UNIVERSITY OF NAIROBI

ASSESSMENT OF THE FATE OF SELECTED PESTICIDES ON VEGETABLES IN NAIVASHA AREA

BY

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DECLARATION

This thesis is my original work 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.

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

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DEDICATION

This thesis is dedicated to my dear husband Dr. Onchari who has been my source of encouragement throughout the research period, my children Maya, Golda, Samuel and Madeline who have been affected in one way or the other by this quest. My late father Samuel and my mother Florence who were always there for me since I was young encouraging me in every step of my educational life, finally to my brothers and sisters for their support.

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ABSTRACT

This study assessed the fate of pesticides used on vegetables in Naivasha area. The harmful effects of pesticides make them pose a serious threat to some of the non-target organisms including human and wild life. The concentrations of two organophosphate pesticides (diazinon and chlorpyrifos) and organochlorine pesticide residues (heptachlor, heptachlor epoxide, aldrin, dieldrin, α-HCH, γ-HCH, β-HCH, δ-HCH, endosulphan I, endosulphan II, *p,p'*-DDE, dieldrin, endrin, endrin aldehyde, methoxychlor, *p,p'*-DDD, *p,p'*-DDT and endosulphan sulphate) were determined in kales, soil and water samples from Naivasha area. Standard procedures were used in sample collection and preparation. Determination of pesticide concentrations in the water, soil and kale samples was done using a GC-MS (GC- 6890, MSD 5972-2) and a gas chromatograph (Agilent 6890N) combined with an auto sampler (Agilent 7683 Series injector), and an electron capture detector (μ-ECD).

The organophosphate pesticides were not recorded in any of the samples. Varying concentrations of organochlorine pesticides were detected in the samples. In kales, methoxychlor was the highest detected pesticide with concentration of 75.41±7.71 μg/kg. aldrin recorded the highest concentration (218.47±6.76 μg/kg) in the soil samples while in the water samples, methoxychlor was the highest detected pesticide with a concentration of 0.68±0.01μg/l. The results suggest contamination of vegetables with pesticide residues that need to be monitored to reduce the risk of exposure to the unsuspecting consumers.

Results of dissipation study of chlorpyrifos revealed concentration in kale leaves at 75.82±3.56 mg/kg on day 0 while on day 7 the residues were 2.82±0.03 mg/kg. In stems, roots and soil samples, initial chlorpyrifos concentrations were 61.36±7.52 mg/kg, <LOD and 42.03±0.00 mg/kg, while the final levels were 1.13±0.06 mg/kg, 1.56±0.00 mg/kg and 1.05±0.04 mg/kg,

respectively. The half-lives in the leaves, stems, roots and soil were 0.63, 0.67, 1.1 and 0.5 days, respectively.

Diazinon concentration in leaves on day zero was 49.02±6.26 mg/kg while final concentration was 3.12±0.14 mg/kg for day 11. Beyond the 11^{th} day the concentration was below detection limit. Diazinon concentrations in stems, roots and soil on day zero were 37.88±3.32, <LOD and 38.25±0.00 mg/kg respectively while the final detectable concentrations were 5.16±0.17, 1.00±0.07 and 1.67±0.02 mg/kg for stems, roots and soil, respectively. The half-lives were 0.42, 0.62 and 0.43 days for stems, roots and soil, respectively. In both dissipation studies (diazinon and dursban), higher concentrations were observed on the leaves in day zero, followed by stems, soil and roots.

From the dissipation studies, chlorpyrifos had longer persistence on the crops and soil compared to diazinon applied under the same environmental conditions. Based on the organophosphate (diazinon and Chlorpyrifos) residue levels detected farmers and consumers should be educated on post-harvest interval to be observed before harvesting of vegetables.

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ABBREVIATIONS

ADI	Acceptable Daily Intake
BDL	Below Detection Limit
DDT	DichloroDiphenyl-trichloro ethane
EPA	Environmental Protection Agency
EPZ	Export Processing Zone
FAO	Food Agricultural Organization
GC	Gas Chromatography
GC-MS	Gas Chromatography Mass Spectrometry
GPS	Global Positioning System
GDP	Gross Domestic Product
HCH	Hexachlorocyclohexane
HPLC	High Performance Liquid Chromatography
KALRO	Kenya Agricultural and Livestock Research Organization
MRL	Maximum Residue Levels
OC	Organochlorine
OECD	Organisation for Economic Co-operation and Development
OP	Organophosphate
OPPs	Organophosphate pesticides
POPs	Persistent Organic Pollutants
RSD	Relative Standard Deviation
SPSS	Statistical Programme for Social Scientists
TDS	Total Dissolved Solids
TSS	Total Suspended Solids
UNEP	United Nations Environmental Programme
USEPA	United States Environmental Protection Agency

WHO	World Health Organization

CHAPTER ONE

1. INTRODUCTION

1.1Background of the Study

Globally, roughly1.8 billion people practice agriculture and most of them use pesticides for economic management of crops and livestock (Alavanja, 2009). Pesticides are categorised into two major groups: agricultural pesticides used against crop pests and diseases and public health pesticides used in public health vector control programs (Alavanja, 2009).

In Kenya, the fast growth in horticultural production has been accompanied by increased use of pesticides coupled with health concerns regarding pesticide use and abuse (Norton *et al.,* 2003). Partly, the heavy use of pesticides occurs because of the high diversity of pests and disease vectors which attack horticultural crops, reducing market value and yield on high-value crops. Pesticides use also brings about safety concerns for agricultural workers who apply them (Norton *et al.,* 2003). Importers and exporters of fresh fruits and vegetables have a potential food safety risk and a market-risk factor from pesticide residues and sometimes, if their shipments surpass acceptable limits, they are rejected (Norton *et al.,* 2003).

There are a number of substances that can fall under pesticides; these include insecticides, molluscicides, fungicides and rodenticides. In addition, plant growth regulators, herbicides and nematicides are also grouped as pesticides (Aktar *et al.,* 2009). Out of these pesticides, organochlorine insecticides, effectively employed in controlling numerous diseases, including typhus and malaria, were controlled or prohibited after the 1960s by majority of the countries due to toxicity to human health and the environment (Aktar *et al.,* 2009). There was a great contribution to pest management and agricultural productivity as a consequence of the introduction of other artificial insecticides such as organophosphate, carbamate and pyrethroid

insecticides introduced in 1960s, 1970s and1980s respectively and the introduction of herbicides and fungicides in the 1970s–1980s (Aktar*et al.,* 2009).

The pattern of division of an agent, its derivatives or metabolites in a living being, compartment, system or population of concern resulting from transportation, transformation, degradation or partitioning is referred to as fate (OECD, 2012). After applying pesticides to the crops, they may be exposed to ecological factors such as sun and wind or they may interact with the plant surfaces. They also may be carried down to water bodies by rain water (OECD, 2012). The pesticide may remain on plant surface or absorption into the plant may take place ending up in the transport system of the plant (OECD, 2012).

Pesticides are designed to be toxic to the pests under attack, however, as a result indiscriminate use, once introduced in the environment; they also affect the non-target species, including man. The widespread application of these chemicals, under the saying, "if little is fine, much more will be better" has caused a lot of harm on human and other life forms (Alavanja, 2009). Because of the extensive use of pesticides, they have become a major group of ecological pollutants (Gilden *et al.,* 2010). Pesticides when used pollute the environment and build up in the food chain leading to harm on human health (Leong *et al*., 2007). The toxic effects of pesticides such as reproductive system interference, foetal development interference together with their ability to cause cancer and asthma (Gilden *et al.,* 2010) is a major source of concern. Some pesticides cause long term exposure because they stay longer in the body (Gilden *et al.,* 2010).

The main source of exposure to pesticides to the general population is as a result of consuming food and taking water polluted with pesticide residues; considerable exposure can happen in or around the residential areas (Shailendra *et al.,* 2013). In relation to the serious harmful environmental effects, many of these adverse effects are dependent on the toxicity of the

pesticide, the safety measures taken while applying, the quantity applied, soil colloids adsorption, the prevailing weather conditions after use and environmental persistence levels (Shailendra *et al.,* 2013).

The health and environmental problems and the dangers associated with the use of chemicals, particularly pesticides, are extreme especially in agriculture (Lee and Seeneevassen, 1998), leading to the chemical build-up of pesticide residues in crops and also to a disruption of plants biochemical parameters (Shailendra *et al.,* 2013). Wrong application methods, poorly maintained or totallyinappropriate equipment for spraying and insufficient storage practices add to these risks (Al-Wabel *et al.,* 2011). The fact that there is use of old pesticide containers for storing food and water has also contributed to the danger of exposure (Damalas and Eleftherohorinos, 2011).

The levels of pesticide residues in plants may be high when they are not used in accordance with good agricultural practices (Iya and Kwage, 2007). Research carried out in the past decade in Ghana and internationally point out the existence of pesticide residues in a number of vegetables, such as onions, cucumber, strawberries, lettuce, cabbage, okra, beans, pepper, tomatoes, oranges and lemons(Hanson *et al*., 2007). Additionally, pesticide residues constitute a danger to soil microfauna and microflora and their toxic effects appear on humans when bioaccumulation occurs along the food chain after initial plant uptake (Hanson *et al*., 2007).

Some of the influencing factors of pesticides fate in soil and water environments comprise of the pesticide properties and the physicochemical properties of the soil and water systems (Ware and Whitacre, 2004). Uptake of persistent residues via plant root is a common form of plant contamination. The amount of pesticides absorbed by a given plant generally depends on the solubility of the pesticide in water, the quantity of pesticide within the soil and the composition of the soil organic matter.

Soil organic matter is the most important soil factor influencing the sorption of residues for non-polar pesticides. The harmful effects posed by the pesticide residues in the plant depends on the toxicity of the residue, the ability of the plant to metabolize or eliminate the residue before it is harvested and the translocation of the residue to the harvested portions of the plant (Akan *et al*., 2013).

Various factors can lead to plant foods contamination by pesticides (Cairns and Sherma, 1992). These include rainfall, wind and chemical reactions induced by oxygen. Others factors include moisture, light and plant enzymes (Cairns and Sherma, 1992). For instance pesticides used in powder form tend to contaminate vegetation to a lesser extent than those that are used in liquid form, but it is also influenced by the structure of the plant in question. Some insecticides build up in the rind of many fruits, more so citrus fruits (Jolanta *et al.,* 2011). It is therefore important to always monitor pesticide residue levels in fruits and vegetables because if this is not done human health can be affected leading to many kinds of diseases (Jolanta *et al.,* 2011).

24% of Kenya's Gross Domestic Product is accounted for by agriculture with approximately 75% of the inhabitants relying on the sector directly or indirectly (PKF Consulting Ltd., and International Research Network, 2005). The main part of the strength and the general weakness in GDP and the increase in income in Kenya can be associated with changes in agricultural performance (PKF Consulting Ltd., and International Research Network, 2005). In the last decade, the horticulture sub-sector has grown and is presently ranked third in terms of foreign exchange income from exports (PKF Consulting Ltd., and International Research Network, 2005). Neighbouring land locked countries which include Uganda, Rwanda and Burundi further increased the import demand for pesticides (Paul *et al.,* 2005). The demand also went up as a result of horticultural farming growth in Kenya in the late 1990's (Paul *et al*., 2005).

Naivasha is one of the towns in Kenya that has experienced fast growth in terms of population. This is due to the expanding horticultural farming businesses. As a result of rapid increase in acreage under horticultural production, Lake Naivasha and its surroundings are experiencing an increase in pesticide use in the horticultural industry.

Earlier studies revealed that poor methods of cultivation enabled the soils found in the lake's environs to be carried by erosion to the lake (Arusei *et al.,* 2002). In addition, some of the flower farms have moved their borders near to the water bodies (Arusei *et al.,* 2002). The fine texture of the soil, high water holding ability and high organic matter content additionally increase the flow of pesticides (Becht *et al.,* 2005). The pesticides residues are therefore easily moved into the lake as a result of erosion. An increase has been observed in the amount of agro chemical residues moving from the flower farms to the lake, this has also been observed in sediments (Becht *et al.,* 2005). There can be additional contribution of pesticides load from farms that are located far away because when these pesticides are used in the field, they are moved by erosion to the lakes, streams and rivers (Getenga *et al.,* 2004; Wandiga, 2001; Wandiga*et al.,* 2002). Additionally, rain and wind can also carry pesticides away from their source of origin, leading to contamination of surface water (Bouman *et al*., 2002; Shomar *et al*., 2005).

1.2 Statement of the Problem

Horticultural intensification in Naivasha has contributed to increased application of pesticides to improve crop yields. Unfortunately, some of these pesticides stay longer in the environment and their residues may contaminate water, soil and plants posing threat to non-target organism such as human and wildlife. As a consequence, toxic effects may manifest on humans as a result of consumption of food with pesticide residues.

Despite the fact that pesticide manufacture is done under very firm guidelines so that they can work with reasonable certainty together with minimum health impacts on human beings and his surroundings, serious issues have come up concerning human health risks as a result of consuming food with pesticide residues (Damalas and Eleftherohorinos, 2011). Pesticide contamination has been singled out as a major environmental effect of agriculture. Parent chemical compounds as well as pesticide metabolites have been found in soil, air and water (Rudel, 1997).

Pesticides vary in the mode of action on human bodies. They also vary in the way they are broken down and removed from the body and also in their toxicity (Sebae, 1986). As a result of these differences, various pesticides show acute effects, whereas others build up in the body leading to sub-lethal health effects. Most of these compounds stay in the environment for long building up in human and human tissues (Sebae, 1986).

Most of the persistent pesticides along with their metabolites are absorbed by plants or remain in the soil and water hence their residues are found in the food chain (Spanoghe *et al.*, 2009). Water sources get polluted by pesticides used in farms. In many cases diffuse pollution of water sources is the most common form of water contamination by pesticides used on crops (Konstantinou, 2006).

There is a significantly high amount of pesticide residues reported in vegetables and fruits and in cereals such as rice and wheat (Miyata *et al.*, 1994). Pesticides residues have also been detected in tomatoes, onions and potatoes (Miyata *et al.*, 1994) as well as oranges and apples in amounts exceeding the maximum residue levels (Roy *et al.,* 1997). The bio-accumulation of persistent pesticides has been reported occurs in living organisms from bacteria and algae to higher plants and animals including man (Roy *et al.,* 1997).

Pesticide residue concentration in organisms increases as the position of that organism increases upwards in the food chain (Jolanta *et al.,* 2011). The current study investigated the levels of pesticide contamination in kales, water and soil samples obtained from Naivasha area and degradation of diazinon and chlorpyrifos in kales and soil.

1.3 Research Questions

1) What is the level of pesticides contamination in vegetables (kales), water and soil from Naivasha area?
2) What is the persistence of diazinon and dursban in soils in Naivasha area?
3) To what extent are the MRLs for post-harvest interval for diazinon and chlorpyrifos in kales.

1.4 Objectives

1.4.1 General Objective

The general objective of this study was to assess the fate and transport of diazinon and chlorpyrifos in Naivasha area.

1.4.2 Specific Objectives

The specific objectives of this study were to:

i. Quantify pesticide residue levels in vegetables (Kales), water and soil samples obtained from Naivasha area.
ii. Study the dissipation of chlorpyrifos and diazinon applied on kale crops in Naivasha area.
iii. Assess the suitability of post-harvest interval on maximum residue of chlorpyrifos and diazinon pesticides used on crops in Naivasha area.

1.5 Justification of the Study

Data on pesticide residues, persistence and maximum residues concentrations in vegetable crops is limited in Kenya. This research is important because it will be a source of information to farmers around Naivasha area and all other parts of the country to support decision making regarding pesticides application to crops.

Secondly, the findings of this study will be important to consumers and policy makers since it will provide information on the level of pesticide contamination in water and vegetables sold in the markets. Horticultural farming, being one of the main foreign exchange earners must be practised in the safest manner possible to ensure that the products meet international standards.

Lastly, the study is important to environmental scientists and other scientists in the area of research since it contributes to understanding of the role they can play in promoting knowledge about best practises in order to reduce pesticides residues in the environment and crop produce.

CHAPTER TWO

2. LITERATURE REVIEW

2.1 General Description and Uses of Pesticides

A pesticide is any compound that can be used to prevent, destroy, repel or control any pest. This includes unwanted class of animals or plants at the time of production, storage, transport, distribution and during food processing (Cairns and Sherma, 1992). The term pesticide also refers to compounds used as defoliants, growth regulators of plants, desiccants, fruit thinning substances and compounds used on the crops before or after harvest to protect the food items from going bad during transportation and storage (Handa *et al.,* 1999 and WHO, 1990).

The term pesticide does not include fertilizers and plant nutrients neither does it include animal nutrients, food additives nor animal drugs (Handa *et al.,* 1999 and WHO, 1990). Tijani and Oshotimehin, (2007) mentioned that pesticides are protective resources that are unique and differ from other productive resources. The reason for this is that they do not affect productivity directly but are applied to eliminate those factors that directly hinder productivity.

Given that their chemical structures, actions and uses are different, the categorization of pesticides becomes hard (Cairns and Sherma, 1992). They can be grouped based on different criteria: toxicity; chemical structure; purpose of application; ecological stability and the pathways through which they enter targeted organisms (Jolanta *et al.,* 2011). Based on structure, pesticides can be categorised into organic compounds or inorganic compounds. Examples of the inorganic pesticides are arsenic fluoride insecticides and arsenic insecticides while the organic include organophosphorus, organonitrogen and organochlorine pesticides (Jolanta *et al.,* 2011).

Organophosphate pesticides are composed of an ester structure and break down fairly easily on the surfaces, in the inner parts of plants as well as in the soil (Cairns and Sherma, 1992).The toxicity of these compounds is through the inhibition of the function of enzymes that control the activities of the nervous system, majorly acetylcholinesterase (Akan *et al.,* 2013). OPPs bind to the enzyme's hydroxylating group in a permanent way thus preventing decomposition of acetylcholinesterase (Jolanta *et al.,* 2011). The blockage of cholinesterase activity leads to an increase in the quantity of acetylcholine at the synapses, ending up to hyper arousal; this is followed by paralysis of the muscles and the major respiratory centres (Akan*et al.,* 2013). Figure 2.1 shows the general structure of organophosphates.

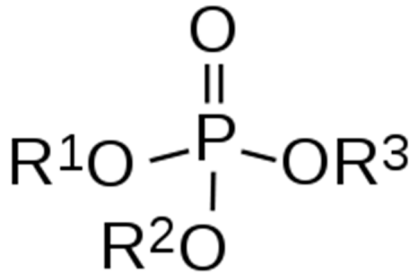

Figure 2.1*: General structure of organophosphates*

2.1.1 Diazinon

Diazinon is an insecticide classified under the organophosphate group and is mainly used to protect most crops against various insects (Abass *et al.*, 2011). Trade names for diazinon include knoxout, Alfatox, Basudin, AG 500, Dazzel, and Gardentox (ATSDR, 2008).Some of its agricultural uses include controlling insects, soil pests as well as foliage on field crops, nuts, fruits as well as vegetables. Prior to its cancellation on home uses in 2004, diazinon was applied on gardens as well lawns to control fleas, ticks and flies (USEPA, 2004).

Diazinon kills by inhibiting the enzyme acetylcholinesterase whose function is to hydrolyse acetylcholine neurotransmitter in cholinergic synapses and in the neuromuscular junctions. This results in an abnormal build-up of the neurotransmitter in the nervous system (Timchalk,

2001). Even though diazinon is found in all environmental compartments, it does not have a tendency to partition to any particular medium (ATSDR, 2008). Table 2.1 shows the physicochemical properties of diazinon and chlorpyrifos

Table 2.1: Physicochemical properties of diazinon and chlorpyrifos

Physicochemical properties	**Diazinon**	**Chorpyrifos**
Chemical name	O,O-Diethyl O-[4-methyl-6-(propan-2-yl)pyrimidin-2-yl] phosphorothioate	O,O-diethyl 0-(3,5,6-trichloro-2-pyridyl phosphorothioate
Empirical formula	$C_{12}H_{21}N_2O_3PS$	$C_9H_{11}C_{l3}NO_3PS$
Molecular weight	304.35 g/mol	350.6 g/mol
colour	Colourless to dark brown	colourless to white
Physical form	liquid	solid
Density	1.116 g/cm3	1.398 g/cm3 (43.5 °C)
Water solubility	0.06 g/L (20°C)	0.73 mg/L (20
Vapour pressure	8.4 × 10 −5 mmHg (20°C)	1.87 x 10-5 mmHg at 25 °C
Boiling point	82–84°C (2.0 × 10 −4 mmHg)	160 °C; 320 °F; 433 K (decomposes)

(USEPA, 2011b)

Diazinon is degraded by biotic and abiotic processes when given adequate time, hence there is no parent compound persistency. Diazoxon and 2-isopropyl-6-methyl-4-hydroxypyimidine are

the degradation products of diazinon. While the toxicity of Diazoxon is high, 2-isopropyl-6-methyl-4-hydroxypyimidine is less toxic but persists in the environment (USEPA, 2004). Oxypyrimidine is the major diazinon degradation product in soil and water (USEPA, 2004). In the atmosphere, conversion of diazinonto diazoxon takes place via ultraviolet (UV) radiation (Timchalk, 2001). The approximate half-lifefor the reaction of the hydroxyl radicals together with the vapour phase of diazinonis estimated to be four hours (ATSDR, 2008).

After the release of diazinon into the soil or surface waters, it may be volatilized or hydrolysed, undergo photolysis or in some cases biodegradation. In the aerobic environment, biodegradation is the main process that takes place for diazinon in relation to soil and water. It can also undergo anaerobic biodegradation (De Vlaming*et al.,* 2000). Diazinon can also undergo hydrolysis in water and soil, especially at low pH (USEPA, 2006). Some of the factors that influence diazinon's half-life in soil comprise of the soil type and pH (USEPA 2004).

Diazinon's release to the environment is mainly attributed to its widespread use particularly as an insecticide in the control of garden pests as well as household related lawn. Its use indoors and as a pest control agent in agriculture has also contributed to its release to the environment. About four million of diazinon's active ingredients are used yearly on agricultural sites (USEPA, 2004). Figure 2.2 shows the structure of diazinon.

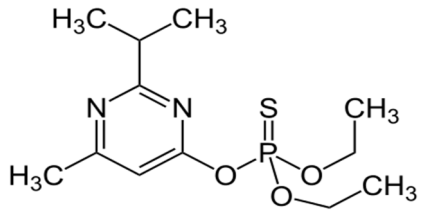

Figure 2. 2*: Structure of diazinon*

Through a number of monitoring studies, diazinons together with its metabolite diazoxon have been detected in surface water (De Vlaming *et al.,* 2000). According to USEPA (2004) diazinon exposure can occur through inhalation, skin penetration and ingestion. Serious additive toxicity

can occur through multiple route exposure. Just like any other organophosphate insecticide, diazinon's symptoms of acute poisoning comprise of sweating, tearing, dizziness, agitation as well as drowsiness. Other symptoms include headache, nausea, and anxiety together with salivation (De Vlaming *et al.,* 2000).

Diazinon is usually harmful to important insects as well as mites which are very helpful in agriculture. For example, USEPA has categorized diazinon as "highly toxic" to honeybees (Allender and Britt, 1994). The lifespan of worker honey bees is also shortened by diazinon There is more sensitivity on newly emerged bees (Leidy *et al.,* 1982). According to Currie *et al.* (1990), diazinon was in the highest toxicity category in a screening program that was carried out internationally for useful insects and mites. Diazinon's effects are similar on predators and parasites of the pecan aphids (USEPA, 1990).

2.1.2 Chlorpyrifos

Chlorpyrifos is acrystalline organophosphate insecticide introduced by Dow Chemical Company in 1965.It is sold as Lorsban and Dursban formulations (Timofeeva and Levin, 2010). It's mode of action on the insects nervous system is through the inhibition of acetylcholinesterase (Hoppin*et al.,* 2002). According to USEPA (2002), most of the indoor use of chlorpyrifos was prohibited in the U.S.A. in 2001.Prior to the ban, chlorpyrifos was among the most frequently used agricultural and residential organophosphate insecticide (USEPA, 2002). Childhood exposure or exposure to chlorpyrifos during pregnancy has been potentially associated with neurological changes that include attention and development problems. It has also been potentially correlated with lower weight at birth (Timofeeva and Levin, 2010). Repeated low-dose or acute exposure in adults may lead to lingering health effects which include a slightly increased risk of wheezing and whistling sound resulting from airway obstruction among agricultural workers exposed to chlorpyrifos (Hoppin *et al.,* 2002).

Chlorpyrifos use in agriculture results in chemical residues on food items (Timofeeva and Levin, 2010). As a consequence, to lessen on exposure to children, the EPA changed the tolerance on tomatoes, apples as well as grapes, decreasing the tolerance on apples together with grapes to 0.01 ppm while eliminating the tomato tolerance in 2006 (USEPA, 2006). Since the residue of chloryrifos on food items like tomatoes, squash and carrots is not allowed, chlorpyrifos' residue on such food items usually represents misuse of chlorpyrifos or spray drift (USEPA, 2006).

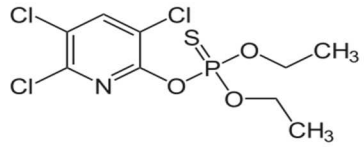

Figure 2.3*: Structure of Chlorpyrifos*

2.1.3 Organochlorine Pesticides

Organochlorine pesticides belong to the group of chemical compounds that are non-polar and toxic, made up of carbon, chlorine and hydrogen. It comprises of three major categories which include: DDT and analogues like methoxychlor as well as dicofol, Benzene hexachloride together with its isomers and the cyclodienes which include endosulfan, endrin, dieldrin, aldrin, chlordane as well as heptachlor (Table, 2.2). The other major groups are chlordecone and Toxaphene (Pope *et al.*, 1994).

Table 2.2: List of Organochlorine pesticides

DDT and analogues	*p,p'*-DDT, *p,p'*-DDD, *p,p'*-DDE, Methoxychlor and dicofol
Benzene hexachloride and isomers	α-HCH, β-HCH, γ-HCH and δ-HCH
Cyclodienes	Endosulfan, endrin, dieldrin, aldrin, chlordane and heptachlor
chlordecone	

Toxaphene	

(Pope*et al.*, 1994)

There has been a large production and use of organochlorine pesticides worldwide until 1970s (Escuderos *et al.*, 2003). The parent compounds together with the degradation products are highly recalcitrant resulting in build-up in environmental media and pollution of soil, food and water (Kim and Smith, 2001). The broad spectrum toxicity of HCH and DDT makes them a potential hazard to the health of human beings (Metcalf, 1997).

Organochlorine pesticides have been banned in most of the countries because of the fact that they are very harmful towards human beings (Escuderos *et al.*, 2003). Their considerable stability makes them to persist in the environment. They can also be moved by air or water far distances (Jolanta *et al.,* 2011). The Stockholm Convention's focus on Persistent Organic Pollutants is on decreasing as well as doing away with the 23 persistent organic pollutants. They include industrial chemicals, Organochlorine pesticides together with two by-products (World Bank, 2001). Pesticide toxicity, stability and mobility in the environment is high concern (Cairns and Sherma, 1992). Their presence in food poses harmful effects on humans (Jolanta *et al.,* 2011).

2.2Pesticides contamination in vegetables

Pesticides are particularly hazardous in fruits and vegetables (Spanoghe *et al.*, 2009). Contamination of plants can occur at any point between the field application to preservation (Ware and Whitacre, 2004). However, consumption of food contaminated with pesticide residues could be of great danger to the health of consumers (Lee and Seeneevassen, 1998).

Generally, the quantity of pesticides absorbed by a given plant depends upon the organic matter of the soil, solubility of the pesticide in water and the amount of pesticide in the soil

(Akan *et al.,* 2013). The total amount absorbed by a single plant increases with time (Akan *et al.,* 2013). For non-polar pesticides, soil organic matter is the most important soil factor influencing sorption of residues (Akan *et al.,* 2013).

The bioaccumulation of contaminants depends on physico-chemical properties (Ware and Whitacre, 2004). For instance, for detritus food chain, the lipophilic contaminants pass on from dead organic matter where they are bound into microorganisms and then to detritus-feeding organisms and their predators all the way to herbivores and carnivores (Akan *et al*., 2013). Any time a higher food chain organism consumes food from a lower food chain organism, the pesticide residues are accumulated by the consuming organism (Ware and Whitacre, 2004). Food chains are not in isolation but interlock with each other and form a food web. Pesticide residue contamination in organisms increases as the position of an organism in the food web increases (Akan *et al.,* 2013).

2.3 Pesticides contamination in soil and water

Surface and groundwater are at a risk of being contaminated by chemicals from diffuse sources other than from point sources when proper field application procedures are followed (Ware and Whitacre, 2004). Examples of point sources include areas on farms where pesticides are filled into sprayers, handled and washed down (Adedeji, 2009). Therefore, Continuous monitoring of environmental and food samples is of utmost importance because of the rampant use of pesticides which has led to the contamination of various strata (Spanoghe *et al.*, 2009; Konstantinous *et al.*, 2006).

Pesticides reach the soil through different pathways. Direct application to the surface is the main pathway where the pesticides affect top few inches of soil (Ware and Whitacre, 2004). The persistence of pesticides is dependent on a number of climatic factors. Some of these

factors include the temperature in the air, intensity of light, direction of wind as well as rainfall (Ware and Whitacre, 2004).

High pesticide dissipation rates are observed in loamy soils with low pH (Adams *et al.*, 1976), and the decomposition is generally accelerated by warm moist soils containing high organic matter. Rotationally grown crops are additionally exposed to pesticide residues in soil and these pesticides hinder valuable microorganisms to crucial levels (Kiu *et al.*, 1995). The soil ecology is altered by excessive amounts of pesticide residues which also have a negative effect on the vegetation together with the metabolic integrity of the soil (Adedeji, 2009). Higher food chain members are prone to pesticides bioaccumulation which is as a result of pesticide residues from the soil flora as well as fauna (Kiu *et al.*, 1995).

There is a risk of environmental contamination when pesticides enter ground water resources and also when there is surface run-off during rainfall (Ware and Whitacre, 2004). Pesticides are washed into the Lake through surface run off, this usually happens during the wet season (Adedeji *et al.,* 2009). There is contamination of water by these pesticides and an interruption of the life cycle of most aquatic organisms hence a significant threat to biodiversity (Furness and Greenwood, 1993).

During the dry season, pesticide use cause serious environmental problems because of low dilution capacity of the water systems, leading to an increase in the concentration of toxic chemicals (Adedeji *et al.,* 2009). Furthermore, it is also a crucial period for several animals particularly birds and fish (Furness and Greenwood, 1993). The direct or indirect water pollution by pesticides can result in high levels of unwanted chemicals in that they not only affect edible fish productivity but also eventually affect human health hence affecting the health of human beings. This may also lead to fish kills and reduce fish productivity (Adedeji *et al.,* 2009).

2.4 The fate and transport of pesticides applied to crops

Pesticides applied to crops may be taken up into the transport system of the plant or remain on the plant's surface (Holland and Sinclair, 2004). On the plant surface, it may undergo volatilization or photolysis. It can also undergo degradation when still on the surface of the plant (OECD, 2012). All these processes not only lead to a reduction of the original pesticide's strength but also introduce new metabolites in the crops (OECD, 2012).

Volatilisation of pesticides normally depends on the pesticide's vapour pressure and environmental conditions (OECD, 2012). Pesticides having a high vapour volatize more quickly as opposed to those whose vapour pressure is low (Holland and Sinclair, 2004). The rate at which pesticides volatize is also dependent on the environmental conditions such as the speed of wind as well as temperature (Holland and Sinclair, 2004).

As soon as molecules absorb sunlight energy, photolysis occurs, this leads to degradation of pesticides (OECD, 2012). Indirect reactions can also be as a result of the breakdown of other chemicals by sunlight and a reaction taking place between the resulting products and pesticides (Ware and Whitacre, 2004).

Pesticides are sometimes used by micro-organisms as nutrients, this leads to a breakdown of these pesticides and in the process carbon dioxide is released together with other substances (Holland and Sinclair, 2004).A disparity in the organic chemicals that occur naturally as well as the pesticide structures can occasionally result in the pesticides not being assimilated by the microbes but it may lead to an alteration at the reactive sites and the end products may possibly be more or less poisonous than the original chemical (Juan *et al.,* 2008).

Agriculture has been intensified in the areas surrounding Lake Naivasha in the last decade. To keep the crops healthier and more productive, more fertilizers and pesticides are being used (Okello and Okello, 2010). It has been reported that a large variety of pesticides are being used

in the area. There may be a great deal of impact on the groundwater whether on a long or a short-term basis if there is a continuous use of pesticides (Okello and Okello, 2010). The transportation of pesticides is majorly by rainfall and wind from where they are applied to nearby plants, land as well as water bodies, where their occurrence may be dangerous or detrimental (Holland and Sinclair, 2004).Since most organochlorine pesticides are highly persistent in the environment, they tend to be detected over a longer period. The detection of some of the organochlorine pesticides is also as a result of long range transportation in the atmosphere (Holland and Sinclair, 2004).

Since most organochlorine pesticides have been banned for use in agriculture all over the world and more so in Lake Naivasha, many farmers now use organophosphate, pyrethroids and carbamate pesticides because they are relatively safe (Mitoko *et al.*, 2008).The widespread use of these pesticides in Lake Naivasha catchment has resulted in pollution to the lake because of agricultural runoff and waste water discharge.

A study carried out in 2014 by Otieno *et al* revealed the presence of chlorpyrifos-ethyl residues in water and sediment samples collected from Lake Naivasha during dry and wet seasons. The highest concentration detected was 35.8±4.6ng/g and 24.9±4.4ng/g in the sediments and water samples collected during the wet season. During the dry season, the highest concentration of pesticide residues detected were 14.4 ±2.9 ng/g and 14.9±3.1 ng/g in the sediment and water samples respectively (Otieno *et al.*, 2014). The same study also revealed the presence of diazinon residues but at lower concentrations. Sediment samples had pesticide residue levels of 9.3 ±3.1 ng/g and 5.7 ±1.2 ng/g during the wet and dry seasons respectively. Water samples had residue levels of 26.7 ±4.3 ng/g and 8.2 ±2.1 ng/g during wet and dry seasons respectively (Otieno *et al.*, 2014).

2.5 Toxic Effects of Pesticide Residues

The extent of harm involved in pesticide use under given conditions is known as hazard and is dependent on the amount of exposure and toxicity of the pesticide (Juan *et al.,* 2008). A measure of the ability of a pesticide to cause harm is referred to as the toxicity of the pesticide (Juan *et al.,* 2008). Determination of toxicity is usually done by subjecting test animals to different dosages of the active component together with its formulations. A pesticide user can lower the potential hazard by choosing pesticides with lower toxicity to control the pests (Maumbe and Swinton, 2003). This will happen when farmers understand the difference in toxicity levels of pesticides (Sesline and Jackson, 1994).

Toxicity can either be acute or chronic. The ability of a chemical pesticide to cause harm to people or animals from a short term exposure is known as acute toxicity (Juan *et al.,* 2008). Acute effects are the damaging effects that come about as a result of short term exposure by any entry point. The routes of entry are oral, eyes, dermal and inhalation (Juan *et al.,* 2008). The quantity of a toxicant that can kill 50% of test species is the measure by which acute toxicity is determined (Jobling *et al.,* 1995). The measure is normally expressed as lethal dose 50(LD_{50}) (Jobling *et al.,* 1995).

The determination of chronic toxicity is through subjecting test species to active components for a long time (Juan *et al.,* 2008). Chronic effects are the damaging effects that come about as a result of exposure to small doses over a long time (Maumbe and Swinton, 2003). Some of the effects that are suspected to be as a result of long term exposure to certain pesticides include toxicity to foetus, birth defects, production of benign or malignant tumours, genetic changes, nerve disorders, blood disorders, endocrine disruption, and reproductive effects (Maumbe and Swinton, 2003). The short term harmful effects of pesticides are easier to establish by way of laboratory tests than chronic toxicity (Juan *et al.,* 2008).

Exposure to pesticides for individuals in a farm situation can occur in various ways (Okello and Okello, 2010). These include eating while spraying pesticides, entry into freshly sprayed fields, exposure on the skin with liquid, consuming food contaminated with pesticides as well as consuming unwashed food (Juan *et al.,* 2008). Being exposed to pesticides can either cause chronic or acute illnesses (Maumbe and Swinton, 2003).

Inappropriate application of pesticides have resulted in high toxicity levels leading toecological risks (Sesline and Jackson, 1994; Joblinget *al.,* 1995). Human beings exposed to small doses of pesticides over a long time via water, food as well as air may eventually suffer from chronic toxicity because of the accumulation of residues in the body over a long time (Kriengkrai, 2006). Cancers, congenital malformations as well as neurological disorders are some of the health problems that are connected with long-term exposure to pesticides. Others include barrenness, impotence, immunological disorders, liver and kidney harm together with skin alterations (Koprucuet *al.,* 2006; Turgut, 2007). It may also lead to an aggravation of an existing illness (Sesline and Jackson, 1994).

The application of large quantities of pesticides has had an effect on water bodies, the atmosphere and soil leading to damage of vegetation and contamination of the environment. According to some FAO report, many countries in Africa stock piled pesticides (chlordane, aldrin, dieldrin, heptachlor and DDT) in some areas and these became waste dump sites (Kriengkrai, 2006).

The groups of people directly exposed to pesticides are, formulators, manufacturers, mixers, suicides, applicators and mass poisoning (Juan *et al.,* 2008). Indirect pesticides impacts on humans include exposure to pesticide residues in the air as well as eating food polluted with pesticides, others include being exposed to pesticide residues in food materials, water, soil,

plants, sediment as well as animals (Kriengkrai, 2006). There is documentation on the connection between contact with pesticides and health issues and defects (Juan *et al.,* 2008).

Pesticides treated crops invariably contain small quantities of these chemicals and the hazard is dependent on the quantity of pesticide residues that remain on the crop and their toxicity (Akan *et al.,* 2013). Research on pesticides residues supports the establishment and control of safe levels of pesticides in food. It is important both for trade purposes and also for ensuring that human health is safe. It is for this reason that maximum residue levels (MRLs) are set so as to ensure appropriate agricultural practices (Juan *et al.,* 2008).

2.6 Review of pesticides residues in vegetables in the world

Pesticides residue analysis in food (vegetables, meat, fruit, baby food, cereals and other processed food) on the Danish market indicated that more residues were present in samples from foreign countries compared to samples of Danish origin (TUD, 2011). In general, fruits and vegetables had higher frequencies of carbamate pesticide residues than the other classes of commodities; vegetables had lower frequencies compared to fruits, also noted was that samples with more than one residue were more frequently found in samples of foreign origin (TUD, 2011). Generally residues exceeding the MRLs were found in 2.6 % of the samples, most commonly in fruit (TUD, 2011).

A study conducted in India regarding the effect of imidacloprid insecticide remains on biochemical parameters in potatoes and its approximation by HPLC showed that potatoes treated with the insecticide had a significant amount of imidacloprid (0.35 mg/kg) during harvest (Shailendra *et al.,* 2013). When the potatoes were washed with tap water and boiled for 20 minutes, the level of the residues went down by 33% and 80%, respectively (Shailendra *et al.,* 2013).

The discovery of the dangerous effects of organochlorine pesticides has made most of the nations that are industrialized and those that are developing to thoroughly investigate and accumulate massive data on the residue status of pesticides in their environment. In the Republic of Benin, a study conducted on health dangers as a result of being exposed to pesticides, along River Kiti, in Dridji, indicated the existence of DDT in the vegetable as well as the fish samples (Yehouenou *et al.,* 2014).

It was observed that DDT and its related compounds together with α-endosulfan had residues up to 403 ng/µg in the amphibians, fish and crabs collected from River Kiti. Also contaminated were bean leaves sampled from the beans planted in the river floodplain and eaten by the residents (Yehouenou *et al.,* 2014). They were polluted with ten pesticides which include hexachlorobenzene, DDT and its related compounds, α-endosulfan, heptachlor, lindane together with dieldrin (Yehouenou *et al.,* 2014). The total DDT levels in the bean leaves were ranging from 274 to 1351 µg/kg dry mass (Yehouenou *et al.,* 2014).

An organophosphorus pesticide residue study in vegetable and soil samples in Borno area of Nigeria indicated that the least residues were detected in spinach roots while the maximum residues of pesticides were detected in the leaf of tomato (Akan *et al.,* 2013).The lowest residues in soil were detected from a depth of 0cm to 10cmwhile high residues were detected at a depth of 21-30cm (Codex, 2009). All organophosphorus pesticide residues in the vegetables and soil samples from the two areas were seen to be at disturbing levels (Akan *et al.*, 2013). The levels were much higher than the acceptable daily intake values (ADIs) and maximum residue limits (MRLs) set for soil and vegetables by the Codex (Akan *et al.*, 2013).

2.7 Review of studies on pesticide residues in Kenya and its neighbouring countries

In a study performed to establish the residues of pyrethroids and organochlorine pesticides in sediments, water together with soil samples along River Nzoia, there appeared to be variation

of pesticide residue levels with season (Tarus *et al.,* 2007). Some pyrethroids and organochlorines (endosulfan sulphate and dieldrin) were within the WHO's MRL (Maximum Residue Limits) (Tarus *et al.,* 2007). In Webuye and Pan-paper areas, *o,p'*-DDE and lindane exceeded the WHO MRL values of water. Lindane in soil was exceeded in Mumias, while *o,p'*-DDE and dieldrin was exceeded in Webuye and endosulfan sulphate in Pan-paper (Tarus*et al.,* 2007). In sediments lindane and dieldrin was exceeded in Moi's Bridge, *o,p'*-DDE in Pan-paper and endosulfan sulphate in Pan-paper Webuye (Tarus*et al.,* 2007).

Banned Orgochlorine pesticides were still found to be used in the lower Yala/Nzoia catchment area (Safina *et al.,* 2011). This is as a result of a study performed to establish pesticide residues in the region during the wet and dry seasons of the year 2009.Organochlorine pesticide concentrations in water from Yala/Nzoia basin were undetected both during the wet and the dry seasons (Safina *et al.,* 2011).

In the same area, the organochlorine pesticide residues found in sediment samples collected during the wet season ranged between 0.05 and 59.01 μgkg^{-1}. During the dry season, the concentrations were ranging from BDL to 24.54 μgkg^{-1}. A majority of the samples had higher residue levels of *p,p'*-DDD and dieldrin as compared to aldrin and *p,p'*-DDT, respectively (Safina *et al.,* 2011). In the water and sediment samples, there were no organophosphates detected. Organochlorine pesticide concentrations in sediments for the two seasons were lower than the recommended WHO guidelines (Safina *et al.,* 2011).

An assessment carried out in Uganda to establish residue levels of pesticide in uncooked Cucumber from Lake Victoria Basin showed small amounts of lindane, endosulfan, DDE, DDT, chlorfenvinphos and fenitrothion in the cucumbers (Nannyonga *et al.,* 2012). The pesticides residue levels were below the recommended European Union Commission maximum residue levels (Nannyonga *et al.,* 2012).

A study carried out in 2011 on carbofuran residues in water, plants and soil samples indicated proof of accessibility of furadan in the veterinary retail shops found in the area (Otieno *et al.,* 2011). This was also true for a similar study conducted on the remains of the African white – backed vultures that had been found dead in Athi River (Otieno *et al.,* 2011). A GC-MS and HPLC analysis of soil, water together with plant samples collected from the farms as well as the water sources showed residues of carbofuran, 3-hydroxycarbofuran together with 3-ketocarbofuran indicating that furadan was widely used in farming ending up in environmental distribution and pollution as a result of the residues. This also meant that small birds as well as mammals were put at risk (Otieno *et al.,* 2011).

Residues of carbofuran together with its two metabolites were also found in a forensic analysis conducted in the feet, beaks and crop content of the dead vulture in addition to that of laced camel carcass and soil samples collected from one of the poisoning sites (Otieno *et al.,* 2004). These findings were in support of allegations that furadan was being used illegally in poisoning wildlife and it was also associated with high death cases of African white-backed vultures in Kenya (Otieno *et al.*, 2011).

Another study carried out in 2012 on carbofuran, diazinon and chlopyrifos ethyl residues in sediment and water in Lake Naivasha indicated higher concentration of chlorpyrifos in sediments (11.2-30.0 ng/g) dry weight in wet season and 4.7 in dry season (4.7-17.4 ng/g dry weight).Diazinon and carbofuran levels were below detection limit in all the analyzed samples (Otieno *et al.*, 2012)

A different study carried out in 2012 on the impacts of climate induced-changes on the distribution of pesticides residues in water and sediment of Lake Naivasha, Kenya showed evidence of increased chlorpyrifos in sediment and water in Lake Naivasha as a result of its increased use in horticulture in the area (Otieno *et al.*, 2012). In this study, higher levels of

chlorpyrifos were reported during the period of high rainfall as compared to levels reported during low rainfall period. Residue levels in sediments ranged between 14.8 ng/g and 32.8 ng/g during the wet season and 8.5 ng/g to 16.6 ng/g during the dry season. Residue levels in water samples ranged between 8.61 µg/L and 22.4 µg/L during rainy season and below detection limit (bdl) −13.6 µg/L in dry season (Otieno *et al.,* 2012).

CHAPTER THREE

3. MATERIALS AND METHODS

3.1 Study area

The study was conducted in Lake Naivasha area. Naivasha sub-county, Nakuru County, has a total area of 3,400 km^2 (Chiramba *et al.*, 2011) and lies within latitude 0°43′00″S and longitude 36°26′09″ E with an altitude of 1915m above the sea level. It has a population of 181,966 (KNBS, 2013) and is among the fastest developing towns in Kenya (Jolicoeur, 2000). The growth is associated with rising vegetable and flower farming business in the areas surrounding the lake. Tourism and its related activities in the area together with relocations from rural to urban areas because of decreasing farming incomes from the conventional cash crops have also been contributing factors towards this growth (Jolicoeur, 2000).

3.1.1 Sampling area

Sampling was done in 8 sites (Figure 3.1), three farms and three markets, a river and the lake. The farms were Kihoto, Malewa and Kenya Wildlife Services (KWS) while the markets included KCC market, Gatara market and Kihoto market. Water samples were collected from Lake Naivasha, River Malewa and KWS farm. A simulation study was also carried out in one of the farms in Naivasha. Figure 3.1 below shows the location of sampling sites. The farming arrangement around Lake Naivasha is such that the farms extend to the areas surrounding the lake. Some of the largest horticultural and floricultural farms in the world surround the lake with 80% of Kenya's floricultural and vegetable farming being carried out in Naivasha (Jolicoeur, 2000).

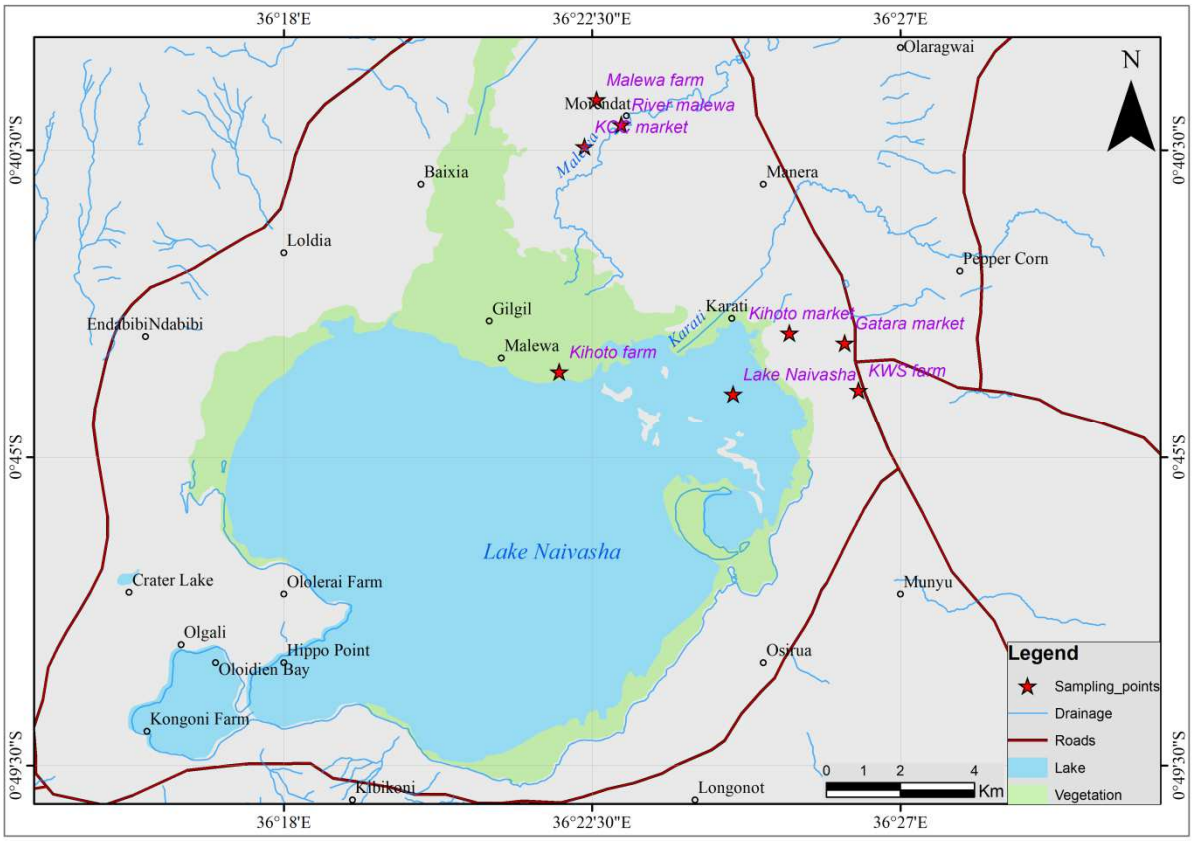

Figure 3.1: Map of Naivasha sub-county, Kenya showing the sampling sites

3.1.2 Description of Sampling Sites

Table 3. 1: GPS coordinates of the sampling sites in Naivasha area

Site	Location common name	GPS Position	Altitude (m)
1	KCC market	036º22’52’’ E 00º40’19’’ S	1,927
2	Kihoto farm	036º25’02’’ E 00º44’05’’ S	1,901
3	Lake Naivasha(Kihoto area)	036º24’56’’ E 00º44’07’’ S	1,905
4	KWS farm	036º26’39’’E 00º44’01’’ S	2,012
5	Kihoto market	036º25’38’’ E 00º43’175’’ S	1,915

6	Malewa farm	036º 22’54’’ E 00º40’075’’ S	1,921
7	RiverMalewa	036º 22’55’’ E 00º40’05’’ S	1,910
8	Gatara market	036º26’19’’ E 00º43’32’’ S	1,989

3.1.2.1 KCC Market

KCC market lies within036º22’52’’ E and 00º40’19’’ S and an altitude of 1,927 m (Table 3.1). It is a small market that deals with retail sale of vegetables, other food items and house hold consumables. There is subsistence agriculture also being practised around this area, mainly involving horticultural farming and rearing of animals such as goats, sheep and chicken.

3.1.2.2 Kihoto Farm

Kihoto farm lies within 036º25’02’’ E and 00º44’05’’ S and an altitude of 1,901 m (Table 3.1).The farm is located at a distance of about 500m from Lake Naivasha. Farming activities around this area involves growing various types of crops (kale, spinach, cabbages, carrots, onions, potatoes, beans, maize among others). Farmers also graze their cows, goat and sheep around this area.

3.1.2.3 Lake Naivasha, Kihoto area

Kihoto area lies within latitudes 036º24’56’’ E00º44’07’’ S and an altitude of 1,905 m (Table 3.1). A variety of crops are grown around this part of the lake. Some of the crops include maize, beans and vegetables (kale, cabbages, carrots, spinach among others). Grazing of animals also takes place around this place.

3.1.2.4 KWS farm

KWS farm is within 036º26’39’’ E and 00º44’01’’ S and an altitude of 2,012 m (Table 3.1).The main activities being carried around this area include subsistence farming and rearing domestic animals on a small scale.

3.1.2.5 Kihoto market

Kihoto market lies within 036º25’38’’ E and 00º43’175’’ S and an altitude of 1,915 m (Table 3.1). Being a market place, the common activities taking place in this area involve sale of various commodities. Some of these include vegetables (kales, spinach, cabbages, carrots and many others) and other food crops like maize, beans and potatoes. About 500m from this market are residential areas.

3.1.2.6 River Malewa

River Malewa lies along036º 22’55’’ E and 00º40’05’’ S and altitude of 1,910 m (Figure 3.1).The river is a watering point for animals and a source of water for domestic use. People also swim in this river. Farmers around this area also use water from this river to water their crops.

3.1.2.7 Malewa farm

Malewa farm lies along 036º 22’54’’E and 00º40’075’’ S and an altitude of 1921 m (Table 3.1). Various kinds of vegetables are grown on the farm which include kales, spinach, onions and carrots among others.

3.1.2.7 Gatara market

Gatara market is within latitudes 036º26'19'' E and 00º43'32'' S and an altitude of 1,989 m (Table 3.1). It is located next to a main road. Various commodities are sold here including vegetables (kales, carrots, cabbages among others). There are shops also located in this area selling household consumables. Table 3.1 shows the co-ordinates of the sampling sites in Naivasha area.

3.2 Chemicals and reagents used

Dichloromethane, n-hexane and acetone (all general purpose) and HPLC grade iso-octane were bought from SCIELAB LTD, Nairobi. The general purpose grade solvents were triple distilled in the laboratory before use. Anhydrous sodium sulphate and aluminium oxide, both analytical grade, were also bought from SCIELAB LTD. High purity Nitrogen, used for reducing samples, was purchased from Gas labs LTD. Hydrogen that is of very high purity, white spot nitrogen together with helium used for gas chromatography were bought from BOC Kenya LTD. High purity Pesticide standards, which were of very high purity, were provided by the PCPB (Pest Control Products Board).

3.3 Equipment and apparatus used

The Soxhlet set up was used in extracting kales and soil samples. It is made up of a heating mantle, a condenser together with a Soxhlet extractor. Extraction of water samples was done using a 2 litre separating funnel. Clean up of the samples was done using a 20 cm long glass column with an internal diameter of 2 cm. The extracted samples were then concentrated using the Stuart rotary evaporator. A fractional distiller was used for distilling the solvents. BINDER E28♯04-71528 oven was used for drying the kales so as to determine the moisture content. Glassware were dried in a Mammoth oven.

Weights for all the samples were taken using the analytical weighing balance (Fisher Scientific A-160). A lab-line explosion proof refrigerator was used to temporarily store the samples before extraction. A HP Agilent GC system equipment with ECD and a GC-MS (HP 6890 PLUS) combined with an auto sampler (Agilent 6890 series injector) were used for quantification of pesticides in the samples extracts.

3.4 Preparation of reagents

Drying of Aluminium oxide was done overnight at 200 ºC in order for it to be 100% active. Deactivation of the Al_2O_3, so as to achieve Al_2O_3 (8% w/w), was done using water. This was done by adding 8ml of HPLC water to 92 g of the Al_2O_3 that had been activated. The process was done in a 250 ml Erlenmeyer flask and it involved shaking the mixture by hand so that all the lumps could be eliminated. These chemicals were then left in the oven again at 200 ºC to condition.

3.5Sample Collection

3.5.1 Sampling plan

Sampling was done twice, in March (during the dry season) and in May 2015 (during the wet season). Samples collected in March captured the dry season when ploughing of the farms was taking place, whereas some farmers also spray their kales with pesticides at this time to kill the invading pests. This is also the time when pesticides are applied to the soil to destroy the different kinds of pests found in the soil in readiness for planting. The samples collected in May captured the rainy season when pesticides applied on the farms at the time of ploughing and planting may be transported by runoff into the rivers and lake.

3.5.2 Soil Sampling

Soil samples were collected from three farms Kihoto, Malewa and KWS and three markets Kihoto, KCC and Gatara. Sampling sites were randomly selected within each farm and market.

Soil cores were dug using a pre-cleaned hoe and scooped using a stainless steel shovel from a depth of 15- 25 cm from five different locations within each farm and market and approximately 200 g of the core scooped. The cores were combined and 500 g of the soil was then placed on clean aluminium foils, wrapped and put inside a black polythene bag labelled' packed in self-sealing bags, put inside cooler boxes and transported to the University of Nairobi's pesticide analytical laboratory. They were then preserved at -20 ºC in the refrigerator prior to extraction (UNEP, 2010). The soil samples were collected in dry season (March, 2015) and wet season (May 2015).

3.5.3 Kales sampling

Sampling for kales was done from 6 sites, 3 markets (Kihoto, KCC and Gatara) and 3 farms (Kihoto, Malewa and KWS). 50 g of the vegetables (kales) was collected in triplicate from each of the six sampling sites. The samples were packed in clean self-sealing bags, clearly labelled and transported to the University of Nairobi's pesticides analysis laboratory for storage in a refrigerator at 4 ºC, awaiting extraction. Kale samples were collected in dry season (March, 2015) and wet season (May 2015).

3.5.4 Water sampling

Water samples for pesticide residue analysis were collected in triplicates from three different sites namely Lake Naivasha (near Kihoto farming area), River Malewa, and at the KWS. Preservation of the water samples was done by adding 100 g of NaCl to the water samples. Sampling was done from each point using 2.5 L amber glass bottles and preserved using 100g of NaCl before being taken to the Laboratory. Sampling was done both during the dry season (March, 2015) and wet season (May 2015). They were analysed for the physico-chemical parameters such as pH, total dissolved solids (TDS) and total suspended solids (TSS). The

samples were then temporarily stored in polyurethane cool boxes and transported to the University of Nairobi's laboratory for analysis.

3.6 Sample extraction

3.6.1 Extraction of soil samples

Soxhlet extraction (EPA method 3540) was used in soil extraction (USEPA, 2006). Before extraction, the soil samples were taken from the freezer and left to thaw for 6 hours. 20 g of anhydrous sodium sulphate was used to dry 20 g of the soil sample; this was done by grinding and mixing thoroughly in a mortar. The mortar containing the dried soil sample was then covered with an aluminium foil and left to stand for about 12 hours. The process was done in triplicates for each of the samples. Extraction was then carried out for sixteen hours in the Soxhlet using a mixture of hexane together with acetone (200 ml) in the ratio of 3:1, respectively. After the sixteen hours, the Soxhlet extractor was turned off and the extracts allowed to cool. This was followed by an addition of 2 ml of isooctane, which acts like a keeper and the extracts concentrated using a rotary evaporator to about 3 ml. The concentrated extracts were thereafter transferred into vials using pasteur pipettes and stored in a refrigerator at 4 ºC pending clean-up.

3.6.2 Extraction of kale samples

Kales were extracted using USEPA method 3510 (USEPA, 2006), which involved using a mixture of hexane and acetone in the ratio of 3:1, respectively. This is a method used for the extraction of pesticide residues in non-fatty crops. Twenty grams of the vegetable samples were dried overnight using anhydrous sodium sulphate in a mortar. This was done in triplicates for all the sites.

The kales were then extracted in a Soxhlet for sixteen hours using a 200 ml mixture of hexane and acetone in the ratio 3:1. The extracts were allowed to cool and 2 ml of iso-octane added to

act as a keeper. Using a rotary evaporator, the extracts were then evaporated to 3ml at 35 ºC. The concentrated extracts were then transferred into clean vials, tightly capped and stored in freezer at 4 ºC pending clean up.

3.6.3 Water samples extraction

Water samples were extracted using the liquid- liquid extraction procedure adopted from USEPA Method 3510 (USEPA, 2006). A glass measuring cylinder was used to measure 2.0 L of water which was then transferred into 3.0 L beaker and the pH recorded. This was followed by an addition of a buffer (50 ml of 0.2 M dipotassium hydrogen phosphate) and the pH recorded. Adjustment of the pH to 7.0 followed by a drop by drop addition of 0.1 M hydrochloric acid or 0.1 M sodium hydroxide solutions while carefully stirring the solution. The next step involved transferring the neutral solution to a 2.0 L separating funnel after which 100 g of NaCl was added to salt out pesticides from the aqueous to the organic phase. Triple extraction was then done using 60 ml of triple distilled dichloromethane (DCM). This involved vigorous shaking of the sample in the separating funnel while releasing pressure. To allow for effective separation, the mixture was left to settle for 30 minutes. This was followed by collection of the lower layer into a cleaned and dried 250 ml conical flask. The process was repeated twice with 60 ml portions of DCM and the extracts combined. 2 ml of isooctane was then added and the extract evaporated to about 3 ml using a rotary evaporator. The concentrated water extracts were then transferred into vials and stored in a refrigerator at 4 ºC awaiting clean-up.

3.7 Cleaning up of extracts

3.7.1 Cleaning up of kale extracts

Cleaning up of the kale samples was done as follows; a 25 cm long chromatographic column with an internal diameter of 1.5 cm was filled with 2 g of activated anhydrous Na_2SO_4 then with 15 g of deactivated Al_2O_3 and topped up with 3 g of activated charcoal (decolourizer) and finally another 2 g of activated anhydrous sodium sulphate. Preconditioning of the column was

done using 15 ml of triple distilled n-hexane. The residue in 3 ml hexane: acetone mixture was poured into the column and the vial rinsed three times with 1 ml hexane. The analytes were then eluted by adding 175 ml of n-hexane into the column. 2 ml of iso-octane was then added to the cleaned extract which was then concentrated to around 3ml under vacuum evaporator. The same process was applied to all the samples. The last extract was reduced to 0.6 ml under a mild stream of nitrogen. At this point the samples were ready for GC analysis.

3.7.2 Cleaning up of water and soil samples extracts

Cleaning up of the water and soil samples was done using a chromatographic column filled with 2 g of activated anhydrous Na_2SO_4 followed by 15 g of deactivated Aluminium oxide and lastly by 2 g activated anhydrous sodium sulphate. The column was conditioned with 15 ml of n-hexane and the sample mixture poured into it then the vial rinsed three times with 1 ml hexane. The analytes were then eluted using 175 ml of n-hexane. 2 ml of iso-octane was then added to the cleaned extract which was then concentrated to around 3 ml under vacuum evaporator. The same procedure was applied to all the samples. The last extract was reduced to 0.6 ml using a mild nitrogen stream. At this point the samples were ready for GC analysis.

3.8 Removal of Sulphur from soil samples

Approximately 1 g of copper powder that had just been activated was added to the already cleaned soil extracts in order to remove sulphur. All extracts containing Sulphur formed copper sulphide as indicated by the black colouration. A glass funnel filled with glass wool together with 2g of activated anhydrous $Na_2SO_4$was used to filter the soil extracts. The anhydrous sodium sulphate was conditioned using 5 ml of HPLC hexane and the samples introduced then 20 ml of HPLC hexane used to elute the analytes into a round bottomed flask. This was followed by an addition of 2ml Iso-octane before it was concentrated. The reduced extracts

were transferred into clean auto vials and further reduced to 0.5 ml under a mild stream of nitrogen ready for GC analysis.

3.9 pH determination for water samples

The pH of the water samples was measured at the sampling sites using a scientific pH meter model IQ 150.Calibration of the pH meter was done using different buffers solutions. The buffer solutions used were of pH 4.0, 7.0, and 10.0

3.10 Determination of moisture content of kales and soil samples

Calculation of the moisture content of the soil and kale samples was done using the difference between the wet and dry weight. This involved a 24 hour (at 105 ºC) heating of 5 g of each of the soil and kales samples in pre-cleaned and pre-weighed watch glass in an oven (model E 28♯ 04-71528). The moisture content was calculated using the formula below;

$$\text{Moisture content} = \frac{\text{Weight of wet sample} - \text{Weight of dry sample} \times 100}{\text{Weight of wet sample}}$$

3.11 Determination of total dissolved solids and electrical conductivity

Total Dissolved Solids (TDS) together with electrical conductivities of the water samples were measured using scientific Martin instrument model Mi 306. This was done in the field. The instrument was calibrated done USING a single point procedure. The EC range was selected and the CAL key pressed. The probe was rinsed with deionised water and immersed into the solution with the sleeve holes being completely submerged. The probe was repeatedly tapped to remove any air bubbles trapped inside the sleeve. The calibration was started with zero, and the dry probe left in air. "REF" and "CAL" indications were displayed and the desired buffer value selected. SHIFT+CFM buttons were pressed to confirm the calibration and when everything was satisfactory, the meter displayed the "StorGood"message and returned to measurement mode.

3.12 Water temperature

Measurement of temperature of the water samples was done using a digital thermometer by dipping it directly into the water body. The measurements were in degree Celsius and were recorded to 1 decimal place.

3.13 Degradation of pesticides study methodology

3.13.1 Planting, sampling and extraction of kales

Kales were planted in Naivasha, at the Kihoto farm on a 9,000 cm^2 plot. Spraying of the kales was done using a hand spray 30 days after transplanting at a concentration of 560 g/ha and 600 g/ha for diazinon and chlorpyrifos, respectively. Watering was done every day for the first week. Three times weekly for the next two weeks after transplanting and twice weekly for the rest of the time. The kales were ready 45 days after transplanting.

The kale farm was divided into two portions with kales on one portion being sprayed with diazinon solution and the other portion being sprayed with chlorpyrifos solution. The vegetables to be sprayed with diazinon were planted 50 cm away from those that were to be sprayed with chlorpyrifos. Sampling for the kales was done by uprooting the whole plant while soil samples were taken around the uprooted kales up to a depth of 25 cm. In determining the maximum residues of pesticides used, pesticides analysis on the kales (leaves, stems and roots) was done on days 0, 2, 4, 7, 11, 14, 21, and 28 using the extraction and clean-up methods illustrated above except for the ratio of hexane and acetone which changed to 1:1 since organophosphates are more polar.

3.13.2 Sampling and extraction of soil

The batch B of the soil samples was first taken to Kenya Agricultural and Livestock Research Organisation (KALRO) for characterization. The collection of samples for the study on degradation of pesticides in the soil samples was carried out from day 0, 2, 4, 7, 11, 14, 21 and

day 28. The sample extraction method was as explained in section 3.6.1 but with the adjustment of the hexane: acetone ratio to 1:1

3.14 Determination of maximum residue levels

Maximum residue levels determination of diazinon and chlorpyrifos pesticides was done through analysis of the vegetable samples that had been sprayed with the two pesticides and periodically determining pesticide concentration for each of the two pesticides over a period of 14 days.

3.15 GC Analysis and quantification of the extract

Kales, soil and water extracts were analysed for OCPs using a gas chromatograph (Agilent 6890N) combined with an auto sampler (Agilent 7683 Series injector), and an electron capture detector (Agilent μ-ECD) and gas chromatography mass spectrometry (GC/MS). The injector and detector temperatures were maintained at 250 ºC and 300 ºC, respectively. 99.999 % Helium gas was used as the carrier gas, it had a constant flow rate of 2 ml/min. On the other hand 99.999% nitrogen was used as make-up gas with a constant flow rate of 30ml/min. Pulsed split less injection mode was used with an injection volume of 1μl. The injection temperature program applied was as follows: 90 ºC (3 min), 90 ºC to 200 ºC (at 30 ºC/ min and hold time of 15 min), 200 ºC to 275 ºC (at 30 ºC/min and hold time of 5 min). DB-5 silica fused high performance capillary column with a length of 30 m, 0.25 mm internal diameter together with a film thickness of 0.25 μm was used. Chemstation software was used in data processing. In the analysis of diazinon and chlorpyrifos, the GC-MS (Agilent HP 6890 PLUS) combined with an auto sampler (Agilent 6890 series injector) was used. The HP 19091J-102 capillary column of 25m x 20μm internal diameter x 0.33 μm film thickness coated with cross-linked 5% phenyl methyl siloxane was used. The carrier gas used was helium at a flow rate of 1.0 ml/min. Oven temperature was maintained initially at 80 ºC for 2 min, increased at 30 ºC/min to 200 ºC, then

at 15 ºC/min to 300 ºC with a total runtime of 22.67. Injection volume was 1µL, which was injected in splitless mode at injection temperature of 250 ºC

3.16 Identification and quantification

Organochlorine pesticides (obtained from IoIc, Poland), Chlorpyrifos and diazinon standards were used at various points in the analysis. Reference standards ranging from 0.01 mg/L to 0.981 mg/L were individually prepared for each standard and quantification was based on calibration curve calculations. Each standard gave a calibration curve with a straight line and the line of best fit drawn from the plot of the response factor (peak area) against standard concentration.

All analyte lines gave a correlation factor (R^2) above 0.99 showing high correlation between analyte concentration and instrument response ratio. Calibration curves are attached in Appendix A1.7. Standard concentrations were obtained by interpolation from the graphs which applies the equation Y= mX +c

Where Y = Normalised peak area (instrument response)

X = Standard concentration

m = Gradient, and

c = Constant

Concentrations of the sample analytes were also obtained in the same way.

3.17 Statistical Data Analysis

All results were recorded in Microsoft excel. The correlations between the seasonal variations and the concentrations of the pesticide residues detected were determined using the Statistical Programme for Social Scientists (SPSS). Representation of the results was done by use of text, graphs and statistical tables to show the interrelationships of various variables such as pH, TDS, electrical conductivity and sample type on levels of pesticide residues in the lake.

CHAPTER FOUR

4. RESULTS AND DISCUSSIONS

4.1Physico-Chemical properties of water samples

4.1.1pH of water samples from Lake Naivasha, River Malewa and KWS farm in March and May 2015

The pH of water from the three sampling sites in Naivasha ranged between 7.41- 7.81 as shown in Figure 4.1 and Appendix 1TablesA.1.1. and A.1.2. The highest pH of 7.81was recorded at Lake Naivasha (Kihoto area) in March while the lowest pH of 7.41 was recorded at River Malewa in May. Samples collected in dry season have higher pH values (Figure 4.1) than the wet season.

The pH values were within the recommended WHO value of 6.5-8.5 for raw water (WHO, 2008). Samples collected in dry season had higher pH values (Figure 4.1) than the wet season. This could be attributed to dilution of the water by the rain. In addition, the changes observed from one site to the other could be partly attributed to the proximity of the study area to Naivasha town and the wide range of human activities in the area. Lake Naivasha (Kihoto area) is located near Naivasha town and is also surrounded by farms thus it is affected by high rate of release of effluent from the growing population as well as run-off from the surrounding farms.

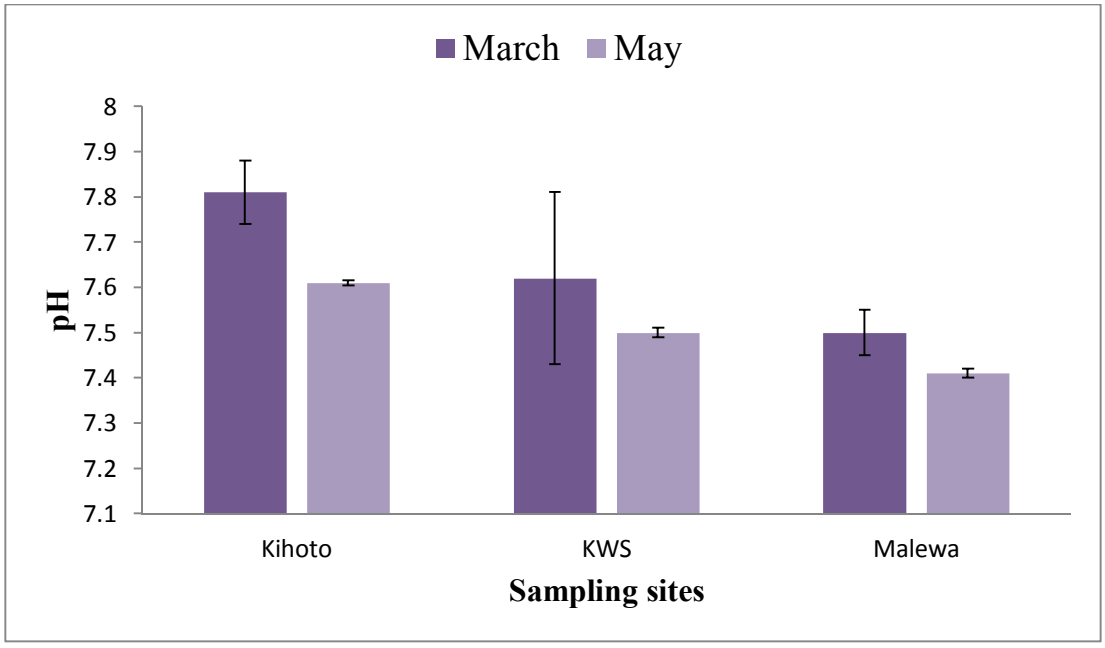

Figure 4. 1: pH of water samples from Lake Naivasha, KWS farm and River Malewa

4.1.2: Total dissolved solids in water samples from Lake Naivasha, River Malewa and KWS farm in March and May 2015

The water samples collected had TDS values ranging between 47.83±0.05 and 438.67±6.11 mg/L (Figure 4.1 and Appendix 1. Tables A.1.1 and A.1.2). The highest TDS (438.67 mg/L) was recorded at KWS farm in May, while the lowest TDS value of 47.83 mg/L was recorded for River Malewa water in March 2015.

In general, the TDS values were within the WHO acceptable limits of ≤ 1000 mg/L for drinking water (WHO, 2008). Slightly higher TDS values were recorded in May as compared to March. This is because during the rainy season the rain water washes inorganic salts and small amounts of organic matter present in solution, dissolving some of them and these end up into the lake thereby increasing the TDS.

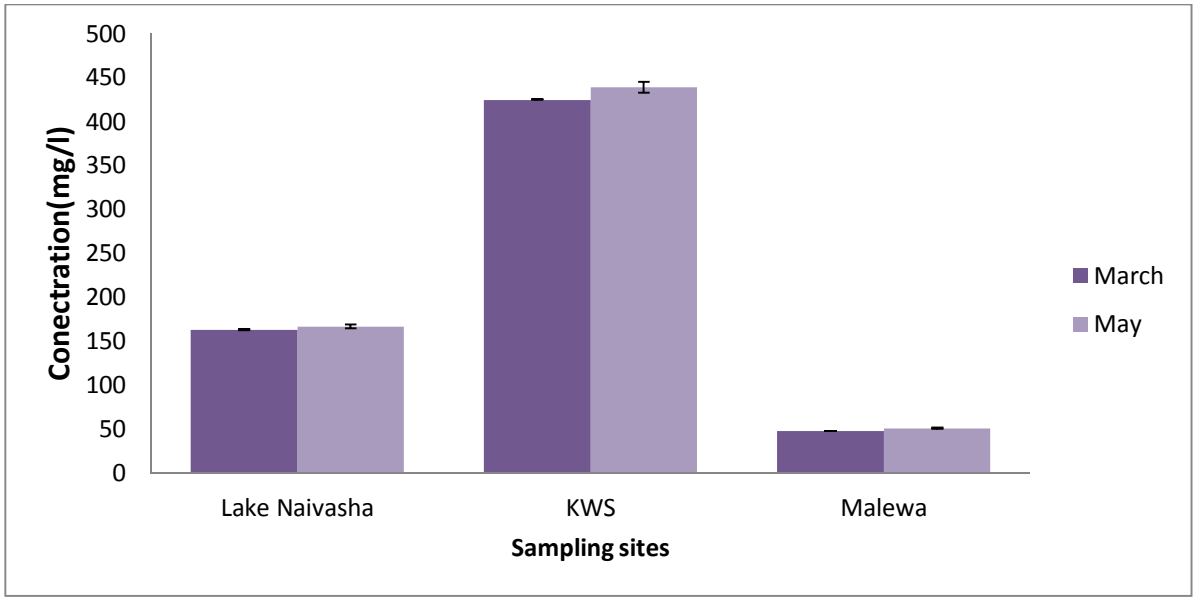

Figure 4. 2: TDS of the water samples for Lake Naivasha, River Malewa and KWS farm in March and May 2015

4.2 Electrical conductivity

The water samples collected had electrical conductivity values ranging between 95.2±0.1 µS/cm and 489.67±1.53 µS/cm (Figure 4.3 and Appendix Tables A1.1 and A1.2). The highest electrical conductivity (489.67±1.53 µS/cm) was recorded in the March at KWS farm while the lowest was recorded for River Malewa in May.

During the rainy season, there was dilution due to increase in water volume from precipitation that lead to low electrical conductivity, as observed for all the sites in May, despite the slight increase in TDS.

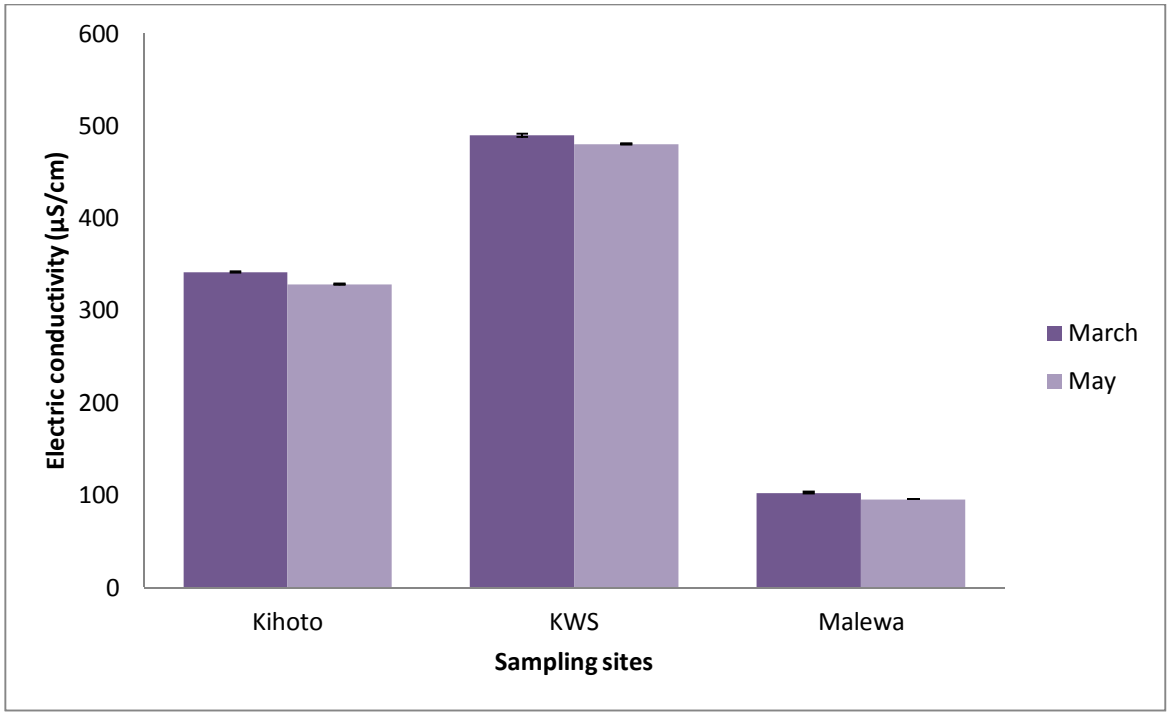

Figure 4. 3: Conductivity of water samples for Lake Naivasha, River Malewa and KWS farm in March and May

4.3 Pesticide residue levels in kales

Organochlorine pesticides were found in the kale samples collected from Naivasha sampling sites. The concentrations varied from one point to the other with the average pesticide levels ranging between below detection limit (BDL) to 75.418±7.71 µg/kg (Table 4.1).

4.3.1 OCP levels in kales in March 2015

OCP residues detected in kales ranged between BDL to 75.418±7.71 µg/kg. The highest concentration was observed for methoxychlor in the kales samples collected from Gatara Market (Table 4.1).

Table 4. 1: Pesticide Residue Levels (µg/kg, dw) in kales in March 2015

Pesticides	KWS farm	Kihoto Market	KCC market	Gatara market	Kihoto farm	Malewa farm
α-HCH	6.59±0.00	72.88±2.74	<1.1±0.1ng/L	<1.1±0.1	<1.1±0.1	<1.1±0.1
β-HCH	<1.6±0.1	<1.6±0.1	<1.6±0.1	0.27±0.05	<1.6±0.1	<1.6±0.1
γ-HCH	<1.6± 0.1	<1.6± 0.1	<1.6± 0.1	<1.6± 0.1	<1.6± 0.1	<1.6± 0.1
δ-HCH	7.23±0.35	0.31±0.04	<0.004± 0.1	2.01±.03	<0.004± 0.1	<0.004± 0.1
Heptachlor	<1.1±0.1	<1.1±0.1	<1.1±0.1	<1.1±0.1	<1.1±0.1	<1.1±0.1
Aldrin	<3.6±0.1	<3.6±0.1	<3.6±0.1	<3.6±0.1	<3.6±0.1	<3.6±0.1
Heptachlor epoxide	<1.1± 0.1	<1.1± 0.1	<1.1± 0.1	<1.1± 0.1	<1.1± 0.1	<1.1± 0.1
Endosulphan 1	<1.1±0.1	<1.1±0.1	<1.1±0.1	<1.1±0.1	<1.1±0.1	<1.1±0.1
***p,p'*-DDE**	<1.8± 0.1	<1.8± 0.1	<1.8± 0.1	<1.8± 0.1	<1.8± 0.1	<1.8± 0.1
Dieldrin	1.03±0.06	0.37±0.00	33.93±1.94	<3.1±0.1	<3.1±0.1	<3.1±0.1
Endrin	<2.2±0.1	<2.2±0.1	<2.2±0.1	<2.2±0.1	<2.2±0.1	<2.2±0.1
Endosulphan 2	<1.5±0.1	<1.5±0.1	67.57±0.94	<1.5±0.1	4.03±1.69	<1.5±0.1
***p,p'*-DDD**	2.84±0.6	1.08±0.27	73.87±11.0	2.08±0.22	4.01±0.09	53.48±16.0
Endrin aldehyde	<2.2±0.1	<2.2±0.1	36.15±0.79	0.336±0.06	1.785±0.39	25.86±1.07
***p,p'*-DDT**	<1.7± 0.1	21.37±5.65	<1.7± 0.1	13.80±1.2	18.40±1.6	52.07±13.8
Endosulphan sulphate	BDL<2.1±0.1	63.22±12.14	53.84±2.25	18.83±1.36	39.31±0.71	44.59±3.25
Methoxychlor	1.62±0.24	18.71±2.72	33.58±1.38	75.41±7.71	16.17±1.69	42.37±3.18

BDL= below detection limits n=6, mean ± standard deviation, dw = dry weight

4.3.2 Comparison of OCPs residue levels in different sampling sites

Figure 4.4 shows pesticide residues detected in different sampling sites. α-HCH was the highest pesticide detected in samples from Kihoto Market at a concentration of 72.88±2.74 µg/kg. The

highest concentration of α-HCH detected in the vegetables was much greater than the set maximum limits of 0.01 µg/kg (Codex, 2009). From Table 4.1, it can be clearly seen that γ-HCH was below detection limit in all the sites, suggesting that there was no recent use of γ-HCH. The high concentration of α-HCH could be an indication of more HCH originating from atmospheric deposition and long-term degradation of γ-HCH to α-HCH, which is also a known isomer under environmental conditions.

The occurrence of *p,p'*-DDT and *p,p'*-DDD in the kale samples may indicate the slow break down of *p,p'*-DDT in the environment or illegal recent use(Yuan *et al.*, 2001). The presence of *p,p'*-DDD in some of the vegetable samples suggests environmental degradation of *p,p'*- DDT to *p,p'*-DDD. On the other hand, *p,p'*-DDE was below detection limit in vegetables samples from all the sites indicating slow degradation of *p,p'*-DDT or potential recent use of *p,p'*-DDT. The highest concentration of methoxychlor (75.41±7.71 µg/kg) was detected in kale samples from Gatara Market.The source of this compounds could not be immediately established, but its presence could be attributed to long range transport and atmospheric deposition. Methoxychlor is documented to undergo slow breakdown in soil, water and air by microscopic organisms and sunlight (Wauchope *et al.*, 1992), which can take several months.

The predominance of endrin aldehyde is an indication of the degradation of endrin to endrin aldehyde. Similarly, the predominance of dieldrin suggests the degradation of aldrin to dieldrin.Out of the two conformational isomers of endosulphan (endosulphan 1 and endosulphan 2), only endosulphan 2 was detected. A high concentration of endosulphan 2 (67.57±0.94 µg/kg) was detected in kale samples from KCC market compared to endosulphan 1 which was not detected, this could be attributed to longer persistence of endosulphan 2 and endosulphan sulphate. Endosulphan 1 readily decomposes and does not build up in the environment the way other organochlorine pesticides do (Cremlyn, 1991).

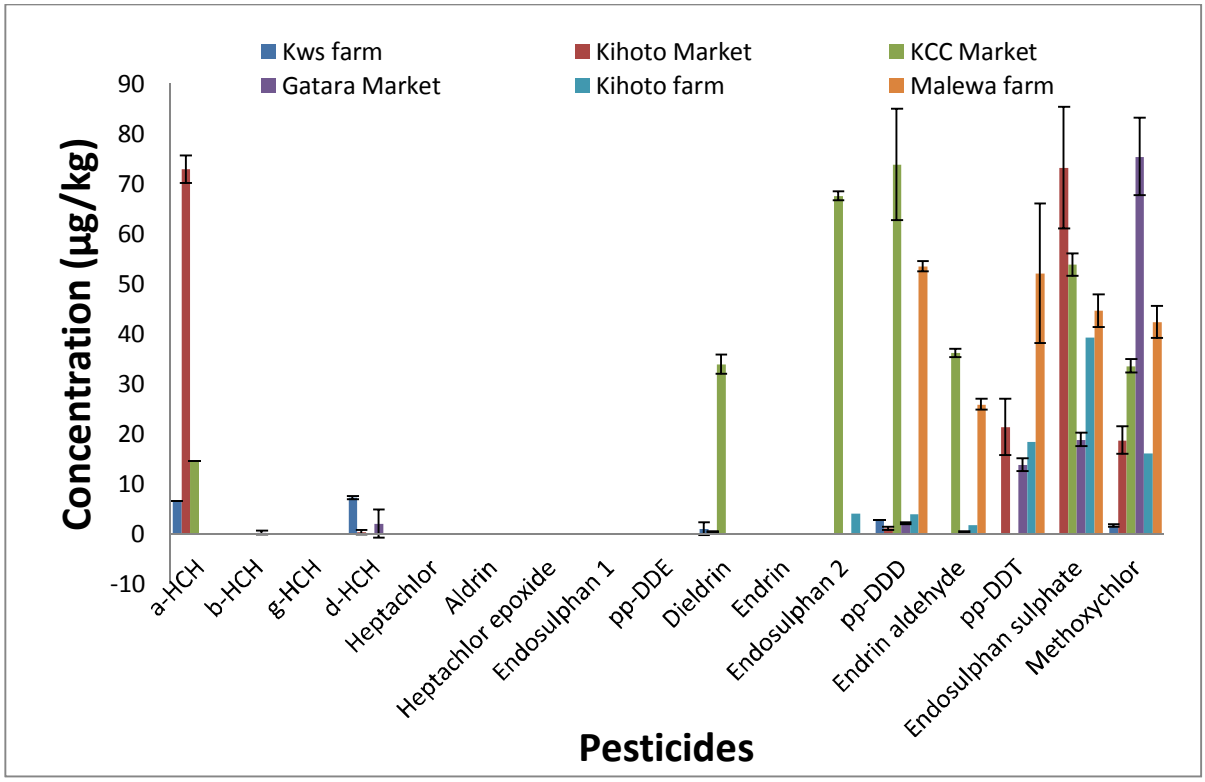

Figure 4. 4: Concentration of OCP in kales from the six sites in March 2015

4.3.3 Pesticide residue levels in kales in May 2015

OCPs residue levels in May ranged between BDL to 74.618±9.07 µg/kg. Methoxychlor was the highest detected pesticide at Kihoto market. Table 4.2 and Figure 4.5 show the OCP residue levels in kales sampled in the month of May from the six sampling sites.

Table 4. 2: Pesticide Residue Levels (µg/kg, dw) in kales in the six sites in May 2015

Pesticides	Kws farm	Kihoto Market	KCC Market	Gatara Market	Kihoto farm	Malewa farm
α-HCH	<1.1±0.1	<1.1±0.1	1.53±0.24	34.39±9.69	2.40±0.15	BDL<1.1±0.1
β-HCH	<1.6±0.1	<1.6±0.1	<1.6±0.1	1.53±10.60	<1.6±0.1	<1.6±0.1
γ-HCH	<1.6± 0.1	<1.6± 0.1	<1.6± 0.1	8.16±0.16	<1.6± 0.1	<1.6± 0.1
δ-HCH	<0.004± 0.1	<0.004± 0.1	<0.004± 0.1	8.50±1.62	<0.004± 0.1	<0.004± 0.1
Heptachlor	<1.1±0.1	<1.1±0.1	<1.1±0.1	24.81±0.07	<1.1±0.1	<1.1±0.1
Aldrin	<3.6±0.1	<3.6±0.1	<3.6±0.1	65.81±2.79	<3.6±0.1	<3.6±0.1
Heptachlor epoxide	<1.1± 0.1	<1.1± 0.1	<1.1± 0.1	3.91±0.81	<1.1± 0.1	<1.1± 0.1
Endosulphan 1	<1.1±0.1	<1.1±0.1	<1.1±0.1	<1.1±0.1	<1.1±0.1	<1.1±0.1
***p,p'*-DDE**	<1.8± 0.1	<1.8± 0.1	<1.8± 0.1	<1.8± 0.1	<1.8± 0.1	<1.8± 0.1
Dieldrin	<3.1±0.1	<3.1±0.1	<3.1±0.1	<3.1±0.1	<3.1±0.1	<3.1±0.1
Endrin	<2.2±0.1	<2.2±0.1	<2.2±0.1	<2.2±0.1	<2.2±0.1	<2.2±0.1
Endosulphan 2	<1.5±0.1	<1.5±0.1	57.57±0.94	<1.5±0.1	4.03±0.69	<1.5±0.1
***p,p'*-DDD**	1.44±0.03	<1.6±0.1	4.65±0.10	1.74±0.09	2.33±0.36	<1.6±0.1
Endrin aldehyde	2.76±0.91	<2.2±0.1	4.94±0.98	4.19±0.83	5.93±0.02	0.44±0.01
***p,p'*-DDT**	3.15±1.31	<1.7± 0.1	31.10±1.33	60.56±6.75	68.10±6.94	<1.7± 0.1
Endosulphan sulphate	24.21±2.98	<2.1±0.1	60.62±11.74	33.41±1.83	30.13±3.58	14.19±4.49
Methoxychlor	44.05±6.42	74.61±9.07	11.65±1.48	41.70±2.22	25.34±1.20	17.739±7.70

BDL= below detection limits n=6, mean± standard deviation, dw= dry weight

4.3.4 Comparison of the concentrations of POPs in kale from the six sites in May 2015

The presence of Methoxychlor in the kale samples from Kihoto Market (Figure 4.5) is explained by the fact that it slowly breaks down in soil, water and air and it may take several months. This explains its presence in the kales. It's presence in the kale samples from Kihoto Market may suggest recent use in the six farms. For the two conformational isomers of endosulphan (endosulphan 1 and endosulphan 2), the same scenario is seen as that observed

during the first sampling (March). Endosulphan 1 was below detection limit for all the sampling sites while the highest concentration of endosulphan 2 (57.57±0.94 µg/kg) was detected in the kale samples from KCC market (Table 4.2). This gives an indication of recent use in farms where these vegetables were grown because endosulphan readily degrades and does not have a tendency to build up in the environment like other organochlorines (Cremlyn, 1991).

From Figure 4.5, it can be observed that α-BHC, β-BHC and δ-BHC, were found in kales from some of the sites. α-HCH was the highest detected (34.39±9.69 µg/kg) from Gatara market. The highest concentration of α-HCH is much greater than the recommended residue limit of 0.01 µg/kg (Codex 2009). From Table 4.2, it can be clearly seen that in the kale samples collected, γ-HCH was below detection limit in all sites except at Gatara market. This therefore suggests present illegal use of γ-HCH.

DDT was found in kales collected from each of the sampling sites except for those collected from Kihoto market and Malewa farm, with the highest concentration being detected at Kihoto farm (68.10±6.94 µg/kg). The presence of DDT is an indication that it degrades slowly in the environment and therefore could be deposited through deposition or there has been a recent illegal use (Yuan *et al.,* 2001). The presence of *p,p'*-DDD in some of the kale samples suggests environmental degradation of *p,p'*- DDT to *p,p'*-DDD and thus its occurrence in the environment and in the kales. A similar scenario is seen in the vegetable samples collected in March as well as in May where *p,p'*-DDE was below detection limit in vegetables from all the sites suggesting slow degradation of *p,p'*-DDD to *p,p'*-DDE. While endrin aldehyde was detected in some of the sites, endrin was not detected in all the sites. Dieldrin was not detected in all the sites while aldrin was only detected at Gatara market. This may suggest illegal current use of aldrin or long range transport in the atmosphere.

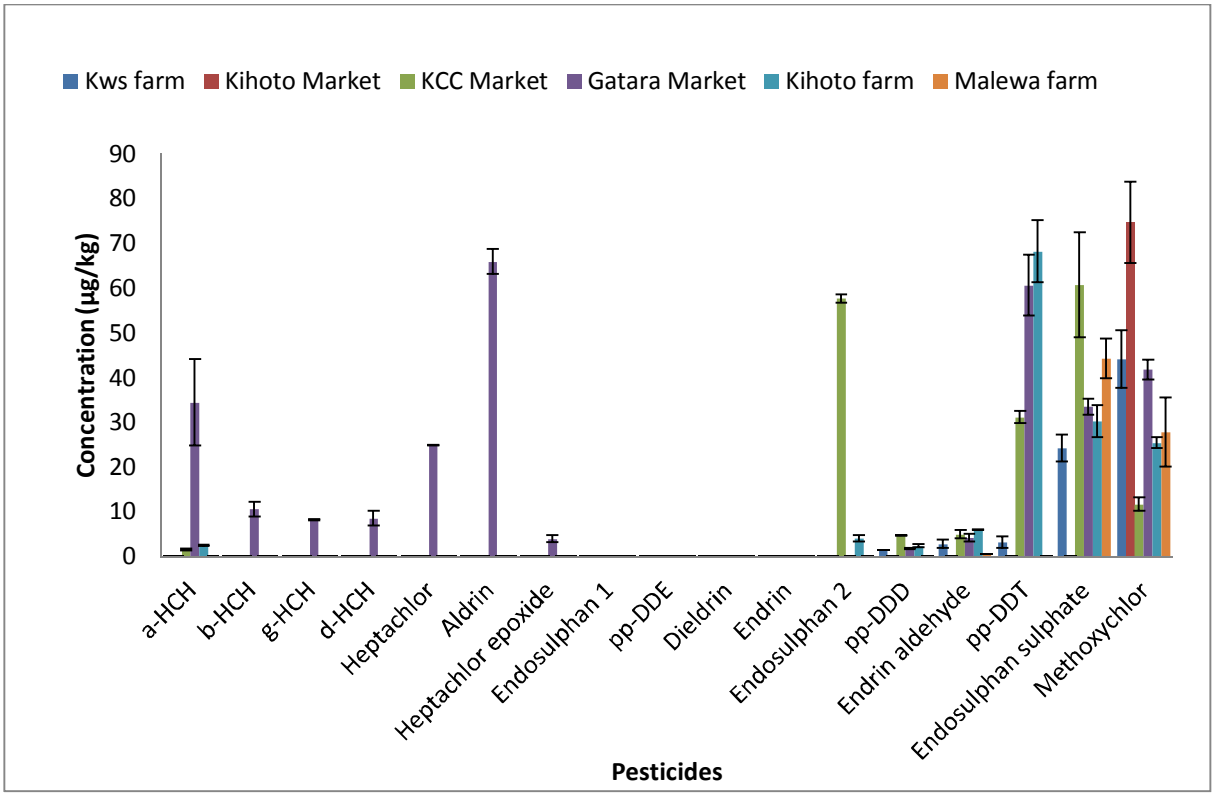

Figure 4. 5: Concentration of OCP in kales sampled in May 2015

4.4 Pesticide residue levels in soil

The concentrations varied from one point to the other with the average pesticide levels ranging between below detection limit (BDL) to 104.16±6.62 µg/kg. Soil samples from Kihoto market collected during the month of May recorded the highest concentration.

4.4.1 Pesticide residue levels in soil (µg/kg) in March 2015

Residue levels of organochlorine pesticides in soil in March ranged from BDL to 65.68±7.98 µg/kg. Endosulphan Sulphate registered the highest pesticide concentration detected in KWS farm. Figure 4.7 and Table 4.3 show the OCP levels in the soil samples collected in March from the six sampling sites.

Table 4. 3: Pesticide Residue Levels (µg/kg, dw) in soil in March 2015

Pesticides	KWS farm	KCC market	Kihoto Market	Gatara Market	Malewa farm	Kihoto farm
α-HCH	14.85±0.45	6.11±0.64	6.15±0.69	0.61±0.31	9.00±0.03	13.67±1.66
β-HCH	1.19±0.06	3.86±0.04	0.34±0.05	0.03±0.00	0.43±0.06	2.47±0.23
γ-HCH	0.55±0.04	13.32±1.40	<1.6± 0.1	0.67±0.07	0.52±0.08	0.09±0.01
δ-HCH	2.07±0.07	48.96±2.77	0.12±0.01	4.27±0.72	5.43±0.99	10.40±1.46
Heptachlor	2.41±0.17	19.31±2.43	0.11±0.06	0.66±0.09	2.32±0.11	4.08±0.78
Aldrin	2.99±0.22	3.81±0.64	1.70±0.05	0.44±0.01	2.74±0.23	2.74±0.17
Heptachlor epoxide	1.29±0.16	0.80±0.01	0.30±0.02	0.07±0.00	0.02±0.00	0.62±0.07
Endosulphan 1	2.75±0.00	2.19±0.01	<1.1±0.1	<1.1±0.1	<1.1±0.1	25.97±1.09
***p,p'*-DDE**	<1.8± 0.1	<1.8± 0.1	<1.8± 0.1	<1.8± 0.1	<1.8± 0.1	1.86±0.13
Dieldrin	17.66±0.81	22.31±6.72	9.68±1.35	<3.1±0.1	1.44±0.01	13.39±1.79
Endrin	11.77±0.16	1.09±0.01	6.03±0.02	<2.2±0.1	<2.2±0.1	0.72±0.05
Endosulphan 2	19.87±0.31	18.27±1.09	13.34±0.63	<1.5±0.1	2.83±0.04	7.58±1.00
***p,p'*-DDD**	45.77±2.25	18.19±0.14	12.02±2.48	<1.6±0.1	61.16±0.32	24.22±2.09
Endrin aldehyde	0.97±0.04	18.05±1.04	5.16±0.97	1.93±0.10	47.20±0.25	26.64±1.70
***p,p'*-DDT**	14.96±3.17	31.42±1.07	18.54±0.91	13.25±2.91	51.31±2.82	26.44±2.23
Endosulphan sulphate	65.68±7.98	41.89±8.21	15.09±1.01	0.46±0.04	56.67±4.82	46.09±3.02
Methoxychlor	33.73±3.63	40.76±3.69	28.18±7.94	25.30±2.32	49.26±2.16	51.46±6.51

BDL= below detection limits n=6, mean± standard deviation, dw= dry weight

The results shown in Figure 4.7 revealed *p,p'*-DDT dominance in soil. This could be related to the slow degradation of *p,p'*-DDT in soil or illegal use (Yuan *et al.*, 2001; Travers *et al.*, 1999). Presence of *p,p'*-DDD suggests break down of *p,p'*-DDT to *p,p'*-DDD. The pre-dominance of endrin aldehyde is an indication of the degradation of endrin to endrin aldehyde. The abundance of methoxychlor in soil can be explained by the fact that it breaks gradually in soil, air as well as in water by sunlight together with microscopic organisms and could take many months (ATSDR, 2002).

The presence of the three isomers of HCH measured were attributed to previous use of γ-HCH. Higher levels of heptachlor were detected as compared to those of its metabolic product heptachlor epoxide could be attributed to recent illegal application on the farms. The existence of isomeric remains of endosulfan in the soil samples suggested use of the technical products in that area. On the other hand, higher residues of dieldrin were detected in most of the sampling sites as compared to aldrin suggesting decomposition of aldrin to dieldrin (Figure 4.7).

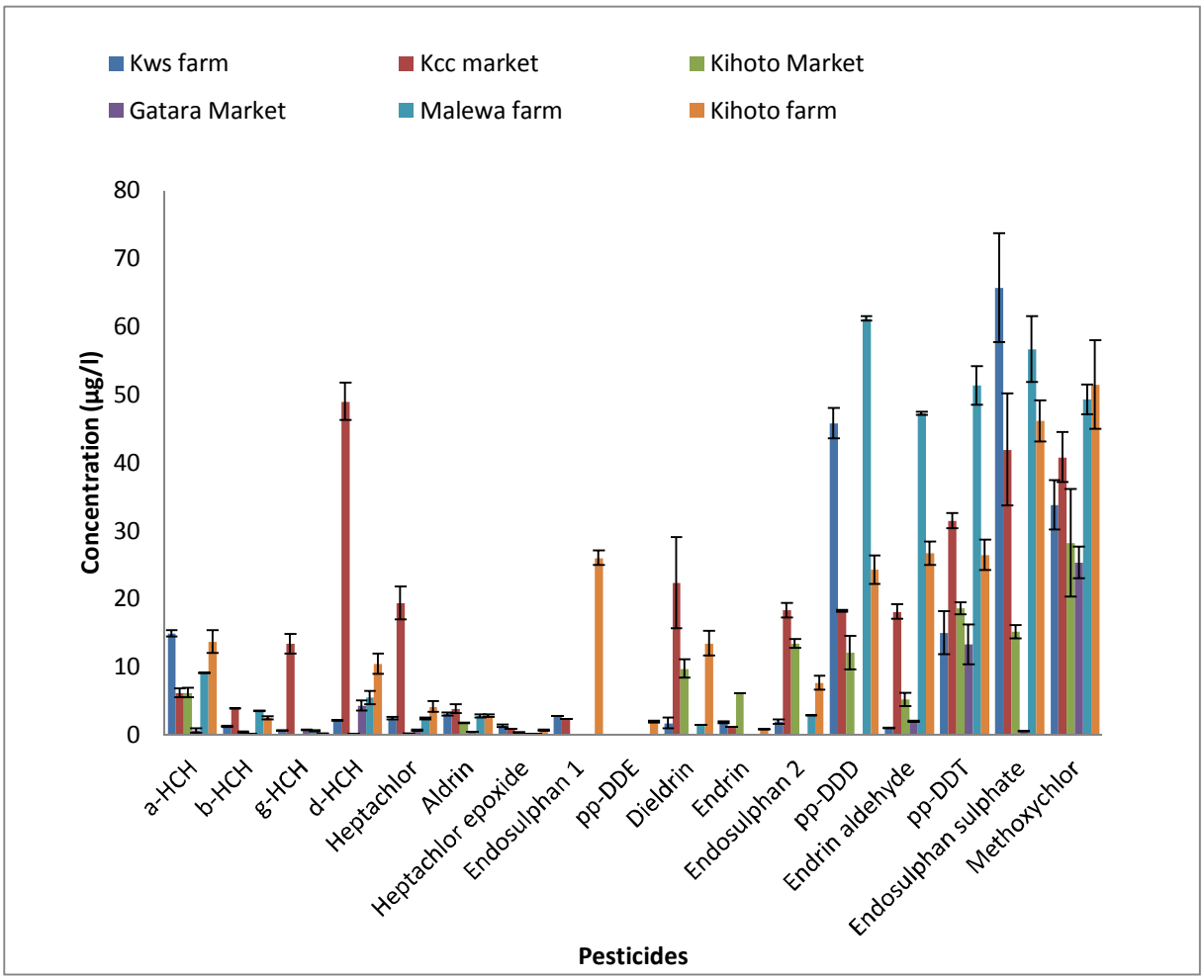

Figure 4. 6: Concentration of OCP in Soil samples collected in March 2015

4.4.2 Pesticide residue levels in soil in May 2015

Organochlorine pesticide residue levels in soil in May ranged from BDL to 104.17±6.62 µg/kg. Endosulphan sulphate was the highest detected pesticide at Kihoto farm in May 2015. Figure

4.8 and Table 4.4 shows the OCP levels in the soil samples collected in the month of May from the six sampling sites.

Table 4. 4: Pesticide residue levels (µg/kg) in soil in May 2015

Pesticides	KWS farm	KCC market	Kihoto Market	Gatara Market	Malewa farm	Kihoto farm
α-HCH	<1.1±0.1	18.72±3.94	67.33±8.31	<1.1±0.1	7.66±0.41	11.46±1.21
β-HCH	<1.6±0.1	3.54±0.88	<1.6±0.1	<1.6±0.1	1.45±0.47	2.85±0.22
γ-HCH	0.55±0.14	13.32±2.40	<1.6± 0.1	0.67±0.01	0.52±0.02	0.09±0.01
δ-HCH	<0.004± 0.1	21.38±1.70	36.64±2.18	<0.004± 0.1	3.08±0.40	11.03±2.94
Heptachlor	<1.1±0.1	30.70±0.61	<1.1±0.1	<1.1±0.1	4.04±0.43	10.45±2.70
Aldrin	<3.6±0.1	218.47±6.76	<3.6±0.1	<3.6±0.1	157.99±1.11	<3.6±0.1
Heptachlor epoxide	<1.1± 0.1	0.43±0.01	<1.1± 0.1	<1.1± 0.1	0.07±0.01	<1.1± 0.1
Endosulphan 1	<1.1±0.1	2.29±0.21	2.55±0.61	<1.1±0.1	<1.1±0.1	<1.1±0.1
p,p'-DDE	<1.8± 0.1	<1.8± 0.1	<1.8± 0.1	<1.8± 0.1	<1.8± 0.1	<1.8± 0.1
Dieldrin	<3.1±0.1	<3.1±0.1	23.31±3.25	<3.1±0.1	0.33±0.07	<3.1±0.1
Endrin	<2.2±0.1	<2.2±0.1	37.93±2.09	<2.2±0.1	1.49±0.11	<2.2±0.1
Endosulphan 2	<1.5±0.1	<1.5±0.1	50.10±0.29	<1.5±0.1	2.84±0.02	16.67±0.00
p,p'-DDD	3.69±0.18	25.38±1.81	11.63±2.71	<1.6±0.1	23.18±4.91	14.35±0.01
Endrin aldehyde	10.41±0.00	6.14±0.04	19.68±3.04	<2.2±0.1	22.29±4.26	23.12±0.01
p,p'-DDT	6.58±0.00	23.37±4.54	67.16±1.71	<1.7± 0.1	30.94±3.70	87.97±0.20
Endosulphan sulphate	38.96±0.00	33.28±4.05	104.15±6.62	<2.1±0.1	39.85±1.58	65.30±0.67
Methoxychlor	14.09±0.79	28.72±.0.27	77.24±2.51	48.40±0.00	63.57±2.44	58.93±0.04

BDL= below detection limits n=6, mean± standard deviation, dw = dry weight

4.4.3 A Comparison of OCP residue levels in soils from different sites in May 2015

Higher *p,p'*-DDT residue levels (Figure 4.8) were noted in most of the sites as compared to those of *p,p'*-DDD, whereas Kihoto farm showed the highest *p,p'*-DDT levels (87.97±0.20 µg/kg). This could be attributed to illegal use of *p,p'*-DDT. Some sites such as KCC and Kihoto markets were located near the farms. Since May was a rainy season, the results showed that some of the pesticides could have been transported by runoff from the farms to these sites or

the pesticide residues could have been as a result of aerial deposition. For endrin and endrin aldehyde residues, a similar situation as that observed in March. Endrin aldehyde was more pre-dominant suggesting degradation of endrin. The high residue levels of methoxychlor in soil in May could be explained by the fact that during the rainy season there is transportation of pesticides residues by rain water. In addition it gradually breaks down in air, water as well as in soil by sunlight together with microscopic organisms and this may take many months (ATSDR, 2002).

The observed residue levels of the three isomers of HCH could be associated with the use of lindane in the area. In some of the sites, higher levels of heptachlor were detected as compared to those of its metabolic product heptachlor epoxide suggesting illegal application on the farms. The existence of isomeric residue of endosulfan in the collected soil samples relates to use of the technical products in the area. High levels of aldrin detected at KCC market (218.47±6.76 µg/kg) and Malewa farm (157.99±1.11 µg/kg) as compared to dieldrin levels suggested potential illegal use or transportation by runoff during the rainy season or aerial deposition

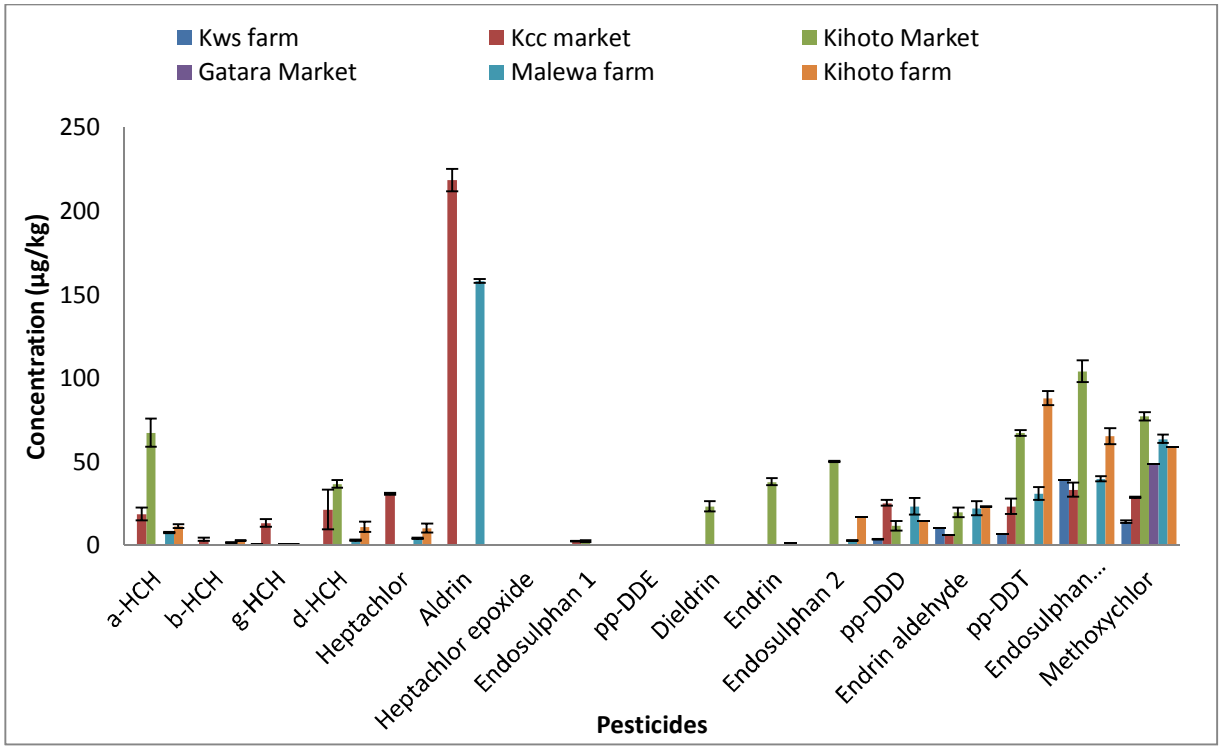

Figure 4. 7: Concentration of OCP in Soil samples collected in May 2015

4.4.5 Soil Physico-Chemical parameters

Table 4.5 below summarizes soil physicochemical properties from the study sites. Soil pH is one of the factors that determine the transfer of pesticides in the soils (Aiyesanmi *et al.*, 2008). The measured pH of the soils ranged from 7.47 at KCC market to 8.56 at Kihoto farm indicating that the soils were generally alkaline (Table 4.5). This could be associated with high sodium and calcium levels in the soils (Aikpokpodion, 2010).

The measured conductivity ranged from 0.29.00 to 22.00 µS/cm. Soils from the study site were characterized by low to medium organic carbon content. The measured organic carbon ranged between 0.83% at Gatara market to 4.62% at KWS farm. This could possibly be attributed to disposal of wastes (Dankyi *et al.,* 2014). The behaviour of inorganic and organic pollutants in soil is dependent on the soil organic matter together with the organic carbon (Aiyesanmi *et al.*, 2008). High percentage of potassium was recorded in all the sites with levels ranging from 3.23% (Gatara market) to 3.95% (KWS farm). The percentage of nitrogen in the soils ranged

from 0.10 % at Gatara market to 0.47 % at KWS farm. The available phosphorus ranged from 15.8 ppm at KCC market to 66.8 ppm at Kihoto farm. High % calcium and Sodium were recorded in all the sites with percentage calcium ranging from 33.9 (KWS farm) to 38.8 (Gatara market). Percentage of sodium ranged from 2.79 (KCC market) to 3.94 (Kihoto farm). The percentage of manganese ranging between 2.78 (Gatara market) to 4.64 (KCC market). Iron levels ranged between 25.90 mg/kg at KWS farm to 200.50 mg/kg at Gatara market. A low copper level (0.84 mg/kg) was recorded at Gatara market while the highest concentration was 2.10 mg/kg at KCC market.

Table 4. 5: Soil Physicochemical parameters

Soil parameters	KWS farm	Gatara Market	Kihoto farm	KCC market
Soil pH	7.93	7.92	8.56	7.47
Total Nitrogen %	0.47	0.10	0.25	0.18
Total Organic Carbon %	4.62	0.83	2.46	1.68
Phosphorus (Olsen) ppm	46.8	16.6	66.8	15.8
Potassium me%	3.95	3.23	3.91	3.87
Calcium me%	33.9	38.8	38.1	37.3
Magnesium me%	3.8	2.78	3.61	4.64
Manganese me%	0.39	0.54	0.74	0.58
Copper ppm	1.04	0.84	2.08	2.10
Iron ppm	25.9	200.5	154.9	114.4
Zinc ppm	96.5	24.50	12.20	12.09
Sodium me%	3.31	3.27	3.94	2.79
Elect. Cond. µS/cm	6.74	1.30	0.29	2

Appendix 1 Table A.1.5 shows the correlation between soil physicochemical parameters and organochlorine pesticide residues in soil.

4.5 Pesticide residue levels in water

The concentrations varied from one point to the other with the average pesticide levels ranging between below detection limit (BDL) to 0.68±0.01 µg/l. The water sample collected during the month of May from Lake Naivasha recorded the highest concentration of pesticides.

4.5.1 Pesticide residue levels in water in March 2015

OCPs residues in March 2015 ranged from BDL to 0.56±0.03 µg/l (Table 4.6).The highest detected pesticide was methoxychlor measured in the samples from Lake Naivasha. Figure 4.10 and Table 4.5 shows the OCPs levels in the water samples collected in March 2015 from the three sampling sites.

Table 4. 6: Pesticide Residue Levels (µg/l) in water from Lake Naivasha, KWS and River Malewain March 2015.

Pesticides	Lake Naivasha	KWS	River Malewa
α-HCH	0.10±0.00	0.01±0.00	0.02±0.00
β-HCH	0.01±0.00	0.01±0.00	0.01±0.00
γ-HCH	0.01±0.00	<1.6± 0.1	<1.6± 0.1
δ-HCH	0.06±0.00	0.02±0.00	0.01±0.00
Heptachlor	0.05±0.01	0.02±0.00	0.02±0.01
Aldrin	0.01±0.00	<3.6±0.1	<3.6±0.1
Heptachlor epoxide	0.02±0.00	<1.1± 0.1	<1.1± 0.1
Endosulphan 1	<1.1±0.1	<1.1±0.1	<1.1±0.1
***p,p'*-DDE**	<1.8± 0.1	<1.8± 0.1	<1.8± 0.1
Dieldrin	<3.1±0.1	<3.1±0.1	0.14±0.01
Endrin	<2.2±0.1	0.02±0.00	<2.2±0.1
Endosulphan 2	<1.5±0.1	<1.5±0.1	<1.5±0.1
***p,p'*-DDD**	0.17±0.01	0.01±0.00	0.05±0.00
Endrin aldehyde	0.07±0.01	<2.2±0.1	0.06±0.00
***p,p'*-DDT**	0.11±0.02	0.02±	0.01±0.01
Endosulphan sulphate	0.22±0.01	<2.1±0.1	0.16±0.02
Methoxychlor	0.55±0.03	<1.6±0.1	0.43±0.03

BDL= below detection limits n=3, mean± standard deviation

4.5.2: Comparison of OCP levels in water from different Sites

Lower levels of organochlorine pesticides were detected in water (Figure 4.10) as compared to the levels found in kales (Figure 4.4) and soil (Figure 4.7) in March 2015. The highest concentration of 0.55±0.03 µg/l (methoxychlor) is much lower than the highest levels of methoxychlor (75.42±7.71 µg/kg) and endosulphan sulphate (65.68±7.98 µg/kg) detected in kales and soil samples, respectively.

Presence of *p,p'*-DDT in the water samples could be majorly due to its persistence in the environment while the detection of *p,p'*-DDD suggested degradation of *p,p'*-DDT to *p,p'*-DDD. On the other hand, the isomers of HCH have high levels of biodegradability, high vapour pressures, high solubility in water and lesser particle attraction and lipophilicity than DDT and its metabolites (Yang *et al.,* 2005).Therefore, these could quickly dissipate, leaving very little residues in water (Yang *et al*., 2005).

High levels of methoxychlor in water from lake Naivasha (Figure 4.10) could be explained by the fact that some of the farms are located just a few metres from the lake and the farmers in that location relied on the use of the lake water for irrigation of their crops. The waste water might eventually get back into the lake causing pesticide contamination (ATSDR, 2002).

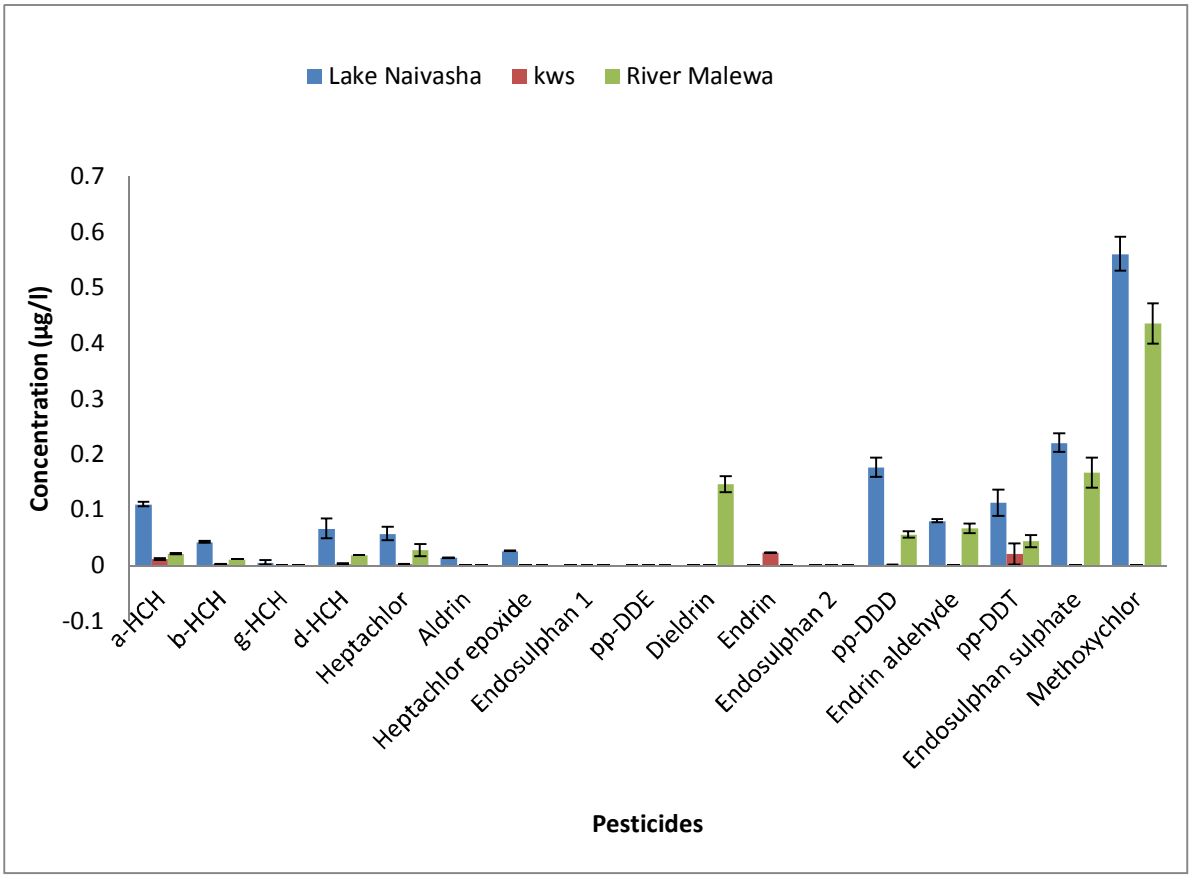

Figure 4. 8: Concentration of OCP in water samples collected in March 2015

4.5.3Pesticide residue levels in water (µg/L) in May 2015

Analysis of the water samples collected in May showed the presence of OCPs ranging from BDL to 0.68±0.01 µg/l. Methoxychlor was the highest OCP detected at in Lake Naivasha samples. Figure 4.11 and Table 4.7 show the OCP residue levels in the water collected in May from the three sites.

Table 4.7: Pesticide Residue Levels (µg/L) in water from Lake Naivasha, KWS and River Malewa in May 2015

Pesticides	Lake Naivasha	kWS	River Malewa
α-HCH	0.14±0.01	<1.1±0.1	0.09±0.01
β-HCH	0.01±0.00	<1.6±0.1	0.03±0.00
γ-HCH	0.01±0.00	<1.6± 0.1	<1.6± 0.1
δ-HCH	0.09±0.01	<0.004± 0.1	0.02±0.00
Heptachlor	0.04±0.00	<1.1±0.1	0.03±0.01
Aldrin	0.03±0.02	<3.6±0.1	<3.6±0.1
Heptachlor epoxide	0.20±0.02	<1.1± 0.1	<1.1± 0.1
Endosulphan 1	<1.1±0.1	<1.1±0.1	<1.1±0.1
***p,p'*-DDE**	<1.8± 0.1	<1.8± 0.1	<1.8± 0.1
Dieldrin	<3.1±0.1	<3.1±0.1	<3.1±0.1
Endrin	<2.2±0.1	<2.2±0.1	<2.2±0.1
Endosulphan 2	<1.5±0.1	<1.5±0.1	<1.5±0.1
***p,p'*-DDD**	0.17±0.01	<1.1± 0.1	0.06±0.00
Endrin aldehyde	0.20±0.02	<2.2±0.1	0.01±0.00
***p,p'*-DDT**	0.58±0.01	<1.7± 0.1	0.04±0.01
Endosulphan sulphate	0.18±0.01	<2.1±0.1	0.04±0.01
Methoxychlor	0.68±0.01	<1.6±0.1	0.59±0.02

BDL= below detection limit n=3, mean± standard deviation

4.5. 4: Comparison of OCPs levels in water from different sites in May 2015

From Figure 4.11, it can be observed that generally higher concentrations of OCPs were detected in May as compared to those detected in March. This could be explained by the fact

that during the rainy season, pesticides are washed off from the farms into the water bodies by the rain or deposited through aerial deposition. Methoxychlor was again the highest detected pesticide in the water samples from Lake Naivasha suggesting slow degradation as well as transportation from the farms by runoff.

Presence of higher levels of heptachlor epoxide as compared to heptachlor in Lake Naivasha suggests degradation product of heptachlor. Similarly, the detection of higher amounts of endrin aldehyde as compared to endrin at Lake Naivasha and River Malewa suggested decomposition of endrin to endrin aldehyde and its transportation from the farms to the water bodies.

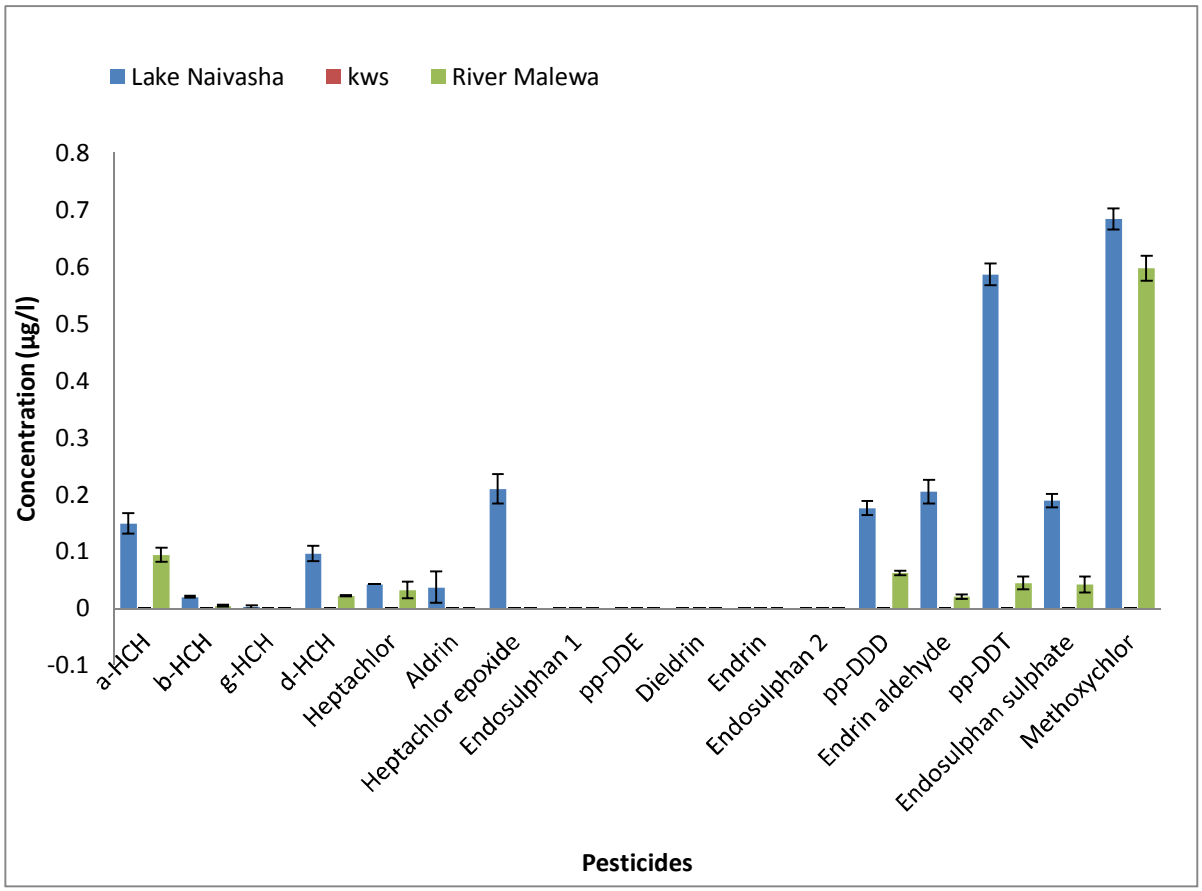

Figure 4. 9: Concentration of OCP in water samples collected from Lake Naivasha, KWS and River Malewa in May 2015

Figure 4. 10: Average concentrations of OCP in water from Lake Naivasha, KWS and River Malewa in May 2015.

4.6 Correlationof OCP residue levels in varous samples

4.6.1 Correlation of OCPs across all the matrices

Additional analysis of the data revealed significant correlations existing between the OCPs in all the matrices (appendix 1 Table A.1.3). There was a direct relationship of OCP levels in vegetables with those in soil from the 6 sampling sites over the sampling period as given by the positive r values. This can be attributed to the fact that these compounds bind tightly to soil, hence their presence in soil long after discharge. Eventually, when crops are planted, there is an uptake of these OCPs by the plants. There, however, existed an indirect relationship between OCPs levels in kales, water and soil. Water samples gave a negative r value and OCPs in soil and water as is given by a negative r value of -0.785 and -0.894 with kales and soil, respectively. This is because of the fact that the release of pesticides from vegetables to water and soil to water occur by slow desorption (Appendix 1 table A.1.3).

4.6.2 Correlation of OCPs residue levels in water and physico-chemical parameters

Appendix 1 Table A.1.4 shows a positive relationship between OCPs in water and water pH (r = 0.559). However a negative relationship was observed between OCPs in water and TDS as well as the Electrical conductivity, with negative r values of -0.704 and -0.414 for TDS and electrical conductivity, respectively.

4.6.3 Correlation of OCPs residue levels in soil with physico-chemical parameters

From appendix 1 (Table A.1.5), there was a positive correlation between OCPs in soil and the soil total carbon, soil phosphorus and soil conductivity as indicated by r values of 0.010, 0.226 and 0.146, respectively. On the other hand, a negative relationship existed between soil OCPs and pH and also soil conductivity (Table A.1.5) as shown by r values of -0.032 and -0.009, respectively.

4.7 Ratios of OCPs

Isomeric ratios of α-HCH/γ-HCH, heptachlor epoxide/ heptachlor, dieldrin/aldrin and *p,p'*-DDD/*p,p'*-DDE in kales, soil and water have been given in Tables 4.7, 4.8 and 4.9.The*p,p'*-DDD/*p,p'*-DDT ratio was higher than 1 at KWS farm and KCC market suggesting previous use of DDT. The ratio of *p,p'*-DDD/*p,p'*-DDT in the kale samples ranged between 0.05 to1.36 indicating a mixture of previous use of *p,p'*-DDT (for the ratios >1) and potential continued illegal application (for ratios <1) (Yang *et al.*, 2005)

Table 4. 8: Ratios of OCPs in Kales from the six sites

Site	**Dieldrin/Aldrin**	**Heptachlor epoxide/Heptachlor**	***p,p'*-DDD/*p,p'*-DDT**	**α-HCH/γ-HCH**
KWS farm	N/A	N/A	1.36	N/A
Kihoto market	N/A	N/A	0.05	N/A
KCC market	N/A	N/A	1.23	N/A
Gatara market	N/A	0.15	0.05	4.21
Kihoto farm	N/A	N/A	0.07	N/A
Malewa farm	N/A	N/A	1.02	0N/A

N/A= Where one or both of the concentrations of the organochlorine pesticide involved in calculating the ratio is below detection limit

4.7.1 Ratios of OCPs in soil

Table 4.9 shows the ratio of dieldrin/aldrin ranging between 0 and 19.38 which indicate past time use of adrin at Gatara market, Kihoto farm and Malewa farm. The ratios obtained for samples from KWS farm, Kihoto market and KCC market were less than one indicating potential recent application. The ratio of heptachlor/heptachlor epoxide ranged from 0.01 to 2.64 partly indicating past use and confirmation of potential recent application as well. Heptachlor degrades under environmental conditions to heptachlor epoxide, which is a more stable metabolite.

Table 4. 9: Ratios of OCPs in soil

Site	Dieldrin/Aldrin	Heptachlor epoxide/Heptachlor	*p,p'*-DDD/*p,p'*-DDT	α-HCH/γ-HCH
KWS farm	0.55	0.53	2.29	13.28
Kihoto market	19.38	2.62	0.27	N/A
KCC market	0.10	0.02	0.79	0.93
Gatara market	N/A	0.11	N/A	0.45
Kihoto farm	4.88	0.04	0.33	132.87
Malewa farm	0.01	0.01	1.02	16.02

N/A= Where one or both of the concentrations of the organochlorine pesticide involved in calculating the ratio is below detection limit.

4.7.2Ratios of OCP residue levels in water from KWS farm, Lake Naivasha and River Malewa

The isomeric ratios for various OCPs in water are shown in Table 4.9. Though the concentrations detected in the water samples (Table 4.5 and Table 4.6) were very low, some of the isomeric ratios were very high indicating past use. Some of the value detected suggest pollution load to the downstream sections of these sites.

Table 4. 10: Ratio of OCPs in water

Site	Dieldrin/Aldrin	Heptachlor/Heptachlor epoxide	*p,p'*-DDD/*p,p'*-DDT	α-HCH/γ-HCH
KWS farm	N/A	N/A	0.03	1.63
Lake Naivasha	N/A	2.38	0.50	36.98
Malewariver	N/A	N/A	1.34	N/A

N/A= Where one or both of the concentrations of the organochlorine pesticide involved in calculating the ratio is below detection limit

4.8 Degradation study of chlorpyrifos in Kales

4.8.1 Recovery and detection limits

Chlorpyrifos standard calibration curve was constructed by plotting analyte concentrations against peak areas. A linearity (y=17,762x -37,858) was obtained with a correlation coefficient of R^2=0.99. Figure 4.13 shows the calibration curve of chlorpyrifos.

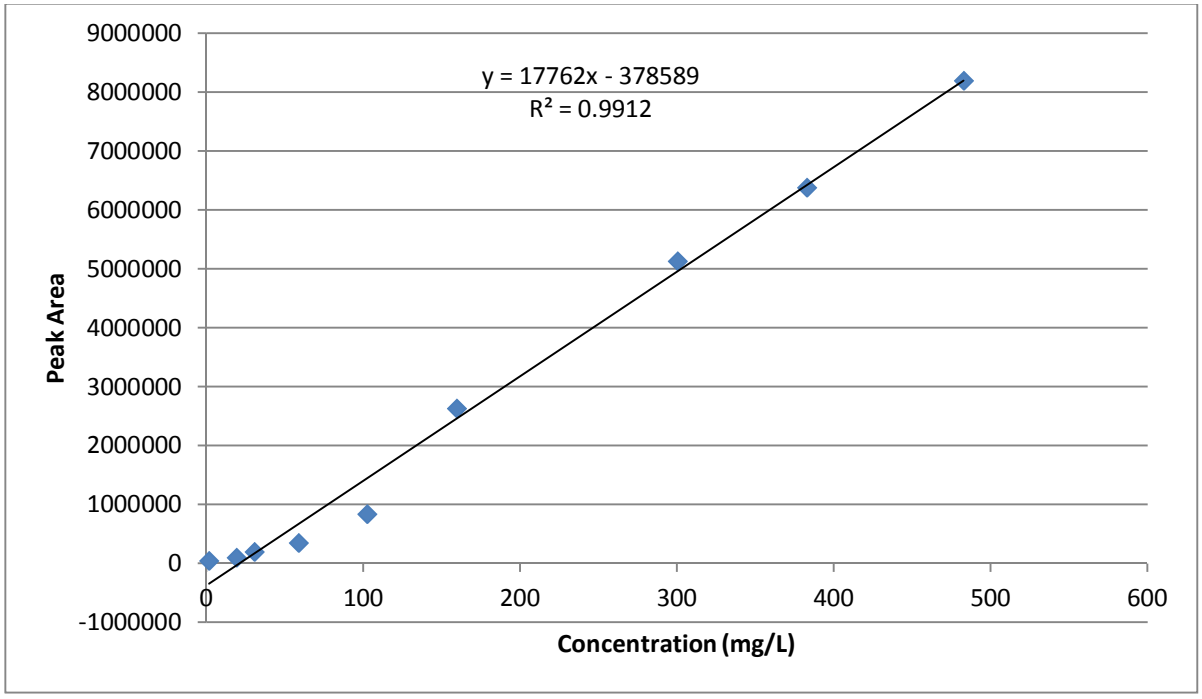

Figure 4. 11: Chlorpyrifos calibration curve

Recoveries were done for the leaves, stems, roots and soil.Fortification was done at 2,000 µg/kg of chlorpyrifos standard obtained from the Pest Control Products Board.Average recoveries from fortified samples for each matrix were in the range of 82.66±3.42 (roots)-84.92±2.91% (leaves).Table 4.11 below shows the recoveries for leaves, stems, roots and soil. The leaves showed the highest percentage recovery (84.92±2.91%).

Table 4.11: Average percentage recovery of chlorpyrifos residue levels (µg/ kg) for different matrices.

Matrix	Leaves	Stems	Roots	Soil
% recovery levels (µg/kg)	84.92±2.91	83.41±6.01	82.66±3.42	83.16±1.82

From Table 4.11, leaves had the highest value (84.92±2.91%) followed by the stem (83.41±6.01%).

4.8.2Degradation of Chlorpyrifos in leaves

The dissipation of chlorpyrifos was obtained by use of the Langmuir-Hinshelwood kinetic model (model of first order function) $C_t=C_o$ x e^{-kt}. The degradation half-life ($t_{1/2}$) of chlorpyrifos in each experiment was calculated using the equation $t_{1/2}$ =ln2/k, where Ct is the concentration (mg/kg) at time t (days) after application Co is the initial concentration (mg/kg) and k is the first order rate constant (for each day).

To obtain the values of the rate constant k and half-life ($t_{½}$), equations 1 to 11below were used:

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

$$\text{Or } r = \frac{dC}{dt} = \frac{kKC}{(1 + KC)} \text{ ---------- (2)}$$

Where r is the rate of reaction (mol/L.min), t is the time (min), C is the equilibrium concentration of analyte (mol/ L), K is the Langmuir constant (L/mol) and k is the rate constant (1/min).

In equation 2 above, the denominator can be ignored when the initial concentration C_0, is <<<1. This reduces it to an apparent first-order rate equation:

$$dC / dt = kKC \text{ ---------- (3)}$$

$$dC / C = kKCdt \text{ ---------- (4)}$$

$$r = dC / dt = kKC(1 + kC) - - - \quad (5)$$

Taking boundary conditions of C = C_0 at t=0 and C = C_t at time t, Integration of equation (3) gives:

$$Ln\ (C_0 / C_t)\ =\ kKt =\ k_{obs} \text{ ----------} \quad (6)$$

Or

$$C_t =\ Coe^{-kt} \text{ ----------} \quad (7)$$

Equation (7) is the first order rate equation which can also be written as:

$$\ln C_t = \ln(C_0) - K_{obs} Xt - - - - - - - - - - - - \quad (8)$$

Where; C_t= concentration at time, t

K_{obs}= first order rate constant

t = time in Days

C_0 = the initial concentration

Taking into Consideration the half-life of a reaction where the concentration of the substance remaining is half the original amount, one obtains $C_t = C_o/2$. Substituting this in equation 7 above gives:

$$Ln\ (C_o / 2C_o = -Kt_{1/2} \text{ ----------} \quad (9)$$

$$Ln\ 0.5 = -Kt_{1/2} \text{ ----------} \quad (10)$$

$$-0.693 / K\ = t_{1/2} \text{ ----------} \quad (11)$$

The results for the dissipation of chlorpyrifos in leaves are shown in Table 4.12 while the disappearance curve of chlorpyrifos in kale leaves is shown in Figure 4.14.

Table 4.12: Concentration of chlorpyrifos in leaves for the different days

Time(days)	Chlorpyrifosconcentration(mg/kg, dw)
0	75.82±3.56
2	41.89±3.41
4	10.05±2.10
7	2.82±0.03
11	<0.34
14	<0.34
21	<0.34
28	<0.34

BDL= below detection limit, n=6, dw= dry weight

From Table 4.12, it can be noted that the concentration of chlorpyrifos on day 0 of application was 75.82±3.56 mg/kg. The concentration levels went down from day 0 to day 7 and at day 7, the residue levels were at 2.82±1.33mg/kg. After day 7, the concentration was below detection limit (BDL). 44.75% of chlorpyrifos degraded within the first two days. On day 4, the residue was 10.05±2.10 mg/kg (86.74% reduction). In day 7, the concentration had reduced to 2.82±1.33 mg/kg which is a 96.28% reduction. From day 11onwards, the concentration was below detection limit (BDL). The initial deposition amount of chlorpyrifos mainly depends on the surface area of the leaves (Laabs *et al.*, 2000). Since Kale leaves at the time of spraying were wide, a high concentration was detected in day 0.

Various factors determine the rate at which pesticides degrade from the leaves of plants. Some of these include vapour pressure of the pesticide and weather conditions such as temperature, rainfall, solar radiation among others (Laabs *et al.*, 2000). In this case, the dissipation of chlorpyrifos was mainly attributed to the weather condition. Rainfall was a key factor in the

dissipation of chlorpyrifos from the leaves as can be seen in dissipation curve illustrated in Figure 4.14.It rained from day one of application and throughout that period. This resulted in fast removal of the pesticide residues from the leaves of the kales and thus a rapid decrease in concentration from day zero to day seven.

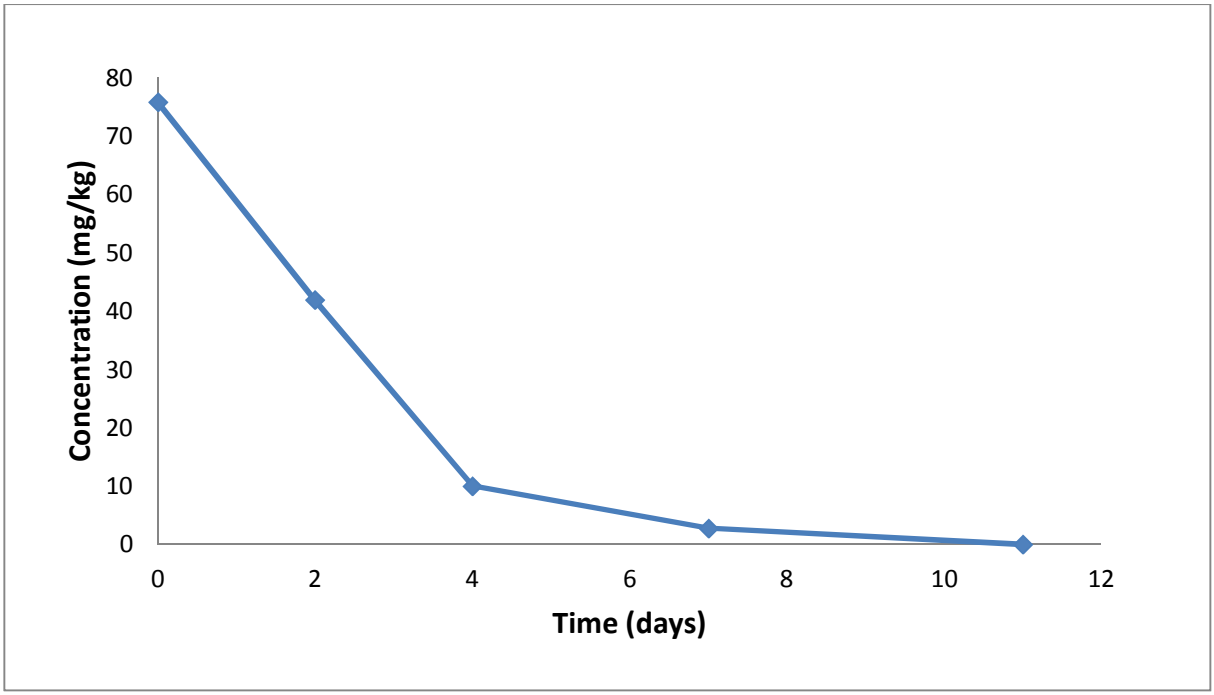

Figure 4. 12:Dissipation curve of chlorpyrifos in kale leaves

Using the rate constant (k) of 0.212 in Figure 4.15, the half life of chlorpyrifos on the leaves was found to be 3.26 days.The values from Table 4.11 were fitted into Langmuir-Hinshelwood kinetic model for reaction rate dependence on initial concentration (Kar *et al.,* 2013).

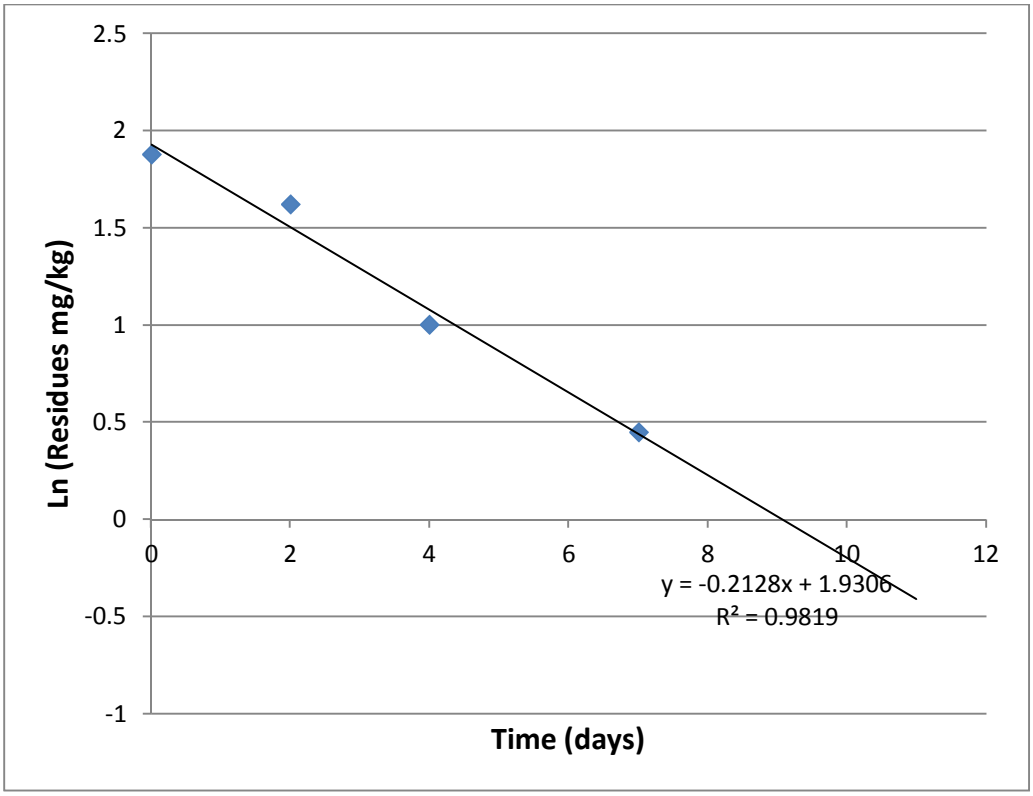

Figure 4. 13:Regression curve for chlorpyrifos residue levels over time in kale leaves

4.8.3Dissipation of chlorpyrifos residue levels from the kale stems

The results for the dissipation of chlorpyrifos from the stems are shown in Table 4.13 and Figure 4.14. Concentration of chlorpyrifos in day zero in the stems was 61.36±7.52 mg/kg. This concentration was lower compared to that measured in the leaves (75.82±3.56 mg/kg) for the same day. This is because while spraying, the leaves were the target area. Therefore the stems were expected to have lower concentration. The residues in the stems declined from day 0 up to day 7.The concentration at day 7 was1.13±0.06 mg/kg. After day 7, the concentration was below detection limit.

Table 4.13:Concentration of chlorpyrifos in kale stemsfor the different days

Time(days)	Chlorpyrifos concentration (mg/kg, dw)
0	61.36±7.52
2	11.56±2.45
4	2.55±0.01
7	1.13±0.06
11	<0.34
14	<0.34
21	<0.34
28	<0.34

dw= dry weight,

The concentration in day two was 11.56±2.45 mg/kg, representing 81.16% drop from day zero. In day four, the concentration was 2.55±0.01 mg/kg while in day seven the concentration was 1.13±0.06 mg/kg (98.15% decrease from day 0).Beyond day seven, the concentration was BDL. The trend of chlorpyrifos disappearance from the stems (Figure 4.16) was similar to that observed for the leaves (Figure 4.14). Lower concentrations were detected in the stems for the different days compared to those detected in the leaves. The trend could be explained by the fact that being a rainy season, much of the pesticide was washed from the stems leading to a rapid decrease in concentration on subsequent days.

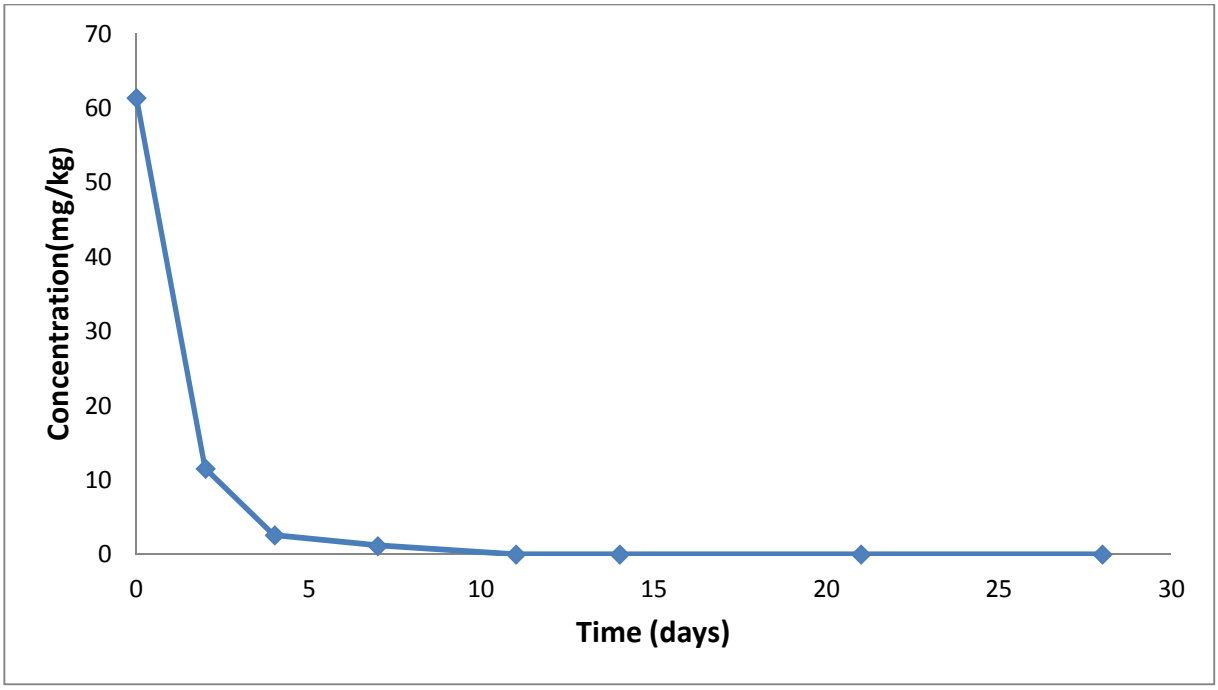

Figure 4. 14: Degradation curve of chlorpyrifosresidue levels in kale stems

The regression curve for the disappearance of chlorpyrifos, obtained when ln of residues were plotted against different time intervals in stems is shown in Figure 4.17. It had a correlation coefficient of R^2 =0.999 and a rate constant of 0.794. Using this rate constant, the half-life was found to be 0.87 days.

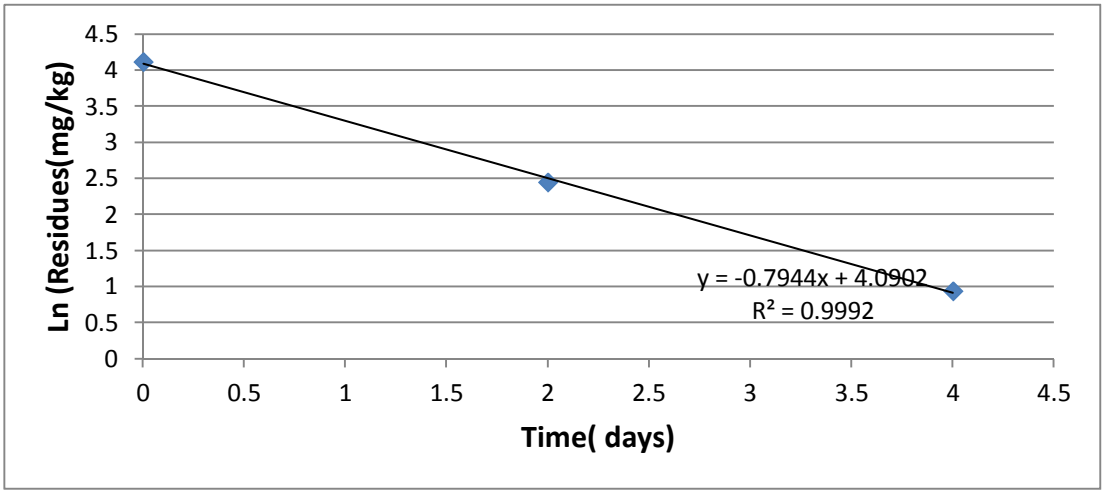

Figure 4. 15: Regression for chlorpyrifos residue levels over time in kale stems

4.8.4:Dissipation of chlorpyrifos in root.

The results for the degradation of chlorpyrifos in roots are shown in Table 4.14 while the degradation curve is shown in Figure 4.15. As can be noted in Table 4.15, no chlorpyrifos was detected in the roots in day zero. This is mainly because of the fact that chlorpyrifos had not been absorbed by the roots by the time the plants were being uprooted.The concentration in day two was 13.03±0.01 mg/kg while that in day eleven was 1.56±0.00 mg/kg.

Table 4.14: Concentration of chlorpyrifos in kale roots in different days

Time (Days)	**Chlorpyrifos concentration in roots (mg/kg, dw)**
0	<0.34
2	13.03±0.01
4	5.41±0.00
7	3.03±0.00
11	1.56±0.00
14	1.06±0.11
21	<0.34

BDL= below detection limit, n=6, dw= dry weight,

The concentration of chlorpyrifos residue in kale roots in day 0 was BDL **(**Figure 4.18). Whereas the leaves and stems recorded 75.82±3.56 mg/kg **(**Figure 4. 14) and 61.36±7.52 mg/kg **(**Figure 4.16) of chlorpyrifos residues in day zero, respetively. The roots recorded the highest residues in day 2 (13.03±0.01 mg/kg).By the fourth day, there was 58.48% decrease in concentration of chlorpyrifos in the roots (Table 4. 12**)**. The residue levels were BDL on the twenty first day (Figure 4.18). The concentration of Chlorpyrifos observed on the first day (BDL) could be attributed to the fact that pesticide residues had no been translocated to the roots on the first day the plants were uprooted. Similar findings were reported in another study by Burner *et al.* (1997). Besides, it had also not rained by the time of uprooting the plants,

hence leaching of the pesticide into the roots zone had not taken place. The presence of the pesticide in the roots in day 2 was attributed to absorption from the soil. Upon spraying of pesticides on the crops, part of this pesticide was washed away by rainwater and the rest was absorbed by the soil and eventually by the roots.

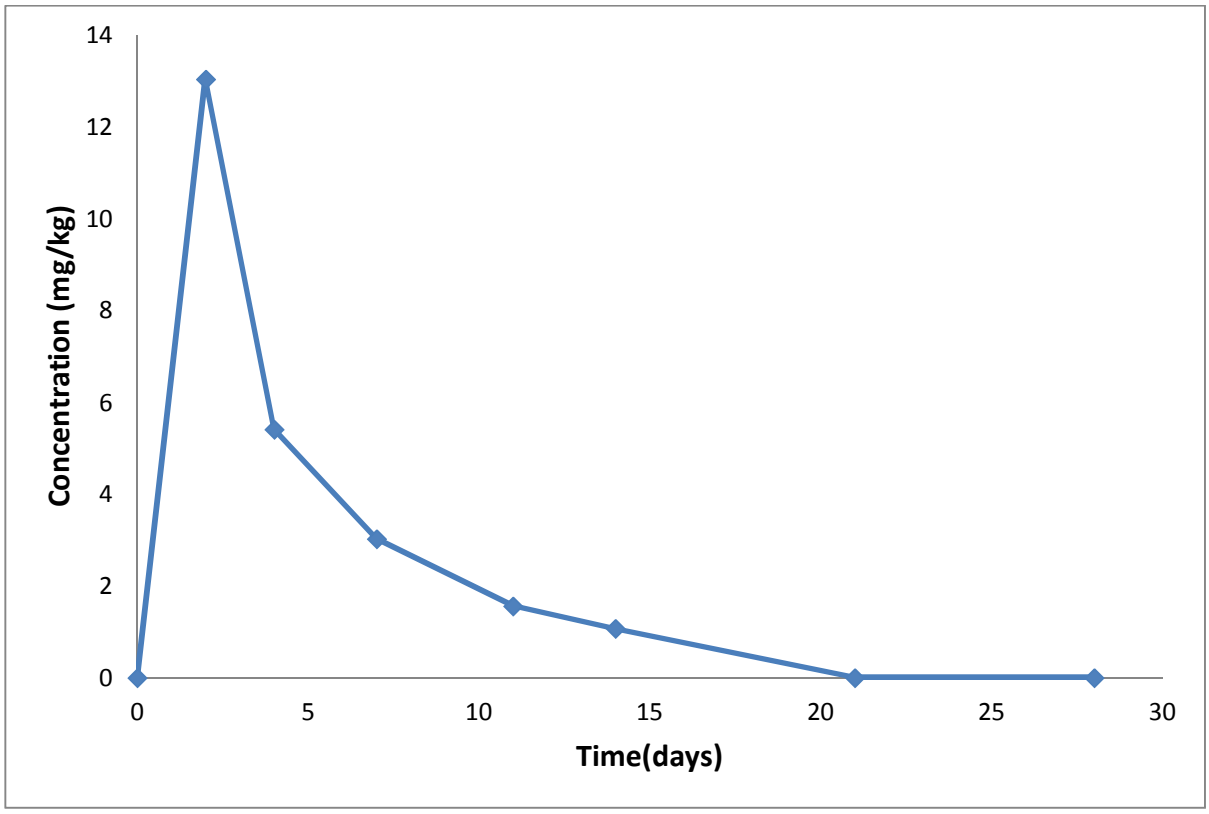

Figure 4. 16:Degradation curve of chlorpyrifos residue levels in kale roots

The regression curve for the disappearance of chlorpyrifos in roots is shown in Figure 4.19.It had a correlation coefficient of R^2=0.953 and a rate constant of 0.197. Chlorpyrifos' half-life in roots was 3.51 days.

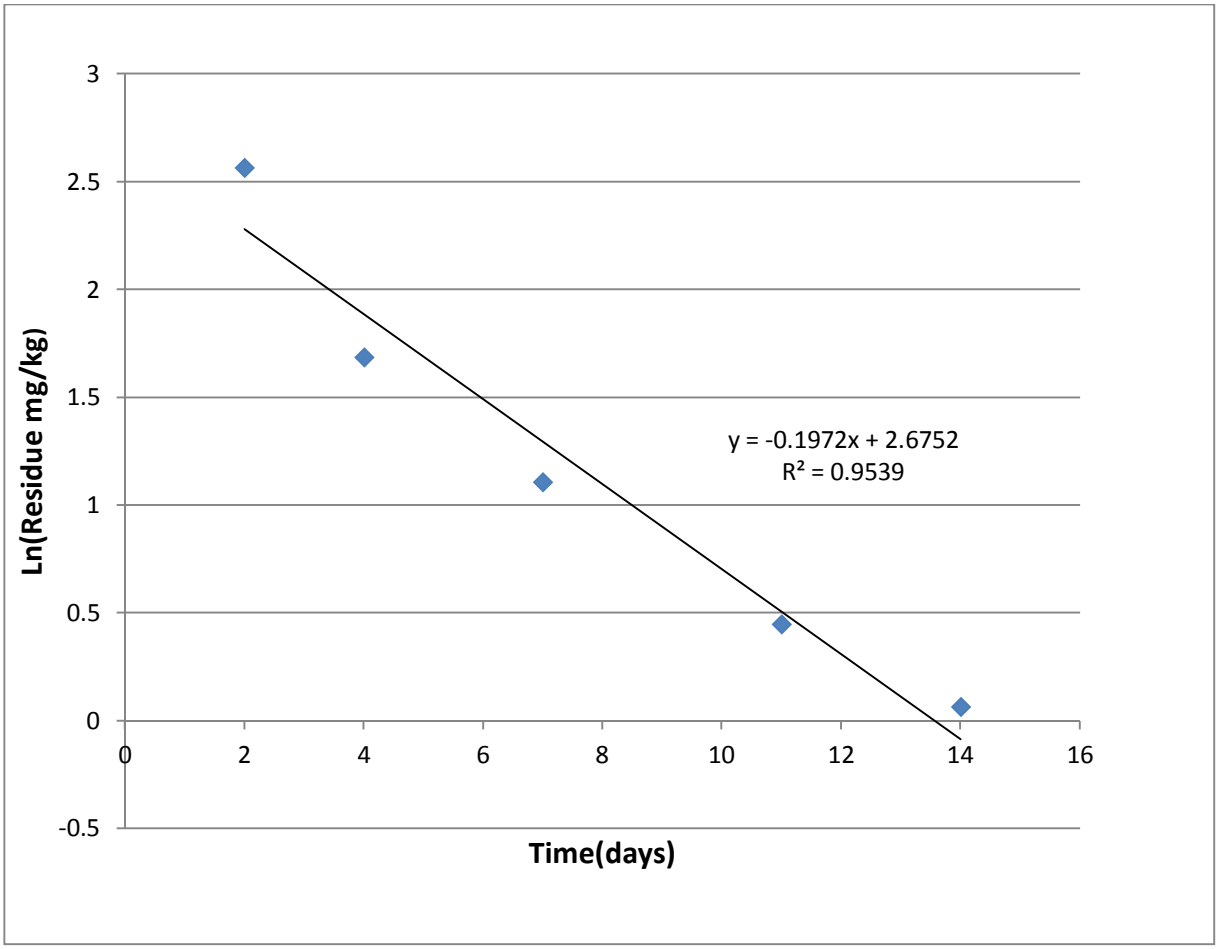

Figure 4. 17:Regression for chlorpyrifos residue levels over time in kale roots

4.8.5: Dissipation of chlorpyrifos in Soil

The results for the degradation of chlorpyrifos in soil are shown in Table 4.15 while the degradation curve is shown in Figure 4.20. The concentration of chlorpyrifos on day zero in soil was 42.03±0.00 mg/kg. On day two, the concentration detected was 11.12±1.30 mg/kg, a 73.54% decrease in concentration from day zero. The concentration on day 21 was 1.05±0.04mg/kg. Beyond day 21, the concentration was BDL (Figure 4.20).

Table 4.15: Concentration of chlorpyrifos in soil in different days

Time	Chlorpyrifos concentration (mg/kg, dw)
0	42.03±0.00
2	11.12±1.30
4	9.07±0.21
7	5.50±0.00
11	2.38±2.51
14	1.91±1.25
21	1.05±0.04
28	<0.34

dw= dry weight,

Figure 4.20 shows that there was a huge decrease in concentration of chlorpyrifos from day zero to day two (73.54%). The rapid dissipation of chlorpyrifos in soil during the first 2 days was followed by a slower second phase.The initial rapid disappearance on the surface of the soil could be attributed to its high vapour pressure (2.19 mPa at 25 ºC), high sorption coefficient, photolysis and physical loss (Laab *et al.*, 2000). This was followed by a slower second phase associated with microbial and chemical degradation in the soil medium. The degradation of chlorpyrifos in the soil was closely associated with climatic conditions at that time. Rainfall played a key role because it resulted in leaching and runoff of the pesticide in the soil (Yang *et al.,* 2005).

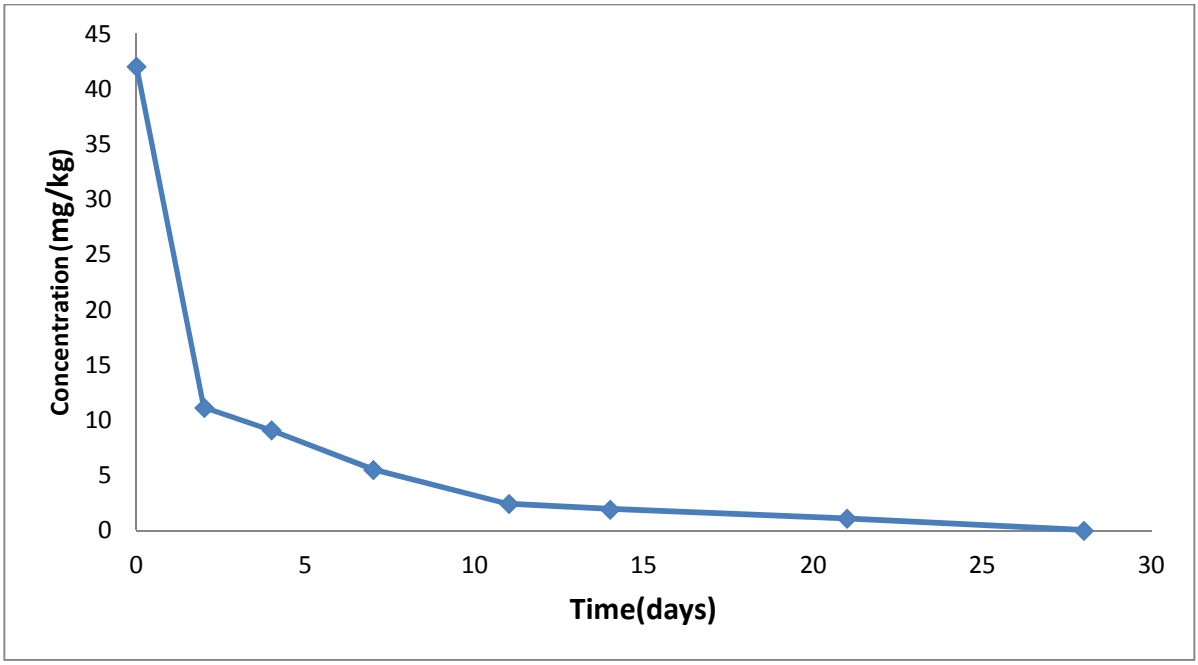

Figure 4. 18: Degradation Curve of Chlorpyrifos Residue Levels in Soil

Degradation of chlorpyrifos in soil followed first order reaction kinetics as can be seen in Figure 4.21 below. A straight line was obtained when the log transformation of the residues levels were plotted against time. It had a correlation coefficient of R^2=0.982 and a rate constant of 0.157. The half life was found to be 4.41 days.

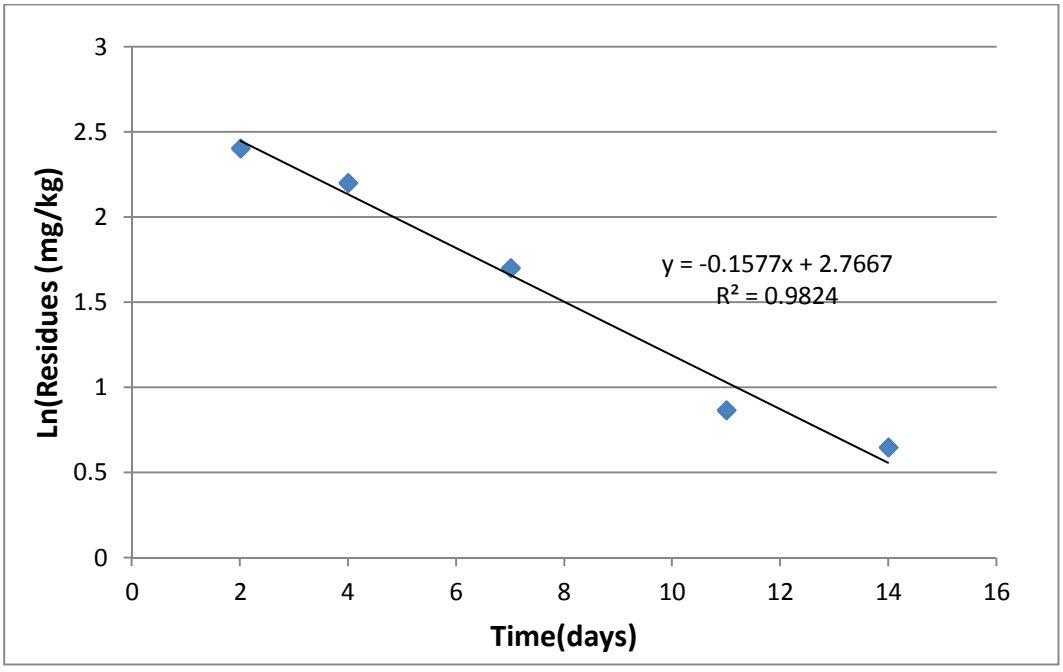

Figure 4. 19: Regression for Chlorpyrifos Residue Levels Over time in Soil

Table 4. 16: Summary of the half-life of chlorpyrifos in kales and soil in Naivasha

Matrix	Equation	Rate Constant	half-life (days)
leaves	$0.693/k = t_{1/2}$	0.212	3.26
stem	$0.693/k = t_{1/2}$	0.794	0.87
roots	$0.693/k = t_{1/2}$	0.197	3.51
soil	$0.693/k = t_{1/2}$	0.157	4.41

4.9:Degradation Study of Diazinon

4.9.1:Recovery and detection limits

Diazinon's standard calibration curve was constructed by plotting analyte concentrations versus peak areas (Figure 4.21). Good linearity (y=15,810x -10,208) was achieved with a correlation coefficient of R^2=0.993. Figure 4.22 shows the calibration curve of diazinon.

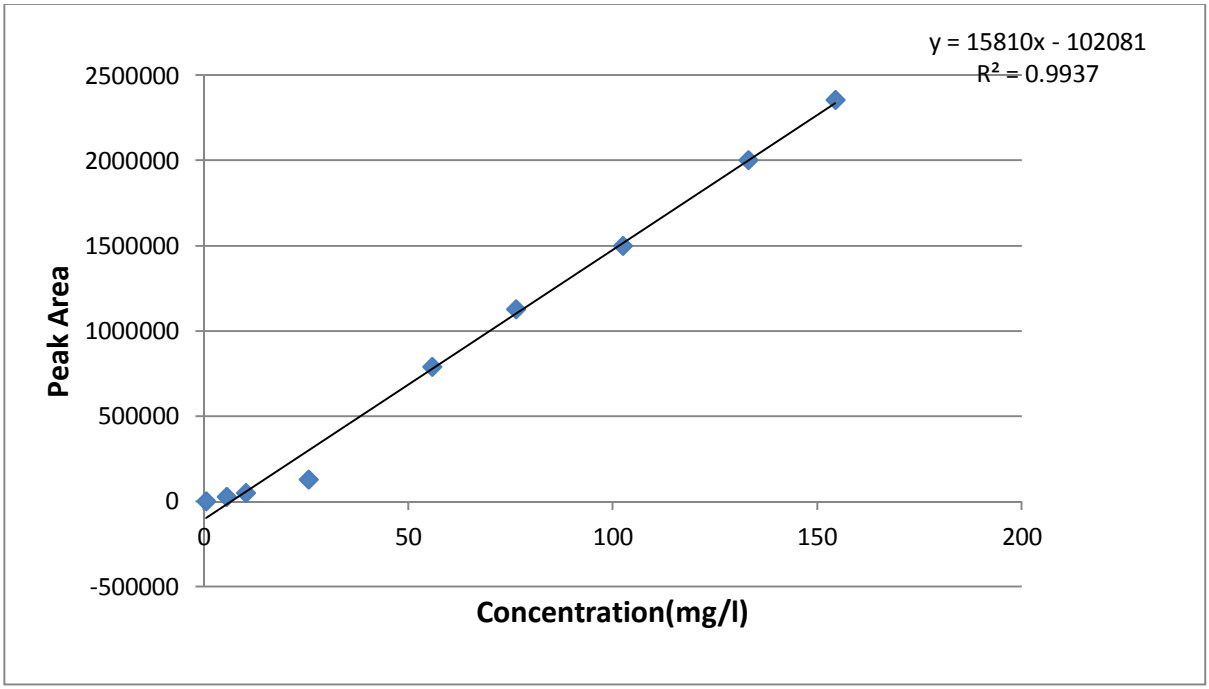

Figure 4. 20: Diazinon calibration curve

The recovery study was done for the leaves, stems, roots and soil.Fortification was done at 1 mg/kg. Average recoveries from fortified samples for each matrix were in the range of 82.92-87.01% and the standard deviation ranged between±1.91 and±5.42 (Table 4.17).

Table 4. 17: Average percentage recovery of Diazinon residue levels (mg/ kg) in different matrice

Matrix	**Leaves%**	**stems %**	**roots %**	**soil%**
% recovery levels (µg/kg)	82.92±1.91	85.41±3.01	85.66±5.42	83.16±2.82

From Table 4.17, the roots had the highest recovery (85.66±5.42%) followed by stem at85.41±3.01%

4.9.2: Degradation of Diazinon on leaves.

Diazinon's dissipation was described by the first order function $C_t=C_o \times e^{-kt}$. The degradation half- life ($t_{1/2}$) of diazinon in each experiment was obtained using equation 11 in section 4.8.2 above. The values from Table 4.18were fitted into Langmuir-Hinshelwood kinetic model for reaction rate dependence on initial concentration.

The results for the dissipation of diazinon in leaves are shown on Table 4.18 while the dissipation curve of diazinon in kale leaves is shown in Figure 4.22. From Table 4.18, it can be noted that the initial concentration of diazinon on the leaves after two hours (day 0) of application was 49.02±0.26 mg/kg. The concentration levels declined from day 0 to day 11. At day 11, the concentration was 3.12.82±0.14 mg/kg. After day 11, the residue was below detection limit.

Table 4. 18: Concentration of Diazinon in leaves in kales in different days

Time (days)	Concentration (mg/kg)
0	49.02±0.26
2	24.64±0.16
4	20.37±0.14
7	10.47±1.03
11	3.12±0.14
14	<0.21
21	<0.21
28	<0.21

Figure 4.22 shows that 58.44% of diazinon degraded within the first four days. On day 7, the concentration had reduced to 10.47±1.03 mg/kg which is a 78.64% reduction (Figure 4.22).From day 11 onwards, the concentration was below detection limit (BDL). The high concentration was detected in day zero because of the wide surface area of kale leaves (Mfalme F1) at the time of spraying. Wash off from the leaves by rain water was also a potential cause of the rapid loses and decrease in concentrations observed from day zero to day seven (Figure 4.22).

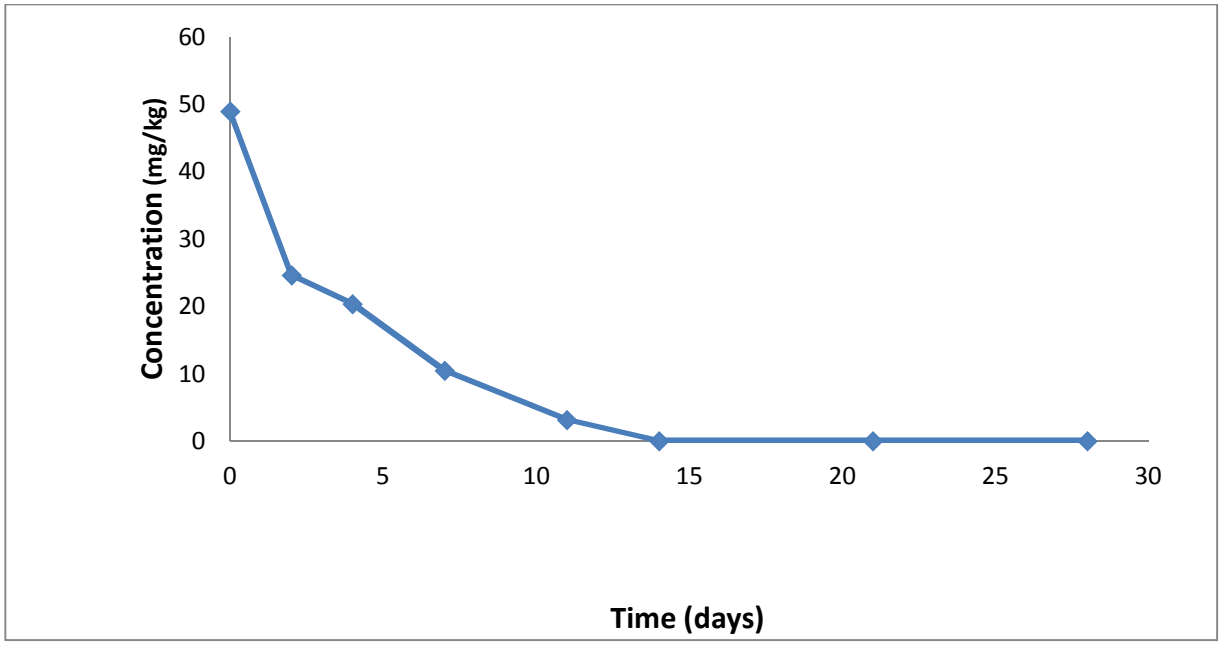

Figure 4. 21: Degradation Curve for Diazinon Residue Levels in Kales Leaves in Days

The regression curve for the disappearance of diazinon, obtained when the natural log of the residues levels in kale leaves was plotted against different time is shown in Figure 4.23. A correlation coefficient of R^2 =0.981 was obtained with a rate constant of 0.238. The half –life for diazinon on the leaves was 2.91 days.

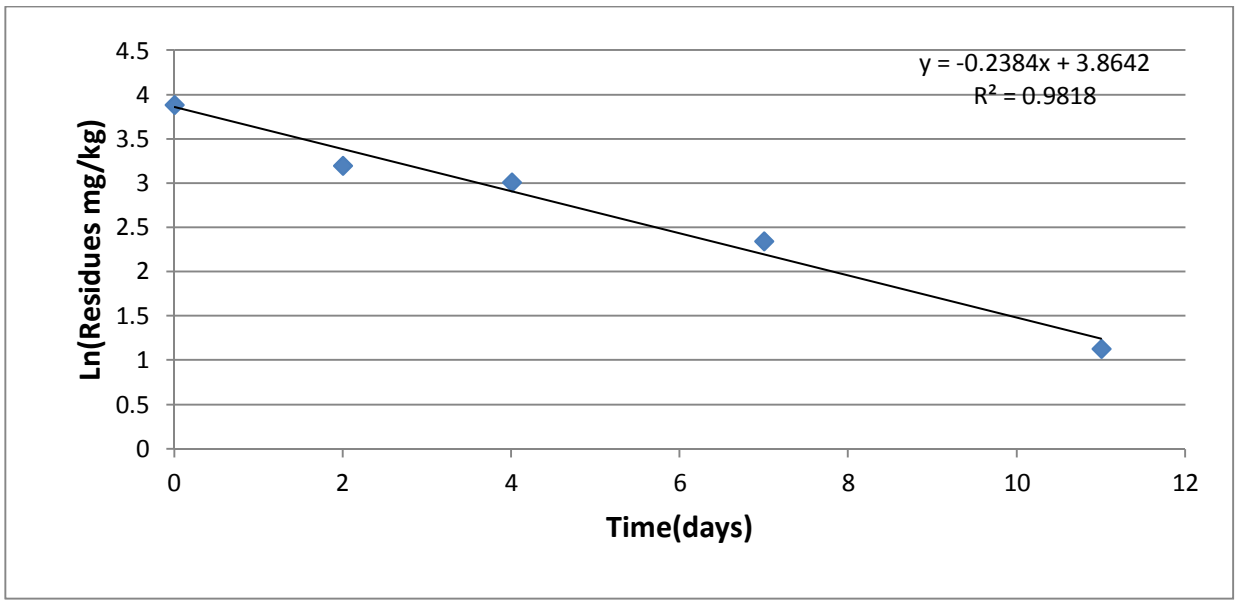

Figure 4. 22: Regression for diazinon residue levels in kales leaves over times in days

4.9.3Degradation of Diazinon residue levels in kale stems in days

Table 4.19 shows the dissipation of diazinon in stems are shown on Table 4.13 while the dissipation curve of diazinon in the stems is shown in Figure 4.24.The initial concentration of diazinon in the stems was 37.88±3.32 mg/kg. This concentration is lower compared to that in the leaves (49.02±0.26 mg/kg) for the same day (Table 4.18). There was rapid decline in residue levels from day 0 to day 7.The concentration on day 7 was5.16±0.17 mg/kg. After day 7, the concentration was below detection limit (BDL).

Table 4. 19:Concentration of diazinon residue levels in stems in different days

Time (days)	Diazinon Concentration(mg/kg)
0	37.88±3.32
2	27.72±3.11
4	12.21±0.39
7	5.16±0.17
11	<0.21
14	<0.21
21	<0.21
28	<0.21

The concentration on day two was 27.72±3.11 mg/kg and 12.21±0.39 mg/kg on day four (Table 4.19). This was a 67.76% decrease from day 0.By the 7th day the concentration was 5.16±0.17 representing 86.37% reduction from day 0. Beyond day seven, the concentration was BDL. Rapid decrease in concentration could be partly attributed to wash off by rain (Figure 4.24).

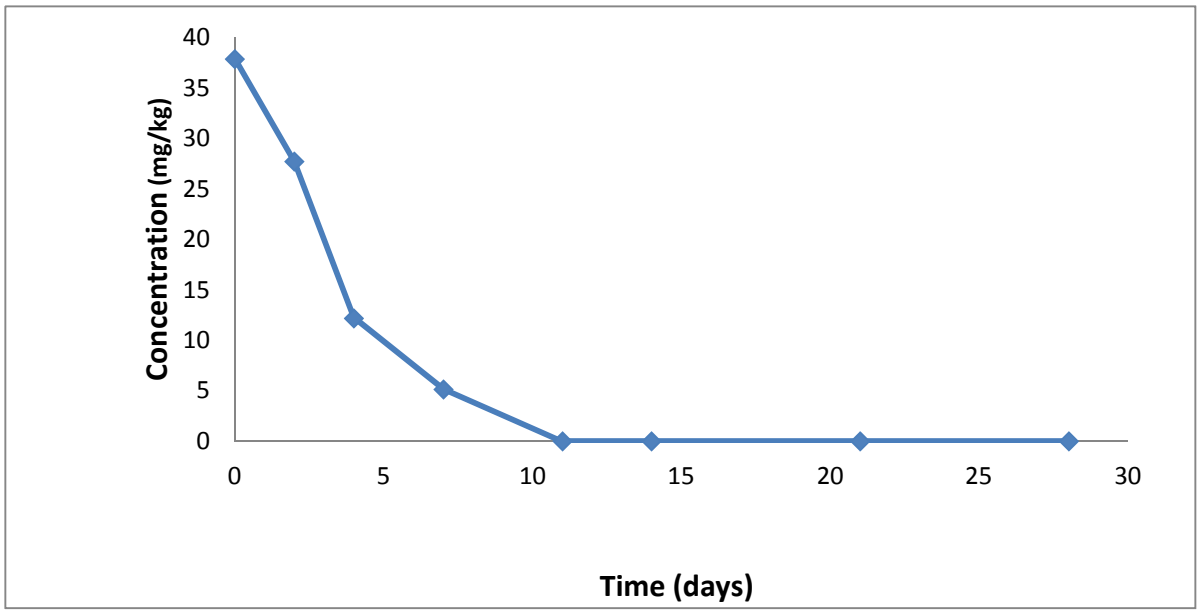

Figure 4. 23: Degradation curve for diazinon residue levels in kales stems in days

The regression curve for the dissipation of diazinon, obtained after log transformation of the concentrations was plotted against time is shown in Figure 4.25, with a correlation coefficient of R^2 =0.981.The rate constant was found to be 0.296 with a half-life of 2.3 days.

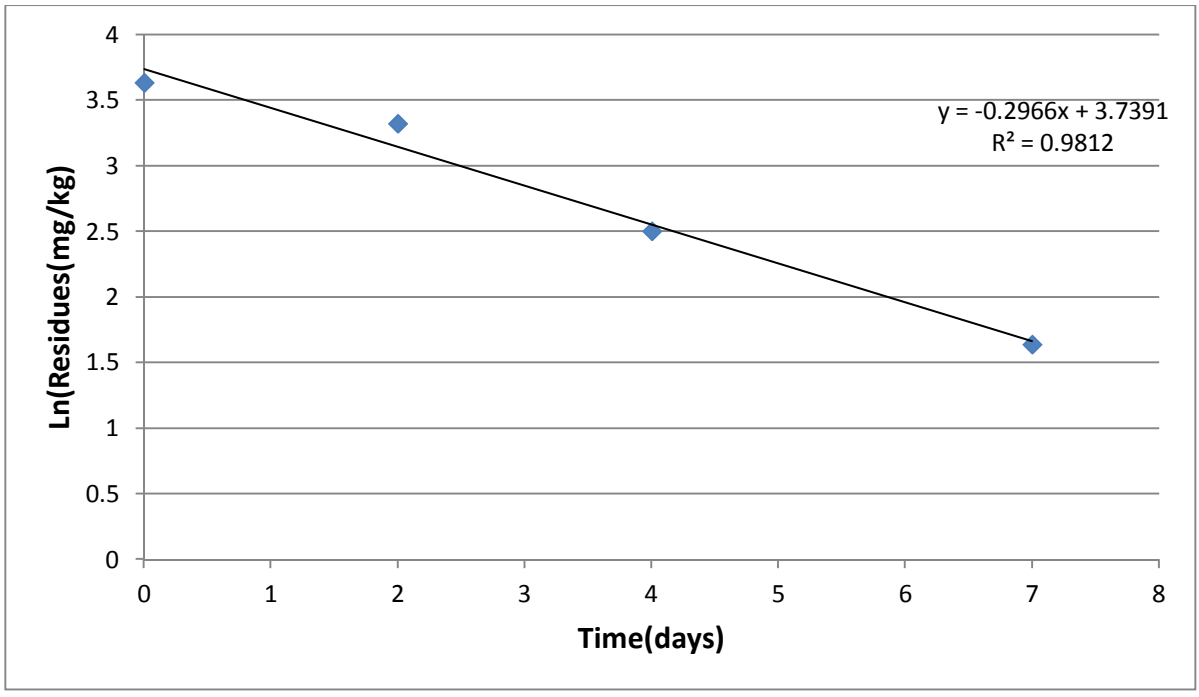

Figure 4.25: Regression for diazinon residue levels instems in days

4.9.4:Dissipation of Diazinon in roots

The results for the dissipation of diazinon in the roots are shown in Table 4.20 while thedissipation curve is shown in Figure 4.26. From Table 4.20, no diazinon was detected in the roots on day zero. This was mainly because of the fact that diazinon had not translocated into the roots by the time of uprooting the plants on day zero. The concentration on day two was 8.10±0.89mg/kg while that on day eleven was 1.00±0.07 mg/kg (Table 4.20).

Table 4.20: Concentration of diazinon in roots on different days

Time (days)	Diazinon concentration (mg/kg)
0	BDL
2	8.10±0.89
4	2.66±0.21
7	1.51±0.04
11	1.00±0.07
14	<0.21
21	<0.21
28	<0.21

Where as the leaves(Figure 4.22) and stems (Figure 4.24) recorded the highest residues on day zero, the roots recorded the highest residues on day 2 (8.10±0.89 mg/kg), which then decreasedfrom day four upto day eleven. Beyond the 11thday, the residues were BDL (Figure 4.26).

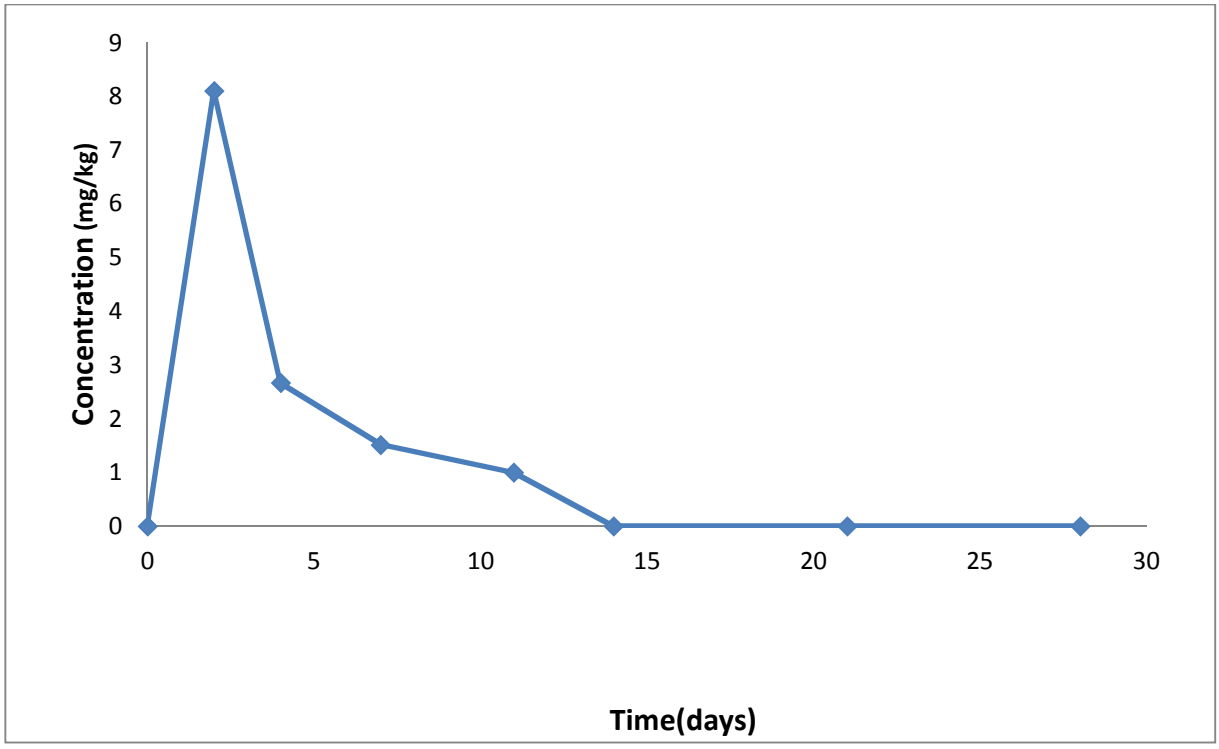

Figure 4. 24: Degradation Curve of Diazinon Residue Levels in Roots in Days

The dissipation of diazinon in roots followed first order reaction kinetics (Figure 4.27).A straight line was obtained when the log transformation of concentrations was plotted against time.The value of R^2 obtained was 0.998 with a rate constant of 0.369.The half life was found to be 3.22 days.

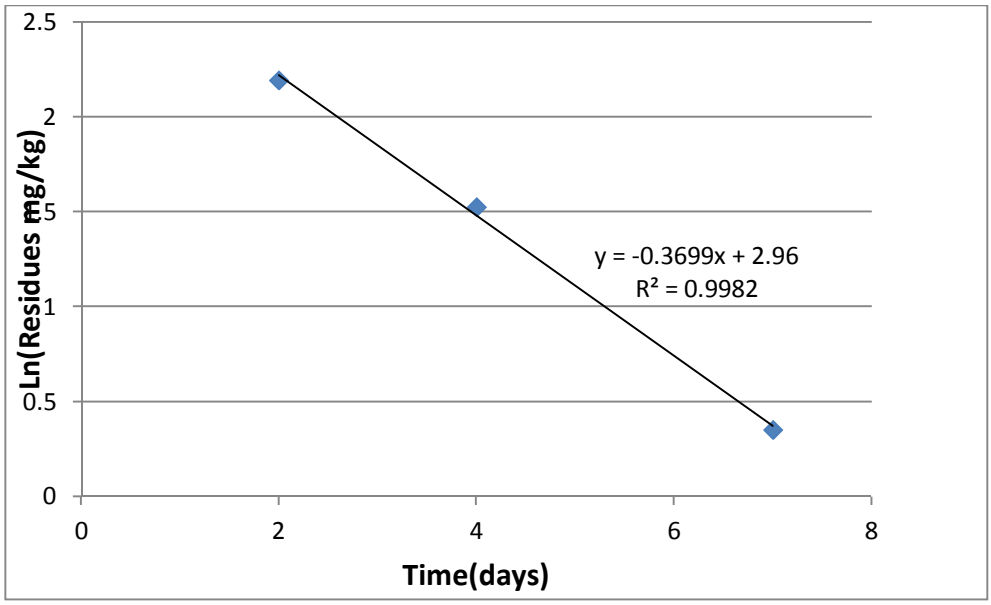

Figure 4. 25: Regression for diazinon residue levels in rootsin days

4.9.5: Degradation of Diazinon Residue Levels in Soil

The results for the degradation of diazinonin soil are shown in Table 4.21 while the degradation curve is shown in Figure 4.28. The initial concentration of diazinon in soil was 38.25±0.00 mg/kg. On day four, the concentration detected was 13.85±1.05 mg/kg, representing 75.93% decrease in concentration from day zero. The concentrations on the 11^{th} and 14^{th} days were 3.09±0.21 mg/kg and 1.67±0.02 mg/kg, respectively. Beyond day fourteen, the concentrations were BDL (Table4.21).

Table 4. 21: Concentration of Diazinon in Soil in Different Days

Time (days)	Diazinon concentration (mg/kg)
0	38.25±3.69
2	19.84±3.57
4	13.85±1.05
7	4.78±0.31
11	3.09±0.21
14	1.67±0.02
21	<0.21
28	<0.21

From the degradation curve (Figure 4.28), there was a huge decrease in concentration from day zero to day four (63.79%). Initially rapid dissipation of diazinon in soil was observed from day 0 to four, but this was followed by a slower second phase. The degradation of diazinon in the soil was closely associated with environmental conditions at that time. For instance rainfall played a key role because it resulted in leaching and runoff of the pesticide in the soil.

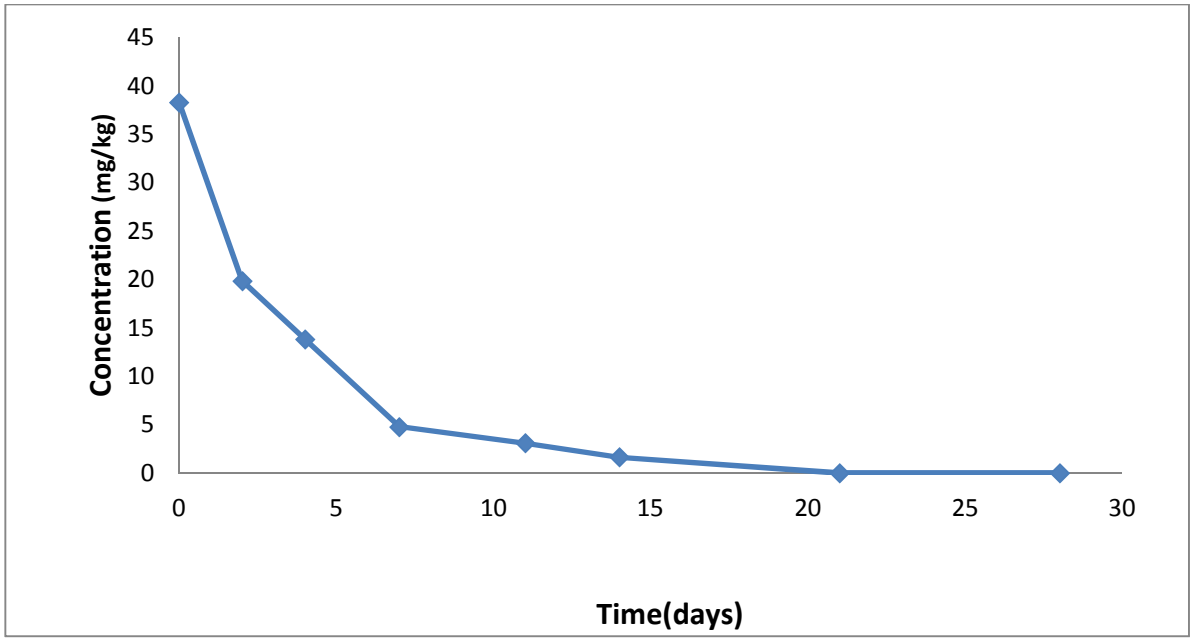

Figure 4. 26: Degradation curve of Diazinon residue level in soil in days

The dissipation of diazinon in soil followed first order reaction kinetics as can be seen in Figure 4.30. A straight line was obtained when the log transformation of concentrations was plotted against time.The value of R^2 obtained was found to be 0.973 with a rate constant of 0.219 and ahalf-life of 3.16 days.

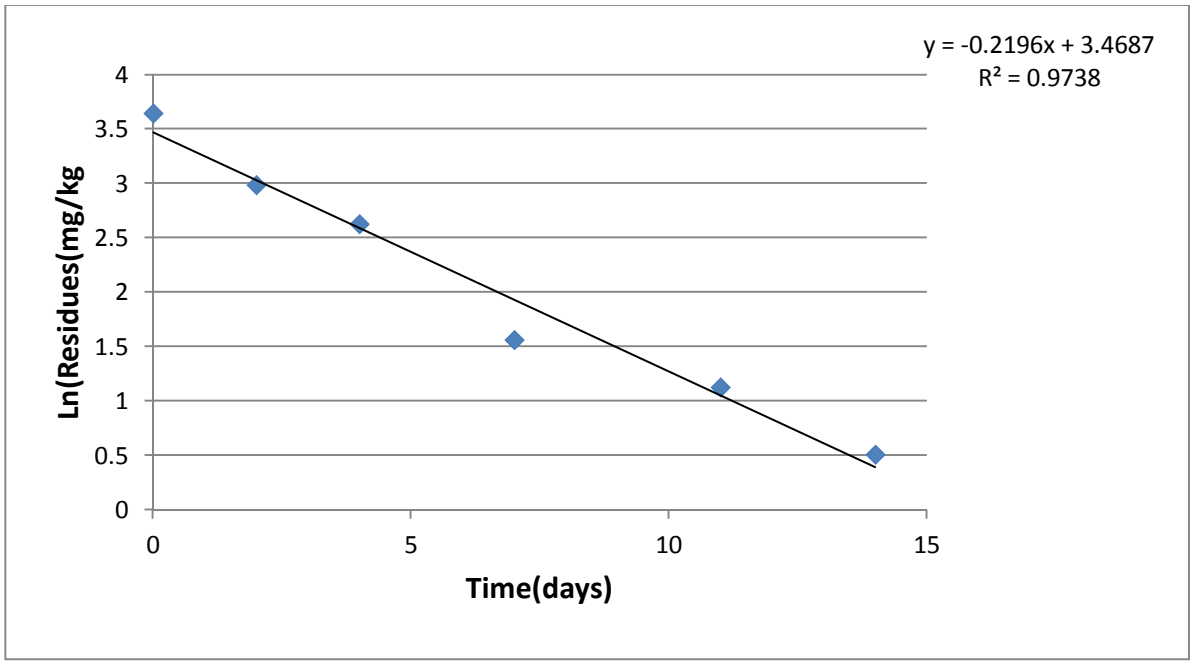

Figure 4. 27: Regression for diazinon residue levels in soil in days

Table 4. 22: Summary of the half-life diazinon in kales and soil in Naivasha

Matrix	Equation	Rate Constant	Half-Life (Days)
Leave	$0.693/k = t_{1/2}$	0.238	2.91
Stem	$0.693/k = t_{1/2}$	0.296	2.34
Roots	$0.693/k = t_{1/2}$	0.369	3.22
Soil	$0.693/k = t_{1/2}$	0.219	3.16

From Tables 4.16 and 4.22, diazinon dissipates faster from the kales than chlorpyrifos. The highest half-life for diazinon 3.22 days while that of chlorpyrifos was 4.41 days. This makes diazinon better pesticide for uses in kales farming since it is less persistent.

4.10 Correlations of Diazinon and Chlorpyrifos Residue Levels

As can be seen in Appendix 1 Table A.1.6, a significant association existed between diazinon levels in the leaves and diazinon levels in stems, roots, and soil as shown by r values of 0.968, 0.280 and 0.993 in stems, roots and soil, respectively.

4.11 Maximum Residue Levels of Chlorpyrifos and Diazinon in kale leaves

The highest concentrations of chlorpyrifos and diazinon in kale leaves were found to be 72.82±3.56 mg/kg and 49.02±0.26 mg/kg, respectively. In both cases, the highest concentrations were seen in day zero. The least detectable residues for both chlorpyrifos and diazinon in kale leaves were 2.82±0.03 mg/kg and 3.12±0.14 mg/kg respectively. These concentrations were observed on day 7 for chlorpyrifos and day 11 for diazinon. After day 7, chlorpyrifos' concentration in kale leaves was below detection limit while in the case of diazinon, the concentration was below detection limit after day 11.However, the European Union maximum residue levels both for chlorpyrifos and diazinon in kales is 0.05 mg/kg, hence

according to the experiment it is safe to harvest kales for consumption after the recommended 14 days.

CHAPTER FIVE

5. CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

From this study, it can be concluded that organochlorine pesticide residues comprising of α-HCH, β-HCH, δ-HCH, γ-HCH, heptachlor, heptachlor epoxide,endosulphan-1, endosulphan-2, endosulpan sulphate, aldrin, dieldrin, endrin, endrin aldehyde, methoxychlor, *p,p'*-DDT, *p,p'*-DDD and *p,p'*-DDE were detected in water, soil and kale samples from Naivasha area.

Higher concentrations were detected in kale and soil samples compared to those detected in water. The concentrations varied from one sampling site to the other and the disparities could be attributed to differences in environmental factors, seasons, site, past and recent use of organochlorine pesticides and their physico-chemical properties.

In kale samples, methoxychlor was the highest detected both in March and May with concentration levels of 75.418±7.7 µg/kg and 76.618±9.07 µg/kg at Gatara and Kihoto markets, respectively. Endosulphan sulphate was the highest detected pesticide in soil samples both in March and May.

From dissipation studies, chlorpyrifos had longer persistence on the crops and soil compared to diazinon applied under the same environmental conditions. Thus diazinon a direct relationship was seen to exist between OCP levels in vegetables with OCP levels in soil from the six sampling sites as indicated by the positive r value of (0.154) while indirect relationships existed between OCPs in vegetables and OCPs in soil(-0.785) and between OCPs in soil and OCPs in water (-0.894). A significant association was seen to exist between diazinon levels in leaves with the diazinon levels in stems and soil with r values of 0.968 and 0.993 for stems and

soil samples respectively. The highest concentrations of chlorpyrifos and diazinon in kale leaves were found to be 72.82±3.56 mg/kg and 49.02±0.26 mg/kg, respectively. In both cases, the highest concentrations were seen in day zero. After day 7, chlorpyrifos' concentration in kale leaves was below detection limit while in the case of diazinon, the concentration was below detection limit after day 11.

5.2 Recommendations

5.2.1 Policy Recommendations

1) Based on the organochlorine residue levels that were detected in kales, soil and water, there is need for constant monitoring of these pesticides in vegetables, soil and water in order to safe guard aquatic biota and end users.
2) The farmers and locals in this area should be informed and trained on the risks involved in the use of pesticides for pest control through awareness creation activities.
3) Based on the OCP residue levels detected, investigations should be carried to determine whether there is current use of the banned organochlorine pesticides and their source.
4) Based on the organophosphate (diazinon and dursban) residue levels detected, farmers and consumers should be educated on post-harvest interval to be observed before harvesting of vegetables.
5) There is need to monitor water used for irrigation so as to minimise contamination of vegetables.

5.2.2 Research Recommendations

1) Research should be carried out on other vegetable varieties and other food crops around this area so as to determine whether they are also contaminated.
2) Further research is necessary on human beings in this area to establish the level of pesticides exposure in their bodies.

3) A comparative study should be carried out around Naivasha area with one set of kales being grown in the field and another set being grown in controlled conditions in a greenhouse to see how different the results would be.
4) Further studies to be carried out to establish the effect of seasonal effects on dissipation rates of the pesticides on the crops.

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APPENDICES

Appendix 1

Table A.1.1: Physico-chemical parameter for Lake Naivasha, River Malewa and KWS farm in March 2015

	pH	*TDS*	Conductivity
Naivasha (Kihoto farm)	7.5±0.05	162.67±0.58	341.67±0.58
River Malewa	7.5±0.05	47.83±0.05	102.23±1.11
Site	7.62±0.19	424.67±0.58	489.67±1.53

Table A.1.2: Physico-chemical parameter for Lake Naivasha, River Malewa and KWS farm in May2015

Site	pH	*TDS*	Conductivity
Naivasha (Kihoto farm)	7.61±0.00	166.33±2.08	328.33±0.58
River Malewa	7.41±0.01	50.5±0.82	95.2±0.1
KWS farm	7.5±0.01	438.67±6.11	480.33±0.58

Table A.1.3: Correlation of the OCPs residue levels in Kales, soil andwater

Correlations

		OCPs in vegetables	OCPs in soil	OCPs in water
OCPs in vegetables	Pearson Correlation	1	.154	-.785
	Sig. (2-tailed)		.771	.425
	N	6	6	3
OCPs in soil	Pearson Correlation	.154	1	-.894
	Sig. (2-tailed)	.771		.296
	N	6	6	3
OCPs in water	Pearson Correlation	-.785	-.894	1
	Sig. (2-tailed)	.425	.296	
	N	3	3	3

Table A.1.4: Correlation of OCPs residue levels in water with physic-chemical parameters

Correlations					
		ocps in water	Water pH	Water TDS	Water Conductivity
ocps in water	Pearson Correlation	1	.559	-.704	-.414
	Sig. (2-tailed)		.622	.503	.728
	N	3	3	3	3
Water pH	Pearson Correlation	.559	1	.196	.523
	Sig. (2-tailed)	.622		.875	.650
	N	3	3	3	3
Water TDS	Pearson Correlation	-.704	.196	1	.938
	Sig. (2-tailed)	.503	.875		.225
	N	3	3	3	3
Water Conductivity	Pearson Correlation	-.414	.523	.938	1
	Sig. (2-tailed)	.728	.650	.225	
	N	3	3	3	3

Table A.1.5: Correlation of OCPs residue levels in soil with physic-chemical parameters

Correlations							
		OCPs in soil	soil pH	soil total Nitrogen %	Soil total carbon %	soil phosphorus	soil conductivity
OCPs in soil	Pearson Correlation	1	-.032	-.009	.010	.226	.146
	Sig. (2-tailed)		.968	.991	.990	.774	.854
	N	4	4	4	4	4	4

soil pH	Pearson Correlation	-.032	1	.158	.176	.863	-.931
	Sig. (2-tailed)	.968		.842	.824	.137	.069
	N	4	4	4	4	4	4
soil total Nitrogen %	Pearson Correlation	-.009	.158	1	1.000**	.566	-.489
	Sig. (2-tailed)	.991	.842		.000	.434	.511
	N	4	4	4	4	4	4
Soil total carbon %	Pearson Correlation	.010	.176	1.000**	1	.586	-.503
	Sig. (2-tailed)	.990	.824	.000		.414	.497
	N	4	4	4	4	4	4
soil phosphorus	Pearson Correlation	.226	.863	.566	.586	1	-.925
	Sig. (2-tailed)	.774	.137	.434	.414		.075
	N	4	4	4	4	4	4
soil conductivity	Pearson Correlation	.146	-.931	-.489	-.503	-.925	1
	Sig. (2-tailed)	.854	.069	.511	.497	.075	
	N	4	4	4	4	4	4
**. Correlation is significant at the 0.01 level (2-tailed).							

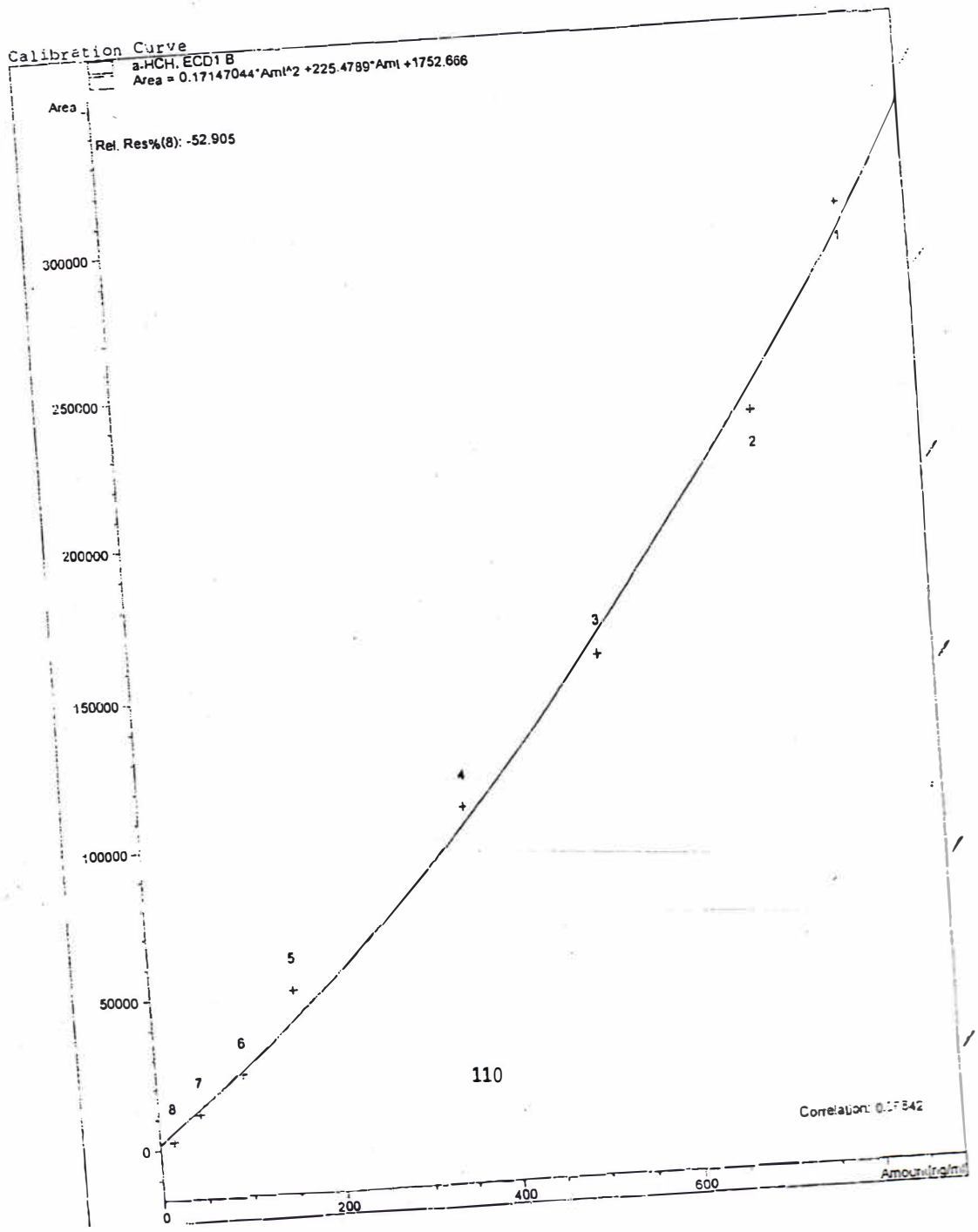
TableA.1.6: Correlation of diazinon and chlorpyrifos residue levels in Leaves, Stems, Roots ad soil the six sampling sites.

Correlations									
		Leaves Diaz	Stems Diaz	Roots Diaz	Soil Diaz	Leaves Chlr	Stems Chlr	Roots Chlr	Soil Chlr
Leaves Diazinon	Pearson Correlation	1	.968**	.280	.993**	.952**	.902**	.266	.953**
	Sig. (2-tailed)		.000	.501	.000	.000	.002	.524	.000
	N	8	8	8	8	8	8	8	8
Stems Diazinon	Pearson Correlation	.968**	1	.444	.977**	.976**	.860**	.420	.897**
	Sig. (2-tailed)	.000		.270	.000	.000	.006	.301	.003
	N	8	8	8	8	8	8	8	8
Roots Diazinon	Pearson Correlation	.280	.444	1	.279	.282	-.060	.994**	.014
	Sig. (2-tailed)	.501	.270		.503	.498	.887	.000	.975
	N	8	8	8	8	8	8	8	8
Soil Diazinon	Pearson Correlation	.993**	.977**	.279	1	.974**	.921**	.261	.960**
	Sig. (2-tailed)	.000	.000	.503		.000	.001	.532	.000
	N	8	8	8	8	8	8	8	8
Leaves Chlorpyrifos	Pearson Correlation	.952**	.976**	.282	.974**	1	.939**	.246	.945**
	Sig. (2-tailed)	.000	.000	.498	.000		.001	.556	.000
	N	8	8	8	8	8	8	8	8

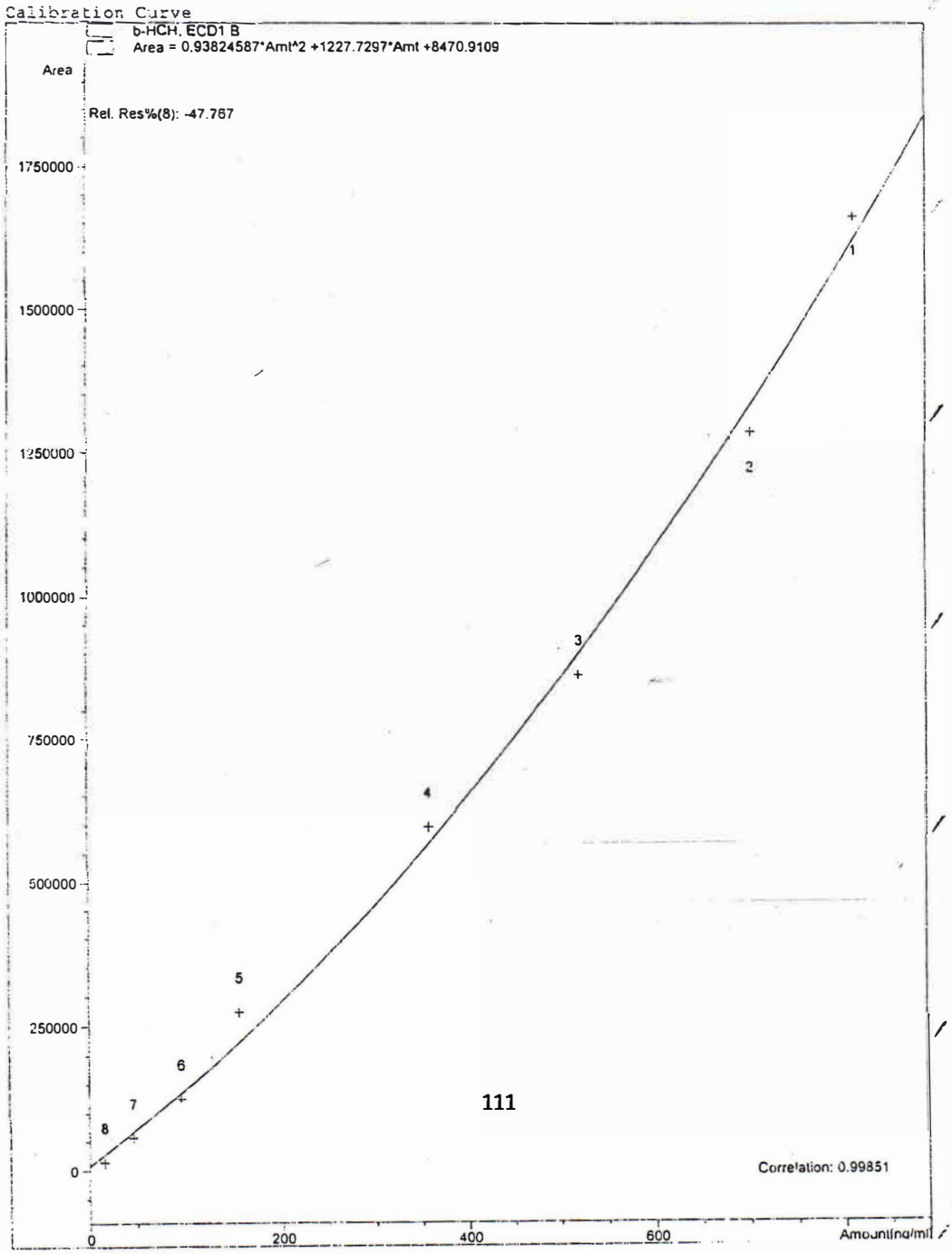
Stems Chlorpyrifos	Pearson Correlation	.902**	.860**	-.060	.921**	.939**	1	-.095	.986**
	Sig. (2-tailed)	.002	.006	.887	.001	.001		.824	.000
	N	8	8	8	8	8	8	8	8
Roots Chlorpyrifos	Pearson Correlation	.266	.420	.994**	.261	.246	-.095	1	-.009
	Sig. (2-tailed)	.524	.301	.000	.532	.556	.824		.984
	N	8	8	8	8	8	8	8	8
Soil Chlorpyrifos	Pearson Correlation	.953**	.897**	.014	.960**	.945**	.986**	-.009	1
	Sig. (2-tailed)	.000	.003	.975	.000	.000	.000	.984	
	N	8	8	8	8	8	8	8	8
**. Correlation is significant at the 0.01 level (2-tailed).									

Figure A4.3: multi-level calibration curves for analyzed OC pesticides

rint of window 66: Calibration Curve



'rint of window 66: Calibration Curve



Print of window 66: Calibration Curve

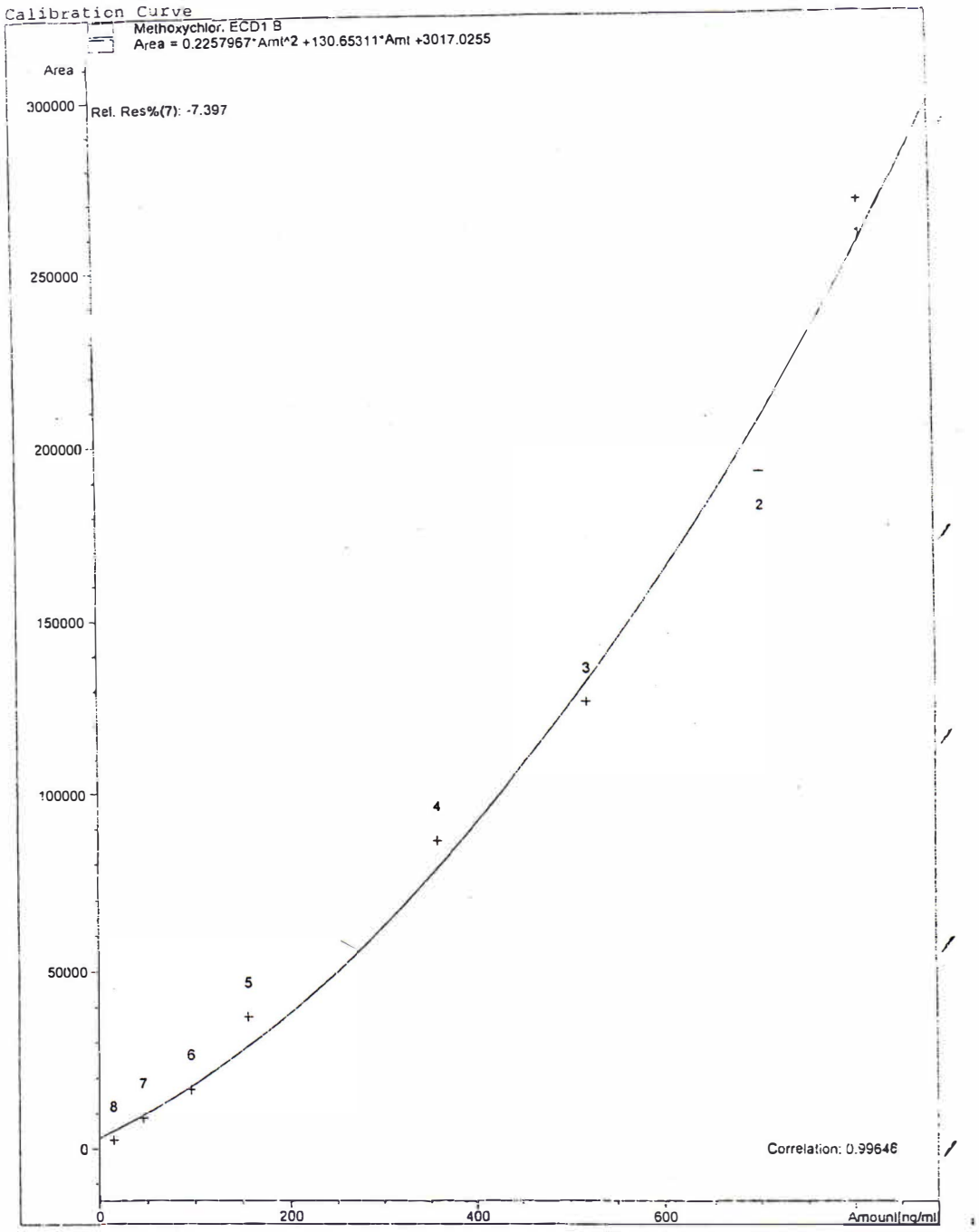


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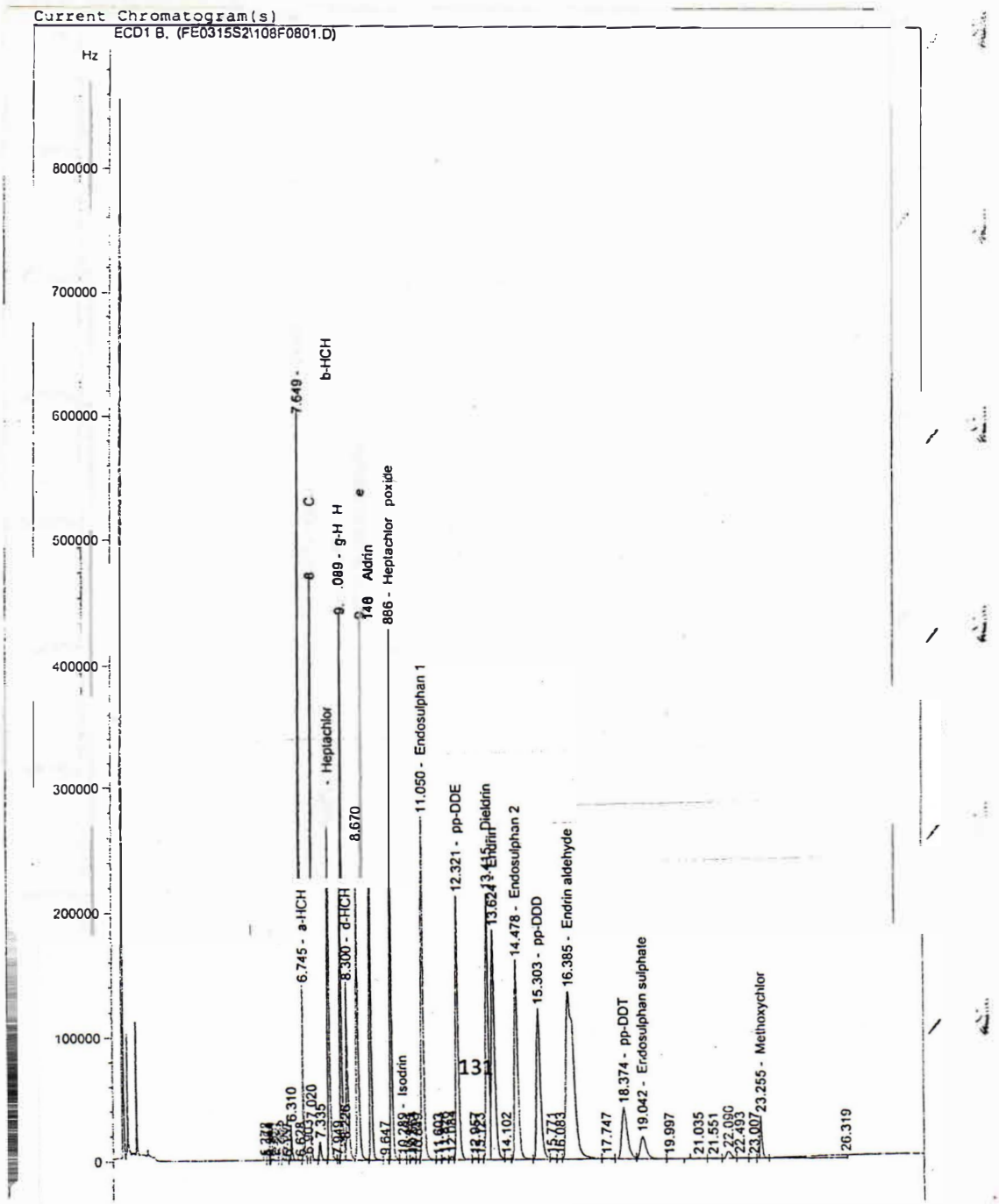
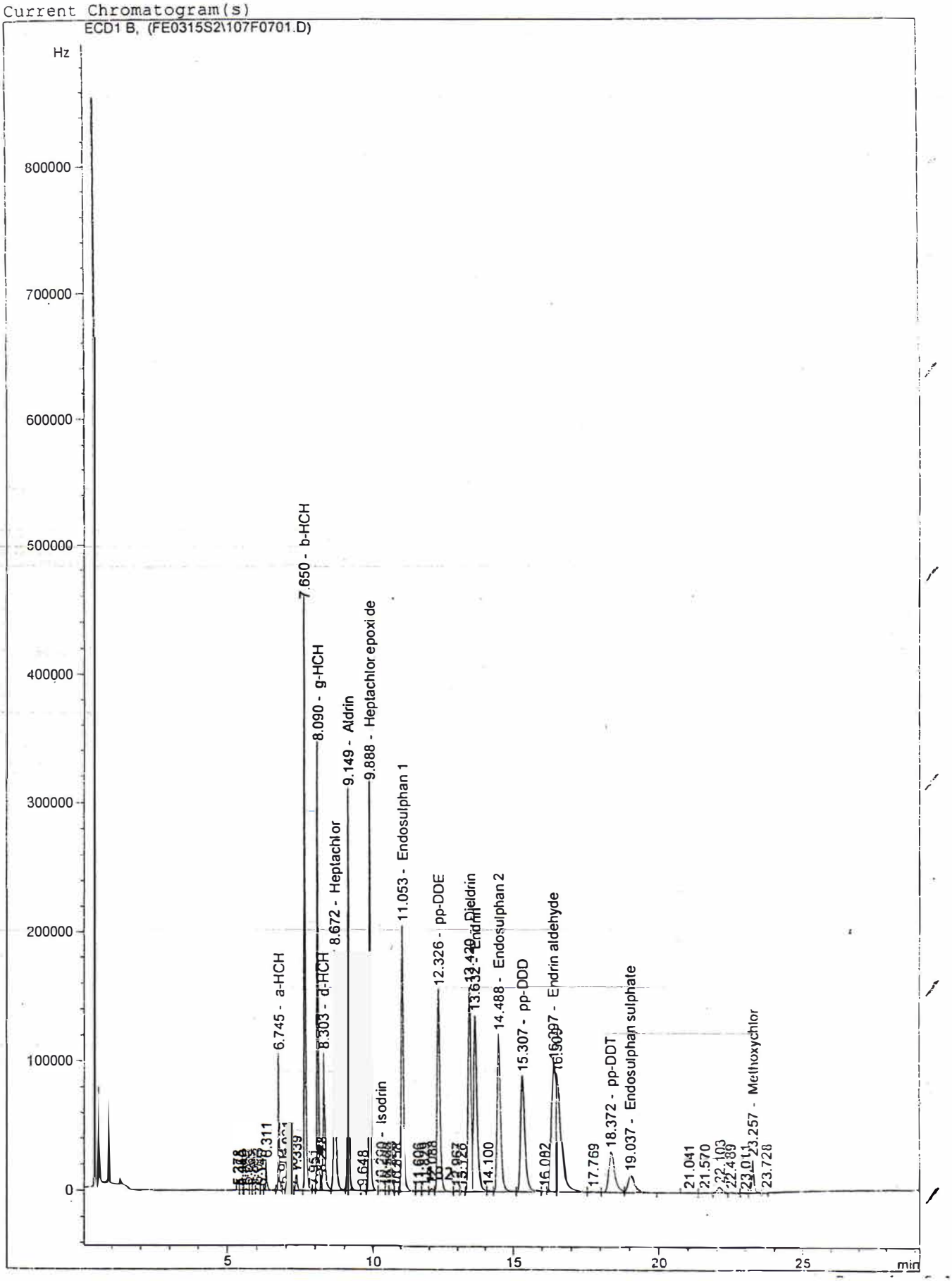
Figure A4.4:Sample calibration standard chromatograms

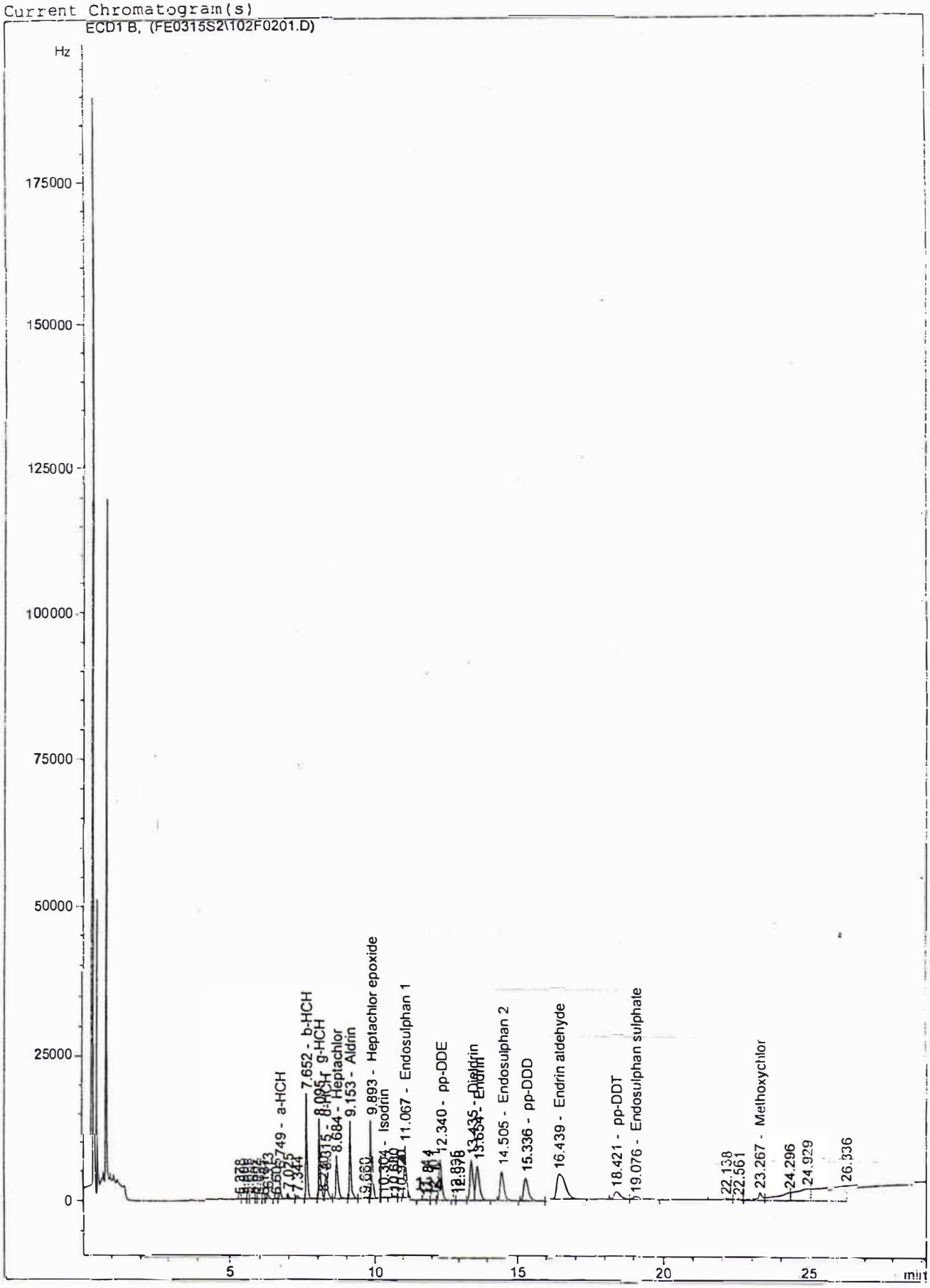
rint of window 38: Current Chromatogram(s)



:int of window 38: Current Chromatogram(s)



Print of window 38: Current Chromatogram(s)



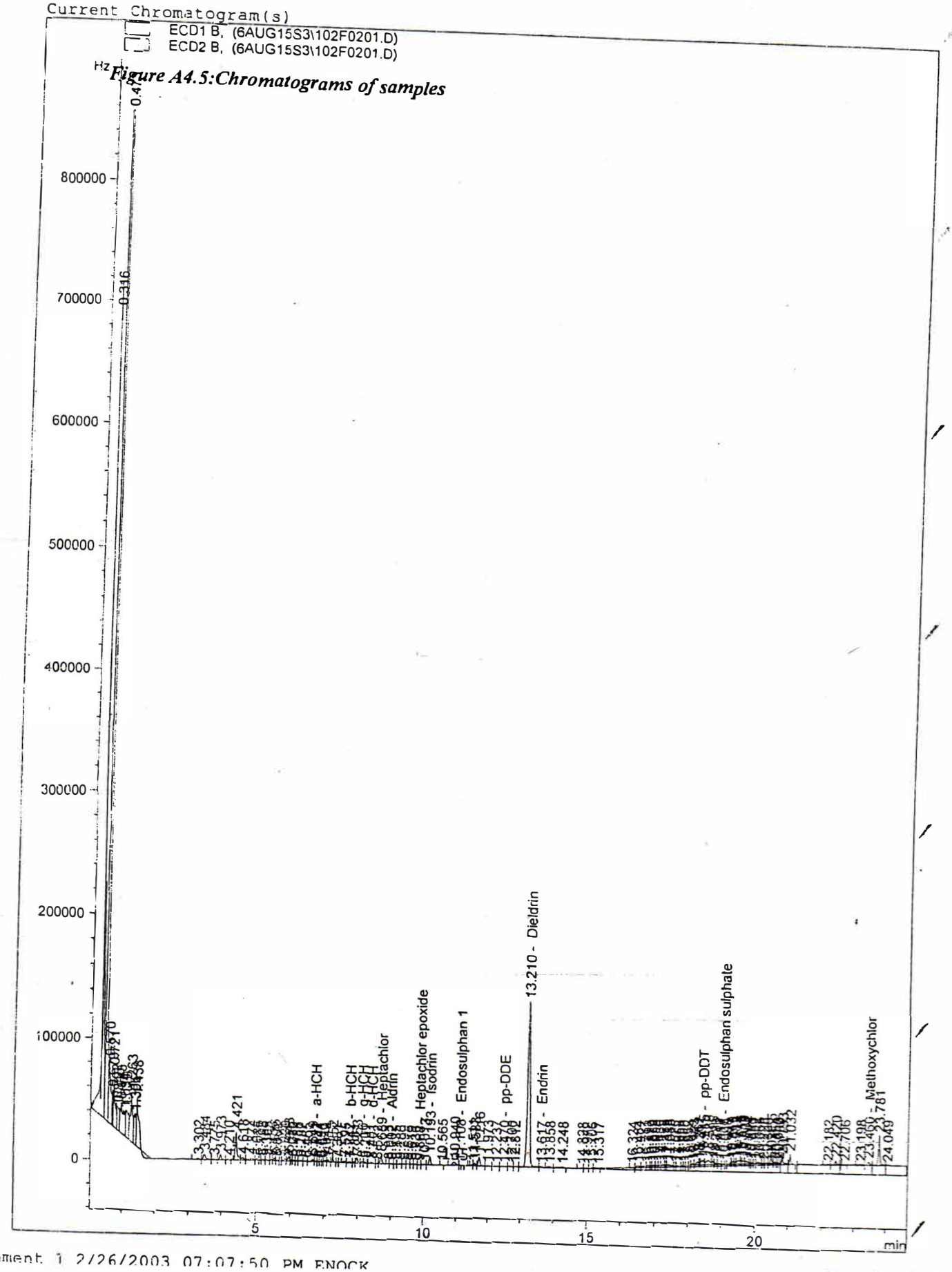
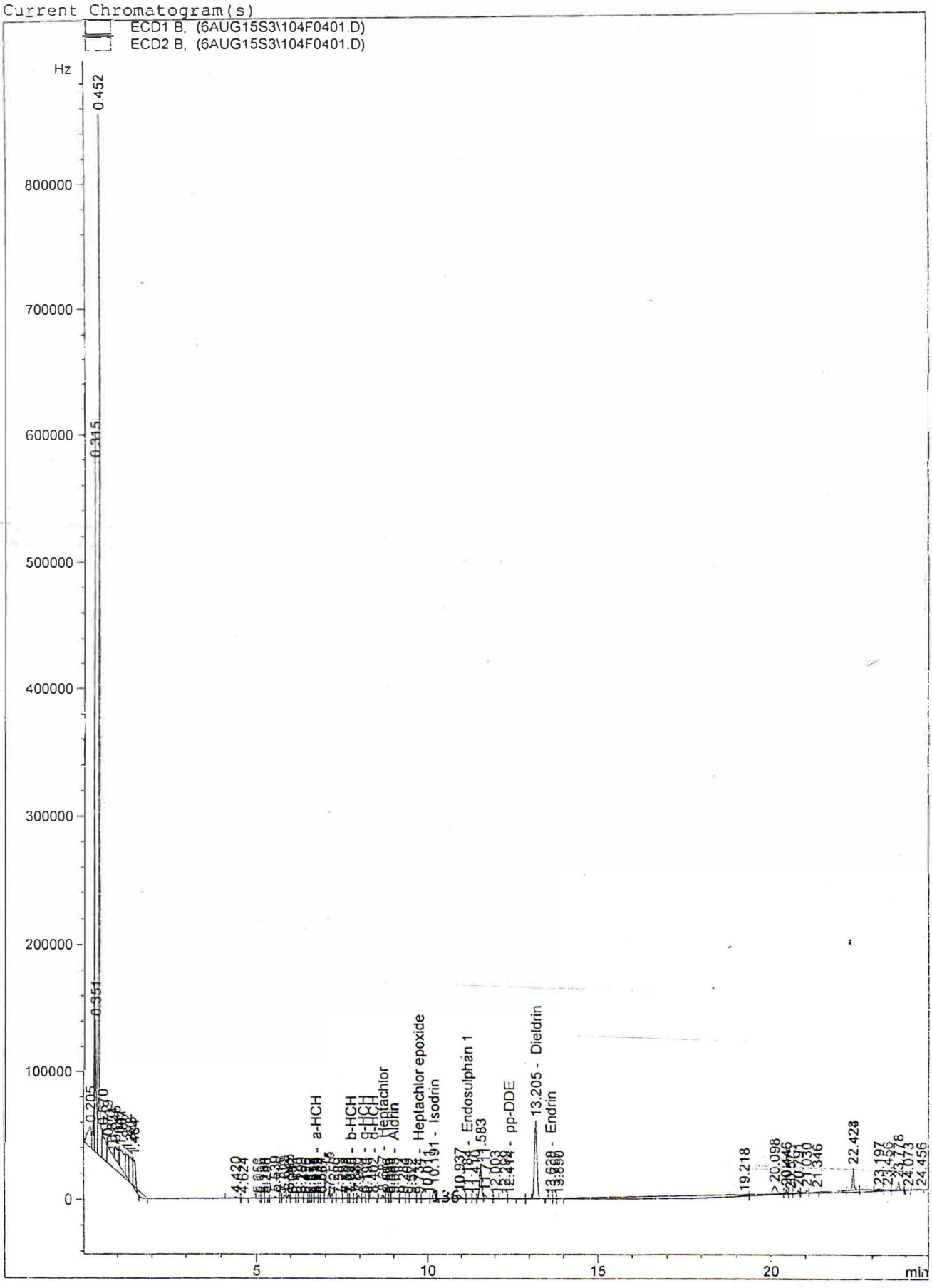


Figure A4.5:Chromatograms of samples

int of window 38: Current Chromatogram(s)



nt of window 38: Current Chromatogram(s)