

**RESIDUES CONCENTRATIONS OF CARBARYL PESTICIDE IN SOIL
AND TOMATOES FROM HIPPO, KINGFISHER AND HARNEKOP
GREEN HOUSE FARMS IN THIKA AND NAIVASHA, KENYA**

By

JACINTA MBITHE KINYUNZU

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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.

JACINTA MBITHE KINYUNZU

(156/68770/2011)

This thesis has been submitted for examination with our approval as university supervisors

.....
Prof. S.O. Wandiga
Department of Chemistry
University of Nairobi

.....
DR. D. A. Abong'o
Department of Chemistry
University of Nairobi

ABSTRACT

Pesticides are of great benefit to agriculture in Kenya due to decreasing quality and quantity of crop production due to insects, weeds, plant diseases, rodents and other pests. They also save lives through control of disease carrying insects. However pesticides are poisons and can contaminate the environment and affect human health. The study sought to determine the fate of carbaryl (1-naphthyl methylcarbamate) in tomatoes and soil was determined in Hippo farm in Thika (Kiambu County), Kingfisher and Harnekop farms in Naivasha (Nakuru County), Kenya.

These areas in which the farms were selected are dominated by intensive irrigated crop farming for local and other markets. Due to the sensitivity of the crop to pest invasion, pesticides and other agro-chemicals are in rampant usage. In addition tomatoes are widely consumed as food stuff in Kenya, its quantity of production and export is increasing since the year 2000, thus chosen for the study. The study focused on carbamate pesticides because they are among the most used pesticides in horticultural sector in Kenya. Carbamates are also known to be the most toxic group of pesticides causing both acute and chronic illness on exposure. Rates of degradation of the pesticides are a requirement to support the enforcement of the legislation, ensure trading compliance and conduct monitoring programs in dietary components.

Samples were collected and soxhlet extracted using organic solvents, investigated and quantified for carbaryl using a gas chromatograph-mass spectrometer (GC-MS). The half life of carbaryl dissipation was calculated using the Langmuir-Hinshelwood kinetic model equation and regression curves were drawn to get the rate constant. Results obtained indicate that carbaryl has a dissipation half-life of 2.92 days and 5.29 days in tomatoes and soil respectively from Hippo farm, 2.02 days and 5.21 days in tomatoes and soil respectively from Kingfisher farm and 5.24 days and 7.19 days in tomatoes and soil respectively from Harnekop farm. therefore Harnekop farm recorded the highest carbaryl half life in tomatoes and soil while Kingfisher recorded the

lowest. The concentration of carbaryl on the pre-harvest interval (PHI) day is 1.65 mg/Kg, 0.28 mg/Kg and 1.75 mg/Kg in tomatoes from Hippo, Kingfisher and Harnekop farms respectively. The inventory data of pesticide use in Hippo, Kingfisher and Harnekop farms indicate that the most commonly used pesticides in the regions are organophosphates, carbamate and pyrethroids. Most farm workers were observed to be aware of the safe use and handling of the pesticides, which results in reduction of injuries and chronic illnesses. All farm workers know the effects of pesticides residue levels on human and environmental health. This is an important awareness step the management of the three farms has taken in the conservation of the environment. All the farm workers investigated had been trained on the minimum pesticide residue levels (MRL) in food.

DEDICATION

This thesis is dedicated to my family: My dear husband Caleb Mulwa and my son Michael Kinyunzu Jnr .

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ABBREVIATION

ADI	Acceptable Daily intake
a.i	Active ingredient
EPA	Environmental Protection Agency
EPZA	Export Processing Zones Authority
FAO	Food and Agriculture Organization
FPEAK	Fresh Produce Exporters Association of Kenya
GAP	Good Agricultural Practice
GDP	Gross domestic Product
GC-MS	Gas chromatography - Mass Spectrometry
GoK	Government of Kenya
HCDA	Horticultural Crop Development Authority
KARI	Kenya Agriculture Research Institute
KEPHIS	Kenya Plant Health Inspectorate Services
MRL	Maximum Residue Limit
PCPB	Pest Control Products Board
PHI	Pre - Harvest Interval

UNEP	United Nations Environment Programme
USEPA	United States Environmental Protection Agency
WHO	World Health Organisation

UNITS OF MEASUREMENT

g	Grams
kg	Kilograms
µg	Microgram
ng	Nanogram
nm	Nanometre
ml	Millilitre
L	Litre
µL	Microlitre
ppm	Parts per millions
ppb	Parts per billions
ppt	Parts per trillions

CHAPTER ONE

INTRODUCTION

1.1. General Background

The agricultural sector is the mainstay of the Kenyan economy, contributing to 24% of national GDP directly and another 27% indirectly, this is by providing income by employing more than 40% of the population, and over 70% of the rural population (MTTI, 2007). However the sector is facing major challenges stagnant or declining levels of productivity, under exploitation of land, inefficiencies in the supply chain due to limited storage capacity, lack of post-harvest services, poor access to input markets and low value addition of most agricultural exports. The objectives of agricultural sector strategy have been increasing agricultural growth [Patrick *et al.*, 2006]. 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 [Ministry of Trade Tourism and Industry, 2004]. The agriculture sectors consist of six subsectors; industrial crops, food crops, livestock, fisheries, forestry and horticulture. Horticulture, the largest subsector, has recorded a remarkable export-driven growth in the past decade and contributes 33 per cent of the GDP and 38 per cent of export earnings [GoK, 2010]. Kenya's success in expanding horticultural exports (fruits, vegetables and cut flowers) is well known. Horticulture ranks second to tea in agriculture export earnings and it accounts for approximately 16 percent of domestic agricultural exports [Kenya Economic Survey, 2012].

Thus the horticulture sector is extremely important for the national economy. The export sector earned the country about US dollars 150 million the year 2003 from a volume of 72000 tones fruits

and vegetables, Over 60 % of these go to UK, the next largest market being Netherlands and France. Consequently it has been critical for the sector to meet not only stricter European Union Legislation on Maximum Residue levels but also the requirements of the European importers and retailers of which most major UK supermarkets now demand certification under EuroGAP standards. Kenya's horticultural sector has received a great deal of attention in her effort to achieve the vision 2030, over the past decade due to the rapid and sustained growth of its exports to Europe [Muendo and Tschirley, 2004]. This impressive growth has undoubtedly contributed to increased rural incomes and reduced rural poverty in Kenya [Muendo and Tschirley, 2004].

Between 40-60% of the horticultural producers are small and medium scale farmers. As many as 60,000 farming families and up to one million Kenyans out of a total population of above 45 million depend directly or indirectly on export of the vegetables for their living [World Bank, 2014]. The horticultural sub-sector employs approximately 4.5 million people countrywide directly in production, processing, and marketing, while another 3.5 million people benefit indirectly through trade and other activities [Horticultural Crops Development Authority, 2009]. Horticulture is a major source of livelihood to farmers generating in excess of \$1.0 billion in foreign earnings annually [HCDA, 2010]. Horticulture production therefore offers the best alternative for increased food self-sufficiency, improved nutrition and ensuring the generation of increased incomes and employment [Ganry, 2007; 2009].

The main horticultural crops grown in Kenya can be broadly grouped into fruits, vegetables and flowers. The major fruits grown include avocados, bananas, citrus, pineapples, mangoes and papaya, while the vegetables include cabbages, spinach, tomatoes, onions, chilies, pepper, carrots, French beans and Asian vegetables (karella, dhudi, brinjals). The area under production for the different horticultural crops occupy about 150,000 hectares.

The production of these crops is for both local and export market. However, a large percentage of the crops are consumed locally. A total of 2.75 million tons of horticultural products are consumed in the domestic market [HCDA, 2010]. Horticultural crops are high value crops generating higher profits than staple food crops per unit of land and the income thus generated can be used for different purposes in terms of eradicating hunger through meeting the food requirements and other necessities. For instance in 2009 the gross production value of banana was USD 317 million compared to USD 199 million in 1997. That of mangoes was USD 60 million in 2009 up from USD 8 million in 1997 [FAOSTAT, 2012].

However, horticulture faces a number of production constraints that must be addressed and managed for increased productivity. Against this backdrop, initiatives that will maximize horticultural production, at national level, are necessary. These include but are not limited to: implementing favourable national policies, fostering the development of holistic crop value chains, improving access to markets and reducing postharvest losses, providing subsidies for farmers to access inputs (machinery, hybrid seed and fertilizer), promoting and facilitating public-private-partnership, increasing investment in research and technology including irrigation, reducing the cost of agricultural equipment and postharvest technologies, improving agricultural extension, developing new crop/varieties for the diverse ecological-zones and meeting the challenges of climate change, documenting, characterizing and conserving indigenous varieties: fruits, vegetable, cereals, root crops, herbs and spices [Wasilwa, 2008].

Production and export of horticultural products are increasing rapidly in many developing countries. From 1970 to 2002 fruit and vegetable production in developing countries almost quadrupled from 256 to 960 million metric tons while exports more than tripled from 9.1 to 6.5 million metric tons [Georges *et al.*, 2003]. Demand for these high value commodities is

stimulated by income growth, reductions in transportation costs and in some cases increased market access. Production for export is often encouraged as means of generating foreign exchange, increasing incomes to producers and providing employment for the farm workers.

Rapid growth in horticultural production has been accompanied by heavy use of pesticides and heightened concern over health effects associated with pesticide use and abuse. Heavy pesticide use occurs in part because numerous pests attack horticultural crops reducing market value and yield on high value crops. Pesticide use raises safety concerns for agricultural workers who apply the pesticides. The concern is high in particular in flower production because of the heavy spraying in enclosed conditions.

Potential food safety risks from pesticide residues are also an important issue for importers of fresh fruits and vegetables. It is a major factor for exporters who may have shipments detained or rejected if residues exceed allowable limits. Thus countries must strike a delicate balance between minimizing pesticides residues and maintaining other aspects of product quality, while also trying to eliminate pest from horticultural crops. Pests, particularly exotic or potentially invasive ones, can cause detentions at the port of entry in the same manner as pesticides residues can. Rejection of even one shipment due to discovery of a pest can result in the exporting country being placed on a quarantine list for a particular commodity thus eliminating an import market. Developing countries are especially vulnerable to detentions as many of their horticultural exports are nontraditional ones for which pre-inspection protocols may not exist. Therefore these countries seek pest management approaches that minimize pesticide use and residues while providing high pest free produce under pre-inspection procedures that can be documented.

1.2 Institutions Involved in the Horticulture Sector

The horticulture industry is governed by various public and private institutions with legal and institutional mandates. Public institutions established under various statutes in Kenya have a national mandate on various aspects of horticulture with a view to improving productivity and service delivery. These institutions include:

1.2.1 Horticultural Crop Development Authority (HCDA)

Recognizing the importance of the horticultural sub-sector, the government established the Horticultural Crop Development Authority (HCDA) in 1967 to develop the sector. The HCDA has been able to help farmers in an advisory and regulatory capacity over the years.

1.2.2 The Kenya Agricultural Research Institute (KARI)

KARI is a premier national institution bringing together research programmes in food crops, horticultural and industrial crops, livestock and range management, land and water management, and socio-economics. KARI promotes sound agricultural research, technology generation and dissemination to ensure food security through improved productivity and environmental conservation. KARI is mandated to undertake research in production, crop management, pre-and post-harvest treatment for insect control and value addition of horticultural crops. The outputs from research activities implemented are to support the national horticultural industry.

1.2.3 Kenya Industrial Research and Development Institute (KIRDI)

This is a parastatal established under the Science and Technology Act (Cap 250). It is mandated to undertake research and development in industrial and allied technologies. KIRDI collaborates with Ministry of Agriculture and other stakeholders in technology development and transfer in processing of horticultural produce.

1.2.4 Universities

Among the universities are the University of Nairobi, the Jomo Kenyatta University of Agriculture and Technology, the Moi University and the Egerton University provide courses at degree and diploma levels related to agriculture, horticulture and environment and are also involved in horticulture research.

1.2.5 Fresh Produce Exporters Association of Kenya (FPEAK)

FPEAK was established in 1975 as an association for horticultural produce exporters. Its functions include: representation and liaison with relevant public and private sector, local and international organizations, and trade associations; promoting exports through overseas exhibitions, trade missions and buyers' missions to Kenya; providing market information on export products and their destinations; training members and their out-growers on production, post harvest handling, packaging and export marketing techniques; and ensuring high quality, environmentally sound and safe products through adherence to an established Code of Practice.

1.2.6 Kenya Plant Health Inspectorate Services (KEPHIS)

KEPHIS is a state corporation that provides regulatory oversight for the government, business sector, scientists and farmers on matters of plant health and quality control of agricultural inputs and produce. Further, it is tasked with the responsibility of establishing linkages with various local and international government and non-government organizations so as to execute its mandate more professionally. In partnership with private institutions it inspects Kenya's horticultural exports to the EU hence ensuring that they conform to the export market requirements.

1.2.7 Ministry of Agriculture (MoA)

The Ministry of Agriculture coordinates the implementation of agricultural, cooperative and rural development policies. The specific functions which are pursued by the Ministry include: rural development policy; agricultural policy; crop production and marketing; land use policy; pests and disease control; agricultural research; phytosanitary services; information management for the agricultural sector; cooperatives and regional development authorities among others.

1.3 Policy That Guides the Horticulture Sector in Kenya

Currently in Kenya, there is no horticultural policy that guides the horticultural sector. However, various pieces of legislation are in place and guide different aspects of the horticultural production. The Agricultural Act, Cap 318 governs the agricultural sector and includes conditions under which fruits and vegetables are grown. The Agricultural Produce (Export) Act Cap 319 provides for the grading and inspection of agricultural produce to be exported and generally for the better regulation of the preparation and manufacturing of agricultural produce for export. The regulations of this Act include Agricultural Produce (Export) (Horticultural Produce Inspection) and the Agricultural Produce (Grading of fruits and vegetables for export).
Inspection and standards: - Regulations and standards for fresh horticultural produce are done at the port of exit by KEPHIS. This status is no longer feasible due to serious emerging challenges both locally and internationally and a National Horticulture Policy is being developed to provide sustainability and further spur growth in the industry.

1.4 Policy That Guides the Pesticide Use in Kenya

The Pest Control Products Board (PCPB) is a statutory organization of Kenya government established under the pest control products act, cap 346 laws of Kenya of 1982 to regulate the

importation and exportation, manufacture, distribution and use of pest control products in Kenya. Several categories of the products included in this are synthetic chemicals, microbial pesticides, botanical pesticides, biochemical pesticides and natural enemies.

The pest control products registration (Amendment) regulation, 2006 requires that the use of genetic modified organisms and living modified organisms as microbial or microbial bio-pesticides shall comply with any other existing laws governing such organisms before an application is made to the board. Bio-safety measures are also put in place to mitigate or protect human health and environment from possible adverse effects of the products of modern bio-technology. The protocol on bio-safety provides comprehensive and holistic regime designed to ensure that the development, handling, transport and use of products of modern bio-technology are undertaken in manner that maximize benefits while preventing or reducing risks to the environment and human health. The protocol is subsidiary agreement to the UN convention on biological diversity (CBD) Kenya signed the bio-safety protocol in 2000 and fulfilled the ratification requirement in 2003. One of the key obligations expected from the parties to the protocol is promotion and facilitation of public awareness education and participation in bio-safety activities as stipulated in article 23.

Bio-safety issues under the mandate of PCPB are:

- i) Micro-organisms for use directly or as active agents in pest control products including genetically modified organisms
- ii) Macro-bials for use directly or as active agents in pest control products including genetically modified organisms
- iii) Bio-chemicals derived from genetically modified organisms, used directly or as active ingredients or in pest control products

In food safety assessment, all pest control products meant for use on edible crops or domestic animals are subjected to health and environmental risk assessment

All pest control products are expected to undergo local biological efficacy trials before registration. Monitoring is also carried out at the time of testing. Some special conditions may be attached to products with high risks

Premises where pest control products are manufactured, packaged and sold are monitored through inspection. For products released and post environmental release monitoring is carried out in collaboration with relevant agencies.

1.5 Pesticide Use in Kenya

The imports of pesticide into Kenya between 2003 and 2009 are attached in appendix III. Analysis of the import quantities by Foxal found out that 50% was fungicides, 20% was insecticides, 20% herbicides and 10% Acaricides, rodenticides and nematicides. It is assumed that this import combination ratio has remained the same in the quantities presented in the table over years. The bulk of the imported pesticides are consumed locally with only 3 % being exported to neighboring countries. Pesticides have been widely used for the control of ticks, mosquitoes, houseflies, post-harvest storage insects, tse-tse flies and as crop pest control and weed control. Frequent application of pesticides has led to the development of resistance, for instance in *Anopheles gambiae giles* resistance to dichlorodiphenyl-1, 1, 1-trichloroethane (DDT) and fenitrotrion. No such resistance was observed for pesticides which are not used for pest control, such as dieldrin, and malathion. The development of resistance to insecticides has been contributor to the re-occurrence of malaria in many regions. However, since resistance is only developed when direct exposure to the insecticide is applied over period of time, replacement of the pesticide or stoppage of the application stops the development of the resistance. This has

been observed in tick when resistance to DDT and dieldrin were eliminated by use of organophosphorus compounds dioxathion and coumaphos in combination with hexachlorocyclohexane (HCH), toxaphene, or by use of new pesticides such as carbaryl, chlorferinphos and formamidenes.

1.6 Overview of Horticultural Production in Kenya

The horticultural sector has continued to attract a lot of interest from a wide range of stakeholders including the Government of Kenya, private sector entrepreneurs, donors and NGOs among others [Harris *et al.*, 2001; Minot and Ngigi, 2002; HCDA, 2008]. It is also an important source of government revenue, foreign exchange earnings and employment, all of which contribute to the national goal of poverty reduction and food security [HCDA, 2008].

The horticultural sector offers opportunities for economic growth both in the medium and high potential as well as the Arid and Semi Arid Lands (ASALs). Over the last two decades, however, Kenya's horticultural sub sector has substantially grown in terms of area under production, commodity and quantities produced. The national production of all horticultural crops in 2007 was estimated to be 7.1 million tones with a wholesale value of at least Ksh120 billion (\$1.85 billion) [KHDP updates, 2008].

The area under pineapple production has been decreasing since 2001 whereas that of mangoes has steadily increased. The decrease in the area under production for pineapples could be due to the increased influx of imported pineapples from regional markets mainly Uganda [Oberthur *et al.*, 2009]. The rapid increase in area allocated for mangoes could be attributed to increased availability of improved varieties of mangoes that attract better prices and product diversification (e.g. juices and dried mangoes). For the vegetables, tomatoes have shown a steady increase in the area allocated and the increase can perhaps be explained by the increased green house tomato

production.

Horticultural production in terms of the quantities produced show mixed trends for various crops. Some crops, particularly onions, chillies and pineapples have shown a decline in production while some like French beans, mangoes and bananas show a general increasing trend after 2001. There has been a marked increase for both cabbage and tomatoes which could be explained by reduced field losses caused by pests and diseases as a result of more farmers adopting green house production (the case of tomatoes) as well as the use of improved cabbage varieties. [Dawson, 2010].

The mixed trends in horticultural production could be attributed to a number of factors. While it is in fact true that climatic factors such as drought are important in explaining the horticultural performance, the major culprits are policy related [[Kang'ethe *et al.*, 2014].

Kenya's horticultural exports mainly fruit and vegetables grew by 9 % per year in the first decade after independence, then 17 % per year from 1974-1983 [Minot and Ngigi, 2002]. The quantities of horticultural produce exported between 2001 and 2007 show mixed trends, in terms of export volumes, with pronounced periodical fluctuations and this also mirrors the area under production and quantities produced. While over 90 % of smallholder farmers in all but the arid regions of Kenya produce horticultural products, fewer than 2 % do so directly for export [Bawden *et al.*, 2002]. The limited horticultural produce for export has been attributable to the stringent sanitary and phytosanitary (SPS) requirements that developing countries have to meet before penetrating the export markets [Wasilwa, 2008; Nyangito and Nzuma, 2003].

1.7 Constraints and Challenges to Horticultural Production in Kenya

Smallholder farmers in Kenya are faced with a number of challenges in their horticultural production activities. These include but are not limited to under investment in agriculture,

disengagement of government from support to agriculture, poor infrastructure, high cost of inputs, limited access to extension services, unreliable weather, and low produce prices [Kang'ethe *et al.*, 2014]. The impact of high cost of inputs has been aggravated by declining soil fertility. There is also a limited access to extension services in most parts of the country with the national extension staff to farmer ratio standing at 1:1,500. The low/uneconomic prices are mostly attributed to weak farmer bargaining power and market cartels. The sector is also subject to lags in policy and legal framework, which are not in line with a liberalized economy [[Kang'ethe *et al.*, 2014]. This situation has hindered most farmers from keeping pace with changing technological advances [Wasilwa, 2008].

1.8 Statement of the Problem

Horticulture is among the leading foreign exchange earner and employer either directly or indirectly. Kenya imports most pesticides from the developed countries. However, pesticide dissipation and degradation rates are carried out at the country of origin of the pesticides 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 application of good agricultural practice (GAP) by farmers. Heavy pesticide use occurs due to numerous pest attacks on the horticultural crops. They are used in agriculture to protect crops from destructive pests both in the field and during storage. They are also used by the department of public health and other areas to eradicate disease vectors and other pests. However, when used, pesticides contaminate the environment and accumulate in the food chain thereby posing hazard to human health [Blasco *et al.*, 2003; Leong *at al.*, 2007 and Pesticide Action Network, 2001]. Thus the residues remaining after harvesting may result to reduced market value of the yield on high value crops. Research on the dissipation of carbaryl in tomatoes grown in green house were very few

in Kenya. Carbaryl is commonly used in Kenya on a variety of crops thus there is need to carry out a study on the fate of carbaryl in tomatoes and soil under green house condition.

1.9 Overall Objective of the study

Study the fate of carbaryl pesticides in harvested tomatoes and soil from Hippo, Kingfisher and Hernekop Farms.

1.9.1 Specific study objectives

- i. Identify the pesticides used on the farm workers in Hippo, Kingfisher and Hernekop farms.
- ii. Determine the dissipation rate of carbaryl pesticide in tomatoes grown in Hippo, Kingfisher and Hernekop farms.
- iii. Determine the dissipation rate of carbaryl pesticide in soil in Hippo, Kingfisher and hernekop farms.
- iv. Determine the residue levels of carbaryl at the time of harvesting in tomatoes from Hippo, Kingfisher and Hernekop farms.

1.10 Justification of the study

Sustainable horticultural production is essential towards realization of vision 2030. However, pesticides abuse and misuse is common in Africa and in particularly Kenya. The study focused on the carbamate pesticides because they are among the most used pesticide in the horticultural sector in Kenya and other developing countries [Mbakaya *et al.*, 1994; Partow, 1995]. Carbamate pesticides are also known to be among the most toxic group of pesticide causing both acute and chronic poisoning to farm workers who are occupationally exposed to them, [Varo *et al.*, 1998]. Chronic exposure of humans to low dosage of pesticides through air, water and food may lead to chronic toxicity due to accumulation of the residues over the long period of time [Sesline and Jackson, 1994]. The recommendations from the study will be used to educate Kenyan farmers on the dangers of pesticide abuse and so ensure appropriate use of recommended products. Tomatoes were chosen for this study because they are widely consumed as food stuff in Kenya, the quantity of production and export is also increasing since the year 2000.

In addition determination of pesticides rate of degradation is a requirement to support the enforcement of legislation, ensure trading compliance and conduct monitoring residue programs in dietary components, their mode of action and movement within the environment [Kennedy, 2006]. The study will be of help following the ban of the use of dimethoate pesticide in horticultural products in Kenya. The ban was prompted by disclosure by Health Authorities in the UK to European Commission that dimethoate had been detected in green beans produced in Kenya which was found to be above the allowed levels. However the horticultural farmers can now continue using the pesticide after the court order in Kenya lifted the ban.

CHAPTER TWO

LITERATURE REVIEW

2.1 Pesticides

Pesticides are substances or mixtures of substances intended for preventing, destroying, repelling or mitigating any pest [Oudejans, 1991]. They help to reduce, and in some cases eliminate, the negative impacts of insects, bacteria, weeds, viruses, parasites and fungi, thereby improving the quantity and quality of agricultural produce as well as human health. The potential of pesticides to cause both short and long term adverse effects to the environment as well public health has attracted global attention. The Montreal protocol of 1987 was designed to protect the ozone layer by phasing out ozone depleting substances like methyl bromide which is used as a soil fumigant. The Stockholm convention of 2001 banned the use of persistent organic pollutants (PoPs) due to their resistance to degrade, bioaccumulation in living organisms, and travel over long distance from the point of source and toxicity to animals and humans (Adelola, 2004, Fernandez and Grimalt, 2003; Scheringer and wania, 2003; Stoeba et al., 2004; Ritter et al., 1995; UNEP, 2001). According to Basel convention of 1989 pesticides are considered to be hazardous substances and should be disposed of in an environmentally sound manner. The 1998 Rotterdam convention on the prior informed consent procedure for certain hazardous chemicals and pesticides in international trade aimed to reduce the environmental and health risks posed by persistent organic pollutants. The legal notice number 120 of Government of Kenya on water quality prohibits pollution of water by discharging or application of any poison, toxic, noxious or other pollutant into aquatic environment. The National Environmental Management Authority (NEMA) is charged with the responsibility of promoting sustainable environment management

however, the pest control product board is mandated to regulate the importation, exportation, manufacture, distribution and use of pest control products. However according to Wandiga (2001) some of the pesticides in spite their ban or severe restrictions could still be available in the market in Kenya. A study done around Lake Naivasha basin showed use of banned or restricted pesticides like endosulfan under various trade names (Njogu, 2011). The government of Kenya in 2012 banned the use of dimethoate on fruits and vegetables for both export and local market (MoA, 2012).

A larger proportion of fresh horticultural produce consumed in Nairobi and exported for foreign exchange is grown the counties of Kiambu, Machakos, Nakuru and Kajiando (Odour *et al.*, 1998). It is that over 300,000 farm families earn the major part of their income through the cultivation and marketing of vegetables (Asaba *et al.*, 2000). Kenya as one of the major horticultural producers in the world, imports approximately 7,000 metric tons of synthetic pesticides worth 4 billion (KES) annually (US \$ 50 million) (Birech *et al.*, 2006). In as much as pesticides have ensured continuous supply of tomatoes, inappropriate use are major concerns due to environmental and health impacts associated with pesticides. Studies have shown build up of pesticides up the food chain and some levels of contamination of water, sediments, eggs, crops and human fluid by pesticides (Njogu, 2011; Wandiga, 2001). The farms were selected in agricultural reproductive areas faced with several environmental challenges among which are and diseases in tomato crop. The proximity of the areas to the capital city of Kenya, Nairobi creates high demand for tomato produce pushing farmers to harvest their tomatoes before the required withdrawal period and increased use of pesticides on tomatoes per season due to pest and disease resistance (Fabro and Varca, 2011; Lichtenberg, 2013). During the control of these pests and diseases farmers could be predisposing themselves and the public to health risks due to

inappropriate handling and use of the pesticides.

This study reports the pesticide residue levels on tomatoes based agro system in selected farms in two counties which supports a large horticultural industry both for export and domestic markets due to increased use of pesticides. Though a lot of work has been done on pesticides in Kenya, no studies have been done on tomato production in the selected farms to establish how farmers use and apply Carbaryl pesticides and especially for the production of tomatoes. There is also lack of inventory of pesticides residue on the crops grown in the regions. The purpose of this study was to create and develop an inventory for the residue concentrations of carbaryl pesticide in soil and tomatoes from the selected farms in Thika and Navaisha regions, Kenya.

2.2 Classification of pesticides

Pesticides are divided into organic and inorganic. Inorganic pesticides are naturally occurring non-carbon elements, 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 bio-accumulative [Hassall, 1990]. Organic pesticides are mainly synthetic compounds containing either aliphatic or aromatic hydrocarbon chains. They are further classified according to their active ingredients (Louis, 1994). They consist of organochlorines, organophosphorus, organosulfur, carbamates and pyrethroids depending on the element bonded to the hydrocarbon system [Wasswa, 2008]. The world health organization (WHO) classifies pesticides in terms of their toxicity; as extremely hazardous (class IA), highly hazardous (class IB), moderately hazardous (class II), slightly hazardous (class III) and unlikely to present acute hazard (class IV) (WHO, 2008)

2.2.1 Organochlorine Pesticides (OCPs)

Organochlorine pesticides are a large class of multipurpose chlorinated hydrocarbon chemicals [Briggs, 1992]. They break down slowly in the environment and accumulate in the fatty tissues of animals. Thus, they stay in the environment and food web long after being applied [Idowu G *et al.*, 2013]. DDT, now banned globally because of its harm to the health of wildlife and people, is a notable example of an organochlorine pesticide. Many organochlorine pesticides are endocrine disrupting chemicals, meaning they have subtle toxic effects on the body's hormonal systems [Lemaire *et al.*, 2004]. Endocrine disrupting chemicals often mimic the body's natural hormones, disrupting normal functions and contributing to adverse health effects, they are very toxic organic compounds, persist in the environment and have the potential for long range transport, posing a serious threat to the environment and its habitats at remote places [Vesna *et al.*, 2001]. Organochlorine Pesticides (OCPs) include dieldrin, heptachlor, chlordane, aldrin, endrin, dichlorodiphenyltrichloroethane (DDT), hexachlorobenzene (HCB), mirex, and toxaphene [Appendix 1]

OCPs were used widely to protect crops, livestock, buildings and households against a variety of pests such as ticks, locust, termites and mosquitoes. Currently, most of these pesticides have been banned, except a few which are under restricted use. Following the ban, large stocks of obsolete OCPs are still in possession by individual farmers, households and government agencies. The probability of these chemicals being released into the environment is very high posing a high risk to animals and human health.

2.2.2 Organophosphorus Pesticides (OPs)

Organophosphorus 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. Examples of OPs include; acephate, dichlorvos, dimethoate, ethion, malathion, mevinphos, chlorfenvinphos, parathion, chlorpyrifos and diazinon [Appendix 1]. 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]. The major disadvantage of organophosphates is the lack of selectivity to non target organisms. These compounds irreversibly inactivate the acetylcholinesterase (AChE) enzyme; an enzyme essential for Neurotransmission and central nervous system of organisms [Moretto, 1998]. This results in the accumulation of acetylcholine (ACh) which interferes with the neuromuscular function thereby producing rapid twitching of voluntary muscles and finally paralysis [Byoung *et al.*, 2003].

OPs are neurotoxic even at very low levels of exposure [Bachmann et al, 2000]. Short-term exposure to these chemicals has been shown to produce muscle twitching, headache, nausea, dizziness, loss of memory, weakness, tremor, diarrhea, sweating, salivation, tearing, constriction of pupils, and slowed heartbeat. Long-term exposure can produce delayed neurotoxicity, such as tingling and burning in the extremities. This delayed neurotoxicity can progress to paralysis and is seldom reversible. Damage may also occur to the liver, kidney, immune system and bone marrow [USEPA, 2009].

Organophosphate pesticides degrade rapidly by hydrolysis on exposure to sunlight, air, and soil, although small amounts can be detected in food and drinking water. Their ability to degrade makes them an attractive alternative to the persistent organochlorine pesticides such as DDT, aldrin and dieldrin [USEPA, 2009]

2.2.3 Organosulfurs

Organosulfurs have sulfur in their structure as the central atom [Briggs S.A, 1992]. Their mode

of action is by disrupting the target organism's metabolism. They have low toxicity to insects and mammals and as a result used for selective purposes [Briggs S.A, 1992]. They are characterized by their toxicity to young and adult insects which is a valuable property. They also cause irritation to the eyes, ears and nose. The common examples are aramite, propargite, tetradifon, and tetrasul [Appendix 1].

2.2.4 Synthetic Pyrethroids

Pyrethrin is a natural insecticide extracted from *Chrysanthemum cineraria folium* (pyrethrum)-the crude flower dust. The synthetic pesticide pyrethroids are derivative of pyrethrins which was designed to improve the biological activity of the active principal of the natural pesticide [Kegley and Hill B. 2007]. Pyrethroids synthesised before 1970 were very sensitive to sunlight, as their molecules split under UV light making them unsuitable for agricultural use but effective for indoor insect pest control. Since 1970s, synthetic pyrethroids with a better photo-stability and low volatility have been produced to suit both agricultural and indoor uses. This class of pesticides poisons the target by contact and causing paralysis [Chapman et al, 1981]. These compounds have low mammalian toxicity, but are highly toxic to insects and aquatic organisms. The common pyrethroids are permethrin, deltamethrin, fenvalerate and tetramethrin [Appendix 1].

2.2.5 Carbamate

They are organic compounds derived from carbamic acid (NH_2COOH). A carbamate group, carbamate ester (ethyl carbamate), and carbamic acid are functional groups that are inter-related structurally and are often inter-converted chemically[Dough *et al.*, 1964]

Carbamates have groups attached to the central carbonyl carbon. R_2 is always an aromatic or aliphatic moiety. The major difference among the carbamate pesticides is in the functional group attached at R_1 . For instance, carbamate insecticides have R_1 as an ethyl group, herbicides have R_1

is an aromatic group, whereas fungicides have R₁ as a benzimidazole moiety. Some of the known carbamates are carbaryl, carbofurans and aldicarbs. Biologically, carbamates resemble the organophosphates in their activity. They inhibit the cholinesterase enzyme required for nerve function in animals. Some carbamates are also suspected carcinogens [USEPA, 2009]. Carbamates are hydrolyzed slowly in neutral and mildly acidic aqueous surroundings, but in the presence of alkali, they decompose rapidly. The half- life of carbaryl, for example, is about 10 days in neutral aqueous suspension (pH 7) but only a few minutes at pH 11 [Briggs, 1992].

2.3 Carbaryl

Carbaryl (1-naphthyl-N-methyl carbamate; Fig. 1) is a carbamate insecticide introduced in 1956 by Union Carbide Corporation. The insecticide is used worldwide and is a substitute for some organochlorine pesticides [Ribera *et al.*, 2001]. Carbaryl controls a broad spectrum of insects on more than 120 different crops [Ware, 2001]. It has also been used to prevent bark beetle attacks in pine trees [Hastings *et al.*, 2001] and as a general garden insecticide [Ware, 2001]. In 2004, approximately 110,000 kg of the insecticide was applied in California alone [California department of Pesticide Regulation -CDPR, 2004]. Annual use in the U.S. is reported to be 4.5-6.8 million kg [Cox, 2004]. Several trade names are associated with carbaryl; the most common being Sevin.

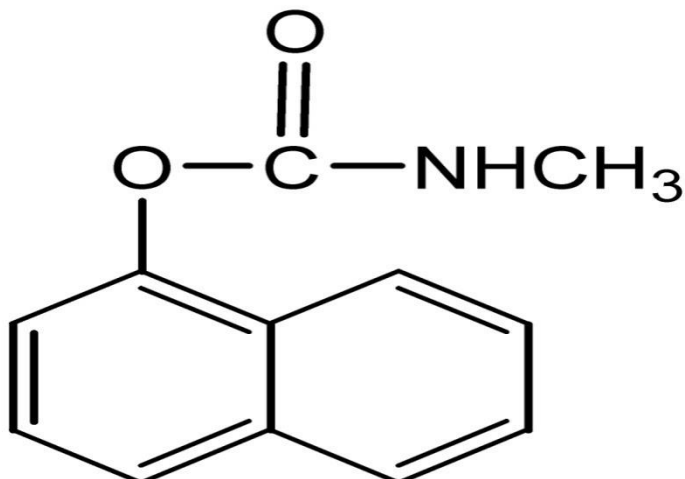


Figure 1: Chemical structure of carbaryl

Active ingredient (a.i.) use rates for carbaryl range from 0.57-4.5 kg/ha [Rajagopal *et al.*, 1984]. It is available in the form of a wettable powder, pellets, granules, suspensions, and solutions. The insecticide is the second most widely detected insecticide in surface waters in the U.S. [Martin *et al.*, 2003].

Table 1. Physical-chemical properties of carbaryl. Pure physical state **Colorless or tan crystal**

Chemistry Abstracts Service registry number (CAS #)		63-25-2
Molecular weight (g/mol)		201.2
Molecular formula		C ₁₂ H ₁₁ NO ₂
Melting point (°C)		142
Vapor pressure (mPa at 23.5°C)		0.041
Octanol-water partition coefficient (log K _{ow})		2.36
Density (20°C)		1.23
Henry's law constant (atm m ³ g/mol at 25°C)		2.74x10 ⁻⁹
Organic-carbon normalized partition coefficient (K _{oc})		290
λ _{max} (nm) ^c		280
Water solubility (mg/L)	20°C ^a	120
	25°C ^d	104
	40°C ^e	40

[Tomlin, 2003; Phillips and Bode, 2004 Sheng *et al.*, 2001; Arroyo *et al.*, 2004; Meister, 2001].

Carbaryl, like most carbamates, inhibits the enzyme that degrades acetylcholine – acetylcholinesterase. Inhibition of this enzyme promotes the buildup of acetylcholine at synapses resulting in uncontrolled movement, paralysis, convulsions, and possible death [Tomlin, 2003].

The physical chemical properties of carbaryl are listed in Table 1. Carbaryl is a low molecular weight compound that is moderately soluble in water and does not readily volatilize. The compound is not compatible with alkaline materials such as lime [Tomlin, 2003].

2.4 Environmental fate of Carbaryl

2.4.1 Air

Carbaryl has a very low vapor pressure, 1.17×10^{-6} mmHg and not readily volatilized in to the air. A low Henry's law constant 2.74×10^{-9} atm gmol⁻¹, suggest that carbaryl has low potential to vaporize from aqueous solution [Lyman *et al.*, 1982]. It might be found in atmosphere associated with air borne particulates or as spray drift but should not be over a large area. If existing in air carbaryl tends to react with hydroxyl radical in the ambient atmosphere. Carbaryl in air was monitored after being applied to large area of forest in Maine for the control of spruce budworm, and the concentrations ranged from 0.0035 to 0.107 µg/m³ [shehata *et al.*, 1984]

2.4.2 Water

Hydrolysis is the primary degradation pathway for carbaryl at PH 7 or above. The compound degrades rapidly between pH 7 and pH 9 at 25⁰C, with half lives of approximately 10-17 days and 3 hrs [Tomlin, 2003] . Carbaryl is moderately soluble in water and its solubility increases with increasing temperature and amount of organic solvents [Tomlin, 2003]. Detections of carbaryl have been found in surface waters of 42 U.S. states at low concentrations (µg/L). In many states, detections were found in both agriculture and urban environments. Several states in

the United States of America reported higher frequency of detections in urban than in agricultural environment. In California, detections in urban environments are less than in agricultural areas. Carbaryl was ranked 8th nationally among pesticides for outdoor home and-garden use in 1992 [Whitmore *et al.*, 1992], and one of four insecticides most commonly detected in urban streams in 2001 [Gilliom *et al.*, 2007].

Agricultural inputs of carbaryl to water systems have also been reported. In Florida, Wilson *et al.*, (2006) detected carbaryl in eight of 457 samples collected from Ten Mile Creek located in an agricultural watershed at concentrations that ranged from 0.33-0.95 µg/L. Lower concentrations of carbaryl (10-100 ng/L) were detected in the Pinios River in Greece with seasonal use of the insecticide in the Thessaly agricultural area [Fytianos *et al.*, 2006]. Higher concentrations have been detected in several locations after carbaryl was used across central California to control the newly introduced glassy-winged sharpshooter pest, *Homalodisca coagulata*. For instance, 6.94 µg/L in a goldfish pond and 1737 µg/L in rain runoff in a drain were detected adjacent to where carbaryl was sprayed [Walters *et al.*, 2003]. Groundwater detections are also reported by LaFleur (1967) who found the presence of carbaryl within two months after application to Congaree soil (well drained loamy soil on river bed) with detections continuing up to eight months. New Jersey had the highest number of carbaryl detections in groundwater across all land use types. Several other states also had groundwater detections mainly in urban and mixed-use areas.

The soil sorption coefficients (K_{oc} = 100 ~ 600), octanol/water partition coefficients ($\log K_{ow}$ = 1.85 – 2.36) and water solubility indicate that carbaryl moderately binds to soils and sediments [Tomlin, 2003]. Thus, suspended particulates or mud in natural water may remove some carbaryl from the aqueous phase. Karinen *et al.*, (1967) reported that 50 % of initial carbaryl disappeared

from estuarine water after 38 days at 80 °C in the absence of mud; in the presence of mud, 90 % of initially applied carbaryl was withdrawn from the water after 10 days at the same temperature. Therefore there was significant removal of carbaryl by mud.

2.4.3 Soil

Carbaryl sorption to soil is rapid at 0.5 hours and 3 hours [Ahmad *et al.*, 2001, Jana and Das, 1997] but persistent (from two to 16 weeks) with a $t_{1/2}$ of 8 days for concentrations ranging from 1-14 mg/L [Rajagopal *et al.*, 1984]. Carbaryl has been found to adsorb more readily in acidic soil (Rajagopal *et al.*, 1984). Both mineral and organic matter in soils has been found to contribute to carbaryl sorption. The mineral interactions are clearly reported in several recent studies. For instance, Sheng *et al.*, (2001) found that potassium (K) saturated smectite clay (a non-ionic, expandable, hydrophilic clay) is a better sorbent for carbaryl than soil organic matter (SOM); the distribution coefficient (K_d) for carbaryl was five times greater in clay (235) than SOM rich soil (muck; 54.2). Sheng *et al.*, (2001) estimated that K saturated clay contributes approximately 35 times more to carbaryl retention than a soil with 2% SOM. De Oliveira *et al.*, (2005) found that its sorption is dependent on the surface charge density and is site specific. For example, the amount of carbaryl sorbed was strongly dependent on the presence of specific exchangeable cations and followed the order of Ba ~ Cs ~ Ca > Mg ~ K > Na ~ Li. The carbonyl group in carbaryl was found to directly interact with the exchangeable cations; Mg²⁺ and Na⁺ interacted strongly with the partial negative charge of the double-bonded oxygen atom on the insecticide [De Oliveira *et al.*, 2005]. A positive correlation between carbaryl sorption with surface area, cation exchange capacity (CEC), and free Al₂O₃ content in Ultisol and Inceptisol soils was made by Jana and Das (1997). Sorption isotherms of carbaryl sorption to Indian soils followed reversible S-shaped curves which suggest multilayer adsorption on the sorbent surface [Jana and

Das, 1997].

Organic matter is another contributor to sequestering carbaryl in soils. For example, carbaryl movement through soil was found to be a function of SOM content; 52% carbaryl was leached in ten rinses from organic rich soil while it took only one rinse to leach the same amount from a sandy soil [Sharom *et al.*, 1980].

Sorption processes are predicted to be highly reversible for carbaryl since the binding is proposed to be nonspecific sorptive binding unlike chemisorption [Rajagopal *et al.*, 1984]. This, along with reported low K_d values, indicate that soils do not have a significant potential to stop carbaryl movement, with time, into water systems and other environmental fate processes (i.e., abiotic or biotic degradation) may play an important role in its dissipation.

Overall, carbaryl is not persistent in soil. It can be degraded through hydrolysis, photolysis as well as by microorganisms. The photodegradation of carbaryl was investigated on soil under artificial sunlight for a total of 30 days [Das, 1990]. In this case, carbaryl was applied on 1-mm soil layers at a concentration of 9.8 ppm. The estimated half-life was approximately 41 days with no findings of major metabolites.

In aerobic soil, carbaryl was quickly degraded with an approximate half-life of 4 days [Miller, 1993]. A significant amount of CO_2 was produced, ranging from 0.1% at day 1 to 59.7% at day 14. Another major degrade is 1-naphthol. Carbaryl degrades more slowly in anaerobic aquatic soil with an estimated half-life of 72 days [Miller, 1993]. 1-naphthol is the major degradate with minor compounds of 1,4-naphthoquinone, 5-hydroxy-1-naphthyl methylcarbamate and 1-naphthyl-(hydroxymethyl) carbamate. None of these minor degradates accounted for more than 2.5% of total applied dose. CO_2 was generated slowly, ranging from none at day 3 to 4% at day 94. At day 126, CO_2 reached the maximum of 23.6%.

Murthy et al., (1989) studied the metabolism of ¹⁴C-carbaryl and 1-naphthol in moist and flooded soils over a 28-day period. More CO₂ was generated from carbaryl treated moist soil than from flooded soil. Most radio-activities existed as soil bound materials and only less than 1 percent of parent was present in extractable radiocarbon. The major degradation was 5-hydroxyl carbaryl in moist soil and 4- and 5-hydroxyl carbaryl in flooded soil.

The adsorption coefficient values (K_{oc}) of carbaryl range from 100 to 600 [WHO, 1994; Jana and Das, 1997], indicating carbaryl moderately binds to soil. Sorption experiments were implemented on two types of soils, Red Bay (AB) and Astatula (AS), which were further separated into two layers, topsoil (0-30 cm) and subsoil (31-60 cm) [Nkedi-Kizza and Brown, 1998]. The properties of individual soil are: AB top (pH 6.3, OM 15.2%), ABsub (pH 5.3, OM 3.9%), AS top (pH 5.6, OM 8.0%) and AS sub (pH 4.8, OM 2%). The sorption coefficient values (K_{oc}) of carbaryl on soils are: 338, 144, 590 and 671 mg/kg on AB topsoil, AB subsoil, AS topsoil and AS subsoil, respectively. The half-lives of carbaryl on the four soils ranged from 8 to 18 days. Given the same type of soil, carbaryl degraded much faster in topsoil than in subsoil.

Terrestrial field dissipation studies were conducted at two locations, one in California and one in North Carolina [Norris, 1991]. Data showed that most residues remain in the first 0-0.15 meters of soil, with only one finding in the layer of 0.3 –0.45 meter. The dissipation half-lives of carbaryl were estimated as from 0.76 to 10.9 days.

2.4.4 Biota

The efficacy of carbaryl for the control of pests is attributed to its ability to inhibit acetylcholinesterase (Ache) in the nervous systems [Barabona and Sanchez-Fortun, 1999]. Given the same mode of action, carbaryl also poses risks to other non-target animals, including human beings. Carbaryl can penetrate the skin, mucous membranes, respiratory tract and gastrointestinal

tract of mammals. However, it can be rapidly metabolized by various animals, and excreted especially in the urine as glucuronides or sulfates [Dorough and Casida, 1964; Fukuto, 1972]. The following metabolites have also been identified: 1-naphthyl N-hydroxymethylcarbamate, 4-hydroxy-1-naphthyl-Nmethylcarbamate, 5-hydroxyl-1-naphthyl-N-methyl-carbamate and 5, 6-dihydroxy-1- naphthylmethylcarbamate.

Carbaryl is relatively safe to mammals although it can temporarily inhibit AchE. Rats given a single oral dose of 560 mg/kg body weight showed a decrease of 42% erythrocyte- and 30% brain-ChE activity within 5 minutes [Carpenter *et al.*, 1961]. However, the activity recovered to normal level after 24 hours Carbaryl and its major degradate, 1-naphthol, are toxic to some ecologically beneficial soil microorganisms such as *Chlorella vulgaris*, *Nostoc linckia* and *Synechococcus elongates* [Megharaj *et al.*, 1990]. Obulakondaiah *et al.*, (1993) reported that carbaryl and 1- naphthol resulted in toxicity at concentrations of 50-100 ppm and 25-100 ppm, respectively. In this case, 1-naphthol was found to be more toxic than its parent compound since it inhibits nitrogen cycling mediated by tested microorganisms. Under other circumstances, carbaryl presented more toxic effect on different microbes than 1- naphthol [Megharaj *et al.*, 1990].

Carbaryl is considered moderately to highly toxic to fish with LC50 values ranging from 4 ppm to 13 ppm [Beyers, *et al.*, 1994; McKim, 1987 and Sinha *et al.*, 1991]. The chemical is especially toxic to the aquatic invertebrate *Daphnia magna* with LC50 values at 48 hours less than 18.6 ppb [Li and Yang, 2000]. Weis *et al.*, (1974) reported that 0.1-ppm carbaryl water solution is able to disrupt the schooling habit for juvenile *Menidia menidia*. 1- naphthol is believed to be the major factor instead of the parent compound. However, schooling behavior was recovered within 3 days.

Carbaryl is slightly or practically non-toxic to birds, with LD50 for young mallard ducks, young pheasants and pigeons of >2179, 2000, 1000-3000 mg/kg, respectively. The effect of low concentration carbaryl (1.68 kg/ha) on nontarget birds, mammals and insects have been investigated in western North Dakota [George *et al.*, 1992]. No evidence was found to conclude that carbaryl depressed brain AChE in birds or small mammals collected from the treated area after 2, 10, 21 days or 1 year.

2.5 Mode of Action of Carbaryl

Carbaryl is a member of the widely used carbonated pesticides. Like most of the carbamates carbaryl acts as an inhibitor to cholinesterase, one of the many important enzymes in the nervous systems of the human vertebrate and insects, [Extoxriol, 2000]. At a specific cholinesterase enzyme, acetylcholinesterase (AChE), plays an important role in breaking down the acetylcholine (Ach), which is the synaptic mediator of nerve impulse in the nervous systems of mammals and insects [WHO, 1994].

The presence of cholinesterase inhibiting pesticides such as carbaryl prevents AChE from breaking down acetylcholine and results in high concentration of Ach in the nervous system. As a result the continuous stimulation of the muscle leads to uncontrolled rapid movement of some muscles, paralysis convulsions and even death [CDPR, 2004]

2.6 Gas Chromatography- Mass Spectroscopy

The theory of GC-MS as instrumental method used in the analysis was developed by Finningan Mat, among other scholars in the year 1983.

Gas chromatography (GC) is a method used to help identify a mixture of compounds by separating compounds according to each compound's retention time. Compounds with a lower molecular weight will elute out earlier than compounds with higher molecular weights due to

differences in boiling points. Smaller structures have lower boiling points and will thus elute faster than those with higher boiling points. It then follows that the compounds with the lower boiling points will have shorter retention times.

Another advantage of GC is that it can be used to determine the purity of compounds. By looking for additional peaks in a sample that are not present in the pure compound, one can gain knowledge about purity. Peak areas of additional peaks can provide an indication of the degree of contamination

Factors other than the boiling points of compounds that determine the separation are: the polarity and physical size of the molecules, the column type (i.e. polar or non-polar), and the number of theoretical plates. The polarity of compounds should be considered because polar compounds will have a longer elution time on a polar column (i.e. the stationary phase) while a non-polar compound will elute in shorter times.

The mobile phase flow rate (how fast the gas is carrying the compounds through) also affects the appearance of peaks on the chromatogram. If the flow is too fast, peaks may not separate out as well, however, if the flow is too slow, band broadening may occur.

Column efficiency is another aspect that must be taken into account. The smaller the height equivalent to a theoretical plate (the more theoretical plates present) the more efficient the column. In the actual process of running a gas chromatograph, a sample is run by using a syringe to inject your compound into the injector port, which leads to a column. A carrier gas (in our case helium) is utilized in order to carry the sample on to the column.

Gas Chromatography–Mass Spectrometry (GC-MS) is a hyphenated analytical technique that combines the separation properties of gas-liquid chromatography with the detection feature of mass spectrometry to identify different substances within a test sample. GC is used to separate

the volatile and thermally stable substitutes in a sample whereas GC-MS fragments the analyte to be identified on the basis of its mass. The further addition of mass spectrometer in it leads to GC-MS/MS. Superior performance is achieved by single and triple quadrupole modes [Sahil *et al.*, 2011 and Jenke, 1996].

GC requires the analyte to have significant vapor pressure between 30 and 300°C. GC presents an insufficient proof of the nature of the detected compounds. The identification is based on retention time matching that may be inaccurate or misleading. GC-MS represents the mass of a given particle (Da) to the number (z) of electrostatic charges (e) that the particle carries. The term m/z is measured in DA/e. GC-MS commonly uses electron impact (EI) and chemical ionization (CI) techniques. The main features of enhanced molecular ion, improved confidence in sample identification, significantly increased range of thermally labile and low volatility samples amenable for analysis, much faster analysis, improved sensitivity particularly for compounds that are hard to analyze and the many other features and options provide compelling reasons to use the GC-MS in broad range of areas [International Organization for Standardization, 2002 and ISO/IEC 17025, 2005].

GC-MS has become a highly recommended tool for monitoring and tracking organic pollutants in the environment. The cost of GCMS equipment has decreased whereas the reliability has markedly increased. The determination of chloro-phenols in water and soil, polycyclic aromatic hydrocarbons (PAH), unleaded gasoline, dioxins, dibenzofurans, organo-chlorine pesticides, herbicides, phenols, halogenated pesticides, sulphur in air is very convenient to be screened by this technique. It can be used to screen the degradation products of lignin in bio-mass research, pesticides in spinach. Analysis of decacyclene, ovalene and even C_{60} degradation analysis of carbamazepine and its metabolites in treated sewage water and steroid can be done without

derivatization [Bliesner, 2006; Amirav *et al.*, 2008].

CHAPTER THREE

METHODOLOGY

3.1 The study areas

The study was conducted in selected horticultural farms in Kiambu and Nakuru Counties, in Kenya. These are among the main agricultural counties with highest produce of kales, cabbage, French beans, tomatoes, horticultural flowers and vegetables. These farms are Hippo farms in Thika of AAA Growers limited, (Kiambu County). Thika is a small town in Kenya located between GPS co-ordinates of 1.03⁰ south latitude and 37.07⁰ east longitude. It is about 1495 meters above the sea level with about 99,322 inhabitants.

Kingfisher and Harnekop farms in Naivasha (Nakuru County) which belong to James Finley limited company. Naivasha town is also a small town in Kenya located between GPS co-ordinates of 0.72⁰ south latitude and 36.43⁰ east longitude. It is 2086 meters above the sea level, with about 38,366 inhabitants. Majority of these produce are sold on the national markets rather than the international markets.

3.1.1 Hippo Farm

Hippo farm was the first farm to be established in the AAA portfolio. The farm covers 100 hectares at 1450 meters above sea level. 3.40 hectares are under covered production for chillies & herbs and the farm is aiming for 5 hectares by the end of 2015. The firm grows crops like beans, tomatoes, butternut, broccoli, sweet corns, sugar snaps, mange tout, onions, peppers baby leafs and other crops as the market requires. The farm has employed 160 people directly out of which 120 are permanent employees and 40 are casual employees. AAA Growers is one of the

leading exporters of premium and prepared vegetables from Kenya. The concept of AAA Growers was born out of a small trial project of growing tomatoes. Initially, setup in conjunction with the lending arm of the World Bank, the International Finance Corporation (IFC), as a micro finance orientated project, today the company harvests 30 metric tonnes of gross products a day and exports annually over 4,000 metric tonnes of fresh produce to Europe and South Africa leading retailers. The company grew from its single production site to four sites, and now cultivates nearly 650 hectares of arable land from its in house production alone, and boasts four custom-built food processing factories.

3.1.2 Kingfisher Farm

Kingfisher farm is one of the farms owned by James Finley Company. The farm is located in Naivasha, Nakuru County, Kenya. The Finlay's Kingfisher farm grows 92 hectares of Tomatoes. The farm has employed 263 people directly and another 1000 people benefit indirectly through the company's activities. The 30-years old Kingfisher farm stands where one of the pioneers of Kenya's flower industry, Sulmac used to be until the year 2000 when it was sold to another flower giant, Homegrown, that was in turn acquired by James Finlay in 2007. In the greenhouses, the farm employs hydroponics technology, reputed as the most economical water and nutrients plant feeding method yet. Plants are grown in a medium fitted with drip lines from a central place where fertilization is done. Crops take only what is required and the rest goes back to the tank for purification and replenishing. The farm practice recycling which has been extended to old greenhouses that are recycled into posts, beehives and nails. Mature rose stocks and papyrus are converted into charcoal, a much used fuel that gives a lease of life to trees.

3.1.3 Harnekop Farm

Harnekop farm is one of the farms owned by James Finley Company. The farm is located in Naivasha, Nakuru County, Kenya. It's the most recently established farm under the Finley portfolio. The farm grows fresh produce both for export and local market. The farm employs 52 people and it covers 10 hectares of land of which 4 hectares is used for tomato farming.

3.2 Pesticide Use Survey

Information on pesticides commonly used in the three farms was obtained using questionnaire which was distributed to a total of 88 respondents (farm workers and management) who were chosen randomly. Thirty two farm workers were interviewed in Hippo farm, forty four in Kingfisher farm and twelve farm workers in Harnekop farm were interviewed. The questionnaire consisted of both open and closed ended questions. Information was obtained on gender, age, designation in the company and level of education of the respondents. Respondents were asked questions on pesticide use and safety information, training on the use and formulation, pesticide-related accidents and their frequency, any known effects of pesticides to the users and the details of the pesticide claimed to have any effect by name. The respondents were also asked questions regarding the technical assistances from agricultural extension workers. 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 and anhydrous sodium sulphate were purchased from SCIELAB LTD, Nairobi. High purity nitrogen used for reducing samples was bought from Gas labs LTD, Nairobi. High purity hydrogen, white sport nitrogen and helium used for

chromatography were 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.

3.4 Equipment and Apparatus Used

Extraction of soil and tomato samples was done using Soxhlet set up comprising of heating mantles, Soxhlet extractors and condensers. Glass column of length 20cm and 2cm internal diameter were used in clean-up procedure, whereas 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. Moisture in soil was determined by heating the samples in BINDER E28#04-71528 oven whereas all glassware were dried in Mammoth oven. All weights were taken using analytical Fisher scientific A-160 weighing balance. 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. A HP Agilent GC system 6890N equipped with MSD was used for qualification and quantification of pesticide in the sample extracts.

3.5 Preparation of Reagents

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

Anhydrous Sodium Sulphate (Na_2SO_4) was prepared by baking out for 16 hours at 200°C to remove all the impurities. Copper powder was activated by shaking with 9ml 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 and hexane were each triple distilled to analytical grade level in a distillation set up.

3.6 Sampling

3.6.1 Sampling of Tomatoes

Sampling of tomatoes in the green house was done five times in September 2013 after the pesticide application in each of the three farms. The first sampling was done two hours after spraying of the tomatoes with carbaryl pesticide. The second sampling was done on the third day after the application of the pesticide, the third sampling was on the fifth day while the fourth sampling was on the seventh days and the last sampling was on the ninth days. Nine days after spraying of the pesticide, the tomatoes were ready for harvesting and selling. The sampling period of nine days was therefore to capture the residue levels of the pesticide at the time of harvesting. The sampling was done by plucking a tomato from marked five different tomato plants using thoroughly cleaned pair of scissors. The tomatoes were then mixed thoroughly well and wrapped in sterilized aluminum foil, fastened with masking tape, labeled and then placed in self sealing polythene bag; the polythene bag was then placed in a polyurethane container with a lid to avoid contamination. The polyurethane bag was labeled and kept in polyurethane cooler box containing dry ice before transportation to the laboratory. This sampling procedure was

repeated in the subsequent sampling periods. At the laboratory the tomatoes were kept in a freezer at -4 °C prior to extraction. The extractions were done at day zero (for the first samples) and not exceeding two days for the subsequent sampling.

3.6.2 Sampling of Soil

Soil samples (0-5 cm plough layers) were collected from five identified points where the tomatoes samples were taken in greenhouse. Soil samples were collected five times at the time when collecting the tomatoes. The soil samples were collected using pre-cleaned stainless steel shovel from five different points in the green house and mixed thoroughly well on the sterilized aluminum foil. The representative sample of about 200 g was placed in aluminum foil, fastened with masking tape, labeled and then placed in self sealing polythene bag; the polythene bag was then placed in a polyurethane container with a lid to avoid contamination, the polyurethane bag was labeled and kept in polyurethane cooler box containing dry ice before transportation to the laboratory. At the laboratory the soils were kept in a freezer at -20°C prior to extraction.

3.7. Extraction

3.7.1 Tomatoes Extraction

Extraction of tomato samples procedure was adopted from EPA method 3540 soxhlet extraction of food. Samples were removed from the fridge and allowed to thaw for 4 hours; the tomatoes were then cut into small pieces using a pre-cleaned knife, and 10 g was weighed then ground using mortar and pestle until homogenous powder was obtained, covered with aluminum foil and left overnight to dry. The dry samples were transferred to the soxhlet thimble and 20 µl of 1ppm PCB 52 solution added as internal standard. 175ml of hexane: acetone (1:1, v/v) mixture was placed in a round bottomed flask before connecting the Soxhlet setup. Extracted was done for 16

hours. To the extracts 1ml of isooctane was added as keeper then concentrated to 1ml using LABCONCO rotary evaporator the temperature was maintained at 30°C after which the extracts were put in vials.

3.7.2 Soil Extraction

Soil extraction EPA method 3540 soxhlet extraction of soil was applied. Soil samples were removed from the freezer and allowed to thaw for about 6 hours prior to extraction. Triplicates of 10g samples were dried with activated anhydrous 10 g Na₂SO₄ and then ground using mortar and pestle until homogenous powder was obtained, 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 internal standard. This was extracted with triple distilled 175 ml of hexane: acetone (3:1v/v) in a 200ml round bottomed flasks for at least 16 hours in the soxhlet extractor set-up. To the extracts 1ml of isooctane was added as keeper then concentrated to 1ml using LABCONCO rotary evaporator the temperature was maintained at 30°C after which the extracts were put in vials awaiting clean-up procedure.

3.8 Samples Clean-Up

The 1ml tomatoes extracts were cleaned up through alumina chromatographic glass column 20 cm long x 2 cm internal diameter (id) packed with 1g of freshly baked anhydrous sodium sulphate, followed by 15 g of deactivated alumina, 1g of activated charcoal and finally another 1g layer of anhydrous sodium sulphate. The column was pre-conditioned with 15 ml HPLC grade hexane and discarded. The sample extract was introduced into the column; the vial was rinsed four times with 1ml portions of HPLC grade 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 1ml using a rotary evaporator at temperature of 30°C and transferred to clean vial and then concentrated to

0.5 ml under a gentle stream of white spot nitrogen gas and taken for GC-MS analysis.

3.9 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 analytical laboratory, University of Nairobi. The DB-5 fused silica capillary column of 30m x 0.25 μ m i.d. x 0.25 μ m film thickness coated with cross-linked 5% phenyl dimethyl polysiloxane was used. The carrier gas was helium (99.99 % purity) at a flow rate of 1.0ml/min. Oven temperature was maintained initially at 70 °C for 1min, increased at 15 °C/min to 175 °C, then at 2 °C/min to 215 °C, at 10 °C/min to 265 °C and finally at 20 °C/min to 290 °C and held for 8min. Injection volume was 1 μ L, injected in splitless mode at injection temperature of 250 °C. Analysis was done in SIM mode.

3.10 Sulphur Removal

To remove sulphur from the cleaned soil extracts, approximately 1g of freshly activated copper powder was added to the sample in a vial. A black coloring appeared to all extracts containing sulphur which indicated a formation of copper sulphide compound. The extracts were then filtered through glass funnel which was packed with glass wool and activated 2g anhydrous sodium sulphate. 5 ml of HPLC hexane was used to condition the anhydrous sodium sulphate and the sample was introduced then eluted with 20ml of HPLC grade hexane into round bottom flask and concentrated to 1-ml using rotary evaporator. The concentrated samples were transferred to clean auto vials and then concentrated to 0.5 ml under a gentle stream of white spot nitrogen gas and taken for GC-MS analysis using the conditions as set in section 3.9

3.11 Recovery Tests

Triplicates of 10 g tomatoes and soil samples were each spiked with 20 μ l of 1 ppm carbaryl standard solution and dried with activated anhydrous 10 g Na₂SO₄ and blended to homogenous powder, before transferring to the Soxhlet thimble for extraction. The extraction procedures and clean-up process were performed as illustrated in sections 3.7.1, 3.8 and 3.9 respectively.

The recovery tests was performed by blending 10g of dried activated anhydrous Na₂SO₄ using mortar and pestle until homogenous powder was obtained (blank sample). The blank sample was spiked with 20 μ l of 1ppm carbaryl standard solution. The extraction, clean-up and analysis prosedures done using the procedures in sections 3.7.1 and 3.9 respectively. The percentage recoveries were calculated.

3.12 Quantification Tests

Quantification was based on calculations from calibration curves in the concentration range of 2.56mg/L to 136.30mg/L for carbaryl. The calibration curve of the standard was drawn.

3.13 Quality Assurance and Quality Control

Quality assurance and quality control were done by spiking each matrix with internal standard (PCB 52) prior to extraction to check extraction efficiency and recoveries, analysis of replicate samples, and field blanks. Field blanks consisting of distilled anhydrous Na₂SO₄ were carried along at every field trip to track field contamination and were then subjected to the entire analytical procedure as the samples. Extraction was carried out in triplicate.

3.14 Physicochemical Parameters of Soil

The soil samples were analysed for carbaryl pesticide residue levels and both physical and chemical parameters to obtain baseline information. The physiochemical analysis of soil was carried out at Kenya Agricultural Research Institute (KARI). 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.

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 15ml mixture of concentrated sulphuric acid and 5% potassium dichromate in 1:2 ratio v/v at 150°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 spectrophotometrically at 600nm by determining the concentration of chromic ions (Cr^{3+}) produced after oxidation.

Total Nitrogen was also analysed using the Kjeldahl 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 Mehlich 1 (double acid) method. Oven dry soil was extracted in 1:5 ratios (w/v) with a mixture of 0.1M hydrochloric acid and 0.5M 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.

3.15 Moisture Content Determination

Moisture content in soil and tomato samples was determined by heating 5 g of the sample in pre-cleaned and pre-weighed watch glass in an oven (model E 28# 04- 71528) at 105°C for 24 hours.

The difference in weight between wet and cool dry sample was taken as the moisture content.

Percentage moisture was calculated as:

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

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 Langmuir 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

RESULTS AND DISCUSSION

4.1 Pesticides Use Survey

4.1.1 Background information on Farming in the Three Farms

The survey was conducted in the three Farms where 88 employees were interviewed on the use, safety, handling, and environmental awareness of pesticides used in the farm. All the three farms had some employees on permanent basis while few were on casual basis and all the three farms practice crop rotation and they grow their plants in green house. The summary of the survey is attached on the appendix II.

4.1.2 Education Background

The interview showed that 22 of the employee had only primary education, 57 of the employee had secondary education while 9 had post-secondary education. Figure 2 shows the employee's education.

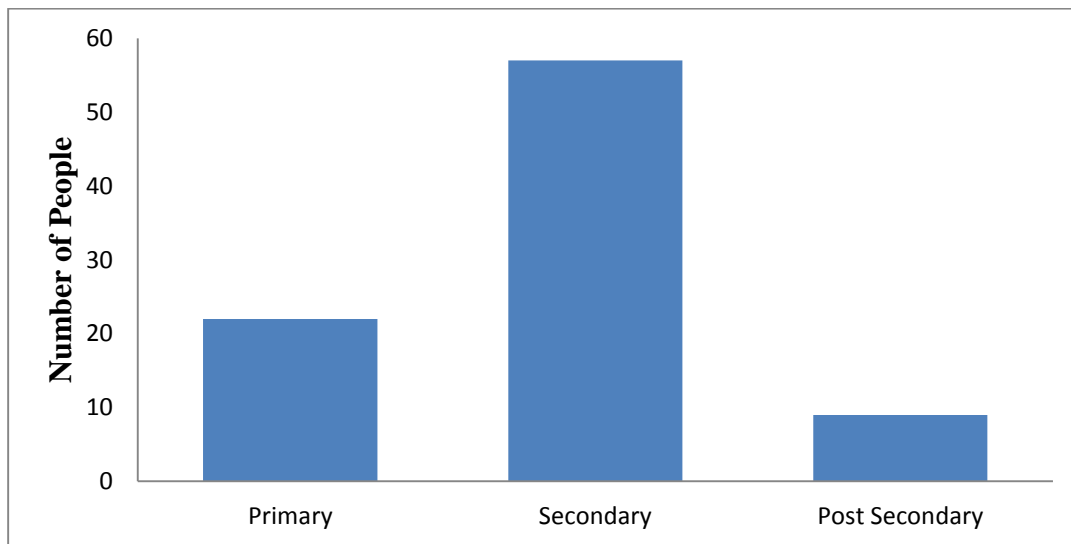


Figure 2: Number of employees and their Education background

4.1.3 pesticides used

From the survey it was found that the most commonly used pesticides in the three farms are organophosphates, carbamates and pyrethroids. All of these pesticides are registered in Kenya by the Pest Control Products Board [PCPB, 2004]. Figure 3 show summary of pesticide used in the three farms.

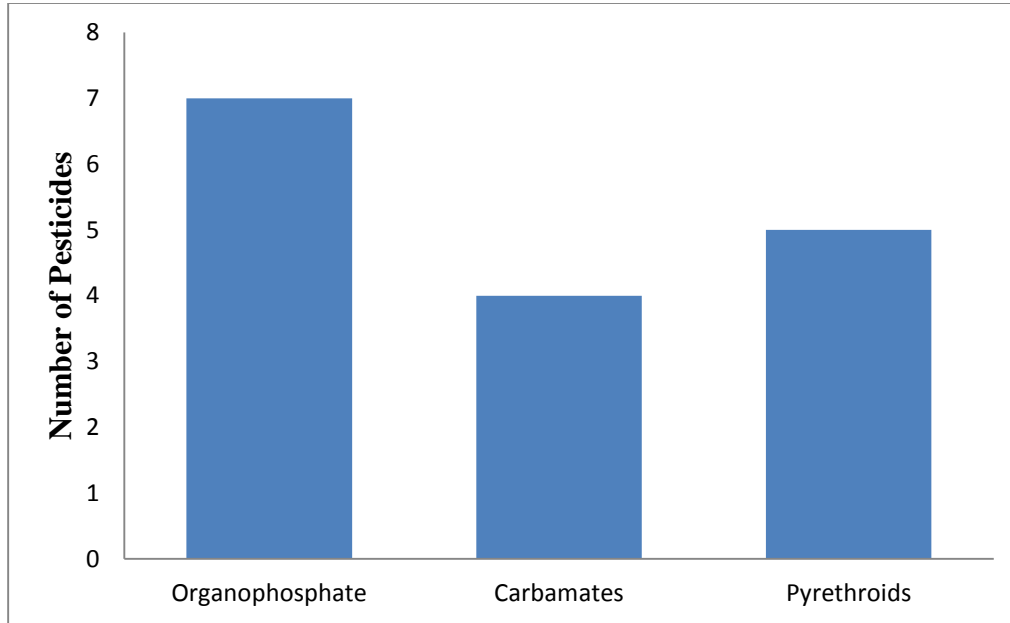


Figure 3: Number and Types of pesticides available in Hippo, Kingfisher and Harnekop Farms.

4.1.4 Factors Affecting Choice of Pesticide

The main consideration for use of a particular pesticide by farm workers from the survey was whether the pesticide enables the farm to get good yield as indicated by 42 of the respondents, followed by cost effectiveness of the pesticide where 32 of the respondents noted it as an important factor. Also 6 used a given pesticide because it was suggested by management of the farm, While 3 used a given pesticide because it was suggested by the agrochemical dealers and the sales agent of the agrochemical industries also 5 of the respondent used the pesticide because it is good for the environment. As shown in Figure 4.

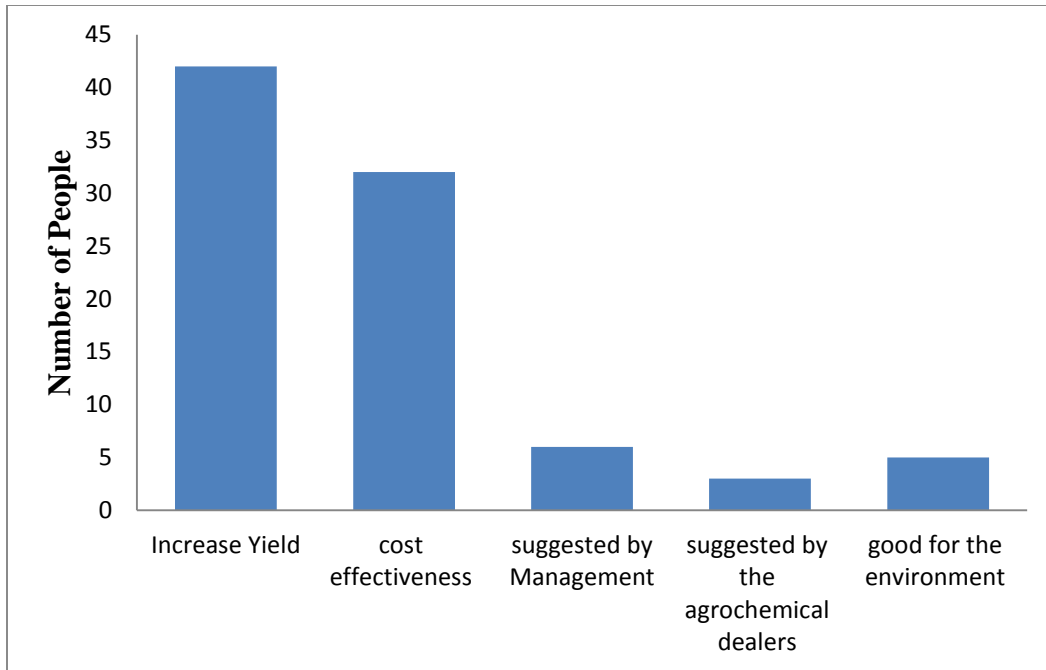


Figure 4: Number of people indicating Factors affecting the choice of pesticide

4.1.5 Pesticide Training and Knowledge

All the respondents were aware of the use of pesticides, but 52 had basic training while 36 had advanced training. All the respondents indicated that they use protective devices when handling pesticides. 98 % of the respondents always read instruction menu on the pesticide before use. The respondents who had post secondary education indicated that they always read instructions on the pesticide use and formulation, while those with secondary education majority said that they 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 indicated that they read the instructions but ask their colleague to explain to them. As shown in Figure 5.

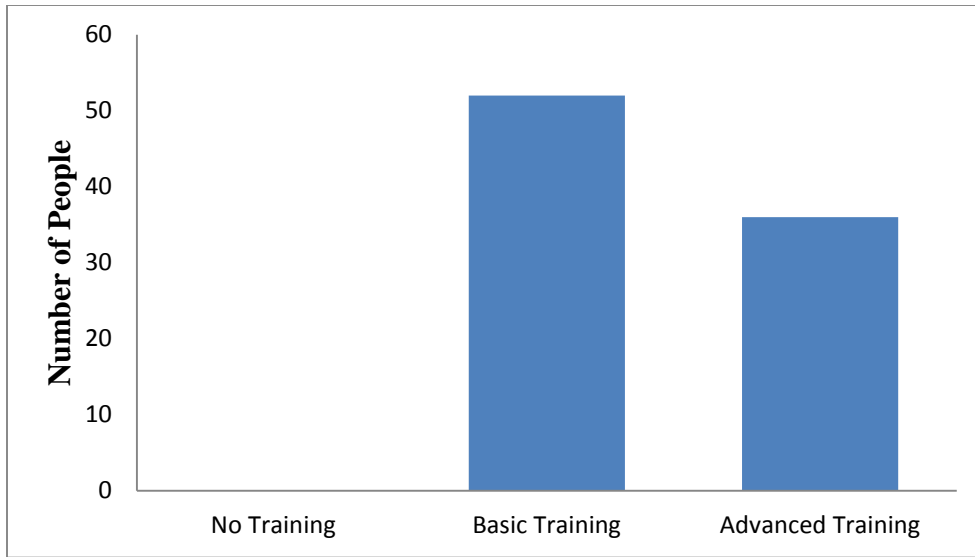


Figure 5: Number of people with training on pesticide use and Safety

4.1.6 Training on pesticides Residue in Food

All the respondents were aware of pesticide residues in food; but 52 had basic training and 36 had advanced training about pesticide residues in food, as shown in Figure 6.

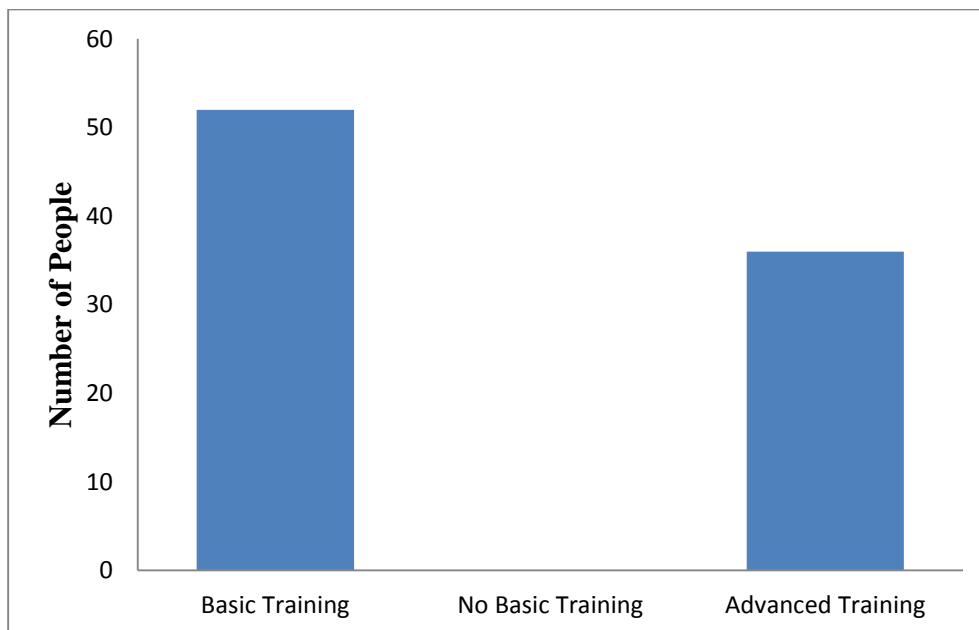


Figure 6: Number of people indicating training on pesticides residues on food

4.1.7 Impacts of Pesticides on the Environment

It was noted that all respondents were aware that the use of a number of pesticides has been banned or restricted in Kenya, while 99 % of the respondents were aware of the effects of pesticides to the environment in case of poisoning the environment with pesticides. There were 2 reported cases of pesticide poisoning in Hippo firm and 3 reported cases of pesticide poisoning in Harnekop firm.

4.1.8 Sources of Information on Pesticide Use

The main information source for the farm's employees on pesticide use are through the firm's agricultural extension workers, management, agro-chemical industries, agro-chemical dealers and media. 66 % of the respondents get information from firm's agricultural extension workers, while 20 % get information from media, 1 % get information from agro- chemical dealers, 3 % get information from the management and only 9% get information from agro- chemical industries as shown in Figure 7.

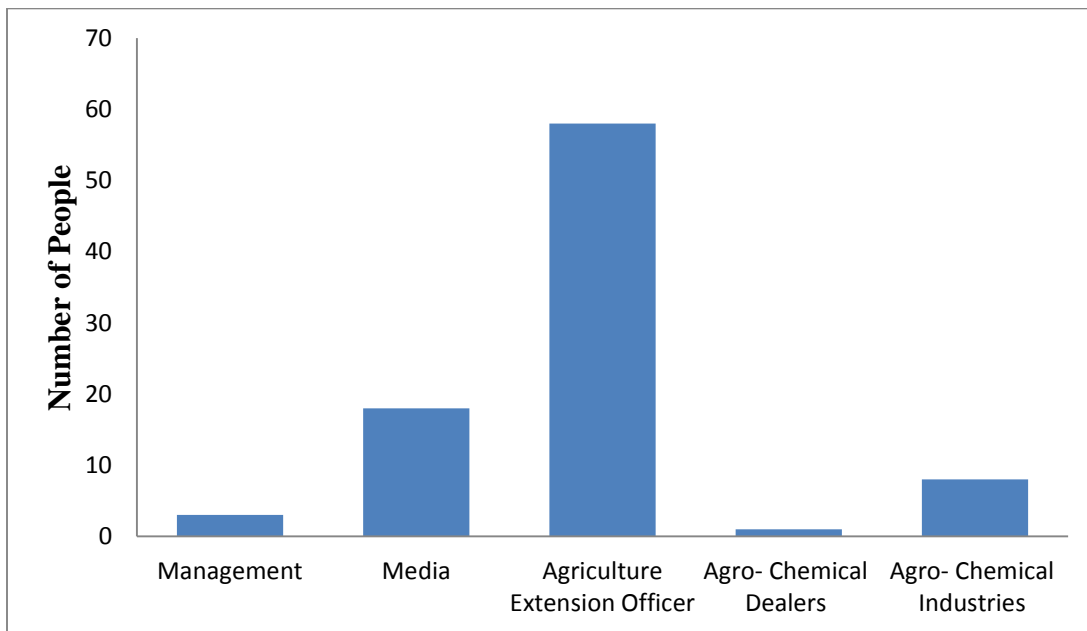


Figure 7: Number of people indicating sources of information

4. 2 Recovery Tests

The recovery of carbaryl was found to be 84.50 % in soil, 93.15 % in tomatoes and 97.95 % in blank samples respectively (Table 1). The recoveries were within the acceptable range of 70 % - 120 % [Hill, 2000].

Table 1: Percent Recoveries for carbaryl pesticide in tomatoes, soils and blank samples

Samples	Carbaryl (% Recovery)
Tomatoes	93.15±0.45
Soil	84.50±1.55
Blank	97.95 ± 6.71

n=3 mean ± standard deviation

4.3 Quantification Tests

Quantification was based on calculations from calibration curves in the concentration range of 1.214 mg/L to 105.368 mg/L for carbaryl. The calibration curve of the standard was a straight line for the compound 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 8 shows calibration curve for carbaryl. Figure 9 and 10 shows chromatogram of carbaryl standard. Sample analyte concentrations were obtained by interpolation from the graphs which applies the equation of the line $y= mx+c$, Where

y = Peak area (Instrument response)

x =Analytes concentration,

m =Gradient, and

c = Constant

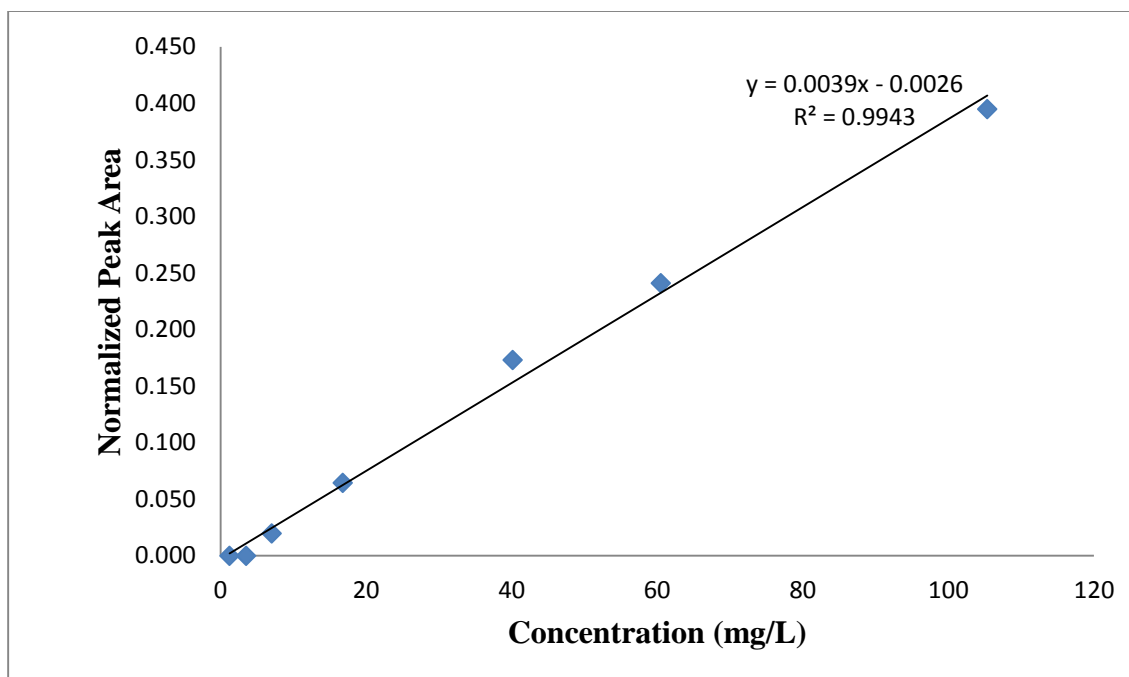


Figure 8: Normalized peak area versus concentration for carbaryl standard

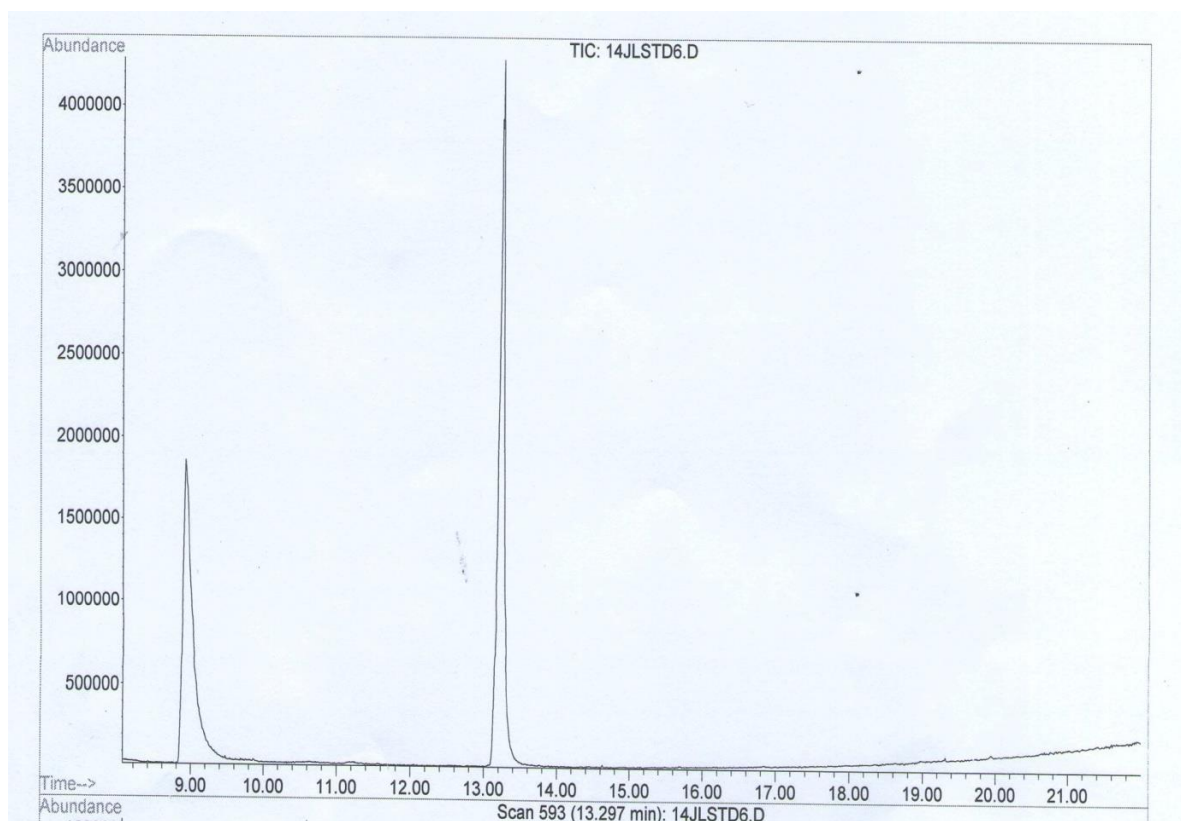


Figure 9: Chromatogram for Carbaryl Standard

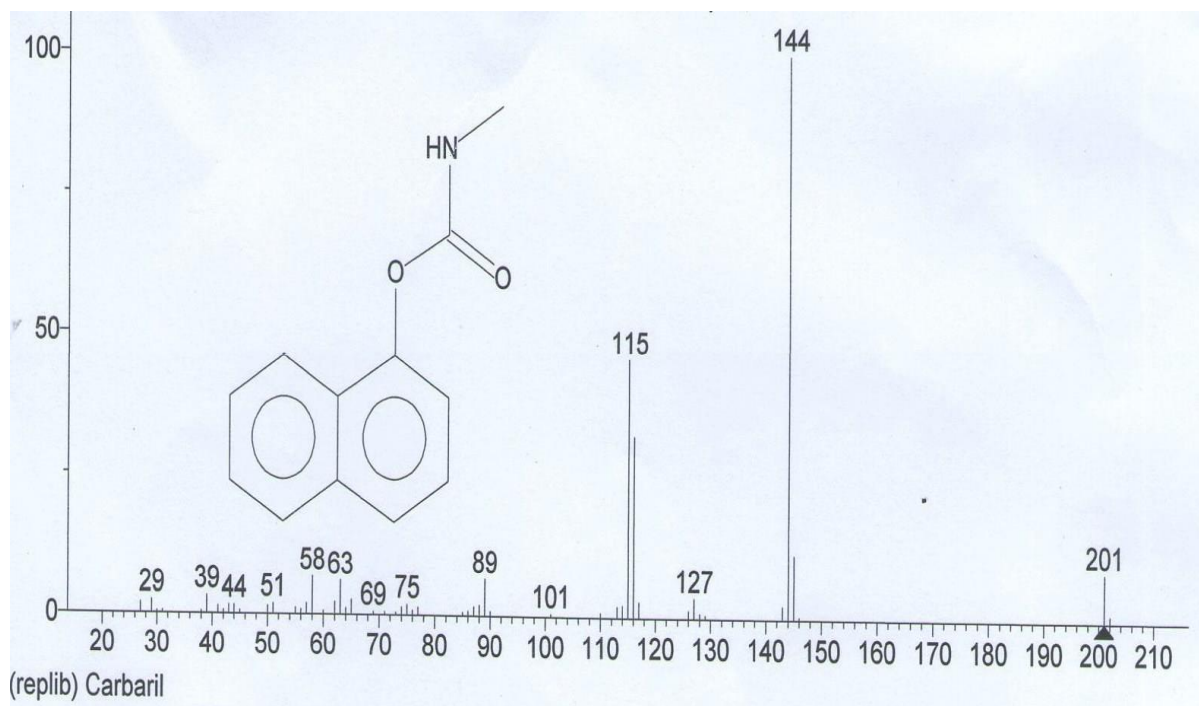


Figure 10: Chemical structure and ionic Mass Spectra for Carbaryl

4.4 Fate of Carbaryl in Tomatoes

4.4.1 Hippo Farm

This study was conducted to establish whether application of carbaryl on tomatoes growing in normal field conditions in a green house result in elevation or reduction of the residue. The results based on dry weight for the dissipation of carbaryl in tomatoes are presented in Table 2.

Table 2: Carbaryl degradation in tomatoes from Hippo Farm (mg/kg, dw)

Time (Days)	Concentration (mg/kg)
0	13.99±2.36
3	4.6±0.04
5	3.22±0.99
7	2.86±0.10
9	1.96±0.00

The trend of degradation (Figure 11) was obtained by plotting determined concentration of Carbaryl versus time in days.

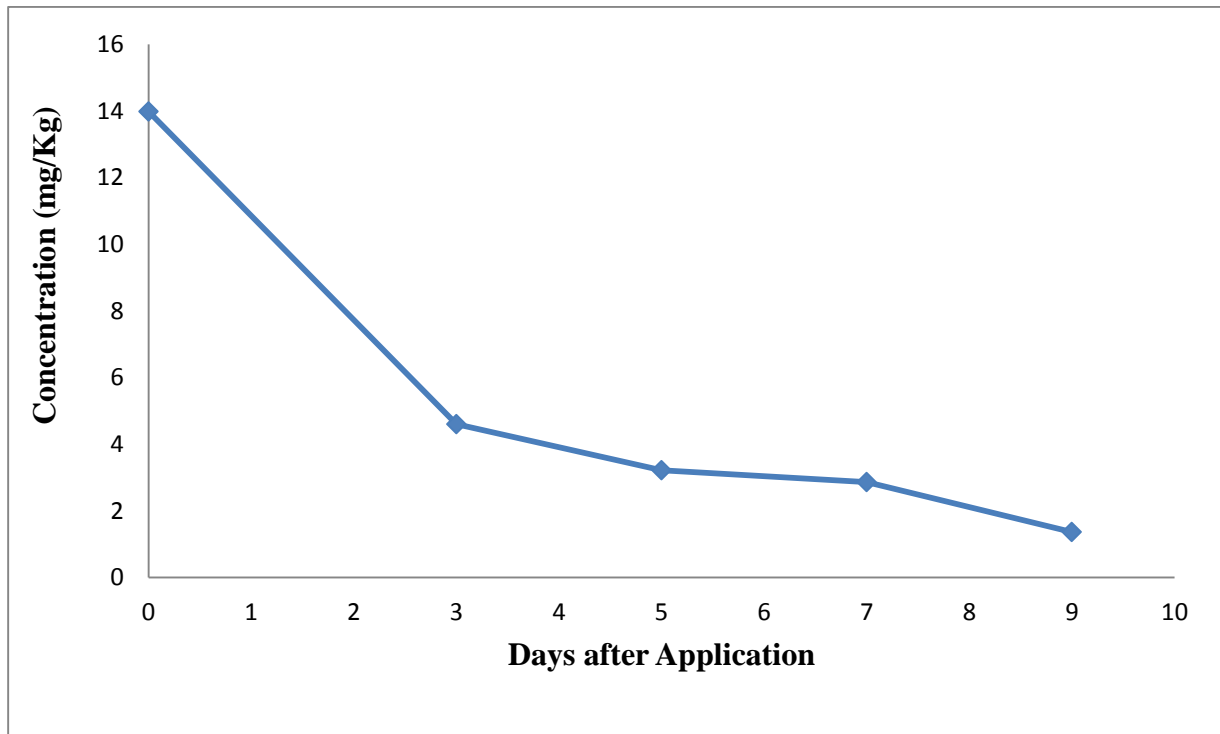


Figure 11: Concentration of Carbaryl against time elapsed after application on Tomatoes in Hippo Farm

The concentration of carbaryl in tomatoes decreased over time (Table 11). The average initial concentration of carbaryl was $13.99 \pm 2.36 \text{ mgkg}^{-1}$ (day 0) and the final residue was $1.96 \pm 0.00 \text{ mgkg}^{-1}$ on the 9th day. After 3 days 33 % of carbaryl remained in tomatoes while 23 % of carbaryl remained in tomatoes by day 5 after the application and 14 % of the initial deposited carbaryl remained in tomatoes by day 9. The results showed that there was rapid dissipation of carbaryl in tomatoes for the first 3 days and that the characteristic two-phase dissipation pattern showing the initial faster dissipation rate followed by slower rate starting after 3 days was seen. This is consistent with other reports from other plants [Wu *et al.*, 2007].

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

$$r = dC/dt = kKC/(1+KC) \quad \text{-----(1)}$$

When the initial concentration C_0 is $\lll 1$, the denominator in equation (1) can be assumed to be 1, and the equation can be simplified to an apparent first-order equation:

$$dC/dt = kC \quad \text{----- (2)}$$

$$dC/C = kC dt \quad \text{----- (3)}$$

$$dC/dt = -Kt \quad \text{-----(4)}$$

Integrating equation 3 and taking boundary conditions of $C = C_0$ at $t=0$, gives

$$\ln(C_0/C_t) = kCt = k_{abs}t \quad \text{-----(5)}$$

Or

$$C_t = C_0 e^{-kt} \quad \text{-----6)}$$

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

$$\ln C_t = \ln C_0 - k_{abs} X t \quad \text{----- (7)}$$

Where; C_t = pesticide concentration at time, t

K_{obs} = first order rate constant

t = time in Days

C_o = the original carbaryl 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:

$$\ln(C_o/2C_o) = -Kt_{1/2} \quad \text{----- (8)}$$

$$\ln 0.5 = -Kt_{1/2} \quad \text{----- (9)}$$

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

The regression curve for the disappearance of carbaryl in tomatoes is shown Figure 12 which was obtained by graph of negative logarithm of the concentration of residues against time and it had correlation of $R^2 = 0.95$

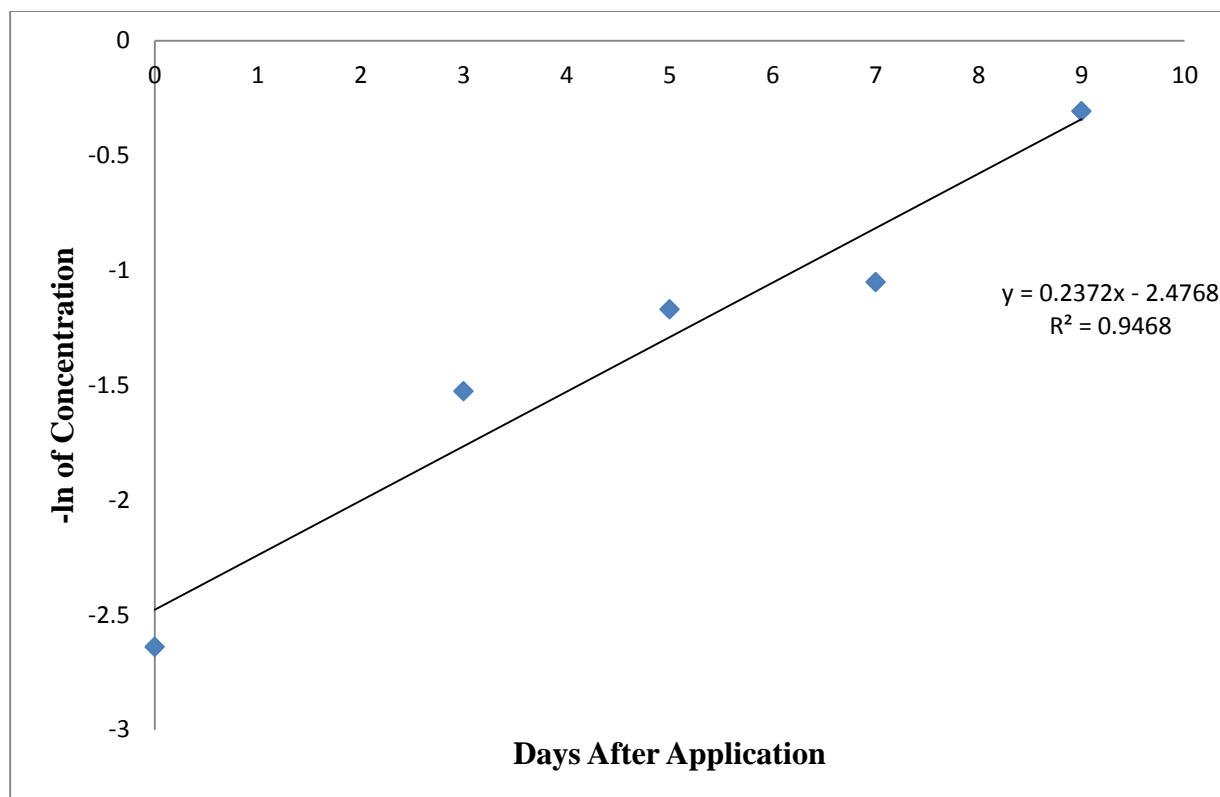


Figure 12: Regression curve for disappearance of Carbaryl from Tomatoes in Hippo Farm

Equation 7 is in the form of $y = mx + C$. A plot of $\ln(C_t)$ versus 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} is 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 12, gave a regression equation, $y = 0.2372x - 2.4768$. A gradient of 0.2372 was obtained (which is equivalent to the constant K_{obs}). Therefore in this study the degradation of carbaryl follows Langmuir-Hinshelwood kinetic equation and using equation (10), the half-life of carbaryl in tomatoes was found to be 2.92 days by the Langmuir-Hinshelwood kinetic model.

4.4.2 King Fisher Farm

This study was conducted to establish whether application of carbaryl on tomatoes growing in normal field conditions in a green house result in elevated/reduction residue. The results based on dry weight for the degradation of carbaryl in tomatoes are presented in Table 3.

Table 3: Carbaryl degradation in tomatoes in King Fisher Farm (mg/kg, dw)

Time(Day)	Concentration
0	6.04±3.77
3	2.88±0.11
5	1.05±0.07
7	BDL
9	BDL

The trend of degradation (Figure 13) was obtained by plotting determined concentration of Carbaryl versus time in days.

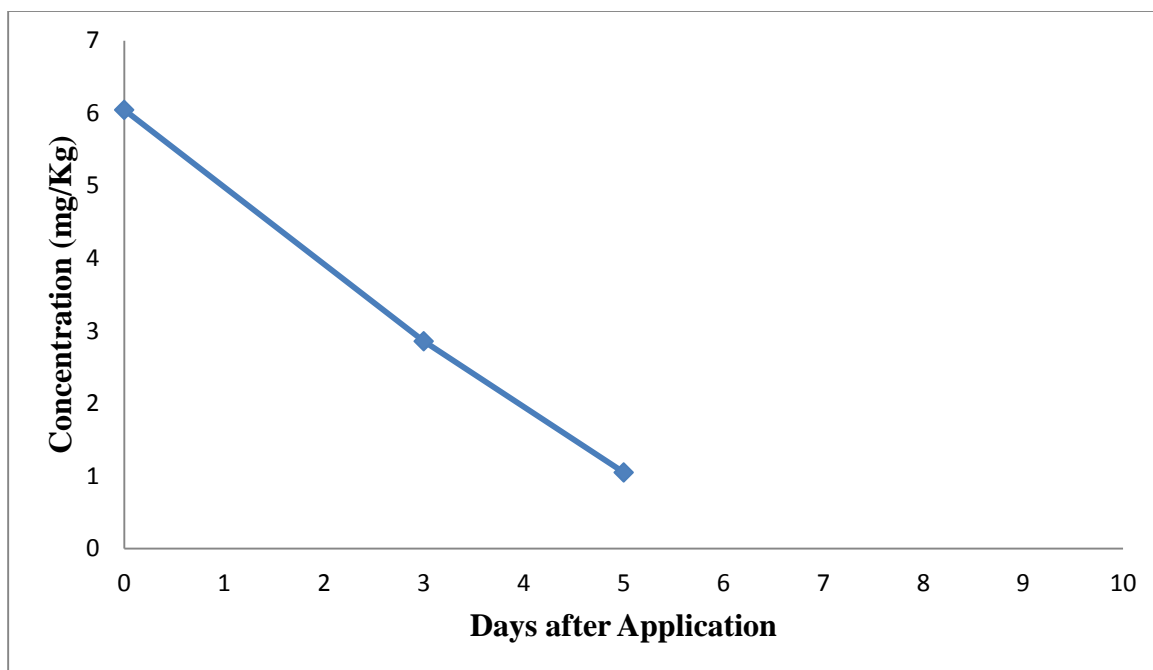


Figure 13: Concentration of Carbaryl against days after application on Tomatoes in Kingfisher Farm

As can be seen in Figure 13, the dynamic curve demonstrated that carbaryl residues dissipated significantly in the first 5 days. The concentration of carbaryl in tomatoes decreased over time (Figure 13). The average initial deposition of carbaryl was $6.04 \pm 3.77 \text{ mg Kg}^{-1}$ (day 0) and the final residue was BDL on day 9. After 3 days 47% of carbaryl remained in tomatoes and 17 % remained by day 5 after the deposition. The half-life of carbaryl in tomatoes was calculated using equation (10) and data obtain (Table 3). The half-life ($t_{1/2}$) of carbaryl was calculated through regression analysis assuming the loss of carbaryl follows Langmuir-Hinshelwood kinetic model, after k (rate constant) was determined and was found to be 2.03 days. The regression curve for the disappearance of carbaryl in tomatoes is shown Figure 14 which was obtained by graph of negative logarithm of the concentration of the residues against time and it had correlation of $R^2 = 0.96$.

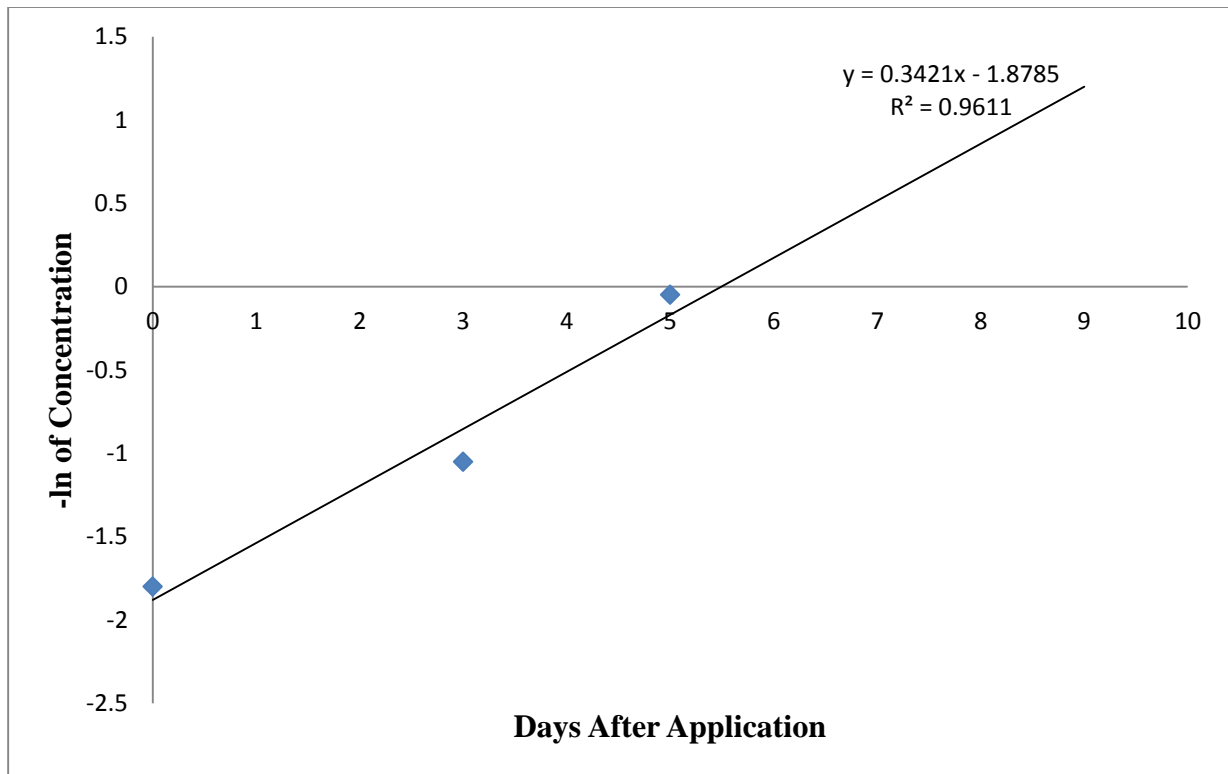


Figure 14: Regression curve for disappearance of carbaryl from tomatoes in King Fisher Farm

4.4.3 Harnekop Farm

This study was conducted to establish whether application of carbaryl on tomatoes growing in normal field conditions in a green house result in elevation/reduction of pesticide residue levels. The results based on dry weight for the degradation of carbaryl in tomatoes are presented in Table 4.

Table 4: Carbaryl degradation in tomatoes in Harnekop Farm (mg/kg, dw)

Days	Concentration(mg/kg)
0	20.41±2.31
3	10.19±0.98
5	6.32±2.74
7	2.26±0.00
9	2.13±0.56

The trend of degradation (Figure 15) was obtained by plotting determined concentration of Carbaryl versus time in days.

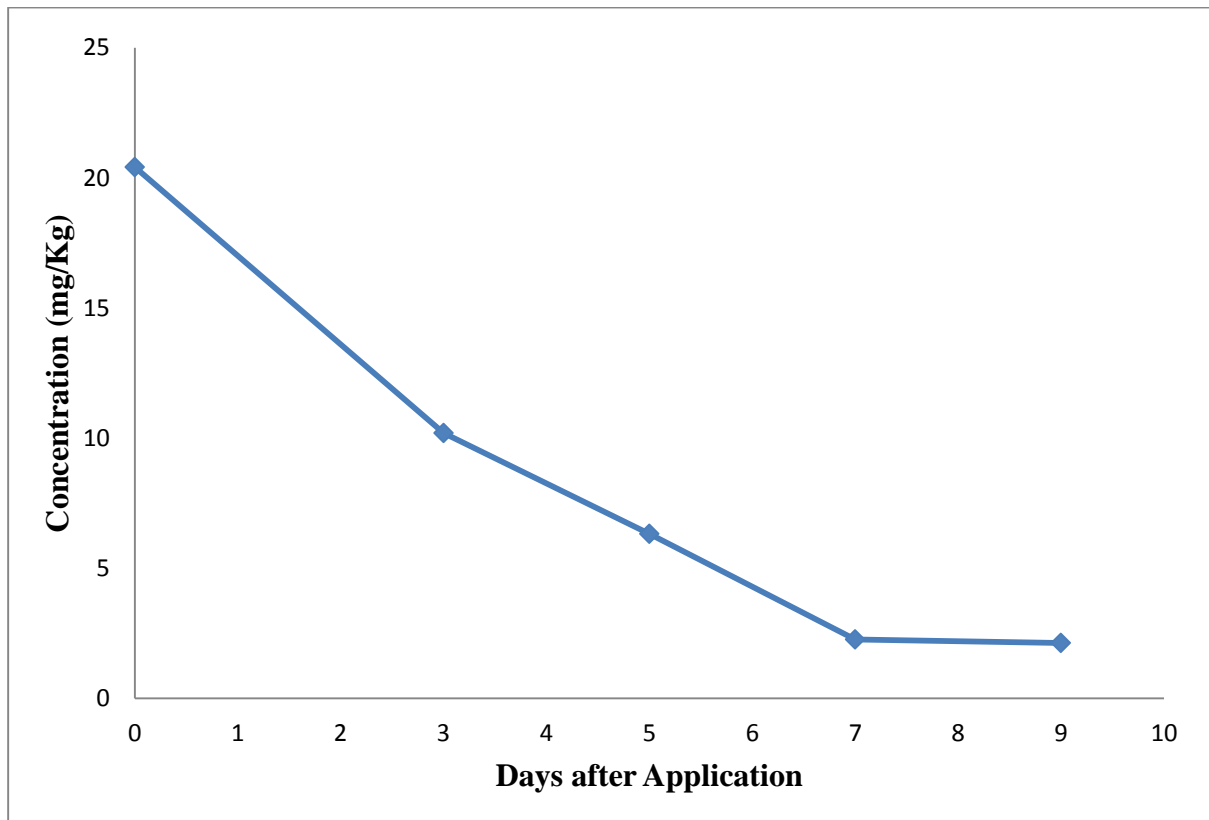


Figure 15: Concentration of Carbaryl against time after application on tomatoes in Harnekop Farm

The concentration of carbaryl in tomatoes decreased over time as can be seen in Figure 15 the dynamic curve demonstrated that carbaryl residues dissipated significantly in the first few days and persisted in tomatoes for extended period of time. The average initial deposition of carbaryl was $20.41 \pm 2.31 \text{ mg kg}^{-1}$ (day 0) and the final residue was $2.13 \pm 0.56 \text{ mg kg}^{-1}$ on day 9. After 3 days 50 % of carbaryl remained in tomatoes while 30 % of carbaryl remained in tomatoes by day 5 after the application and 10 % of the initial applied carbaryl remained in tomatoes by day 9. The results showed that there was a rapid initial dissipation for the first 3 days which is characteristic of a two-phase degradation pattern showing the initial faster degradation rate followed by lower rate starting after 3 days. The half-life of carbaryl in tomatoes was calculated using equation (10) and using data in (Table 4). The half-life ($t_{1/2}$) of carbaryl was calculated through regression analysis with the assumption that the loss of carbaryl follows Langmuir-Hinshelwood kinetic model, after k was determined and was found to be 2.54 days. The regression curve for the disappearance of carbaryl in tomatoes is shown in Figure 16 which was obtained by graph of negative logarithm of the concentration of the residues against time and it had correlation of $R^2 = 0.957$

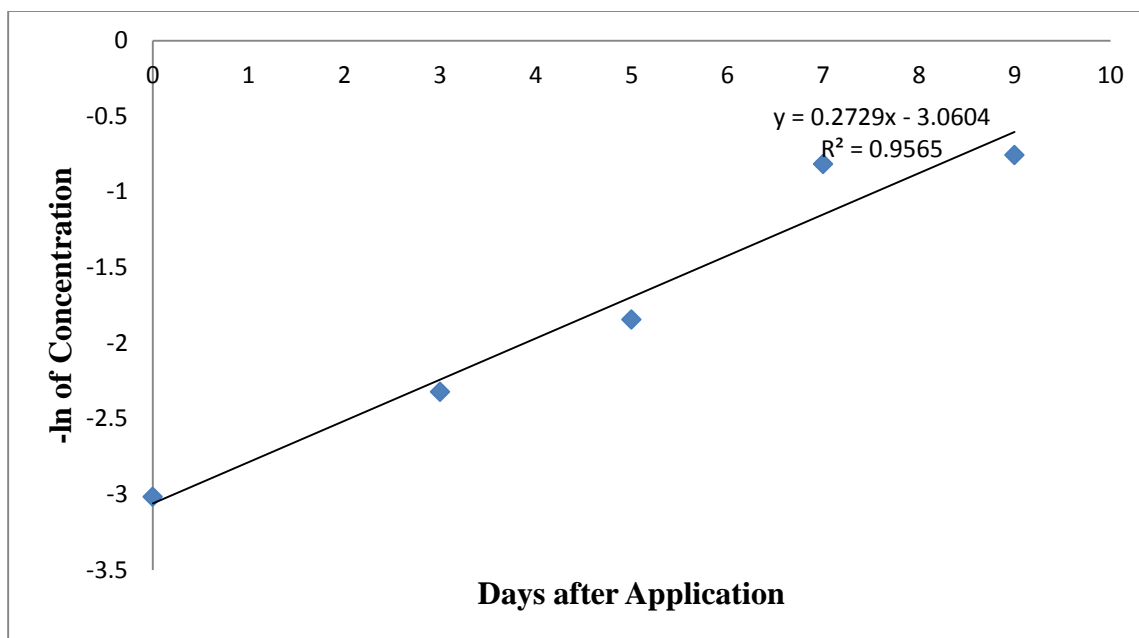


Figure 16: Regression curve for disappearance of carbaryl from tomatoes in Hamekop Farm

4.5 Fate of Carbaryl in Soil

4.5.1 Hippo Farm

This study was conducted to establish whether application of carbaryl on soil in normal field conditions in a green house result in elevated/reduction of residue of carbaryl in soil. The results based on dry weight for the dissipation of carbaryl in soil are presented in Table 5.

Table 5: Results of Carbaryl Degradation in Soil in Mg/Kg

Days	Concentration (mg/Kg)
0	4.6±0.87
3	2.86±0.01
5	2.03±1.24
7	1.66±0.66
9	1.45±0.33

The trend of degradation (Figure 17) was obtained by plotting determined concentration of Carbaryl versus time in days.

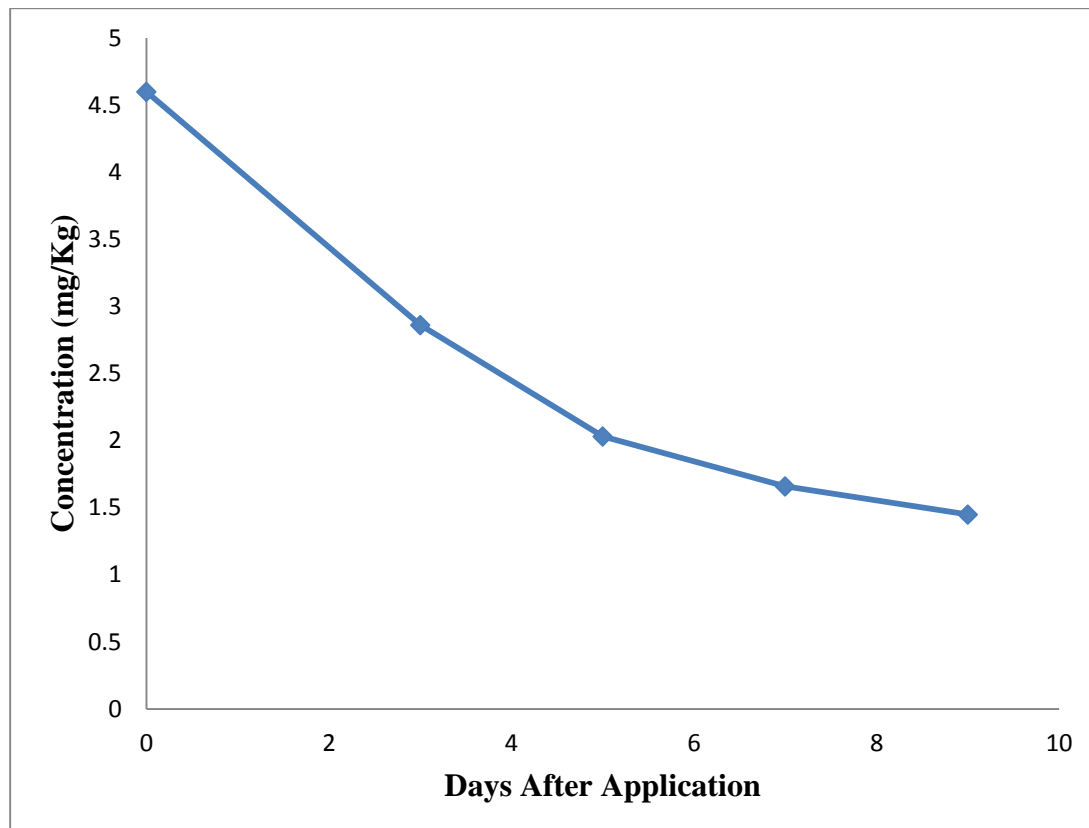


Figure 17: Concentration of carbaryl against time after application on Soil in Hippo Farm

The concentration of carbaryl in the soil decreased over time (Figure 17). The average initial deposition of carbaryl was $4.6 \pm 0.87 \text{ mgkg}^{-1}$ (day 0) and the final residue was $1.45 \pm 0.33 \text{ mgkg}^{-1}$ on day 9. After 3 days 62 % of carbaryl remained in soil while by day 5 after the application of carbaryl in soil, 44 % of the initial applied pesticide remained in soil and 32 % of the initial applied carbaryl remained in soil by day 9. The results showed that there was rapid dissipation of carbaryl in soils for the first few days and that the characteristic two-phase dissipation pattern showing the initial faster dissipation rate followed by lower rate. The half-life of carbaryl in soil was calculated using equation (10) and data obtain (Table 5), the half-life ($t_{1/2}$) of carbaryl was

calculated through regression analysis assuming the loss of carbaryl follows Langmuir-Hinshelwood kinetic model, after k was determined and was found to be 5.29 days. The regression curve for the disappearance of carbaryl in soil is shown in Figure 18 which was obtained by graph of negative logarithm of the concentration of the residues against time and it had correlation of $R^2 = 0.973$.

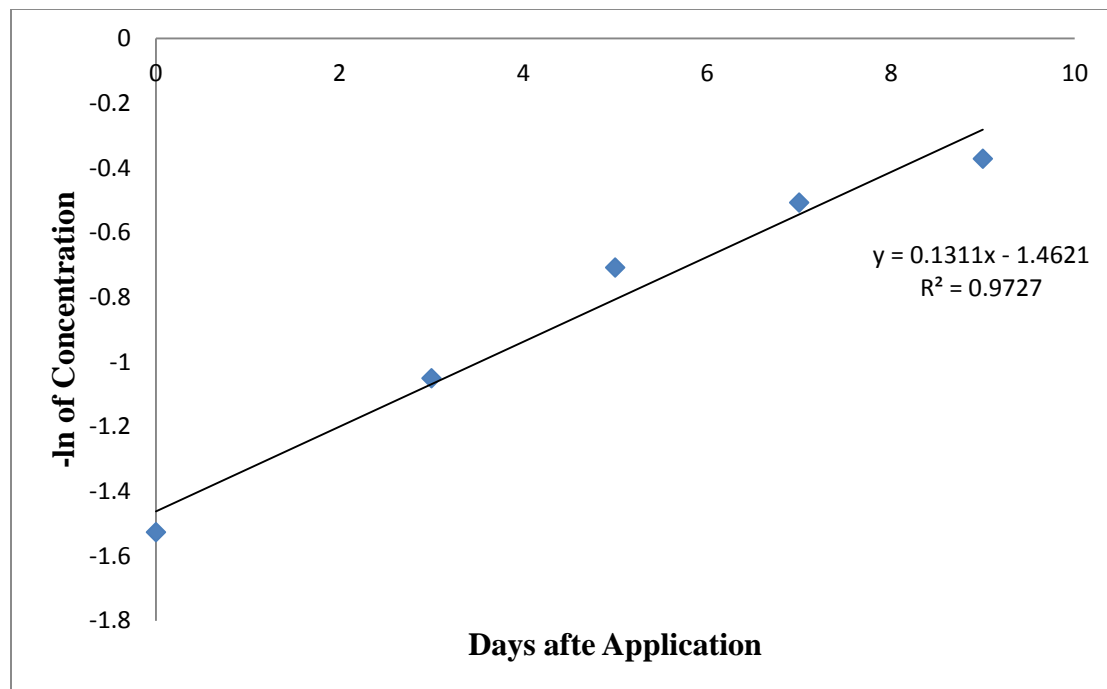


Figure 18: Regression curve for disappearance of Carbaryl from Soil in Hippo Farm

4.5.2 King Fisher Farm

This study was conducted to establish whether application of carbaryl on soil in normal field conditions in a greenhouse result in the elevation/reduction of pesticide residue levels of carbaryl in soil. The results based on dry weight for the dissipation of carbaryl in soil are presented in Table 6.

Table 6: Carbaryl degradation in Soil in mg/kg

Days	Concentration (mg/Kg)
0	3.46±0.00
3	1.95±0.01
5	1.76±0.08
7	1.24±0.00
9	1.02±0.05

The trend of degradation (Figure 19) was obtained by plotting determined concentration of Carbaryl versus time in days.

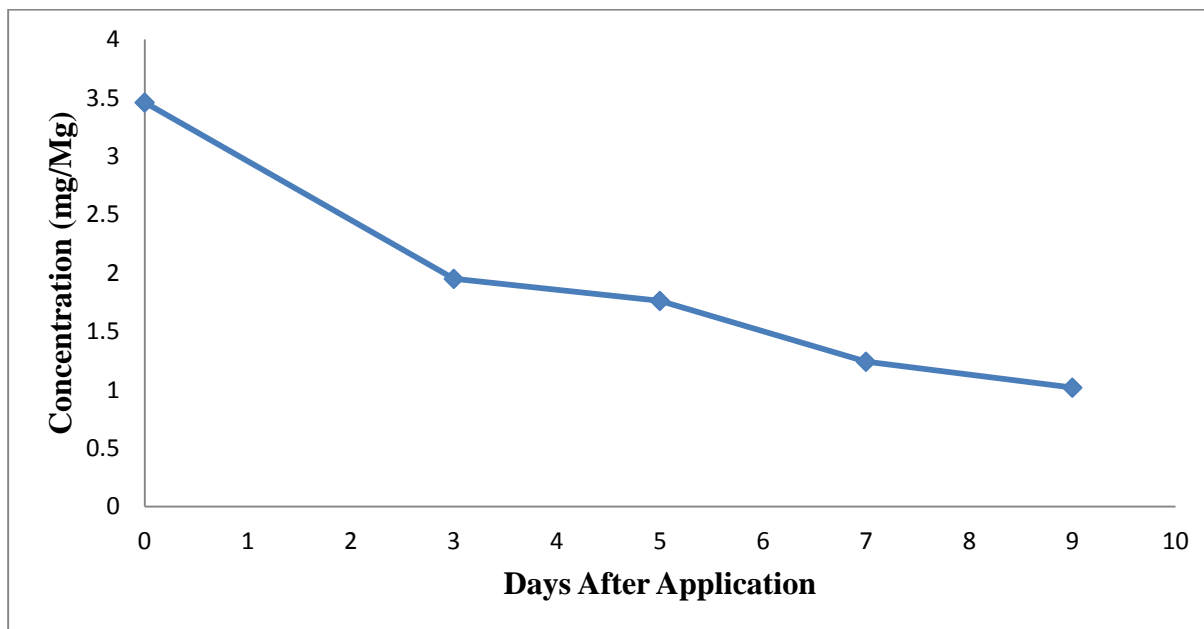


Figure 19: Concentration of Carbaryl against time after application on Soil in Kingfisher Farm

The concentration of carbaryl in soil decreased over time (Figure 19). The average initial deposition of carbaryl was $3.46 \pm 0.00 \text{ mg kg}^{-1}$ (day 0) and the final residue was $1.02 \pm 0.05 \text{ mg kg}^{-1}$ on day 9. After 3 days 56 % of carbaryl remained in the soil while by day 5 after the deposition of carbaryl in the soil, 51 % of the initial applied pesticide remained in the soil and 29 % of the initial applied carbaryl remained in the soil by day 9. The results showed that there was rapid dissipation of carbaryl in the soils for the first 3 days and that the characteristic two-phase dissipation pattern showing the initial faster dissipation rate followed by lower rate. The half-life of carbaryl in soil was calculated using equation (10) and data obtain (Table 6), the half-life ($t_{1/2}$) of carbaryl was calculated through regression analysis assuming the loss of carbaryl follows Langmuir-Hinshelwood kinetic model, after k was determined and was found to be 5.21 days. The regression curve for the disappearance of carbaryl in soil figure 20 which was obtained by graph of negative logarithm of the concentration of the residues against time and it had correlation of $R^2 = 0.98$

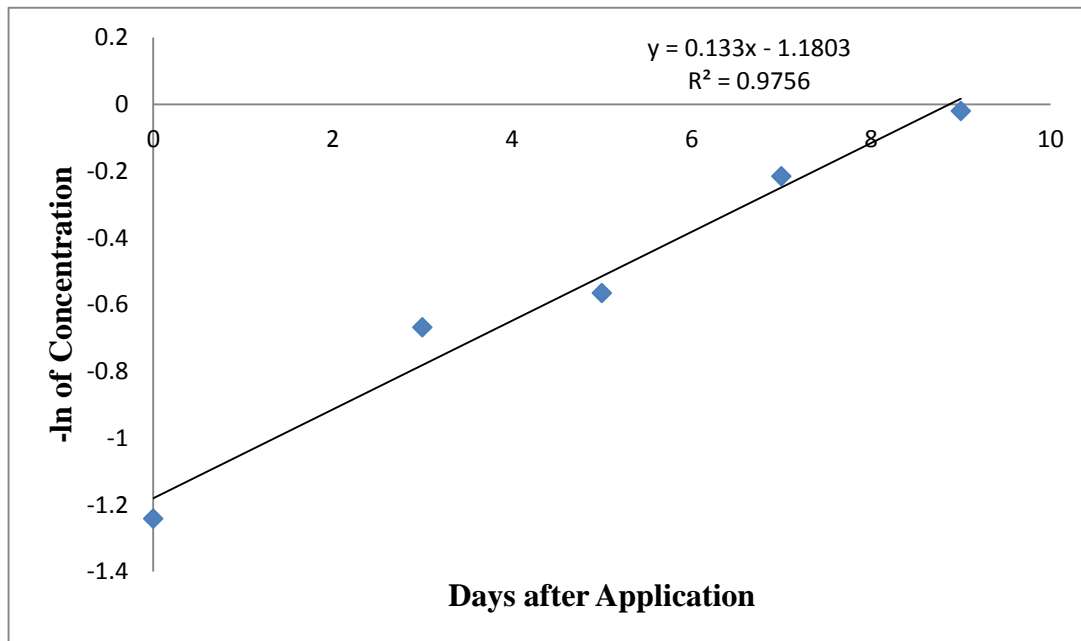


Figure 20: Regression curve for disappearance of Carbaryl from Soil in Kingfisher Farm

4.5.3 Harnekop Farm

This study was conducted to establish whether application of carbaryl on soil in normal field conditions in a greenhouse result in elevation or decrease of pesticide residue levels of carbaryl in soil. The results based on dry weight for the dissipation of carbaryl in soil are presented in Table 7.

Table 7: Results of Carbaryl Degradation in Soil in mg/Kg

Days	Concentration (mg/Kg)
0	7.02±1.19
3	4.63±0.67
5	4.12±1.02
7	3.08±0.98
9	3.03±0.84

The trend of degradation (Figure 21) was obtained by plotting determined concentration of Carbaryl versus time in days.

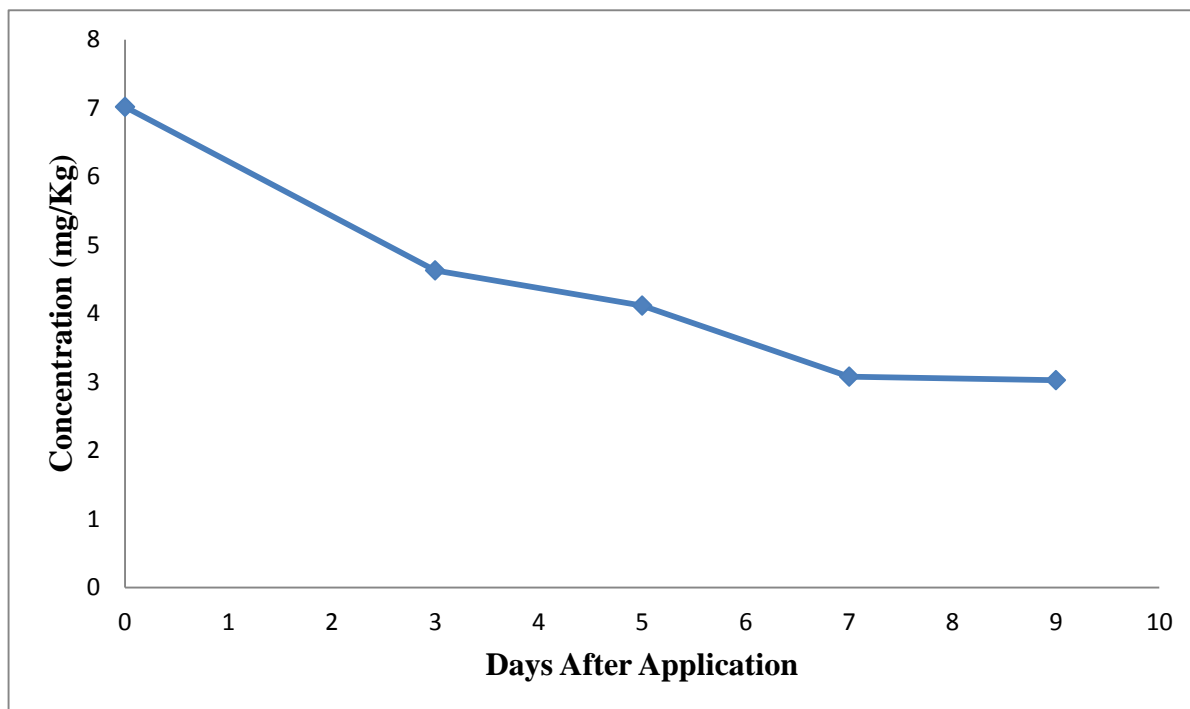


Figure 21: Concentration of Carbaryl against time after application on Soil in Harnekop Farm

The concentration of carbaryl in soil decreased over time (Figure 21). The average initial concentration of carbaryl was $7.02 \pm 1.19 \text{ mg kg}^{-1}$ (day 0) and the final residue was $3.03 \pm 0.84 \text{ mg kg}^{-1}$ on day 9. After 3 days 66 % of carbaryl remained in the soil while by day 5 after the application of carbaryl in soil, 58 % of the initial applied pesticide remained in soil and 43 % of the initial carbaryl remained in soil by day 9. The results showed that there was rapid dissipation of carbaryl in soil for the first few days and that the characteristic two-phase dissipation pattern showing the initial faster dissipation rate followed by lower rate. The half-life of carbaryl in soil was calculated using equation (10) and data obtain (Table 7), the half-life ($t_{1/2}$) of carbaryl was calculated through regression analysis assuming the loss of carbaryl follows Langmuir-Hinshelwood kinetic model, after k was determined and was found to be 7.19 days. The regression curve for the disappearance of carbaryl in soil figure 22 was obtained by graph of negative logarithm of concentration of residues against time and it had correlation of $R^2 = 0.95$.

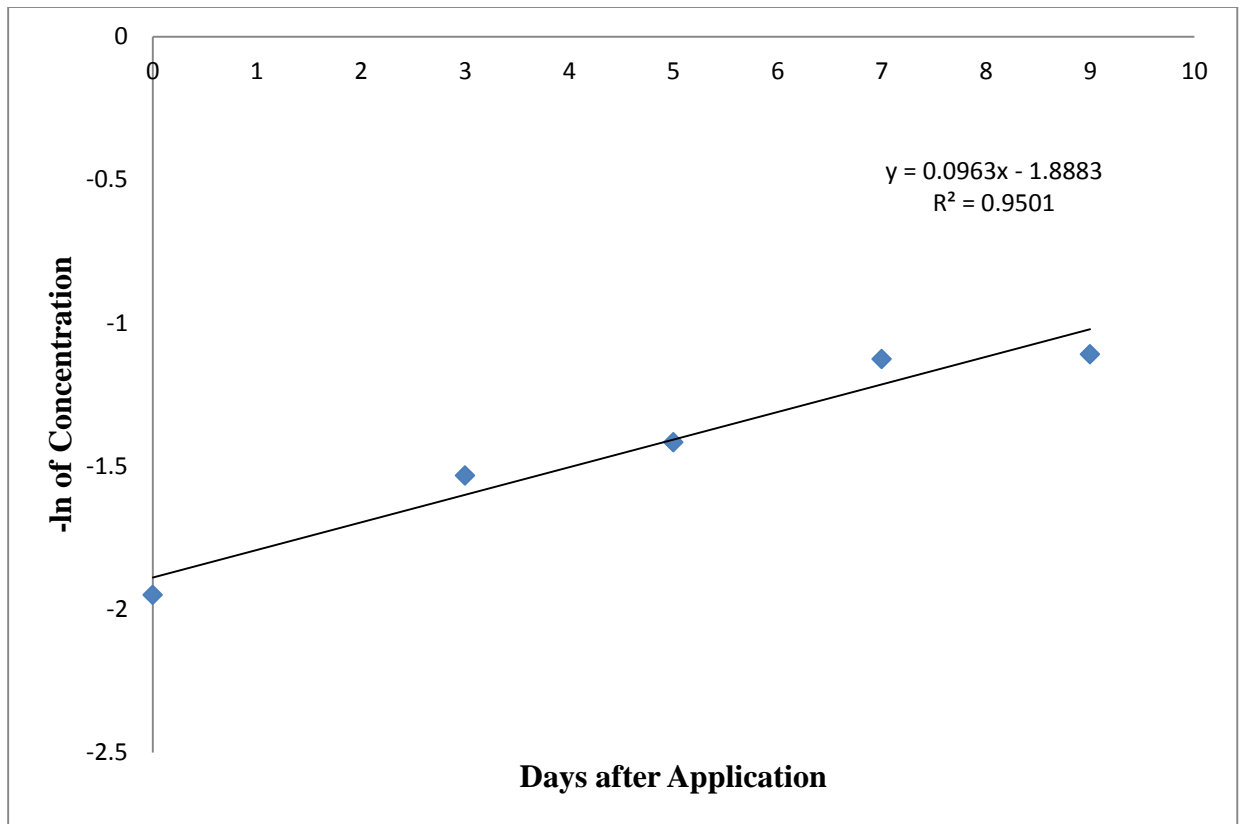


Figure 22: Regression curve for disappearance of Carbaryl from Soil in Harnekop Farm

4.6 Physicochemical Parameters of Soil

The Hippo farm soil was ranked to be 75 % clay, 8.1 % sand, and 17 % silt. The soil had a bulk density of 0.7g/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 %. A summary of the characteristics of the soil is presented in Table 8.

Table 8: Soil fertility, texture and physico-chemical properties at Hippo Farm

Parameters	Test Soil
pH	6.72
Total Nitrogen %	0.48
Organic carbon %	4.03
Phosphorous (ppm)	29.5
Potassium (me %)	1.21
Calcium (me %)	4.3
Magnesium me %	1.9
Manganese me%	0.30
Copper (ppm)	2.33
Iron (ppm)	61.5
Zinc (ppm)	2.98
Sodium me %	0.10
Clay %	75
Silt %	16.9
Sand %	8.1
Bulk Density	0.7

The Kingfisher farm soil was ranked to be 72 % clay, 10.2 % sand, and 17.8 % silt. The soil had a bulk density of 0.91 g/cc. It was slightly alkaline with a pH of 8.2. The percent total nitrogen was 0.46 % while the organic carbon was 5.23 %. A summary of the characteristics of soil is presented in Table 9

Table 9: Soil fertility, texture and physico-chemical properties at Kingfisher Farm

Parameters	Test Soil
pH	8.2
Total Nitrogen %	0.46
Organic carbon %	5.23
Phosphorous (ppm)	31.6
Potassium (me %)	1.0
Calcium (me %)	5.7
Magnesium me %	1.4
Copper (ppm)	1.99
Iron (ppm)	56.2
Zinc (ppm)	6.87
Sodium me %	0.18
Clay %	72
Silt %	17.8
Sand %	10.2
Bulk Density	0.91

The Harnekop farm soil was ranked to be 68 % clay, 9.3 % sand, and 22.7 % silt. The soil had a bulk density of 0.89g/cc. It was slightly alkaline with a pH of 8.4. The percent total nitrogen was 0.51% while the organic carbon was 4.88 %. A summary of the characteristics of soil is presented in Table 10.

Table 10: Soil fertility, texture and physico-chemical properties at Harnekop farm

Parameters	Test Soil
pH	8.40
Total Nitrogen %	0.51
Organic carbon %	4.88
Phosphorous (ppm)	28.0
Potassium (me %)	0.99
Calcium (me %)	4.12
Magnesium me %	2.1
Manganese me%	0.33
Copper (ppm)	1.89
Iron (ppm)	66.8
Zinc (ppm)	7.21
Sodium me %	0.15
Clay %	68
Silt %	22.7
Sand %	9.3
Bulk Density	0.89

4.7 Discussion

Kingfisher farm had the least initial deposited concentration of carbaryl (6.04 ± 3.77 mg/kg) followed by Hippo farm (13.99 ± 2.36 mg/kg) while Harnekop farm had the highest initial concentration of carbaryl (20.41 ± 2.31 mg/kg). It is presumed that the initially deposited carbaryl amount mainly depended upon the surface area of the tomato which the pesticide was sprayed on in spite of the tomato characteristics, such as tomato roughness, content of cuticular waxes, etc. which contribute little to the initial depositions. Therefore, the concentration of the

initial deposition is directly proportional to the tomato area; likewise the concentration of the applied pesticide determines the initial concentration of carbaryl on the tomato. The three farms had different initial concentration of the pesticide that is directly proportion to the amount of pesticide used. When the employee of the three farms were asked questions concerning the type and the concentration of the pesticide used, they all said that the amount of pesticide used depended on the occurrence of a given pest or disease. There was a difference in the initial concentration of the pesticide from the three farms these can be attributed to the use of different concentration of the pesticide and hence all the three farm workers do not use the manufacturer's specification on the pesticide. This is very dangerous to the environment and even for human consumption. Also during the survey it was found that the farm workers mix more than one pesticides depending on the pest or disease on the tomato crop and they use different market brands of the pesticide which differ in the concentration of the active ingredients. Deshmukh *et al.* (2012) reported only 5.4 ppm of initial deposit, which might be due to the use of lower dosage (0.8 kg/ha). Kavadia and Shanker (1976) however, reported deposit of (6.5 to 7.7 ppm) on tomato fruits from 0.25 per cent carbaryl application. This could be attributed to the fact that the insecticide was applied only once, while Stephen and Meera (2010) recorded initial deposit of Carbaryl on brinjal fruits of 11.47 ppm from 0.2 % Carbaryl spray and dissipated to 9.93 ppm within one day after treatment recording thereby a decrease in residue to about 13.40 %, and Chia-chang *et al.*, (2007) recorded initial deposit of Carbaryl on tea tree of 23.41ppm from 2.50Kg/ha carbaryl spray and 76.72 ppm from 1.25 Kg/ha carbaryl spray.

Tomatoes from Hippo farm recorded dissipation rate of 2.92 days of carbaryl, while Tomatoes from Kingfisher farm had dissipation rate of 2.02 days, and Tomatoes from Harnekop farm had dissipation rate of 2.54 days of carbaryl. The average dissipation rate of carbaryl is 2.48 days.

This is within reported range of field dissipation half-life of 0.76 – 10.9 days [Norris, 1991] and less than 1.25 days reported in tomato [Galhotra *et al.*, 1985]. As compared to other plants the persistence of carbaryl on plants has been investigated by several research groups [Choudhary *etal.*, 1988; Galhotra *et al.*, 1985; Iwata *et. al.*, 1979, Rao and Ramasubbaiah, 1988]. Sevin 80W were applied on mature orange and lemon trees at the rate of 11.5 lb a.i. (1200 gal)-1 acre-1 in Orange County and Riverside County California, respectively (Iwata, *et al.*, 1979). After 5 days, foliar residues for orange were 5.6 µg/cm² and lemon 2.4 µg/cm². The residues after 60 days were 0.36 and 0.41 ug/cm² on orange and lemon, respectively. The half-lives of carbaryl on oranges and lemons were reported as 14 and 22 days, respectively. In other experiments, the dissipation half-lives of carbaryl were 1.80-1.94 days in sesame plant [Choudhary *et al.*, 1988 and Galhotra, *et al.*, 1985]. Galhotra (1985) reported the carbaryl residues in potato foliage and tuber, 64-94 days after application at the rates of 1 – 5 kg a.i. /ha, were below detectable level (0.03 – 0.10 ppm). Comparing the three farms, Hippo farm had the highest dissipation rate followed by Harnekop and Kingfisher had the least dissipation rate. This shows that the rate of dissipation depends on the initial concentration of the pesticide.

The concentration of carbaryl 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 carbaryl at $t = 9$, C_o is concentration of carbaryl at $t= 0$ and k is the first order rate constant. The concentration of carbaryl on the PHI day was found to be 1.65 mg/kg, 0.28 mg/kg and 1.75 mg/kg for tomatoes from Hippo, Kingfisher and Harnekop farms respectively. All the three farms had carbaryl residue above the EU MRL of 0.02 mg/Kg for food.

In soil, Kingfisher farm had the least initial deposited concentration of carbaryl ($2.46 \pm 0.00 \text{ mg Kg}^{-1}$) followed by Hippo farm ($4.6 \pm 0.87 \text{ mg Kg}^{-1}$) while Harnekop farm had the highest initial concentration of carbaryl ($7.02 \pm 1.19 \text{ mg Kg}^{-1}$). Stephen and Meera (2010) reported initial deposits (residues recovered after 1hr of application) were 12.6 and 25.92 ppm in agroecosystem at low (17.24 :g gG1) and high (34.48 :g gG1) levels of fortification respectively. The residues progressively declined up to 60 days but became non-detectable during the next sampling at 75th day.

Soil from Hippo farm recorded dissipation rate of 5.29 days of carbaryl, the average initial deposition of carbaryl was $4.6 \pm 0.87 \text{ mg kg}^{-1}$ (day 0) and the final residue was $1.45 \pm 0.33 \text{ mgkg}^{-1}$ on day 9. Soil from Kingfisher farm had dissipation of 5.29 days, the average initial deposition of carbaryl was $3.46 \pm 0.00 \text{ mg kg}^{-1}$ (day 0) and the final residue was $1.02 \pm 0.05 \text{ mgkg}^{-1}$ on day 9. Soil from Harnekop farm had dissipation rate of 7.19 days of carbaryl, the average initial deposition of carbaryl was $7.02 \pm 1.19 \text{ mg kg}^{-1}$ (day 0) and the final residue was $3.03 \pm 0.84 \text{ mg kg}^{-1}$ on day 9. The dissipation of insecticides was faster during the first 8 days as compared to the latter period. The dissipation of residues at low level of fortification was, in general, significantly faster, than at high-level fortification. Similar results have also been reported by other workers [Lichtenstein *et al.*, 1971 and Gajbhiya, 1989] for organo-chlorine pesticides. The pH of soil during the study was 6.72, 8.2 and 8.4 for Hippo, Kingfisher and Homekop farms respectively, organic carbon content was 4.03 %, 5.23 % and 4.88 % for Hippo, Kingfisher and Homekop farms respectively and moisture content was 8.42 %, 3.36 % and 4.83 % for Hippo, Kingfisher and Harnekop farms respectively. Soil moisture content and temperature plays important role in rapid microbial degradation of pesticides. Besides the insecticides, were applied on the surfaces which are subjected to rapid loss by volatilization and photo-gradation.

According to reports available, the organic matter in soil firmly adsorbs the insecticide molecules, rendering it non- available to microbial degradation and other losses such as leaching, and volatilization resulting in increased persistence of insecticides. Similar observations were made by Chapman *et al.* (1981). They observed that 74 % of the initially applied (1ppm) delta methrin remained in organic soil as compared to 52 % in mineral soil after 8 weeks of treatment. The results are also in close conformity with the studies made by Biswas *et al.* (1991) and Ali *et al.* (1994). Overall, carbaryl is not persistent in soil. It can be degraded through hydrolysis photolysis as well as by microorganisms [Das, 1990]. The photo-degradation of carbaryl was investigated on soil under artificial sunlight for a total of 30 days [Das, 1990]. In this case, carbaryl was applied on 1-mm soil layers at a concentration of 9.8 ppm. The estimated half-life was approximately 41 days with no findings of major metabolites.

The interviews indicated high awareness among farm workers about risks and safe handling of pesticides, all the farm workers used protective devices when handling pesticides. The dose used and the spraying intervals seldom correlate with those recommended by the manufacturer, Many farm workers use safety information and recommendations of dose on the pesticide because they read the instruction manual but the dose used is determined by the presence of a given disease or pest. From interview results it is clear that all farm workers were aware of the ban or restriction imposed on some pesticides in Kenya [PCPB, 2008], this is a good move which will ensure that the banned pesticides can't find their ways into the region from obsolete stock piles [NES, 2006]. 99% of the farm workers are aware of the effects of pesticides to the environment.

Study conducted by Abong'o *et al.*, (2014) in Nyando River catchment, documented a list of agro-chemicals used along the river drainage basin, and the recommended rates of applications, environmental and human health impacts and toxicity to birds and bees. Further the study

documented most of the pesticides used in Nyando River 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 in this area are ignorant of the safe use and handling of the pesticides, which results in some injuries and chronic illnesses.

CHAPTER FIVE

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

The study investigated the residual behavior of carbaryl in tomatoes and soil from Hippo farm in Thika, Kingfisher and Harnekop farms in Naivasha, Kenya. Carbaryl remained more in soil than in tomatoes in all the three farms investigated. The carbaryl pesticide half-life was found to be 2.92 and 5.29 days in tomatoes and soil respectively from Hippo farm, 2.02 and 5.21 days in tomatoes and soil respectively from Kingfisher farm and 5.24 and 7.19 days in tomatoes and soil respectively from Harnekop farm. Harnekop farm recorded the highest carbaryl half life in soil (7.19 days) while Kingfisher farm recorded the lowest (5.21 days). The rate of dissipation depended on the initial concentration of the applied pesticide and therefore it was suggested that Harnekop farm used high concentration of the pesticides. The concentration of carbaryl on the PHI day was found to be 1.65 mg/Kg, 0.28 mg/Kg and 1.75 mg/Kg for tomatoes from Hippo, Kingfisher and Homekop farms respectively. This is above the European Union MRL (0.05 mg/kg) of carbaryl in food. This shows that the pesticide applied resulted into elevated levels during the time of harvesting in tomatoes.

Most of the pesticides used in the three farms are organophosphates, carbamates and pyrethroids and some are highly hazardous. Most farm workers are trained on the safe use and handling of the pesticides, which results in reduction of injuries and chronic illnesses. All the farm workers are trained on pesticide residue levels limit in food.

5.2 Recommendations

On the basis of this study, the following recommendations are made;

The regulatory authorities like HCDA and KEPHIS should monitor the quality of produce marketed locally and internationally to ensure that consumers are not exposed to high levels of pesticide residues.

National Pesticide Residues Monitoring and Surveillance is recommended on agricultural food products 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.

The ministry of agriculture and private partners ought to train farmers on safe use of pesticides.

This study recommends a further research on the alternative methods to pests and disease control in tomato farming.

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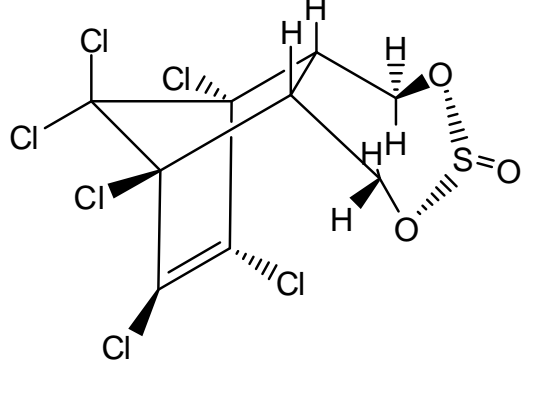
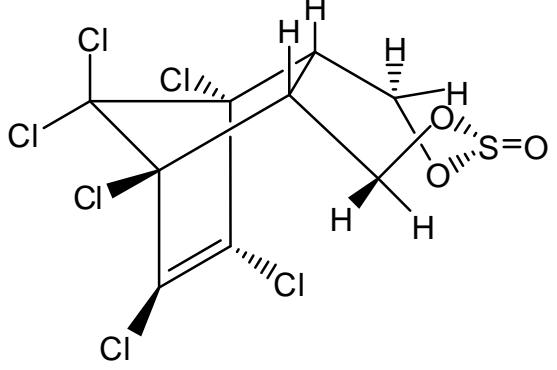
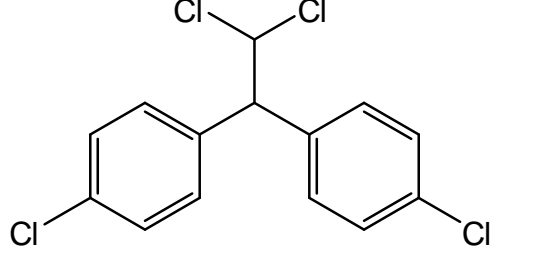
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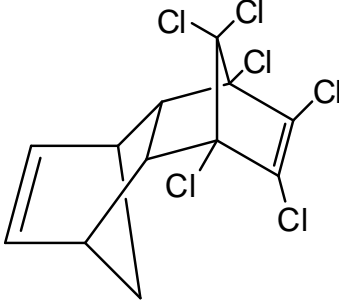
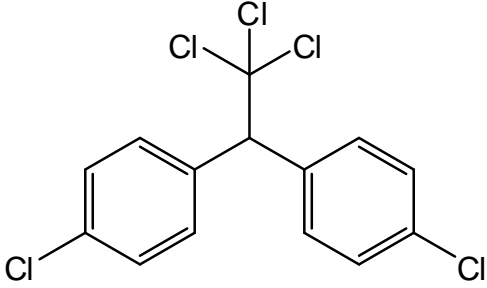
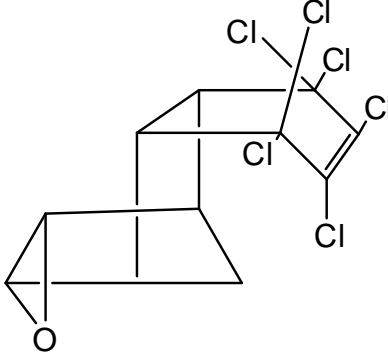
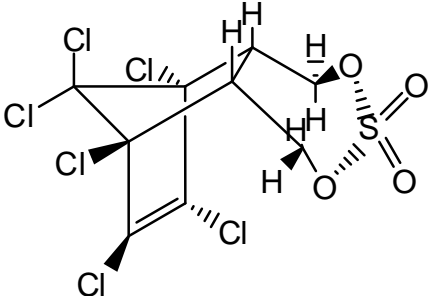
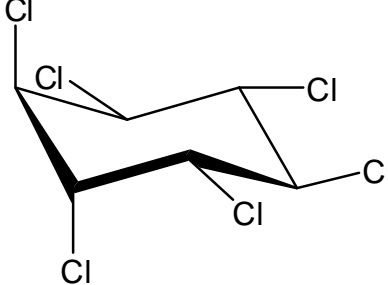
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APPENDIX

Appendix I

Figure 1.1: Chemical Structures of organochlorine Pesticides

SN	Name	Structures
	α -Endosulphan	
	β -Endosulphan	
	(1,1-dichloro-2,2-bis(4-chlorophenyl)ethane) <i>p,p</i> DDD	

	Aldrin	
	dichloro-diphenyl-trichloro-ethane (<i>pp</i> -DDT)	
	Dieldrin	
	EndosulphanSulfate	
	hexachlorocyclohexane (HCH),	

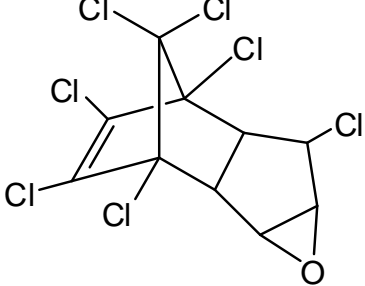
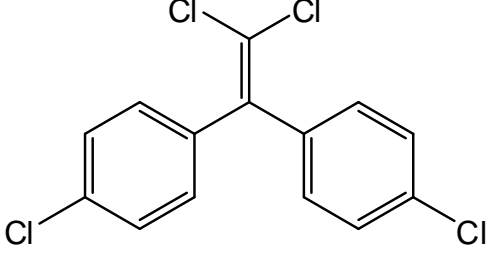
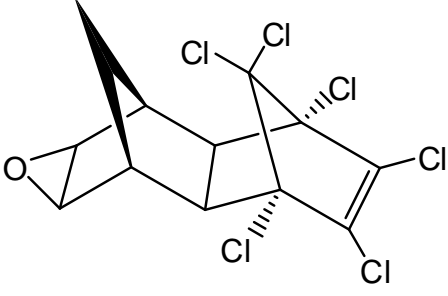
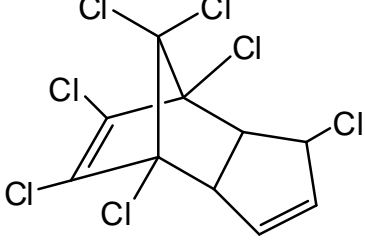
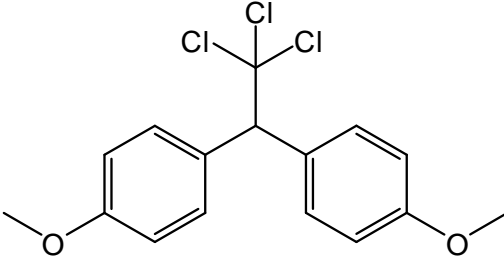
	Heptachlor epoxide	
	2,2-bis p-chlorophenyl, 1-dichloroethylene- p,p'-DDE	
	Endrin	
	Heptachlor	
	Methoxychlor	

Figure 1.2 : Some Organophosphorus pesticides

SN	Name	Structures
	Dichloros	
	Acephate	
	Dimethoate	
	Ethion	
	Chlorfenvinphos	

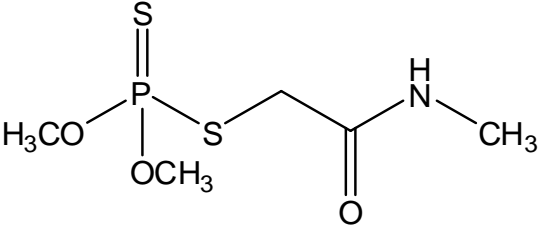
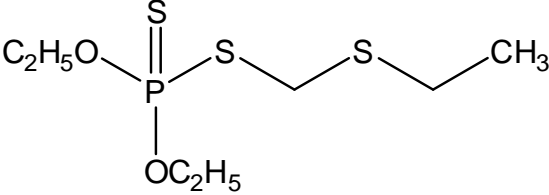
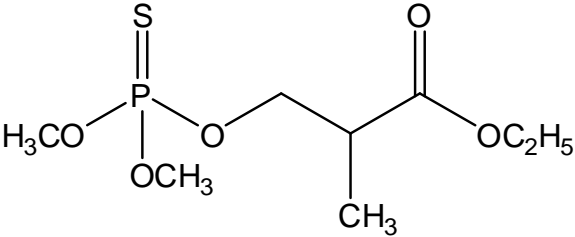
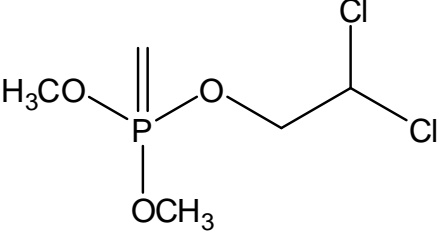
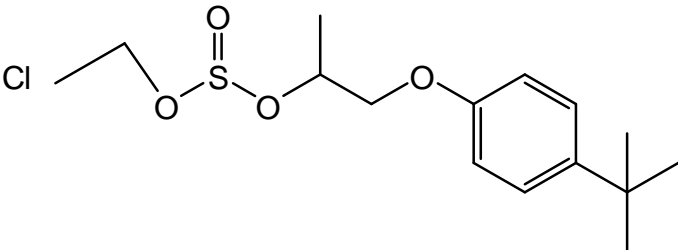
	Diazinon	
	Disulfoton	
	Mevinphos	
	Dichlorvos	

Figure 1.3: Some Organosulfur Pesticides

SN	Name	structures
	Aramite	

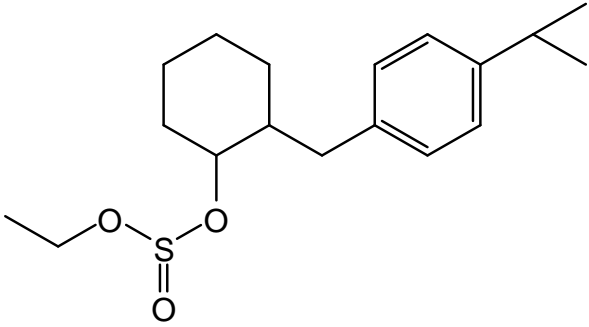
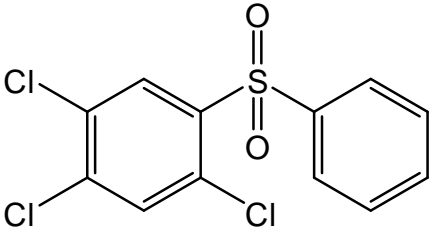
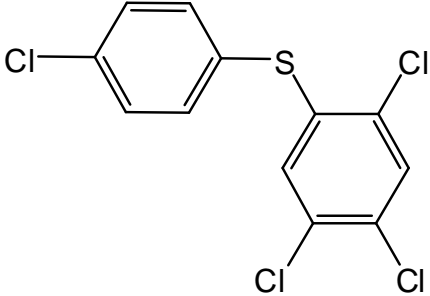
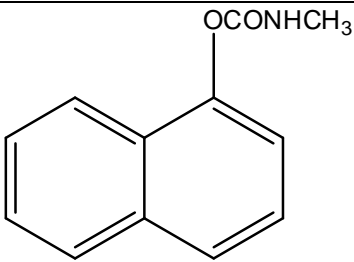
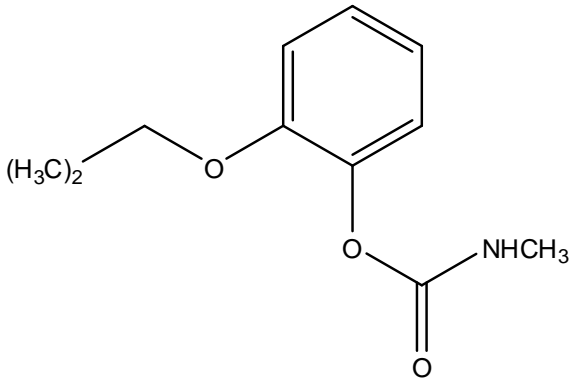
	Propargite	
	Tetradifon	
	Tetrasulf	

Figure 1.4: Some Carbamate Pesticides

SN	Name	structures
	Carbryl	
	Carbofurans	

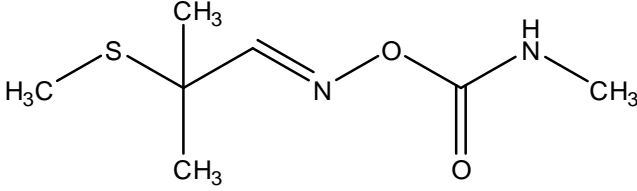
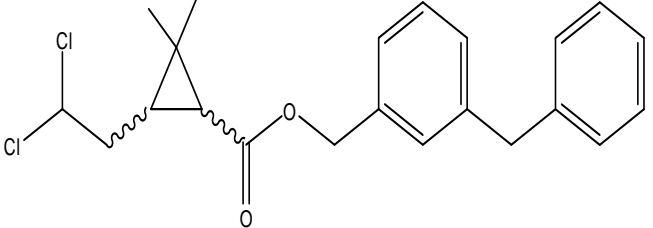
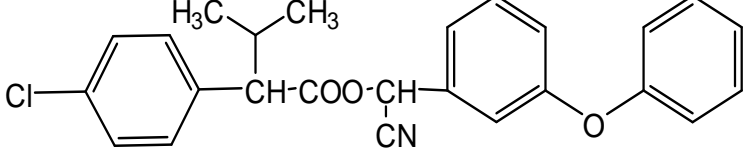
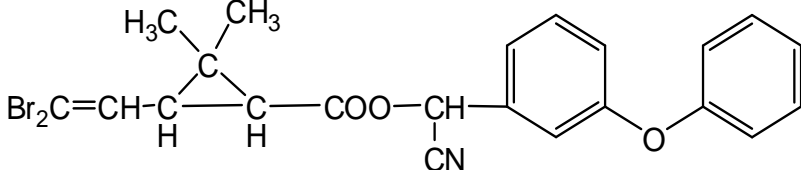
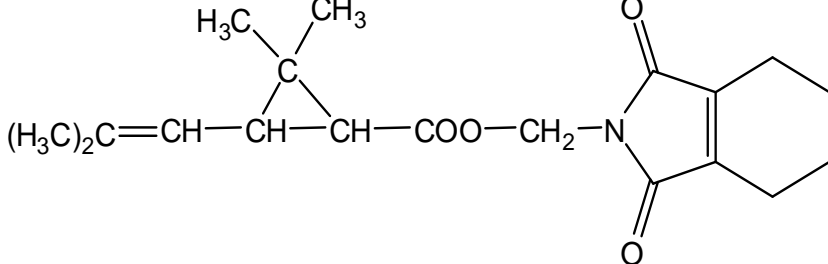
	Aldicarbs	
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Figure 1.5: Some pyrethroids Pesticides

SN	Name	structures
	Permethrin	
	Fenvalerate	
	Deltamethrin	
	Tetramethrin	

.....
.....

5.

- a) When do you plant your crops and why?.....
- b) How many times do you plant this type of crop(s) per year?.....
- c) When do you harvest the crop(s)?.....
- d) What problems have you experienced with the crop(s)?.....

.....
.....
.....
.....

- e) Is it a common problem,.....
- f) How do you solve it?.....

C) Use of pesticides in farming

a) Do you use any pesticides in your farm YES.....NO.....

b) If [No], why?

.....
.....
.....

c) If [yes], which ones

.....

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

.....

e) How and when do you apply the pesticides

f) Where do you get Pesticide(s) from?.....

g) What is the cost per unit?.....

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

- j) Which factors do you consider when choosing a given pesticide?

- Are there any guide lines given to you before buying any pesticides?-----who gives them ----
 -----, -----, -----
5. Have you ever had any training on pesticides managements and safety?-----
- a). In which institution were you trained? -----
- b). How long did the training take? -----
- c). what role did the government play in your training-----
- d). Do you use any form of protection when handling pesticides chemicals? -----
- e). If yes which one? -----,-----,-----,-----,-----
7. Where do you dispose containers after use? -----,-----,-----
- 8.Do you have information on the pesticide related pollution in this area ? -----if yes give
 some details.-----
9. a) Have you ever used any unlabelled pesticide -----
- b) If yes where did you get the pesticide from? -----
10. a) Do you know any banned pesticide?-----

(D) Health problems associate with use of pesticides

- (a) Have you experienced any health problem suspected/or due to exposure to the
 b) Pesticide(s)? [Yes].....[no].....
- c) If [yes], when?
- d) How was it treated?.....
- e) If [no], have you gone for any medical check-up?.....
- f) 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 Farms.

Gender	Males				Female			
Age (years)	18-24	25-34	35-44	over 45	18-24	25-34	35-44	Over 45
Number	38	16	4	2	11	9	7	1
Purpose of using pesticides	To control pests that destroys crops and vegetables. To control ticks and fleas in livestock, To control mosquitoes.							
Designation								
Gardener	19	11	2	0	5	3	2	0
Extension worker	1	2	0	1	2	0	0	1
Management	1	0	1	1	0	1	1	0
Others (Carsual)	17	3	1	0	4	5	4	0
Factors Affecting the Choice of Pesticide								
Increase Yield	18	10	2	1	8	6	3	0
Cost Effective	18	4	1	0	2	3	3	1
Suggested by Management	2	0	0	0	1	0	0	0
Suggested by Agro-Chemical dealer	0	2	1	1	0	0	1	0
Good for Environment	0	0	1	0	1	0	3	0
Training on pesticides handling								
With basic training	26	10	2	0	9	7	4	0
With no basic training	0	0	0	0	0	0	0	0
Advanced training	12	6	2	2	2	2	3	1
Pesticide Resdue in Food								
With basic training	26	10	2	0	9	7	4	0
With no basic training	0	0	0	0	0	0	0	0

Advanced training	12	6	2	2	2	2	3	1
Safety and Control								
Always read instruction menu	9	13	6	2	2	15	12	2
Not aware of instruction menu	10	4	2	0	4	6	10	4
Do not read instruction menu	19	8	3	0	1	9	1	0
Education Level								
Primary	26	6	3	0	4	8	4	0
secondary	9	8	0	0	4	1	2	1
Post-Secondary	3	2	1	2	3	0	1	0
Pesticide Ban								
Awere of the ban	38	16	4	2	11	9	7	1
Not aware of the ban	0	0	0	0	0	0	0	0