t=0, gives

$Ln(Co/Ct)= kKt=k_{abs}$----------------------------------- (5)

Or

$Ct= Coe^{-kt}$ --- (6)

This is the first order rate equation, also written as:

$\ln C_t = \ln(C_0) - K_{obs}Xt$ −−−−−−−−−−−−−-------(7)

Where; C_t= pesticide concentration at time, t

K_{obs}= first order rate constant

t= time in Days

C_o= the original chlorpyrifos concentration

Consider the half-life of the reaction where the remaining concentration of the pesticide is half the original amount; $C_t= C_o/2$ and substituting in equation 7 above gives:

$Ln(C_o/2C_o=-Kt_{1/2}$--(8)

$Ln\ 0.5=-Kt_{1/2}$ ---(9)

$-0.693/K =t_{1/2}$ --(10)

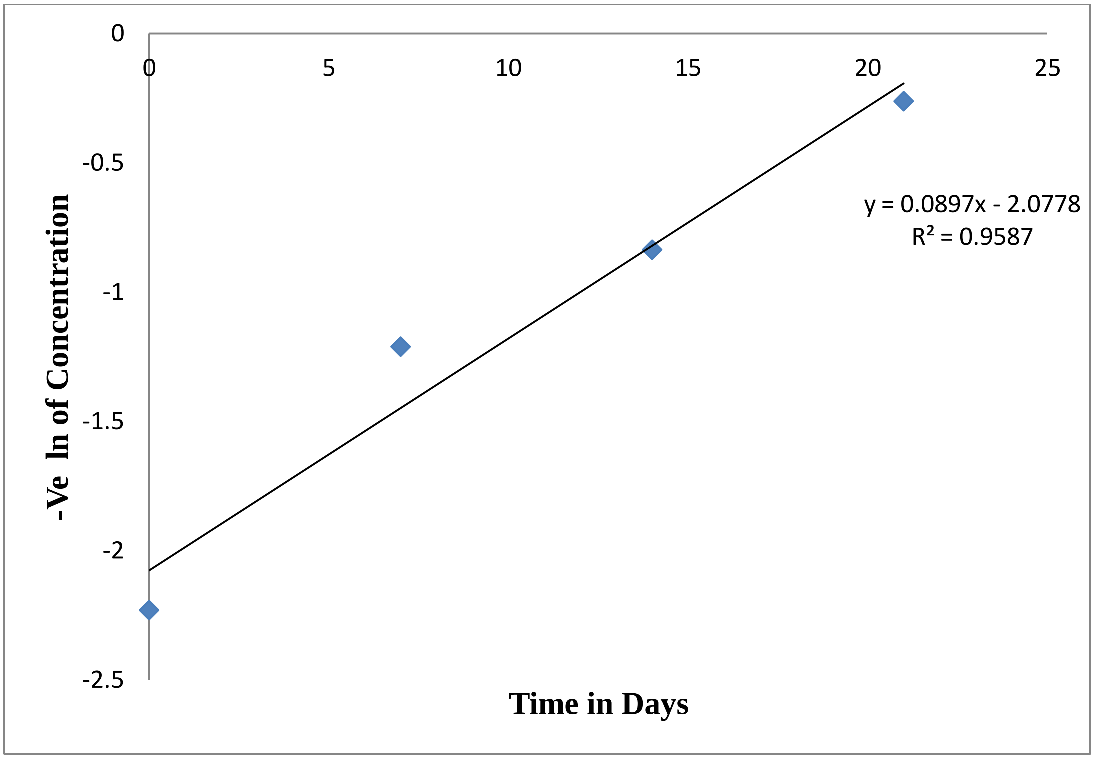

Figure 4. 14: Regression curve for disappearance of Chlorpyrifos from Soil

Equation 7 is in the form of y= mX + C. A plot of ln(C_t) verses time (t) gives a straight line, the slope of which upon linear regression equals the apparent first- order rate constant $K_{obs.}$ In this case, the K_{obs} are the observed degradation rate constant. The values obtained by this analysis were the same as that of the exponential regression analysis. Based on first order kinetic, a plot of negative ln concentration of residues versus time t (days) Figure 4.14, gave a regression equation, y = 0.0897x-2.0778. A gradient of 0.0897 was obtained (which is equivalent to the constant K_{obs}). In this study the degradation of chlorpyrifos follows Langmuir-Hinshelwood kinetic equation and using equation 10, the half-life of chlorpyrifos in soil was 7.8 days by the Langmuir-Hinshelwood kinetic model [Langat, 2011 and Lalah *et al.*, 2009].

This is within reported ranges from previous studies in which laboratory experiments, reported a half- life in the range of 3–8 days [Singh *et al.*, 2006]. Further it was observed that chlorpyrifos persisted in a low pH soil, i.e., less than 3 % of the pesticide had degraded after 10 days and more than 50% of chlorpyrifos was dissipated at a higher pH soil (pH 8.5) [Singh *et., al* 2006]. Another study reported that the half-lives in humid tropical soils from Malaysia were typically 7–120 days, however, it was also reported that some half-lives were 257 days in the soils containing less soil microbial populations [Chai *et al.,* 2013]. In the literature, it was reported long environmental dissipation half-lives of chlorpyrifos, of up to 4 years, depending on application rate, ecosystem, and pertinent environments [Gebremariam *et al.,* 2012]. Since chlorpyrifos presented low water solubility and a higher log K_{ow}, it had a strong tendency to sorb to organic matter and soil. Stability and effectiveness had made chlorpyrifos one of the most popular pesticides worldwide but on the other side its persistence had raised environmental concerns [Kamrin, 1997]. Since this study was done in a container in a green house the result shows that chlorpyrifos most probably was lost through volatilization or conversion to other metambolites.

4.6 Fate of Chlorpyrifos in French Beans

The spray mixture applied to the French beans contained Chlorpyrifos. The plants growing on the soil had non detectable residues of chlorpyrifos. The French beans that matures in 60 days were treated with chlorpyrifos, 21 days before the expected first harvest day. Collected samples were analysed and the results obtained is presented in Table 4.4, and the dissipation trends of chlorpyrifos in French beans is presented in Figure 4.15.

Table 4. 4: Results of Chlorpyrifos Dissipation in French Beans in mg/Kg (Dry Weight)

Day	Treated French Beans	Untreated French Beans
0	33.72±1.87	<LOD
7	1.47±0.47	<LOD
14	1.41±0.14	<LOD
21	<LOD	<LOD

LOD: Limit of Detection

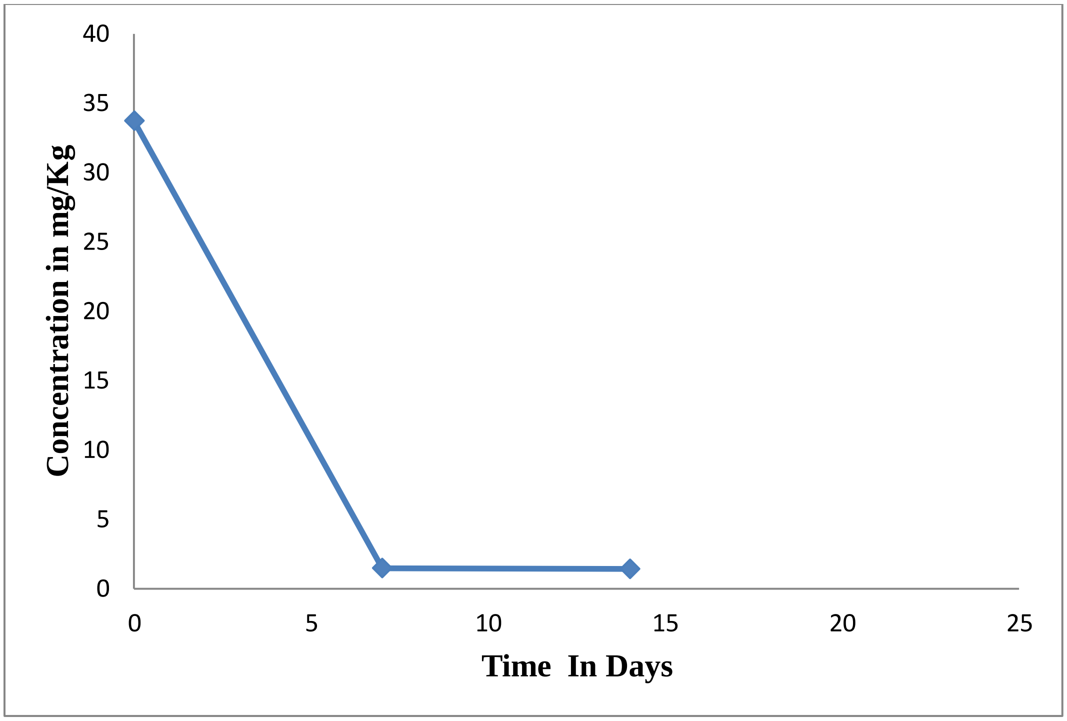

Figure 4. 15: Trends of Chlorpyrifos Dissipation in French Beans

As can be seen in Figure 4.15, the dynamic curve demonstrated that chlorpyrifos residues dissipated significantly in the first few days and persisted in the crops for extended period of time. The concentration of chlorpyrifos in French beans decreased over time (Figure 4.15). The average initial deposition of chlorpyrifos was 33.72±1.87 mg Kg^{-1} (day 0) and the final residue was BDL on day 21. The results showed that there was rapid dissipation of chlorpyrifos in French beans during the first 7 days and that the characteristic two-phase dissipation pattern showing the initial faster dissipation rate followed by lower rate starting after 7days was seen and which is much consistent with other reports from other soils [Fang *et al.,* 2006].

Half-life of chlorpyrifos in French beans was calculated using equation 10 and data obtain (Table 4.4). The half-life ($t_{1/2}$) of chlorpyrifos was calculated through regression analysis assuming the loss of chloripyrifos follows Langmuir-Hinshelwood kinetic model, after k was determined and was found to be 3.05 days. The regression curve for the disappearance of chlorpyrifos in French beans is shown below which was obtained by graph of negative logarithm of the concentration of the residues against time and it had correlation of R^2 =0.7598

As compared to its half- life in Brassica chinensis (5.81 days), Lettuce (3.92 days), Celery (5.45 days), Asparagus lettuce (3.90 days), Pepper (2.64 days), Eggplant (3.00 days) [Xiang-Yang Yu *et.,* *al* 2014]. The concentration of chlorpyrifos on the pre-harvest interval (PHI) day, (21) was calculated using the equation $C_t = C_o e^{-kt}$ Where, C_t is concentration of chlorpyrifos at t = 21(PHI), C_o is concentration of chlorpyrifos at t= 0 and k is the first order rate constant. The concentration of chlorpyrifos on the PHI day was found to be 0.05 mg/Kg. Because of chlorpyrifos' high hydrophobicity (high K_{ow} value), the pesticide would readily enter into the inner parts from the surfaces resulting in high residue levels. A portion of the residues may be transferred from leaves to the growing plant. The amount of residue at harvest depends upon factors such as the application rate, time interval between last application and harvesting, and the type of crop. The minimum residue levels (MRL) for European Union is 0.05 mg/kg for chlorpyrifos. The calculated residue level of the plant in study is the same as the EU MRL this shows that if the pesticide is applied appropriately it does not result to elevated residue levels.

4.7 Assessment of Chlorpyrifos Residues in French Beans

Eleven French beans samples were analysed for chlorpyrifos residues. The survey targeted twelve samples but supermarket M did not have the commodity at the time of sampling. The results of the tested samples are presented in table 4.5.

Table 4. 5: Results of Chlorpyrifos Residues in French beans

Seasons	**Kangemi Market**	**Muturwa Market**	**Supermarket M**	**Supermarket U**
Warm and dry (January)	<LOD	<LOD	<LOD	<LOD
Long rains (March)	<LOD	<LOD	<LOD	<LOD
Cool and dry (July)	<LOD	<LOD	*	<LOD

* Commodity not available in the market at the time of sampling.

The results show that chlorpyrifos residues were not detected in French beans from two open air market outlets and two supermarket outlet surveyed. This could be attributed to the fact that the GC-MS machine might be having high detection limit than the available pesticides residue in the food. This case is good since all the produce being sold in the four sites had below the European Union limit of 0.05 mg/Kg.

4.8 Assessment of Dimethoate Residues in French beans

Eleven French beans samples were analysed for dimethoate residues. The survey targeted twelve samples but supermarket M did not have the commodity at the time of sampling in July 2014. The results of the tested samples are presented in Table 4.6.

Table 4. 6: Results of Dimethoate Residues in French beans

Seasons	Kangemi Market	Muthurwa Market	Supermarket M	Supermarket U
Warm and dry (January)	<LOD	<LOD	<LOD	<LOD
Long rains (March)	<LOD	<LOD	<LOD	<LOD
Cool and dry (July)	<LOD	<LOD	*	<LOD

* Commodity not available in the market at the time of sampling.

The results show that dimethoate residues were not detected in French beans from two open air market outlets and two supermarket outlet surveyed. This could be attributed to the fact that the GC-MS machine might be having high detection limit than the available pesticides residue in the food. This is good since all the produce being sold in these four sites had below the European Union limit of 0.05 mg/Kg.

4.9 Discussion

Farmers in Kiambu County use pesticides to control insect pests and weeds, Insect pests that are commonly encountered by farmers in Kiambu County, Kenya included diamondback moth, *P. xylostella*, cutworm, *Agrotis ipsilon* (Hufnagel) (Lepidoptera: Noctuidae), cabbage white butterfly, *Pieris brassicae* (L.) (Lepidoptera: Pieridae), aphids, *Brevicoryne brassicae* (L.), *Lipaphis erysimi* (Kaltenbach) and *Myzus persicae* (Sulzer) (Homoptera: Aphididae), fruit borer, *Heliothis armigera* (Hu¨ bner) .

The choice of a given Pesticide by farmers depends on whether the pesticide enables the farmer to get yield as indicated by 46% of the respondents, followed by cost effectiveness of the pesticide with 30% of the respondents noting it as an important factor. Also 6% used a given pesticide because it was suggested by NGO, While 4% used a given pesticide because it was suggested by the agrochemical dealers and the sales agent of the agrochemical industries. Also 14% of the respondents said they were suggested by other farmers. Out of the fifteen commonly used pesticides in Kiambu County 7% are classified by World Health Organization [WHO 2002] as highly hazardous, 40% moderately hazardous and 53% slightly hazardous by WHO (Table 4.1).

The interviews indicated a low awareness among farmers about risks and safe handling of pesticides, 68 % of the farmers even those who had training on how to handle and the effects of pesticides did not use protective devices when handling pesticides. The dose used and the spraying intervals seldom correlate with those recommended by the manufacturer, Many farmers miss safety information and recommendations of dose on the pesticide because they do not read the instruction manual this is very risk to both the farmers and the environment. From interview results it is clear that 35 % of the farmers in Kiambu County are not aware of the ban or restriction imposed on some pesticides in Kenya [PCPB, 2008], these pesticides can easily find their ways into the region from other counties such as Nakuru and Kajiando where obsolete stock piles have been reported [NES, 2006]. 80 % of the farmers are aware of the effects of pesticides to the environment.

Study conducted by Abong'o et al., (2014) in Nyando catchment, documented a list of agro-chemicals used along the River Nyando drainage basin, and the recommended rates of applications, environmental and human health impacts and toxicity to birds and bees. Further the study documented that most of the pesticides used in Nyando catchment area are organophosphate and are moderately hazardous. However some individual farmers still used banned or restricted organochlorine pesticides. There are major pests' problems in River Nyando catchments and therefore an active pest management programme is necessary to secure the harvest in the region. Most farmers are ignorant of the safe use and handling of the pesticides, which results in some injuries and chronic illnesses.

In the dissipation of chlorpyrifos in soil it was observed that the concentration decreased over time (Figure 4.13). The average initial deposition of chlopyrifos was 9.3±0.25 mg/kg (day 0) and the final residue was 1.34±0.06 mg/Kg on day 21. The dissipation curve for the pesticide showed that the dissipation of the residues has initially fast rate and later slow rate. The half life was found to be $t_{1/2}$ = 7.8 days, This is within reported ranges from previous studies in which laboratory experiments, reported a half- life in the range of 3–8 days [Singh *et al.,* 2006]. The into metabolites, conversion of the same into bound residues in the soil, volatilization to the atmosphere, leaching and microbial mineralization. The dissipation of chlorpyrifos pesticide was initially fast because the processes responsible for the degradation of chlorpyrifos are concentration dependent; initially the concentration of the pesticide is high. As time advances the concentration of chlorpyrifos decreases and this reduces the rate of dissipation of chlorpyrifos.

Study by Singh et al., (2006) reported that the laboratory experiments half- life days for chlorpyrifos in the range of 3–8. Further it was observed that chlorpyrifos persisted in a low pH soil in which less than 3 % of the pesticide had degraded after 10 days and more than 50 % of chlorpyrifos was dissipated at a higher pH soil (pH 8.5). Another study reported that the half-lives in humid tropical soils from Malaysia were typically 7–120 days, however, it was also reported that some half-lives were 257 days in the soils containing less soil microbial populations [Chai *et al.,* 2013]. Long environmental dissipation half-lives of chlorpyrifos, of up to 4 years, have been reported depending on application rate, ecosystem, and pertinent environments

[Gebremariam *et al.,* 2012]. Since chlorpyrifos presented low water solubility and a higher log K_{ow}, it had a strong tendency to sorb into organic matter and soil.

In comparison to studies carried out in other pesticides Getanga et al (2000) reported half- life of malathion and dimethoate, of $t_{1/2}$ value of 17 days for malathion and 72 days for the dimethoate. The results clearly show that malathion dissipated faster than dimethoate from the soil. The results showed that dimethoate is more persistent than malathion in the soil. Faster dissipation of malathion was accelerated by the degradation of the bound residues, which would normally increase the persistence of a pesticide in the soil since they are sequestered in the soil. Malathion is not efficiently absorbed from the soil by the pea plant due to its low solubility in water and high log Ko/w. Dimethoate in the soil is readily available to the pea plant by water mass flow through the xylem [Getenga *et al.,* 2000].

In the dissipation of chlorpyrifos in french beans the concentration decreased over time (Figure 4.14). The average initial deposition of chlopyrifos was 33.72±1.87mg/Kg (day 0) and the final residue was 1.41±0.14mg/Kg on day 14. The dissipation curve for the pesticide show that the dissipation of the residues is initially fast and slow in the later stages. The half life was found to be $t_{1/2}$ =3.05 days, This is within reported ranges from previous studies in which laboratory experiments, reported a half- life in the range of 0.91 days for pepper plants, 3.92 days for lettuce plant, 3.92 days for asparagus lettuce plant, 5.82 days for brassica chinensis plant, 3.00 days eggplant plants and 5.46 days celery plant [Xiang-Yang Yu *et al.,* 2014]. One of the key factors for the degradation of the pesticide on the plant could be photodegradation of chlorpyrifos [Nieto *et al.,* 2009]. The leaf characteristics may affect how the pesticide would be retained on the surfaces of the leaves and then the penetration into the plant tissues, leaf surface roughness [Gaskin *et al.,* 2005], plant species, nature of harvested crop and metabolic activities like rate of uptake, growth, translocation storage and excretion [Edwards, 1975],as well as the content of water repellent cuticular waxes [Bargel *et al.*, 2006]. In addition environmental factors such as temperature, precipitation, humidity and air movement (wind) influence the persistence of pesticides on plants. The total quantity and form of a pesticide reaching plants and soil depends on the site and method of application, type of equipment together with the formulation type. These consequently influence pesticide persistence on both the plants and soil [Edwards, 1975].

The assessment of chlorpyrifos and dimethoate in french beans from two open air market and two supermarkets within Nairobi gave results that were below detection limit. These can be attributed to the fact that the amount of residue at harvest depends upon factors such as the application rate, time interval between last application and harvesting, and the type of crop, hence it might be that the farmers apply the pesticides and leave the plants on the field long enough before the time of harvesting.

Studies conducted by Musila (2011) reported chlorothalonil in French beans samples collected from two supermarkets and two open air markets in Nairobi. Higher residues were observed during the warm and dry season ranging from 1.60 to 21.40 µg/Kg, compared to the long rains season that reported 0.81µg/Kg. No detectable residues were reported during the cool and dry season.

Another survey conducted by the Pesticide residue committee (PRC) of the UK in 2008 where 4129 samples were tested reported that around half the samples tested did not have detectable pesticides residues while the percentage of food tested which contained residues above trading standards and the MRLs remained at 1.2 %. The monitoring programme aimed at foods where residues were expected to be found. In this programme, a total of 2309 samples of fruits and vegetables were tested for up to 212 pesticides. Residues were found in 1484 samples (64.3 %)

with 49 samples (2.1 %) containing residues above the MRL. Residues above MRL were reported in apples, beans in pods chilli peppers, Chinese cabbage, cucumber, grapes, melons, oranges, pears, peas in pods, potatoes, spinach, tomatoes and yams. Chlorothalonil residues were not detected in any of the samples; however, four samples of beans in pods originating from Kenya contained dimethoate residues above MRL, one contained omethoate residues above the MRL while the other three had detectable residues of the same pesticide. One of the four samples contained residues of methomyl above MRL and detectable residues of dicofol in addition to the dimethoate and omethoate. Produce from other countries including India, China, Egypt, Ghana and Morocco Contained pesticide residues. These countries compete for the EU market with Kenya, and therefore Kenya must strive to maintain the market by meeting the trade requirements.

CHAPTER FIVE

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusion

The study investigated the residue behavior of chlorpyrifos in French beans and soil in greenhouse experiment. Chlorpyrifos was found to persist more in soil than in French beans with a half-life of 3.02 days and 7.8 days in French beans plants and soil respectively. Chlorpyrifos residue on the pre-harvest day was 0.05mg/Kg which is the same as both the EU and Codex MRLs. This shows that if the pesticide is applied in the right way it will not result into elevated levels during the time of harvesting. The present studies clearly show that in the green house French beans sprayed with chlorpyrifos at recommended dosages and at normal harvesting interval of 21 days after spraying are safe. All the French beans samples collected from the local open air market and supermarkets from Nairobi County had concentration that was below detection limit.

Most of the pesticides used in farms in Kiambu County are organophosphates, carbamates and pyrethroids and some are highly hazardous. Most farmers are ignorant of the safe use on handling of the pesticides, which results in some injuries and chronic illnesses, therefore training and pesticide handling is necessary for all the farmers. There are major pests' problems in Kiambu County and therefore an active pest management programme is necessary to secure the harvest in the region. From the results of this study and other studies conducted in Kenya Musila (2011), Maundu, 2009 and Gitanga et al., 2000 it would be important to monitor and ascertain the residue levels of pesticides in soil and various horticultures. This would give information to be used in surveillance programs for pesticide residue levels in the agricultural Kenya.

5.2 Recommendations

From the survey it was found that generally there was low level of understanding on the safe use and handling of pesticides, therefore Steps should be taken to educate the public on the safe use of pesticides in order to reduce contamination of the environment with pesticide. These should be done with the help of the government, agrochemical industries and NGOs.

More sampling times is suggested for study of dissipation rate of chlorpyrifos and the sampling should be done after every two days as the pesticide degrades fast.

National Pesticide Residues Monitoring and Surveillance is recommended on produce sold in Kenyan markets and those destined for export to protect consumers, assess implementation of GAP, detect unauthorized or misuse of pesticides and support trade.

Further study on the dissipation trends of chlorpyrifos and dimethoate in tropical soils cores to establish the dissipation rate is recommended. This could be coupled with a leaching ability of the pesticide in tropical soils.

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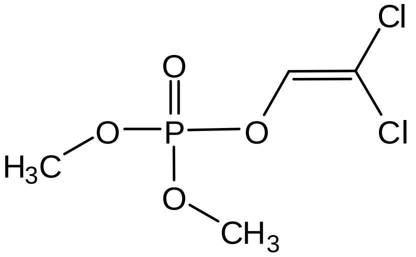
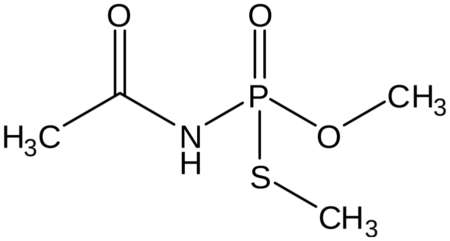
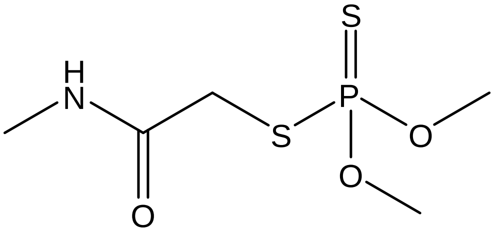
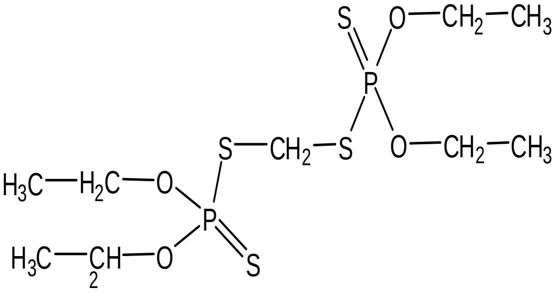
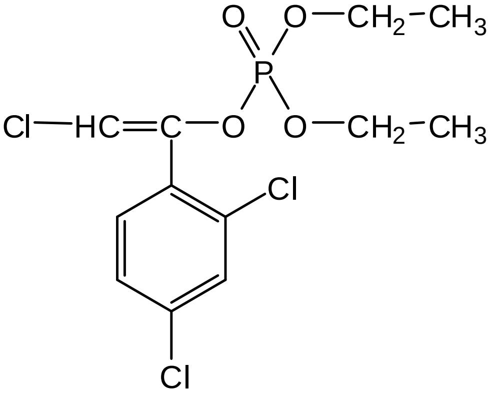
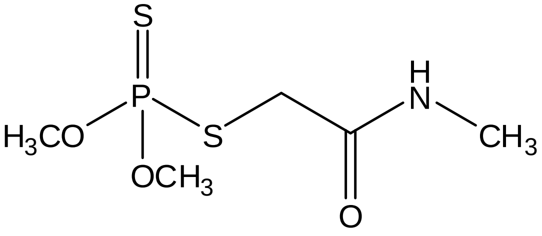
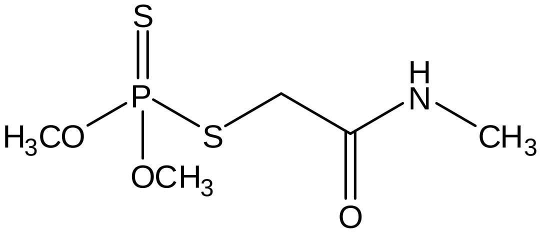
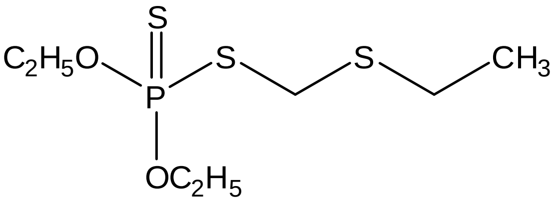
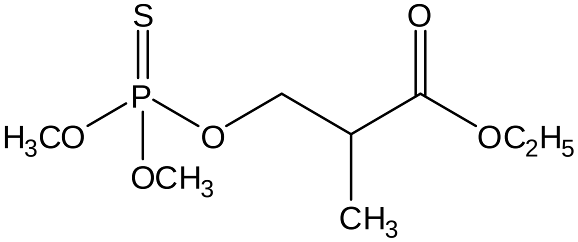
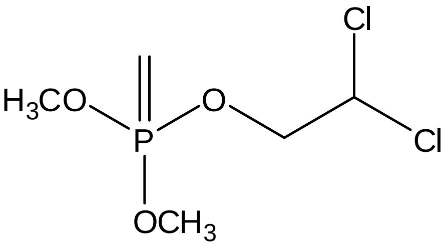
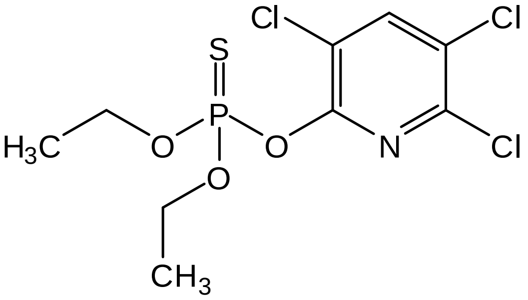
APPENDICES

Appendix I

Figure 1.1 : Some of Organophosphorus pesticides

SN	Name	Structures
	Dichloros	
	Acephate	
	Dimethoate	
	Ethion	

	Chlorfenvinphos	
	Diazinon	
	Dimethoate	
	Disulfoton	
	Mevinphos	
	Dichlorvos	

	Dichlorvos	

Appendix II

QUESTIONAIRE ON THE USE OF PESTICIDES IN KIAMBU COUNTY.

Sub County…………………. ...Location ……………..Sub-Location……………..

At……………Sampling Point Date of interview………… Questionnaire Number……

Topography of the region………………

(A) Farmer's Particulars

Gender male ( ) Female ( )

Age?

How long have you lived in this area?

The highest level of education reached please tick (Primary, Secondary and post secondary)

Most important source of income for the household?

(B) Information on Farming activities

How many hectares of land do you have? ……….. Ha

Which Type of farming do you practice? [A] Small scale farming [B] large scale Farming.

What type of crops do you grow?

Which crop(s) do you commonly grow for export purposes?

Why this crop(s) and not any other?

How much land have you devoted for this crop?

For how long have you been using this piece of land for this crop(s)?

Do you practice any crop rotation? [Yes] [No]

If No, Why?

If [Yes], for which crops?

When do you plant your crops and why?

How many times do you plant this type of crop(s) in a year?

When do you harvest the crop(s)?

What problems have you experienced with the crop(s)?

Is it a common problem, how do you solve it?

(C) Use of pesticides in farming

Do you use any pesticides for your crop(s)? [Yes], [No]

If [No], why?

If [yes], which one(s)?

How long have you been using the pesticide(s) on the farm(s)?

How much of each pesticide(s) do you use per hectare and what is the yield?

How and when do you apply the pesticides?

Are there any guide lines given to you before buying any pesticides chemicals?

Who gives the guidelines?

Do you read and understand the instructions and procedures before using pesticides?

Do you use any form of protection when handling pesticides chemicals?

If yes which one?

Where do you dispose containers after use?

What is the cost per unit?

Have you ever had any training on pesticides managements and safety?

In which institution were you trained?

How long did the training take?

Have you ever received any training on quality, food safety pertaining to pesticide residues?

If yes from who did you receive the training?

What role did the government play in your training?

Do you use any form of protection when handling pesticides chemicals?

If yes which one?

if yes give some details

Do you know of any banned or restricted pesticides in Kenya?

(D) Health problems associate with use of pesticides

Do you have information on the pesticide related pollution in this area?

If yes give some details?

Have you experienced any health problem suspected/or due to exposure to the Pesticide(s)?

[Yes], [no]

If [yes], when? How was it treated?

If [no], have you gone for any medical check-up?

Do you have any or had any health problem apart from the one(s) above.

Appendix III

Table 3.1: Summary of Field Questionnaire on the use of pesticide in the area.

Gender	Males				Female			
Age (years)	18-24	25-34	35-44	over 45	18-24	25-34	35-44	Over 45
Number	3	5	12	18	1	7	11	7
Purpose of using pesticides	To control pests that destroys crops and vegetables. To control ticks and fleas in livestock, To control mosquitoes.							
Factors Affecting the Choice of Pesticide								
Increase Yield	2	2	4	8	0	3	4	2
Cost Effective	1	2	5	7	1	2	3	2
Suggested by NGOS	0	0	1	2	0	0	1	1
Suggested by other farmers	0	1	1	0	0	2	2	1
Suggested by Agro-Chemical dealer	0	0	1	0	0	0	1	0
Good for Environment	0	0	0	1	0	0	0	1
Training on pesticides handling								
With basic training	0	1	3	12	1	3	5	5
With no basic training	3	4	7	3	0	3	6	1
Advanced training	0	0	1	3	0	1	0	1

Training on pesticides Residue in Food								
With basic training	0	1	3	15	1	4	5	5
With no basic training	3	4	7	3	0	3	6	1
Advanced training	0	0	1	0	0	0	0	1
Safety and Control								
Always read instruction menu	2	4	6	15	1	5	8	5
Not aware of instruction menu	0	0	1	0	0	2	1	0
Do not read instruction menu	1	1	4	3	0	0	3	2
Education Level								
Primary	2	0	5	4	0	3	6	1
secondary	0	5	6	6	0	3	3	1
Post-Secondary	1	0	1	8	1	1	2	5
Pesticide Ban								
Aware of the ban	1	4	5	13	0	5	7	6
Not aware of the ban	2	1	8	5	1	2	4	1
Effects of Pesticides to the Environment								
Aware	3	4	10	18	1	7	10	7
Not aware	0	1	2	0	0	0	1	0

Sources of Information								
NGOS	0	1	6	6	0	4	6	3
Radio	2	3	3	6	1	3	3	2
Agriculture Extention Officer	0	1	1	2	0	0	1	1
Agro- Chemical Dealer	1	0	1	1	0	0	1	0
Agro- Chemical Industries	0	0	1	4	0	0	0	1
Incidents and Accident reported	5							
Technical support	none							

Table 3.3: Irrigation water Suitability Parameters

Parameters	Irrigation water	Critical level
pH	7.9	N/A
Conductivity(µs/cm)	310	1
TDS (mg/L	155	N/A
Sodium (m.e/L)	6.21	N/A
potassium (m.e/L)	0.42	N/A
Calcium (m.e/L)	0.35	N/A
Magnesium (m.e/L)	0.01	N/A
Carbonates (m.e/L)	ND	N/A
Bicarbonates (m.e/L)	2.73	N/A
Chlorides (m.e/L)	10.65	N/A
Sulphates (m.e/L)	5.775	N/A
Sodium Adsorption Ratio (SAR)	14.64	5.0

Note

Note Applicable is used because the quality of irrigation water is depended on SAR and EC. The SAR is a ratio of Na ions to Ca and Mg ions expressed as;

$$\mathbf{SAR} = \frac{\mathbf{NA^{+}}}{\sqrt{}\,(\mathbf{Ca^{2+} + Mg^{2+}})/2}$$

Table 3.4: Test soil Fertility evaluation Parameters and Physicochemical properties

Parameters	Test Soil	Critical level	Comment in relation to French beans Growing
pH	6.72	5.5	Slightly Acidic
Total Nitrogen %	0.48	0.2	Adequate
Organic carbon %	4.03	0.5	Adequate
Phosphorous (ppm)	29.5	30 ppm (Mehlich 1)	Low
Potassium (me %)	1.21	0.2	Adequate
Calcium (me %)	4.3	2.0	Adequate
Magnesium me %	1.9	1.0	Adequate
Manganese me%	0.30	0.11	Adequate
Copper (ppm)	2.33	1.0	Adequate
Iron (ppm)	61.5	10.0	Adequate
Zinc (ppm)	2.98	5.0	Low
Sodium me %	0.10	2	Adequate
Clay %	75	40	Clay soil, texture grade C
Silt %	16.9	-	
Sand %	8.1	-	
Bulk Density	0.7	-	
PF 0	84.48	-	Saturation point
PF 2	62.17	-	Field capacity
PF 2.3	42.67	-	Field capacity
PF 4.2	20.45	-	Permanent wilting point

Table 3.5: Volume of Pesticides Imported from Financial Year 2003/2004 – 2009/2010 (PCPB, 2010).

	2003-2004	2004-2005	2005-2006	2006/2007	2007/2008	2008/2009	2009/2010
Category	*Quantity in tones*	*Quantity in tones*	*Quantity in tones*	*Quantity in tones*	*Quantity in tones*	*Quantity in tones*	*Quantity in tones*
Insecticide	2165	2881	2844	2475	2887	2995	3181
Fungicide	1657	2031	2361	3190	2651	2340	2415
Herbicide	1396	1538	1311	1859	2289	2933	1840
Others	723	597	1192	1225	1330	1413	1396

Table 3.6: Value of Pesticides Imported from Financial Year 2003/2004 – 2007/2010(PCPB, 2010).

Category	2003/2004	2004/2005	2005/2006	2006/2007	2007/2008	2008/2009	2009/2010
	Value in ‘000 000’Kshs	*Value in ‘000 000’Kshs*	*Value in ‘000 000’Kshs*	*Value in ‘000 000’Kshs*	*Value in ‘000 000’Kshs*	*Value in ‘000 000’Kshs*	*Value in ‘000 000’Kshs*
Insecticide	2,411	2,077	2,031	1,181	3909	2,079	2,493
Fungicide	925	1,113	1,506	1,251	602	3,153	3,874
Herbicide	571	650	620	324	206	944	939
Others	142	133	337	362	191	1,167	918