ADSORPTION AND PHOTODEGRADATION OF PESTICIDE RESIDUES IN SELECTED PLANTS GROWN IN ORGANIC CONTAINER GARDEN: FOOD SECURITY PHENOMENON

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JAMES KAMAU MBUGUA

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DECLARATION

This is my original work and has never been submitted to any institution for any academic award.

JAMES KAMAU MBUGUA

156/79134/2012

DATE……………………………

SIGN…………………………………

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

SUPERVISORS

Professor G. N. KAMAU   Dr. D. MBUI

SIGN……………………   SIGN………………………...

DATE…………………....   DATE …………….................

DEDICATION

This research work is dedicated to my family for their moral and financial support during the course of this work, my friend, mentor and inspiration, Professor G.N. Kamau for his support, guidance and advice and Dr. D. Mbui for her professional advice.

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ABSTRACT

This work focuses on the fate of pesticide residues mainly; pentachlorophenol, lambda cyhalothrin, chlorothalonil and chlorpyrifos in organic container farming in soil and crop surfaces. Adsorption of pesticide residues, photo-degradation of pesticide residues by light, pesticide levels in various crops and methods of removal have been discussed.

Food insecurity in the world has led to improvement of farming methods to modern and more sustainable methods which require less rainfall, land and agricultural inputs. These methods translate to high yields and shorter time to crop maturity. Organic container gardening methods is practical in areas where land is scarce, for example in slums and therefore has been adopted by some slum dwellers. Most farmers, who practice this type of farming, grow vegetables, maize, beans and *nappier* grass in sacks, plastic bags, flower vases and plastic containers. Questionnaire administered to farmers revealed that 70% have prior knowledge of organic farming. Most of them said they did not wash their produce before use or selling. 78% of the interviewed people do not know where the produce they eat/use come from. Some farmers admitted to applying pesticides in their farms.

The adsorption phenomenon of chlorpyrifos by loam soil particles where the crops were grown in an aqueous solution was studied using a Freundlich isotherm model which assumes the adsorption/ desorption relations: $nX + S \Leftrightarrow SX_n$, $K = [SX_n]/[X]^n[S]$ and $ln[x]_{ads} = ln\,(nK') + nln[x]_e + [sx_n]_w$, where is the chemical species of interest; S is the substrate; is the adsorption/desorption equilibrium constant; is the particle-pesticide complex. The apparent adsorption equilibrium constant; $[]_{ads}$ is concentration of in adsorbed state in water suspension. $[]_e$ is the concentration of in solution at equilibrium and $[]_w$ is the pesticide adsorption site complex in the suspension at equilibrium. The amount of chlorpyrifos adsorbed was determined against variation of mass of sediment, concentration of chlorpyrifos and contact time using UV-Visible spectrophotometer at 254nm. 89-99.1% of chlorpyrifos molecules were adsorbed regardless contact time with the process equilibrating after 30 minutes. The data obtained in this study best fitted the quasi Langmuir adsorption isotherm with regression values of up to 0.992. The calculated values of the apparent K, n and ΔG were found to be 118.665, 0.244 and -11.7946kj/mol. The negative value for ΔG confirmed the fact that adsorption reaction occurs

spontaneously. Moreover, adsorption of chlorpyrifos onto suspended/dissolved sediment particles decreased with increase in mass of the substrate and variation of concentration.

Photo degradation of pentachlorophenol, lambda cyhalothrin, chlorothalonil and chlorpyrifos by sunlight, 40w, 60w, 75w and 100w light bulbs on the surface of spinach and tomatoes was also studied. The results obtained indicated that up to 84% pentachlorophenol, 71% chlorpyrifos, 72% lambda cyhalothrin and 85% chlorothalonil degraded on the surface of spinach on exposure to 100w bulb for 60 minutes. Photo-degradation of these residues was found to be dependent on temperature, time of exposure, light intensity and surface of exposure.

Analysis of pentachlorophenol, lambda cyhalothrin, chlorothalonil and chlorpyrifos on tomatoes, potatoes and spinach from organic container garden was also studied. Extraction was done using AOAC 2007.01 method without cleanup step. The samples were analyzed using reversed phase high pressure liquid chromatography. The results indicated presence of significant levels of chlorothalonil, pentachlorophenol and chlorpyrifos in spinach and high levels of PCP in both tomatoes and potatoes. Pentachlorophenol (PCP) levels exceeded CODEX limits by 26.47, 89.13 and 44.44 % in spinach, tomatoes and potatoes, respectively, while chlorothalonil and chlorpyrifos in spinach exceeded MRL levels by 20.00 and 28.57 %, respectively.

Spinach and tomatoes were washed with; 0.9% NaCl, 0.1% $NaHCO_3$, 0.001% $KMnO_4$, tap water and 0.1% acetic acid before extraction and analyzed with the UV-Vis spectrophotometer. For the washing solution treatments, 0.001 % $KMnO_4$ washing solution was found to be most effective in reducing the pesticide residues which was most probably due to the high degree in the pesticide degradation.

Key words: Pesticide Residue, Organic Container Gardening Vegetables, Quechers, Adsorption, Photo-Degradation.

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LIST OF ABBREVIATION AND ACRONYMS

AAS   - Atomic Absorption Spectroscopy

A, B and g are isotherm constants of Redlich-Peterson isotherm

ADI   - Average daily intake

ATSDR -The Agency for Toxic Substances and Disease Registry

C_0 - initial concentration of solution

C_e - concentration at equilibrium

C_{Ae} - amount adsorbed on solids at equilibrium

ECD - Electron Capture Detection

EDA - External detector adapter

FID   - Flame ionization detector

FPD -   Flame photometric detector

GC - Gas Chromatography

HPLC -   High Pressure Liquid Chromatography

K_a - adsorption equilibrium constant of Langmuir isotherm

K_F & $\Delta G°$ - Freundlich isotherm and Gibb's free energy change respectively

Kd - distribution coefficient

K_R - dimensionless separation factor

MS   -   Mass spectroscopy

MRL - Maximum residue levels

NPD -   Nitrogen phosphorus detector

n - Empirical constant of Freundlich isotherm

UNEP - United Nation environmental program

PID   -   Photo-ionization detector

ppm - parts per million

q_e & q_m - equilibrium adsorption capacity and maximum adsorption capacity respectively

QuEChERS – Quick, Easy Cheap, Effective, Rugged and Safe

SPE - Solid Phase Extraction

WHO - World Food Organization

CHAPTER ONE

1.0   INTRODUCTION

1.1   Food security in Kenya

The world's population is expected to grow from 6.8 billion people currently to 9.15 billion by 2050 (WHO, 2014). In order to guarantee that everyone in the world can be fed by the year 2050, agricultural production needs to increase by 70% (GTZ, 2010). Production of enough food for the growing population in Kenya is a great challenge. Unpredictable weather patterns, poor planning and slow adoption of modern farming methods negatively influence food security. Data from the International Food Policy Research Institute (IFPRI,) shows that food security has worsened in the last two decades. Food security is a situation in which all people, at all times, have physical, social and economic access to sufficient, safe and nutritious food which meets their dietary needs and food preferences for an active and healthy life (Kenya Food Security Steering Group, 2008). In the recent years, and especially starting from 2008, the country has been facing severe food insecurity problems. These are depicted by a high proportion of the population having no access to food in the right amounts and quality. Official estimates indicate over 10 million people are food insecure with majority of them living on food relief. Households are also incurring huge food bills due to the high food prices. Maize being staple food due to the food preferences is in short supply and most households have limited choices of other food stuffs. The current food insecurity problems in Kenya are attributed to several factors (Ministry of agriculture, 2013)**:**

Poor food distribution mechanisms: There exist in efficient mechanisms to distribute food after harvesting to low production regions and urban centers at competitive and affordable prices. The prevailing food shortages in such regions increase demand for food, pushing the prices high. In the circumstance, we have witnessed scenarios where food has been rotting in farms in high production regions in the north and central Rift Valley, while people in low food production regions of North Eastern, Coast and part of Eastern provinces are exposed to famine.

Unstructured markets: Lack of organized market systems for major food commodities has led to long and inefficient value chains, affecting the availability of food at affordable prices.

Low investment in irrigation: Over-reliance on rain-fed agriculture in the country has led to food shortages whenever we experience poor weather conditions. Irrigation has been adopted mainly for rice, horticultural crops and, only lately, maize under the Economic Stimulus Programme in Bura Irrigation Scheme in North Eastern Province.

Over-dependence on a limited number of staple foods: Many Kenyan communities grow and utilize staple foods like maize, beans, rice and wheat and their corresponding products. This has culminated in a high demand for these commodities, and at the same time portends hunger if any of them is in short supply.

Low mechanization in food production: Most farmers in Kenya are small-scale operators working holdings of less than 2.5 acres. This is due to increasing population pressure as well as expanding urbanization, both of which require more land for settlement, thus reducing the amount of available land. Mechanization is minimal in these circumstances, which actively contributes to low productivity.

Poor post-harvest management: It is estimated that over 40% of the food produced is lost across the value chain of food/agricultural commodities because of poor post-harvest management. Poor storage facilities as well as inadequate value addition equipment and skills create a shortage in the market, thus contributing to rising food prices.

The impact of food insecurity in some regions in Kenya is depicted in figure 1. The government has set policies to curb food insecurity disasters. The policies include**;** Supply related policies, price related policies, and Income related policies.

Food and nutrition security expected to improve through March 2013.
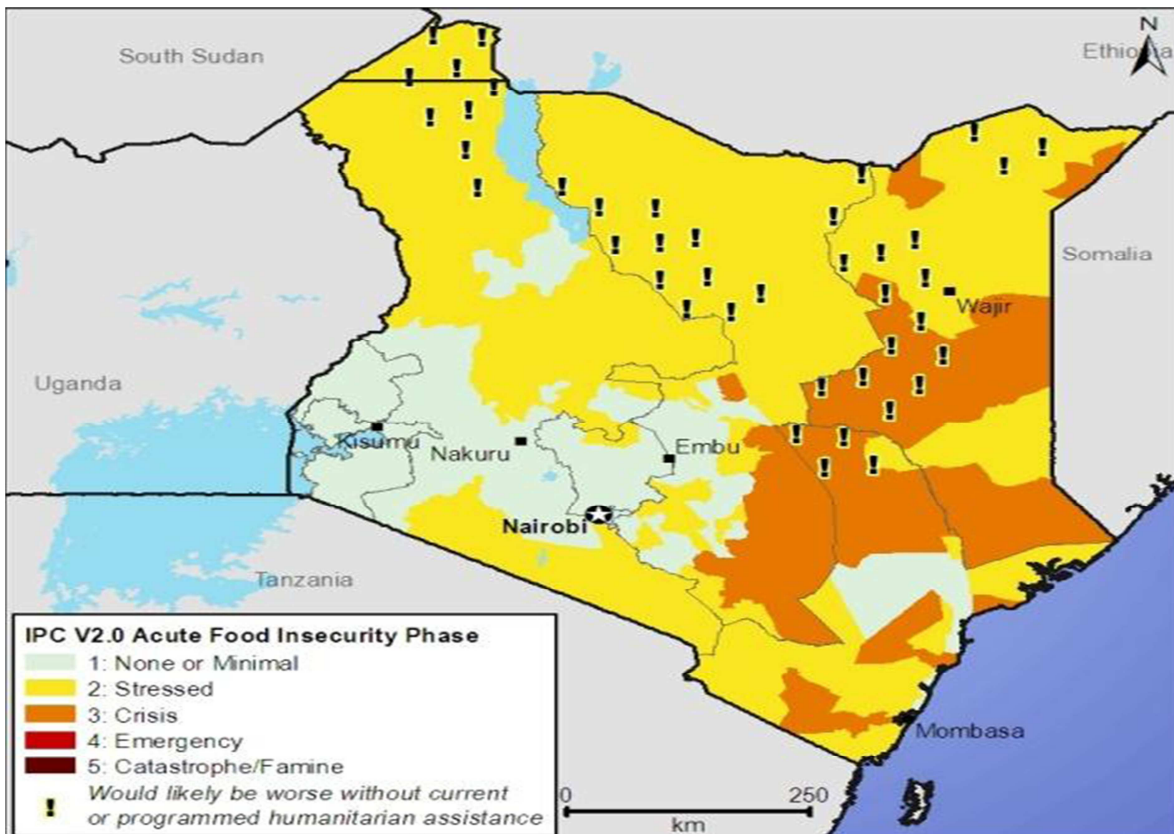
(Kenya food security outlook, Government of Kenya and world food program;

Figure 1.1: Food security outcomes, October 2012 (*source: Kenya agricultural research institute*).

1.2   Vegetables in Kenya

Vegetables are part of daily diets in many households in Kenya and a major source of vitamins, fibers and minerals essential for human growth and development. Vegetables are made up of cellulose, hemi-cellulose and pectin which give them their texture and firmness (Sobuka and Dairo, 2000). Consumption of good quality vegetables is important for better health. More often than not most consumers consider undamaged, dark green and big leaves as characteristics of good quality leafy vegetables. However, external morphology of vegetables does not guarantee un-contamination. In Kenya the most commonly consumed vegetables include; *sukumawiki*, spinach, cabbages, onions, pigweeds and tomatoes. Fruit, cereals and vegetables contamination mainly results from pesticide residues sprayed during plant growth or from irrigation using waste water and heavy metals from the

industrial and domestic wastewater and from sewage sludge applied as manure in vegetables gardens (Cited from Daily Nation DN2, November 7, 2012). With small pieces of land in the slums and cities, slums and cities dwellers have resulted to organic container gardening to ensure vegetables is part of their diet. Hence the importance of the current study aimed at determining the extent of pollution of vegetables especially the mode of contact (adsorption/desorption).

1.3 Organic container gardening

Organic gardening emphasizes soil improvement through the regular addition of organic matter, and biological and genetic diversity to manage insect and disease problems. A growing numbers of Kenyans are interested in buying and growing organic produce to reduce exposure to chemical pesticides. For most gardeners, "organic" means no chemical fertilizers or pesticides. Fortunately, it's possible to grow container vegetables organically. Mini-gardening is practical for those who do not have sufficient yard space for a huge garden. Even persons living in apartments and condominiums can grow at least a few vegetables by planting a mini garden.

1.3.1 Crops

The basic rule for deciding which crops to plant is to grow what you like to eat and what your growing conditions allow. In most cases, farmers' control of the soil, and therefore light is the most limiting factor. Most vegetables require a minimum of six hours of direct sunlight a day. Leafy vegetables (lettuce, spinach, chard and various other greens) can tolerate more shade than root crops (beets, carrots, potatoes). Fruiting crops (tomatoes, pepper) cannot thrive at all in a shady spot. It is important to grow varieties adapted to cool, cloudy climate, especially of such heat-loving crops as tomatoes and pepper.

1.3.2 Containers

Any container used for growing plants must have holes near the bottom to allow excess water to drain out. Holes should be made on the sides of containers right near the bottom, but not on the bottom itself. They should be at least 1/4 inch in diameter. If the basic need for drainage is met, any container that will hold soil is suitable for growing plants. Some commonly available cheap or free containers include: plastic or metal buckets that restaurants get vegetable oils or other foodstuffs in, plastic milk containers with the tops cut off, old leaky pails, bushel baskets or fruit boxes lined with plastic to hold

soil, plastic garbage cans, or nursery pots or flats. Terra cotta clay pots are another widely available container. When clay pots, are used, watering is done frequently, because they dry out much more quickly than plastic containers. Heavy plastic bags of varied capacity can be used, too. In Britain, tomatoes are commonly grown in soil-filled plastic bags. Generally, large plants require wider and deeper growing spaces than small plants. Large containers make more efficient use of space and serve as a heat reservoir to protect plants from freezing in winter or baking on warm summer days. But, smaller containers are easier to move and may be better for warm-season crops that you want to start inside or move to protected areas occasionally. Shallow containers, 8 to 10 inches deep, are fine for most vegetables, but they dry out faster than deeper ones. Some crops, such as tomatoes, peppers, carrots and other long-root crops require deeper containers.

Figure 1.2: Pictures of organic container garden next to a house.

1.3.3 Insects, Diseases, and Weeds

Container-grown plants are susceptible to the same insect and disease problems as any other crops. Weeds can take over potted plants, robbing crops of needed nutrients and sunlight. Fortunately, weeds are easier to control in containers than in open garden spaces. Pulling young weeds or shallow cultivation are the best controls. Herbicides are not appropriate.

1.3.4 Watering

Over-watering and under-watering are the most common problems. The water in the container is the only water the plants can get. They cannot send their roots deeper to find water. Large plants take a lot on warm days, and they must be watered often. Water does not drain in a container as easily as it may in a garden. A good light potting mix is essential for soil drainage. The best guide to whether or not a container planting needs watering is to stick a finger 2 or 3 inches into the soil and see if it is moist.

1.3.5 Fertilizer

Soilless mixes are very low in nutrients, so fertilizers are added. Initially, to each 16 gallons or 2.5cubic feet of mix, the following are added:

1 cup dolomite lime and

1 cup 5-10-10 fertilizer

In place of the 5-10-10, a "complete" organic fertilizer can be made from:

1 cup cottonseed meal or 2/3 cup blood meal and

2 cups bone meal and 1 cup kelp meal

Organic fertilizers are released slowly and will not be available to your crop as quickly as synthetic ones. This has advantage of less burning the plants from over-applications.

1.3.6 Advantages of organic container gardening

- It's perfect for all kinds of people; people with physical limitations, college students, renters, novice gardeners, and any gardener wanting to cut back, downsize, and save time. Watering and harvesting of 10 containers can be done in 10 minutes.
- There is no digging or tilling. Gardening can be done in the rain without getting muddy!
- Container gardening is virtually weed-free.
- It's inexpensive to get started. Few tools are needed.
- Helps to overcome some common gardener complaints: backyards that are too shady for tomatoes, compacted, poor quality soils and soils, contaminated with lead, persistent soil-borne

disease like Fusarium wilt of tomato.

- Temporary or permanent containers (including balcony, deck, stoop, concrete pad, or any part of your yard which means they can be moved anywhere.
- Containers can be located in a convenient place (place the tomatoes in full sun and the lettuce in partial shade.)
- Better control over growing conditions (water, sunlight, nutrients) can lead to higher yields with less work than a conventional garden (10 sq. ft. can produce 50 lbs. of fresh organic produce).
- Container gardens are easier to protect plants from weather extremes, insect pests and bigger critters.
- Vertical growth saves space and allows use of exterior walls; window boxes can be fitted to any location.

1.4   Pesticide Residues

Pesticide and/or pesticide residues are defined as any substance or mixture of substances intended for preventing, destroying, repelling or mitigating any pest, including vector of human and animal diseases, unwanted species of plant or animals causing harm or interfering with production, processing storage, transport and even marketing of food, agricultural produce, animal feedstuffs or substances. Pesticide may be administered to animals or crops to control insects, pathogens or diseases. The term pesticides includes substances intended for use for plant growth, plant regulator, defoliant or agent for thinning fruits or preventing premature fall of fruits and substances applied to crops either before or after harvest to prevent produce from deterioration during harvest or storage (Food & Agricultural Organization of United Nations 2002). There are several forms a pesticide may adopt e.g. biological, chemical substances, antimicrobial and disinfectants.

Agricultural production has been accompanied by continuous agrochemical applications. The use of pesticides is normally associated with environmental contamination and human health problems in the world, currently more than 1900 pesticide active ingredients are commercially available products and are registered for agricultural use to maximize food production for the growing population (Winteringham, 2007). Pesticides are essential in modern agricultural practices but due to their biocide activity and potential risks to consumers, presence of pesticide residues in food is a growing source of concern for general population and environment. According to Miller (2004), 98% of sprayed pesticides

and 95% of herbicides reach a different destination from the target species including air, water and soil. Pesticides and heavy metals are among the major environmental pollutants and contribute to high soils contaminations. Pesticides uses biodiversity, reduces nitrogen fixation, contributes to pollinator decline, destroy habitats and threatens endangered species. Some pests form resistance to pesticides which translate to more pesticides use or use of new pesticides (table 1). This causes ambient pollution problem (Rockets, 2007; Wells, 2007; Haefeker, 2000; Zeifssloff, 2001; Palmer et al.2007; Winteringham, 1971).
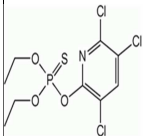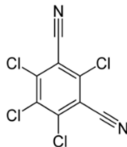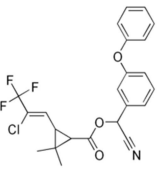
Pesticides are very dangerous to consumers, workers and close bystanders during manufacture, transport, during or after use (U.S. Environmental Protection Agency, 2007). Uncertainty exists regarding the long-term effects of low dose pesticide exposures. The WHO and UNEP estimate that each year, 3 million workers in agriculture in the developing countries experience severe poisoning from pesticides with 18,000 of these dying (Winteringham, 1971). Annually 25 million workers suffer mild pesticides poisoning (Food Additives and Contaminants, 2010). There have been many studies of farmers intended to determine health effects of occupational pesticide exposure.
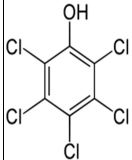
Human beings are always exposed to pesticides in the food they eat, water they use and the air they breathe. There are three main channels for pesticides in our body; dermal, respiratory and oral. This means contacts with concentrated products during mixing or use posses a great risk. The level of absorption of these contaminants depend on formulation and body part exposed. Human health risks may be caused by short term or long term exposure (table1.0).

The pesticides need to undergo extensive efficacy, environmental, and toxicological testing to be registered by governments for legal use in specified applications. The applied chemicals and/or their degradation products may remain as residues in the agricultural products, which becomes a concern for human exposure. Therefore, maximum residue levels (MRLs) (or "tolerances" in the U.S.), which limit the types and amounts of residues that can be legally present on foods, are set by regulatory bodies worldwide. In Europe, EU Council Directive 91/414/EEC describes the regulatory framework by which MRLs are set. If the farmers apply the pesticides properly on crops for which the pesticides have been registered, and appropriate harvest intervals are given, then it is very unlikely that regulatory limits will be exceeded. Unfortunately, not all farmers follow recommended legal practices, and due to the

tremendous number of pesticides and crops in production, there is a need for routine multi-residue pesticide monitoring using methods with wide analytical scope (Fernández-Alba, 2008).

Table 1.0: Selected pesticides residues

Brand Name	Chemical name	Structural formula	crops	Pests controlled	Mode of action
Dursban	Chlorpyrifos		Cabbages Onions Tomatoes beans, Flowers, ornamentals	Lepidopteron larvae, grass hoppers, army worms, cut worms, bollworms, Cutworms, aphids and termites, Ants, Leaf worm, bollworms, Aphids	Contact Stomach Vapor action
Daconil	chlorothalonil			Army worms, cut worms, bollworms, Cutworms, aphids, termites, Ants, Leaf worm and bollworms	Eye contact, inhalation, ingestion and skin contact
Karate	Lambda cyathrin		Vegetables, maize, cotton	Aphid ,Cabbage stem flea beetle ,Pollen beetles ,Rape stem weevil ,Seed weevil Termite bud weevil , Imported cabbage	Contact, stomach action, and repellent properties

				looper Diamondback moth, Cabbage armyworm, Beet semi-looper, Tomato pinworm and Green peach aphid . Sweet potato whitefly, Spider mites, aphids, American bollworm, Leaf miner	
Pentachlorophenol	pentachlorophenol		Vegetables	Ants, weevils and aphids	Contact, stomach

1.5   Photo-physical and Photochemical Processes of pesticide residues

1.5.1   Photo-physical Processes

Sunlight photolysis is highly dependent on UV absorption profiles of the pesticide, the surrounding medium, and the emission spectrum of sunlight. The energy to break chemical bonds in pesticide molecules usually ranges from 70 to 120 kcal mol^{-1}, corresponding to light at wavelengths of 250–400 nm (Watkins 1974), spectral irradiance of sunlight detected near the ground becomes important in determining the photo-degradation profiles of pesticide. By passing through the atmosphere, sunlight intensity significantly decreases to about 10% in the troposphere, and no light is transmitted at wavelengths from <290 to 295 nm, mainly due to absorption by ozone (Zepp and Cline 1977; Parlar 1990). As a result, sunlight near the ground exhibits a maximum at around 440–460 nm, and its intensity at the UV region responsible for photo-degradation of pesticide becomes approximately 5%–6% of the total intensity. There are many photo-physical pathways of sunlight absorption (Turro 1978; Roof 1982;

Parlar 1990). When a photon is subjected to a pesticide molecule, molecular excitation occurs via interaction between the electric field of a pesticide molecule and that of light at a time scale of femto seconds without a change of molecular geometry (Franck–Condon principle). Each photon can activate only one molecule in the ground state (S_0) with a certain probability to the excited singlet state (Stark–Einstein rule), and usually the lowest excited state (S_1) is involved in further photo processes. Generally, pesticide molecules exhibiting a UV-VIS absorption spectrum at >290 nm have a substituted aromatic moiety, sometimes being conjugated with the lone-pair electrons or the unsaturated bonds such as carbonyl or carbamoyl group, and hence $\pi \rightarrow \pi^*$ or $n \rightarrow \pi^*$ transition takes place upon irradiation.

There are three possible photo-physical pathways from the S_1 state: non radiative internal conversion, emission of fluorescence, and inter-system crossing to the excited triplet state (T_1). The first pathway means the relaxation from higher vibrational levels ($_10^{12}$ sec^{-1}) in the S_1 state followed by decay to a lower electronic state with the same multiplicity (106–1012 sec^{-1}). The second one is a radiative deactivation process. The fluorescence spectrum is usually close to a mirror image of that of absorption due to the Franck–Condon principle but shifted to the red. The lifetime of fluorescence is very short (nanoseconds to microseconds) due to the transition between states with the same multiplicity. The last pathway is a spin-forbidden process ($S_1 \rightarrow T_1$), followed by slow radiation less deactivation or emission of phosphorescence. The $T_1 \rightarrow S_0$ process is also spin-forbidden, and hence the lifetime of phosphorescence usually becomes an order of milliseconds to 102 sec.

The foregoing consideration can also be applied to pesticide molecules in the solid phase, but adsorption onto these media is most likely to affect the photo-physical processes. Molecular motion would be highly restricted, and interactions with these heterogeneous surfaces result in modification of their electronic states. In this case, the reflectance spectrum of a pesticide gives more useful information than an absorption spectrum, and this is described by the relationship of Schuster and Kubelka-Munk (Parlar 1984) instead of the Beer–Lambert law:

$$\mathbf{F(R_\infty) = (1 - R_\infty)2/2R_\infty = K/S}\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\mathbf{1.1}$$

The diffuse reflectance, $F(R_\infty)$, represents the radiation penetrating into the powder and resembles the usual transmission spectrum. R_∞ is the ratio of reflectance of a sample to that of a standard and thus the relative diffuse reflectance of an infinitely thick layer compared to a non-absorbing standard such as magnesium oxide; K and S are the absorption and scattering coefficients, respectively. Adsorption can produce unequal displacement of the ground- and excited-state potential curves, which would result in a different vibronic band shape. Thus, spectral changes by adsorption are characterized by a spectral shift; changes of extinction coefficient, broadening of absorption bands, and appearance of new bands (Wendlandt and Hecht 1966; Nicholls and Leermakers 1971; Parlar 1984) are based on the literature survey. Both bathochromic (red) and hypsochromic (blue) shifts on adsorption have been reported, which are considered to depend on the type of an electronic transition. It is known that a blue shift almost always occurs with $n \rightarrow \pi^*$ transition and often a red shift with $\pi \rightarrow \pi^*$ transitions (Nicholls and Leermakers 1971). In the case of the former transitions, the change of a non-polar environment to polar causes more stabilization of the ground state via hydrogen-bonding and dipole–dipole interactions than the excited state, resulting in a blue shift. For $\pi \rightarrow \pi^*$ transitions, the excited state is more stabilized by polarization in the polar environment, resulting in a red shift. The alteration of emission spectrum by adsorption is likely, but the corresponding information is limited. Villemure et al. (1986) have reported the significant increase of fluorescence intensity of paraquat when adsorbed onto clays. Fluorescence with an emission maximum of 345 nm was very weak in aqueous solution, but adsorption resulted in the increase of its intensity with a blue shift by 20 nm. The increase of intensity is most likely to stem from an inhibition of radiationless quenching by counteranion Cl– by intercalation of molecules into the interlayer of clays.

1.5.2   Photochemical Processes

Unless the energy of an excited-state molecule is lost as heat or emission of light, it causes various types of chemical reactions in the excited molecule. There are two types of photochemical reactions, well known as "direct" and "indirect" photolysis (Roof 1982; Miller and Zepp 1983). Direct photolysis means the photo-reaction proceeds by absorbing light energy, whereas indirect photolysis is defined as reaction of a ground-state molecule with the other excited molecule or photo-chemically produced reactive species. The former indirect photolysis is called photo-sensitization or quenching, and

the latter is a photo-induced reaction with a reactive oxygen species. The average rate of direct photolysis in a well-mixed system can be estimated by using the GCSOLAR program based on spectral irradiance of sunlight, absorption profiles, and quantum yield of pesticide (Leifer 1988). In contrast, when pesticide molecules exist as deposits on soil and plant surfaces, the heterogeneous micro-environment makes such estimation difficult. For example, many researchers have reported the quantum yield for pesticides in solution photolysis, but the information is very limited on solid-phase photolysis (Krieger et al. 2000; Samsonov and Pokrovskii 2001). In the case of soil photolysis, Balmer et al. (2000) introduced a model function of light attenuation in soil with diffusion of a pesticide molecule to better describe the dissipation profiles.

1.6   Pesticides in Kenya

Ochora et al., 2009-2010 found out that in Kenya, pesticides are used extensively on large farms and by parastatal organizations, which are largely concerned with export crops. The use of extremely and highly hazardous insecticides was observed (Epstein and bassein,.2003). 67% of those surveyed attested to frequent change in pesticides to combat resistant strains affecting farm produce.

Among the most commonly used pesticides were Methomex 90sp and Diazol 60ec. Insecticides were frequently used followed by herbicides and fungicides based on the crop grown and area. Farmers relied mainly on commercial sources for information about pesticides and on suppliers whose main aim is to maximize profit. This resulted in misuse of pesticide residues; inadequate personal protection equipment and consequently poor personal hygiene were inadequate. The major concern of the pesticides users is lack of gloves, nose mask and apron which were practiced by more than half of farmers. This has been reported to be a source of contaminations through skin absorption and inhalation (Berg 2001, Mathews et al., 2003, Burleigh et al., 1998 and Yildirim, 2007).

In developing countries, adequate protective clothing is neglected for reasons of discomfort and/or high cost. There are no regulations requiring farmers working with pesticides to observe specific precautions (Wilson and Tisdell 2001). Proper pesticide waste disposal is very important in controlling environmental contamination. Accidental and uncontrolled discharge of residues in the environment has been reported to be harmful (Damalasb et al., 2008) especially careless container disposal. These containers may retain unacceptable quantities of residues if not rinsed properly (Miles et al., 1983). In

other countries like Germany, USA, France, Sweden, there are policies on where to take these containers for reuse or proper disposal but in Kenya the containers are sold to dealers whose intention on containers recycles is unknown.

There is need for a comprehensive intervention to change farmers' pesticide use pattern. Both short-term and long-term measures on appropriate use of pesticides should be implemented. Limiting access to hazardous pesticides, government and farmers collaboration on usage is needed.

Knowledge alone doesn't translate to practice (Murray and Tayler, 2002). A broad variety of factors play a role in shaping farmers actual pesticides usage since they act rationally within the context of their resources and socioeconomic objectives (Rola and Pingali, 1993).

1.7   STATEMENT OF THE PROBLEM

Pesticides are essential in agriculture, both in livestock and crop production. They are widely employed to prevent and cure crop diseases as well as pest control. This has led to increased food production as well as improved livelihood in agricultural countries in the world.

Although they have many beneficial factors, poor and excess pesticide use is hazardous to life due to environmental, soil and surface water contamination as well as food intoxication. Over the years pesticide residues has been reported in food crops including vegetables, cereals and animal products. Bio-accumulation of these harmful residues has led to nervous problems, paralysis, reduced IQ and sudden death resulting from inhalation or ingestion. Neurological and gastrointestinal problems, as well as problems in the endocrine and hormonal systems have been linked to pesticides (Maluniu, Gniob, Joseluisu, Krystle et al, 2013). The risk is more pronounced in young children.

Despite the numerous risks our people are exposed to while using pesticides in their farms, pesticides application cannot be abolished as crops need to be produced. Organic farming seems to be the solution to pesticide residues contamination in farm produce since crop pest and diseases and weed control is based on biological methods as well as non-residual methods though it's very expensive and may not be practical. Many city dwellers have resolved to organic container gardening to sustain their family due to limited land resources. They spray pesticides to their crops to ensure market quality and increased produce. Without knowing how much of these harmful pesticide residues are left in the food, they offer the produce to the market to another group who cares not where and how the crop has been grown. Over

76% Kenyans do not wash these produce and use them as obtained thereby posing great health risk.(Cited from Daily nation-Zuka November 7, 2012.Germs in a bowl (Nairobi 's deadly *sukumawiki*) To be able to evaluate the effects of these contaminants, there is need to evaluate their levels of pentachlorophenol, chloropyrifos, chlorothalonil and lambda cyhalothrin in various staple crops grown by organic container gardening, their photo-degradation and adsorption in organic container garden as well as their mode of removal before consumption.

1.8   OBJECTIVES

1.8.1   Overall Objective

To determine the level of pesticide residues in specific crops grown by organic container gardening method, assess adsorption and photo-degradation levels of residues and assess possible methods of pesticide removal

1.8.2   Specific Objectives

1. To determine the level of pesticide residues in spinach, tomatoes and potatoes grown using organic container gardening and comparing them with those allowable by WHO and NEMA.

2. To study adsorption phenomenon of chlorpyrifos as applied to organic container gardening soils and determine apparent thermodynamic properties *(Assumption: adsorption of chlorothalonil, lambda cyhalothrin and pentachlorophenol have similar adsorption properties as chloropyrifos)*.

3. To fit the adsorption of chlorpyrifos data to Freundlich, Langmuir, Temkin and Redlich-Peterson adsorption isortherm models and compare the obtained thermodynamic properties.

4. To study the photo-degradation of pentachlorophenol, chlorothalonil, lambda cyhalothrin and chlorpyrifos by sunlight, 40w, 60w, 75w, and 100w bulbs.

5. To assess methods of removal of pentachlorophenol, chlorothalonil, lambda cyhalothrin and chlorpyrifos by washing with tap water, 0.9% NaCl, 0.1% NaHCO$_3$, 0.001% KMnO$_4$ and 0.1% acetic acid.

1.9   Justification

Organic container gardening especially by slum and most city dwellers is becoming more pronounced in many countries. This is due to the increased urbanization and population growth. Organic container gardening is easier to monitor, inexpensive, does not require digging or tilling. It can also be used by all kinds of people since it requires little space. To protect the crops from various diseases and pest, many farmers apply pesticides to their crops. This has increased the contamination levels in both soil and crops and thereby making human beings vulnerable due to toxic effects of these chemicals. More often than not some of these pesticides e.g. chlorpyrifos and malathion have resulted to paralysis and sudden death as many of the users do not read the prescription documents enclosed in the pesticides packet.. This study will fully describe the fate of residues in organic container garden. This will help consumers on various residue levels in order to take adequate measures before consuming sprayed produce. There is therefore need to study the levels of these pesticides from Organic container gardening produce, the contamination levels of soil due to spilled pesticides and their biodegradation under different environmental conditions in order to create awareness of pesticide levels in these crops.

<center>**CHAPTER TWO**</center>

2.0   LITERATURE REVIEW

Soil and water pollution has attracted many scientists to explore the level of pesticides contamination extent in the environment. Previous researchers have shown that bio-availability of pesticides in soils depends strongly on chemical form and binding modes (Arrebola et.al., 2003). As a result, single and sequential extraction schemes have been developed to evaluate the mobility or bioavailability of pesticides in surface water, crops, soils and sediments. Pesticide residues are known to undergo; photolysis, microbial degradation and hydrolysis on the earth surface.

2.1   Organic Container Gardening

Vegetable gardens range from mini-gardens (containers) to max-garden (acre and more). Container gardening is practical in apartments, slums and other areas where land is insufficient. Areas suitable are along fences and in fence corners, in and around flower beds, adjacent to walks and drives, near the foundation of the house, on patios, porches and balconies, and even on roof-tops. Such small-scale container culture can be both practical and ornamental if properly and imaginatively done (James 2001). Organic gardening emphasizes soil improvement through the regular addition of organic matter, and biological and genetic diversity to manage insect and disease problems. For most gardeners, "organic" means no chemical fertilizers or pesticides (Maggie et al., 2002).

A groundswell of interest in organic gardening has developed over the past few years in Kenya with the government promoting adoption of this method because of its low cost to initiate, insufficient land in cities and climatic changes. Kenya agriculture research institute has been training groups of farmers on this new farming method. Emphasis has been put in ensuring there are no chemical pesticides applied on these gardens (KARI).

2.2   Nairobi case study

Around 3 million people residing and foreign visitors in Nairobi eat vegetables (kales) on regular basis (DN2 2012). The population of city resident is expected to rise to 25 million in the next decade. This is quite a market for practicing and aspiring farmers. On estimate, there are 3700 farmers within a

20km radius in Nairobi practicing agriculture, with a 50% using poor quality water and agricultural practices. According to a research by university of Nairobi and Sweden, kales from the city contains full spectrum of disease causing organisms. Spinach, *sukumawiki*, cabbages, pigweed and tomatoes have been major accompaniment for *Ugali* a major staple food in Kenya. This is a substitute for those who cannot afford meat and due to splinted campaign by nutritionist. "The greener the vegetables, the better " has been the slogan but it should be noted that external morphology doesn't necessarily mean the most nutritious (East African Medical Journal 2012).

Vegetables are often grown on small plots, bags and plastic basins and along sewer lines due to the increasing cost of living for commercial and domestic purposes. Farmers regularly use untreated industrial water effluent for vegetables farming. For example Nairobi river water is used by city residents wherever it passes for farming, domestic and even industrial activities (East African Medical Journal 2012).

In Dandora Wastewater Treatment Plant, more than 10 acres out of 500acres is being used for vegetable farming and other agricultural activities though restricted. Water is used for irrigation while sewage sludge has been applied as manure. These waste water sources consists of thousands cubic liters of industrial and domestic effluent from million homes and over 5,000 industrial activities. A report published in East African Medical Journal says that quite a considerable number of Nairobi residents are eating highly contaminated vegetables (Ngugi et al., 2010). Researchers sampled kales grown along Athi River, Ngong and Wangige and those sold in Kawangware, Kangemi and Githurai, which markets proved the vegetables to be health hazard. They tested positive for coli forms, *e-coli, and salmonella* bacterium (Karanja et al., 2010).

Contamination by feaces and urine originating from animal and human waste disposed into water sources used for irrigation and also wrong manure use has been reported by a research conducted by Karanja et al., 2010. According to researchers from University of Nairobi, farmers were found to be using liquid slurry from a sewer line in Kibera a slum in Nairobi city while a farmer was found watering kales in soil-filled sack at her doorstep with waste water from the same sewer. These vegetables usually take short time to mature due to highly nutritious manure and the watering practices.

An earlier study by University of Nairobi and Kenyatta University carried out in Khadiha's Kibera neighborhood a slum in Nairobi city and Maili Saba along Ng'ong River, in Nairobi city a tributary of the Nairobi river basin was found to be heavily contaminated with heavy metals and germs. The contaminants were mainly found in stem and leaves and this is a health concern as leaves and stems are harvested for consumption. The soil and plant samples contained high bacterial and parasitic loads (Journal of tropical and sub-tropical agro ecosystems, Bacterial contamination of kale along the supply chain in Nairobi and its environs by Kutto et al., 2004). Water used for irrigation from Ng'ong River was blamed for heavy metal and germs. An earlier study on kales by the same group in Nairobi had indicated the presence of heavy metals, pesticide residues and fertilizers residues in the samples (Kutto et al., 2004).

2.3   Factors Controlling Photolysis on Plant Surfaces

2.3.1   Environmental Factors

A number of factors such as meteorological conditions, formulation type, sprayer characteristics, and affinity of plant surface to formulation are considered to determine the amount of pesticide attached to the surface as well as ground cover and canopy thickness of plants (Willis and McDowell 1987). Zongmao and Haibin (1997) extensively investigated factors controlling dissipation from tea plant surfaces for 16 pesticides. Photo-degradation was found to be one of the most important factors in dissipation process except for evaporation, rainfall elution, and growth dilution. Both photolysis and rainfall elution were found to play a great role in the dissipation of diflubenzuron in a conifer forest (Rodriguez et al. 2001). Garau et al. (2002) examined the extent of pesticide loss from a cellulose membrane due to evaporation and co-distillation in the presence or absence of underlying water. They found that; evaporation, co-distillation, and photolysis all contributed to dissipation of pyrimethanil and cyprodinil with slight variation, and the controlling factor for azoxystrobin and fludioxinil was found to be photolysis. The existence of tomato fruit wax mostly retarded evaporation and co-distillation of pesticides and exhibited a screening effect against sunlight. For a pesticide with higher vapor pressure and less photo-reactivity, volatilization loss became predominant in dissipation as observed for chloropyrifos (Meikle et al. 1983). In addition to these factors, penetration of pesticide into cuticle and biotic metabolism therein are also considered important (Bentson 1990; Katagi and Mikami 2000)

2.3.2   Illumination Conditions

Spectral irradiance of sunlight at the plant surface is most important to understand the effect of photolysis. Because the window glass used in ordinary greenhouses absorbs a considerable amount of light in the UV-B region (280–320 nm), this filtering effect is likely to reduce the overlap between the solar emission spectrum and the near-UV absorption spectrum of many pesticides (Kleier 1994). Garau et al. 2002 realized that photo-degradation was measurably reduced by covering the Petri dish as a model of the greenhouse window. Fukushima et al. (2003) examined the photolysis of 14C-fenitrothion on tomato fruit in a greenhouse with a ceiling made of quartz or borosilicate glass. The intensity of sunlight at <360 nm was significantly reduced in the borosilicate glass greenhouse, and neither the corresponding oxon nor the *S*-isomer generated by photolysis in the quartz greenhouse was detected. Furthermore, transmission through the greenhouse window is also known to be reduced by glass pollution, and its extent was larger in the shorter wavelength region (Van Koot and Dijkhuizen 1968). The structure of greenhouse changing the intensity and spectral irradiance of the transmitted sunlight is known to give insignificant effect on dissipation of chlorpyrifos. Type of crop and season were the most relevant factors (Martı́nez Vidal et al. 1998), similar results were obtained for fenpropathrin (Martı́nez Galera et al. 1997), while degradation of methomyl was found to depend on the type of greenhouse (Gil Garcia et al. 1997).

Degradation of pesticides in the greenhouse or outdoors was compared by Cabras et al. 1990 to examine the controlling factors in foliar dissipation. They applied carb to lettuce in a greenhouse and in field. No significant differences occurred in half-lives of total carbamates, but greater formation of these degradation products was observed in the field. The comparative degradation study of parathion using a growth chamber, greenhouse, and open field with and without motorized covering exhibited more formation of the oxon and *S*-isomer in the field (Joiner and Baetcke 1973). Based on these results, the experimental conditions of growing plants should be monitored and compared with the real environment as much as possible to investigate the most realistic pesticide photo-degradation process.

2.3.3   Effect of Formulation

Pesticide formulation is composed of an active ingredient, carrier such as clay, surfactants as wetting and spreading agents, non-evaporating viscous stickers, humectants, and penetrating agents such

as crop oils (Hazen 2000). These additives which have hydrophobic and hydrophilic parts provided a very complex medium for photolysis of pesticides. Their aromatic moiety becomes a possible photo-sensitizer or quencher (Nutahara and Murai 1984; Thomas and Harrison 1990). Baker et al. (1983) investigated extensively the changing nature of epicuticular waxes on the impact of several formulations containing ^{14}C-labeled pesticide using scanning electron microscopy, X-ray analysis, and micro-autoradiography.

2.3.4 Pesticide on the Leaf

Leaves are covered with protective cuticles that function by decreasing water loss and protecting the plant from infection by various pathogens. The cuticle is a complex structure consisting of a pectin layer that binds the cutin to the epidermal cell walls and a layer of epicuticular wax on the outside, this structure is known to depend on plant species (McFarlane 1995; Bianchi 1995). When the stomata are open, gas molecules can diffuse in and out and interact with a large hydrophilic area of water-covered mesophyll cells. Most pesticides are hydrophobic molecules, and thus the large lipid-covered surface of leaves (cuticles) forms an ideal sink for accumulation of pesticides. The fine structure of the wax layer greatly differs between plant species and is morphologically classified by using light microscopy into four main forms: needles, rods, granular layers and films (Baker 1982). Use of the electron microscope has revealed that the aerial surfaces of all higher plants carry a partial or continuous coverage of amorphous wax and that formation of crystalline wax is frequently superimposed on amorphous layers. Penetration through these wax regions and the underlying cutin layer has been extensively studied, for example, by using the diffusion cell method (Scho¨nherr and Riederer 1989). Radiant energy of sunlight is considered to interact with the leaf structure by absorption and scattering. Sunlight is reflected and scattered by hairs, leaf pubescence, and the glaucous leaf surface, and a portion of the light enters into the leaf (Robberecht and Caldwell 1980; Holmes and Keiller 2002). This light is critically reflected internally at the cell walls in the intercellular space as a result of the difference of refractive index between air and water in tissues (Gates et al. 1965). Pesticides by foliar application are considered to distribute mainly on the epicuticular wax layer, but a portion may enter into the plant directly through stomata opening or diffusion; thus, depth and spectral distribution of penetrated sunlight would be important when photo-degradation is considered. Many studies have been conducted to investigate this

using a fiber optic probe (Vogelmann and Bjo¨rn 1984). About 90% of the penetrating monochromatic light (310 nm) was attenuated within the initial one third of the leaf (100–150 μm) of *Brassica napus* L., mostly at the epidermal cells; polychromatic radiation (280–320 nm) exhibited a relatively uniform spectral distribution within the leaf (Bornman and Vogelmann 1991; Cen and Bornman 1993). UV-B radiation was found to reach the epidermis and mesophyll in other measurements for this leaf (Alenius et al. 1995). Day et al. (1994) measured UV absorption spectra and the epidermal transmittance spectra at 280–350 nm of foliage from 42 plant species and demonstrated that some flavonoids act as a UV-absorbing agent. These observations imply that pesticide molecules in the leaf can absorb some part of the radiation energy of sunlight irrespective of their location, and chromophores in leaf tissue can also affect their photo-degradation.

2.4   PESTICIDES RESIDUES

Thousands of pesticides of different chemical class e.g organochlorine, organophosphate, pyrethroids, carbamates are used for agricultural and nonagricultural purposes throughout the world today.

2.4.0   Method of analysis

Widespread use of pesticides has led to development of multi-residue analytical methods for analyzing environmental and food samples which may contain residues of pesticides, pesticide transformation products and other environmental toxicants.

Various analytical methods have been applied in determination of the level of pesticide residue in vegetables and other crops. The choice of method used depends mainly on the availability of the equipment, type of crop analyzed, efficiency, accuracy, cost and sensitivity. Some of the methods are briefly highlighted below:

2.4.1   Spectrometric methods

2.4.1.1 UV-visible spectrophotometry

The use of UV-visible spectroscopy as a primary method of determination in organo-phosphorus (OP) pesticide residue work has declined to an insignificant level in recent years (W P Cochrane.,1981). This method is based upon the measurement of the absorbency of the pesticides or derivative pesticides. For example, Turner has described a procedure using 4- (4-nitro-benzy1)-pyridine as a

spectrophotometric reagent for most OP pesticides, which is sensitive to low microgram amounts. The direct utility of a UV-visible spectroscopic method in pesticides residue analysis is limited because of its relatively low sensitivity and selectivity.

2.4.1.2 Infrared spectroscopy

The sensitivity of infrared instrumentation and techniques have increased in the past years with the improvement of instrumentation, the use of infrared spectroscopy in pesticide residue work is limited to conditions where microgram or greater amounts of pesticides are present in the sample matrix. Infrared spectroscopy is very useful for confirming the identity of a pesticide residue (Ruzicka et al., 1973) . Gore et al have compiled the infrared and UV spectra of 76 pesticides for this purpose. The use of infrared spectrometry as a selective detector in chromatographic methods appears to have good potential for future applications in the pesticide area (Ram et al., 1982).

2.4.1.3 Chemiluminescence spectroscopy

A highly sensitive method for the determination of some alkyl phosphates based upon chemiluminescence has been developed by Fritsch (1980). The alkyl-phosphate is reacted with sodium perborate ($NaBO_4$) or hydrogen peroxide (H_2O_2) to produce a peroxophosphate, which then oxidizes an amine such as luminol in alkaline medium to produce the chemiluminescence. This method can also be employed for spectrophotometric or fluorometric measurement when the appropriate amine is substituted for the luminol. This method has only been applied to phosphorus-containing nerve gases thus far, but application to OP pesticides appears to be possible (Fritsch et al., 1978).

2.4.2   Electrochemical methods

2.4.2.1 Polarography

The polarographic determination of OP pesticides in foodstuffs has been reviewed (Davidek.,1980). Electroanalytical techniques are applicable to those OP pesticides which possess nitro- (e.g. parathion) or other electrochemically-active substituents. It appears that sulphur-containing OP pesticides may be determinable after a hydrolysis step at a mercury electrode in an anodic mode (Davidek., 1980) . However, a chromatographic separation step would be desirable to reduce interferences from the sample matrix. A piezoelectric crystal detector which is sensitive to OP pesticides

has been reported (Schiede et al., 1972) . This detector, although useful for gas-phase determinations, requires further development before it can be more widely applied.

2.4.3 Enzymatic methods

The inhibition of acetyl-cholinesterase activity can be useful for the sensitive detection of OP pesticides (Alsen et al., 1981), especially when used in conjunction with chromatographic separation (Hormann et al., 1975), by using a substrate with favorable spectrophotometric or fluorometric measurement properties. However, when used by itself, this technique is non-selective in that no information as to the identity of the inhibitor is provided, and thus its use is possible only under very carefully controlled conditions. The high cost and the difficulty in maintaining consistent activities of the enzyme preparation are important limitations to be considered. The determination of blood acetyl-cholinesterase activity in farm workers is a good indicator of OP pesticides (Toy., 1976), but, again, the identity of the pesticides must be determined by other means.

2.4.4 Chromatographic methods

2.4.4.1 Thin layer chromatography

Considerable advances in the separating power of thin layer chromatography (TLC) have been made in recent years through improvement in sample application and plate technology. After separation, the plates are normally dried and scanned with a densitometer or fluorometer to quantitate the components. In many cases, including the trace-level determination of OP compounds, treatment of the plate with a development reagent is necessary to obtain adequate sensitivity and selectivity. Because the utility of TLC in OP pesticide residue analysis depends to a large extent upon the detection scheme, considerable effort has been made to devise sensitive and selective spray reagents for OP pesticides (Ebing., 1970). For example 4-(4-nitrobenzy1)-pyridine reacts with most OP compounds and results in a blue spot which can be quantified to low microgram amounts. The formation of hetero poly-molybdenum blue can be employed as a TLC detection technique after in-situ mineralization of the OP compound on the plate (Murty et al., 1980). The detection limits are greater than 0.1 microgram using this technique (Murty et al., 1980). Inhibition of acetyl-cholinesterase provides a more sensitive detection scheme (Bhasar et al., 1981). While TLC is used to a limited extent as a primary method for

pesticide residue analysis (Hulpke et al,., 1980), it is especially valuable for screening (Ambrus et al., 1981) and confirmation of identity (Hulpke et al., 1980; Biros 1971).

2.4.4.2 Gas chromatography

Numerous papers have been written about gas-liquid chromatography since the first description by James and Martin (James et al., 1952). It has been applied most frequently in modern analytical chemistry and has been used to solve a wide range of problems in medical, biological, and environmental science areas, as well as having industrial applications. In spite of developments in spectroscopy and liquid chromatography, gas chromatography remains the most widely used separation tool in analytical chemistry and is likely to remain so for the foreseeable future. This technique has more resolving power and sensitivity for the separation and determination of volatile organic compounds than any other method in analytical chemistry. The limitations of the technique are established primarily by the thermal stability of the samples and chromatographic substrate (Cochrane et al., 1976).

Generally, one is restricted to an upper temperature of around 400 °C and a molecular weight of less than 1000, although higher temperatures have been used and larger molecular weight samples have been separated in a few instances (Cochrane et al., 1976). In gas chromatography, the sample or some convenient derivative samples must be thermally stable at the temperature required for volatilization. Gas chromatography has become the method of choice for pesticide residue analysis because of the excellent sensitivity and selectivity afforded by the specialized detectors which are available (Aue 1975; Cochrane et al., 1976; Ewing 1987; Willard et al., 1988). The detectors which are the most useful in the determination of op pesticides are the flame photometric detector (FPD), thermionic detector (TID) and the electron capture detector (ECD). The FPD operates by combusting the OP compounds in a hydrogen-rich medium, which results in the formation of electronically-excited HPO. The luminescence is monitored at 526 nm. The FPD is very reliable and achieves detection limits of the order of 100 pg or less for most OP compounds (Aue., 1975). The TID (also known as the alkali flame ionization detector) is sensitive to both nitrogen and phosphorus. The TID is about ten-fold more sensitive than the FPD but is less reliable (Cochrane et al.,1976) • The ECD is the second most widely used ionization detector (23.84) and it owes much of its popularity to its unsurpassed sensitivity to a wide range of toxic and biologically-active compounds. Consequently, it is widely used in trace analysis for the determination of pesticides, herbicides, industrial chemicals in the environment, drugs and other biologically active

compounds in biological fluids, and for the determination of the fate of the volatile organic compounds in the upper atmosphere.

These highly selective and sensitive detectors have enabled the development of GC methods for the residue-level determination of OP pesticides which have excellent signal-to-noise ratios at legally important limits. These methods have been applied in determination of OP pesticide residues in fruit and vegetables. Their clean-up procedure consisted of extraction, evaporation and column adsorption prior to GC analysis. The selectivity of the TID and FPD permits the use of a less rigorous sample clean-up procedure than is the case for highly sensitive detectors such as the electron capture detector (Aue., 1975). Figure 2 highlight the various components of GC instruments.
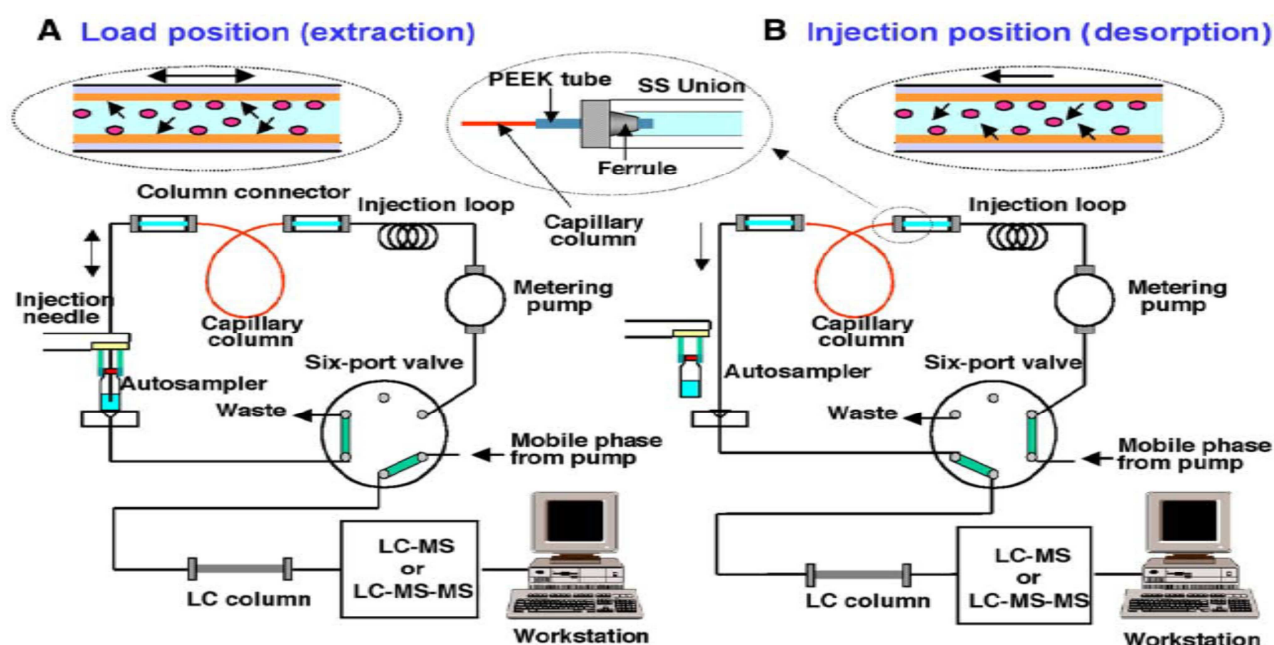
Figure 2.1: Schematic flow chart of gas chromatography instrument (Shimadzu Corporation)

There are six selective detectors readily available which can cover the requirements for the GC analysis of the majority of op pesticides. No one detector can fulfill all residue requirements and often there is a choice between several detectors for a given application. However, the percentage of published paper on FPD, TID, ECD, MS, FID and NPD GC detectors are 30.89, 16.26, 14.63, 10.57, 9.76 and 4.88, respectively and the publishing percentage for LC-MS is 13.01. (Aue., 1975).

2.4.4.3 Gas chromatography-mass spectrometry

A chromatogram gives quantitative (peak height or area), and qualitative (retention parameter) information of the components in a mixture. The identification is based solely on retention. Even for a simple system, a peak at a certain position in a chromatogram may be a substance other than the one anticipated (two or more components may elute exactly with the same retention). The identity can be firmly established, when the selectivity of information from the chromatogram is very good. Spectroscopic techniques provide a rich source of qualitative information with high degree of certainty, but have, two practical limitations: It is often difficult to extract quantitative information from the signals, and pure or single-component samples are required. Thus chromatographic and spectroscopic techniques provide complementary information about the complexity and the concentration of components in the sample. Their tandem operation provides more information about a sample than the sum of the information gathered by either instrument independently (Zlatkis et al., 1977), thus combinations of this type can be particularly fruitful. The coupling of gas chromatography with mass spectrometry was at the forefront of the development of combined analytical instrumentation "hyphenated" systems.

The principal hyphenated techniques are gas chromatography interfaced with mass spectrometry (GC-MS), Fourier transform infrared spectrometry (GC-FTIR), and optical emission spectroscopy (GC-OES); liquid chromatography combined with mass spectrometry (LC-MS), Fourier transform infrared spectrometry (LC-FTIR), and nuclear magnetic resonance spectroscopy (LC-NMR).

GC-MS has had an impact on OP pesticide residue analysis (Vander et al., 1975). The technique of selected ion monitoring (SIM) can be operated at very high sensitivity for a mass selective chromatographic detector, and selectivity is obtained because the mass is a substance specific parameter. Selected ion monitoring is now a widely used technique in the area of biomedical (Millard., 1978; Garland et al., 1981; Halpen., 1981) and environmental analysis.

2.4.4.4 High performance liquid chromatography (HPLC)

The role of high performance liquid chromatography in pesticide residue analysis has been assessed by several authors (Sieper et al., 1973; Lawrence 1980; Moye 1981; Hankset al., 1981) and its potential is beginning to be more fully explored. It is generally accepted that HPLC detectors must be

improved for applications to pesticide residue analysis to be fruitful. Since the first reported use of HPLC in an OP pesticide residue determination in 1971 (Henry et al., 1971), a number of publications have appeared in this area and are highlighted below to illustrate the approaches towards detection which have been taken. Most workers have employed UV detection of the intact pesticides. For example, Wilson and Bushway (1981) determined Azinphos-methyl and its Oxon analogue in fruit and vegetables using reversed-phase HPLC with UV detection set at 224 nm. The precision at the lower level of determination (0.16 ppm) was less than 4%. A further example of the use of a UV detector in the determination of op pesticide residues by HPLC is from the work of Cabras et al.,1981 Several OP pesticides were determined in grapes by simple extraction with benzene, evaporating to dryness and reconstituting the extract in the mobile phase, followed by injection. Detection was accomplished at 221 nm and detection limits were in the range 0.04 to 0.2 ppm. UV detection is applicable only to those pesticides which possess suitable chromophoric substituent and which are in relatively uncomplicated sample matrices. The UV detection sensitivities for most OP pesticides have been compiled (Hoodless et al., 1978; Lawrence 1980). Figure 2.1 represent various parts of HPLC instrument.
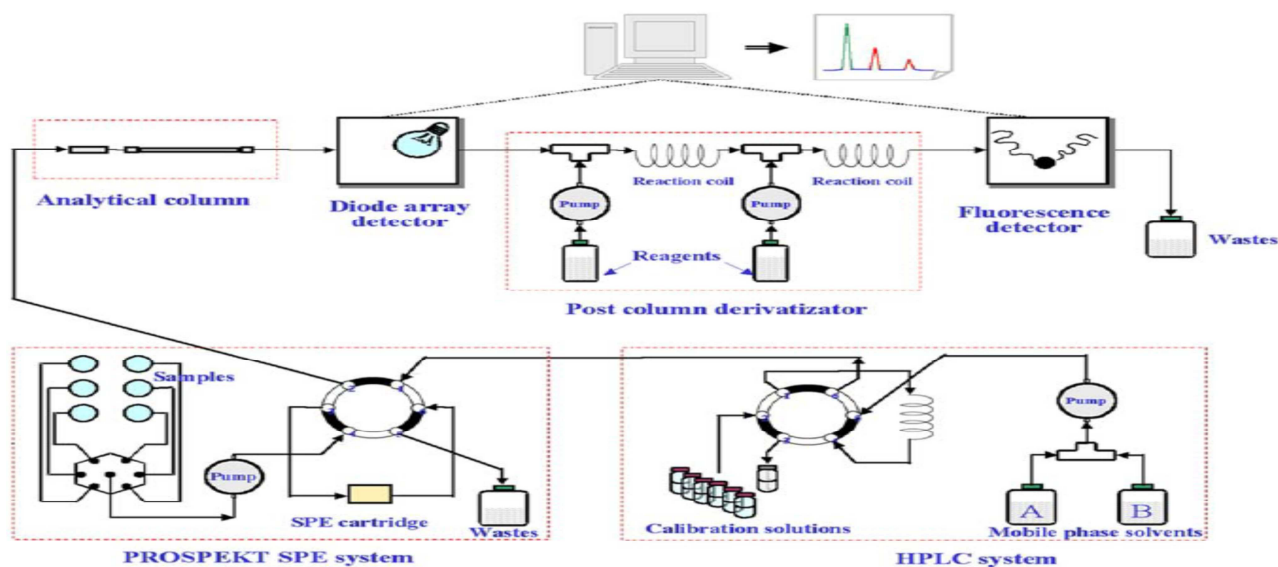
Figure 2.2: Schematic flow chart of HPLC instrument (Shimadzu Corporation)

Several attempts have been made to devise alternative detectors for OP compounds which are more sensitive and selective. Acetyl cholinesterase inhibition has been used to detect OP pesticides by coupling HPLC with an auto analyzer. The combination of HPLC (Ott,., 1977) and the auto analyzer has

also been exploited by Att in connection with the determination of parathion and it's Oxon in dust samples. A diazotization reaction was used, but low detection limits were not achieved. The specificity of the auto analyzer detection allowed confirmation of the UV response. Some workers have attempted to adapt flame spectroscopy techniques for detectors in liquid chromatography. McGuf fin and Novotny have demonstrated the potential of an FPD used in conjunction with micro-column HPLC. A detection limit of 2 ng was achieved. Chester examined the problem of quenching of HPO emission by organic solvents and found that alcohols and acetone did not cause quenching at moderate concentrations, but acetonitrile caused nearly complete quenching at concentrations above 10%. Szalonti has used flame ionization detector for his study of the normal-phase HPLC of op pesticides. Graphite furnace atomic absorption has been employed for the detection of op compounds (Tittarelly et al., 1981) , but further work is needed on this technique to increase sensitivity and to decrease processing time. Cope investigated a rotating molecular emission cavity detector for possible applications to OP compounds, but found it to be relatively insensitive and noisy. The use of electrochemical detectors in the determination of pesticide residues by HPLC has been reviewed. Electrochemical detector is expected to be applicable only to the few OP pesticides whose structural features permit it, i.e. samples component is electro-activity (e.g. parathion).The applicability of on-line LC-MS was demonstrated by Parker and co-workers for OP pesticides. The use of liquid chromatography-mass spectrometry (LC-MS) has been successfully applied by several workers in recent years (Lee et al., 1986; Henion et al., 1985; Niessen 1986;). The work of Barcelo was aimed at expanding the general insight into the usefulness of PCI and NCI and chloride-enhanced negative ionisation (ClENI) for the determination of some organophosphorus compounds in on-line LC-MS. OP pesticides are thermally-labile, such as trichlorfon, or polar such as parathion. Because of these problems, the analysis of organophosphorus pesticides and their corresponding metabolites has been carried out by LC using UV and selective MS detectors (Barcelo et al., 1988; Farran et al., 1988).

The on-line combination of liquid chromatography-mass spectrometry (LC-MS) plays an important role in environmental organic analysis as compared with gas chromatography-mass spectrometry (GC-MS) (Barcelo et al,., 1988)

2.4.4.5 Combined HPLC-MS

The introduction of HPLC has made it possible to separate and also identify highly polar compounds which are not gas chromatographable. If compared with capillary GC, HPLC has two major disadvantages. 1) There are only a few detection methods: ultraviolet (UV), fluorescence and electrochemical detection. 2) The separation efficiency of HPLC is considerably poorer than that of capillary GC. This lower performance increases the probability that several components co-elute and cannot be differentiated by non-specific detectors. A mass spectrometer represents a specific and at the same time sensitive detector. Unfortunately HPLC-MS coupling is far more difficult than GC-MS coupling as the vacuum system of the mass spectrometer has to handle up to 2 ml min -1 of solvent (corresponding to - 2000 ml min -1 gas), and soft ionization methods are required for polar compounds (Barcelo et al., 1988).

2.5   Sample Extraction and Clean Up

QuEChERS is the acronym of Quick, Easy, Cheap, Effective, Rugged and Safe, a matrix dispersive solid-phase extraction mainly based on the PSA bulk adsorbent, is carried out on the acetonitrile extract of the crop to be analyzed. The bulk adsorbent is dispersed after extraction, some salts are added (magnesium sulphate, sodium chloride, and a citrate buffer), and then the extract can be directly analyzed after centrifugation. The QuEChERS extraction followed by LC–MS–MS assay is, therefore, a valuable tool for pesticide residues analysis, allowing good analytical performance and high throughput. The QuEChERS sample preparation procedure consists of extraction, clean-up, and solvent exchange. The solvent exchange provides a final solvent that is more amenable to split less injection. Care must be taken to adequately and thoroughly homogenize the sample. When analyzing grains such as rice, water must be added during the homogenization step and taken into consideration in the final calculations of spikes and standards. To perform liquid-liquid extraction requires water. Also, the water helps mix the rice during the homogenization step. The most common techniques in modern multi-residue target pesticide analysis are gas chromatography and liquid chromatography coupled to mass spectrometry (GC-MS; LC-MS) and/or tandem mass spectrometry (GC-MS/MS; LC-MS/MS) with triple qua-druple mass analyzers (Valenzuela, A. I.,et.al,2001).

2.6 Theory of adsorption phenomenon

Burchill et al., (1981) proposed an adsorption model of binary dilute solution, based on kinetics of chlorpyrifos on loam soil. This model is adopted in this work. The apparent thermodynamic data is also calculated. The characteristic adsorption of pesticide by soils or sediments can be described by the Freundlich empirical isotherm (Graham-Bryce, 1981):

$$C_{ads} = k_F C_e^n ....(1)$$

Where the Freundlich constant, C_{ads} is concentration (mg/ml) of the pesticide adsorbed by the soil/sediment in a colloidal solution and C_e is the concentration of the pesticide in the solution (mg/ml) at equilibrium (Hance, 1965; Bowman and Sans, 1977). By taking batches of known mass of sediments (adsorbent), and mixing with solutions of known initial concentration of pesticides, followed by shaking and the equilibration, the concentration of the adsorbed pesticide (C_{ads}) and that at equilibrium (Ce) can be estimated. The Freundlich factor is a constant for a given system and therefore may be used to compare the degree of adsorption of different solutes onto various sediments. On the other hand, n is regarded as a measure of adsorption non-linearity between solution solute concentration and adsorption.

The adsorption process of pesticides on soils was reviewed by Burchill et al., (1981). They attested that several factors need to be considered in conducting adsorption studies. They include; kinetics and energies involved nature of interactions between the solute and the adsorbents and initial and equilibrium conditions.

In order to obtain the adsorption/desorption, equilibrium, thermodynamic and kinetic data, there is need to come up with a functional adsorption/desorption equilibrium model, from which the apparent equilibrium constant and kinetic information can be calculated. Assuming that the adsorption of pesticide solute by the colloidal/sediment or both particles occurs during the shaking period, implying when the sediment is in suspension, then the adsorption/desorption equilibrium can be described as follows [Seungman et. al., 2005]:

$$nX + S \Leftrightarrow SX_n ....(2)$$
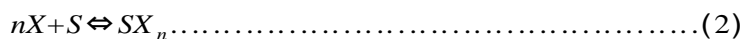
$$K = [SX_n]/[X]^n[S] \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots (3)$$

On re-arrangement:

$$[SX_n] = K[X]^n[S] \dots \dots \dots \dots \dots \dots \dots \dots \dots (4)$$

Where X is the pesticide molecule of interest; S is the adsorbent/substrate or adsorption site on the sediment or colloidal particle in solution and K is the adsorption/desorption equilibrium constant. SX_n is the particle-pesticide adsorption complex n is the number of molecules adsorbed. Also, one notes that S is a solid whose mass is very large compared to that of the solute. Therefore, the $[S]$ can customarily be taken to be unity thereby reducing equation 4 to:

$$[SX_n] = K[X]^n \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots (5)$$

And on taking logs we have:

$$\log[SX_n] = \log K + n \log[X] \dots \dots \dots \dots \dots \dots (6)$$

It means, since equation (6) is linear, the value of K can be obtained from the slope and intercept of the $\log[SX_n]$ versus $\log[X]$ plots respectively. In addition, the standard Gibbs free energy of activation ΔG, can be estimated by use of the conventional equation:

$$K = e^{-\Delta G/RT} \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots (7)$$

Considering the assumption that the adsorption of chlorpyrifos by colloidal and/or soil particles occurs during the shaking (suspended particles) and also that all the adsorbed pesticide goes to the sediment on settling, then the concentration of pesticide adsorbed to the suspended particles $[X]_{ads}$ can be obtained using equation 8 below:

$$[X]_{ads} = [X]_i - [X]_e \dots \dots \dots \dots \dots \dots \dots \dots \dots (8)$$

Where $[X]_i$ represents the initial pesticide concentration before a known mass of sediments is added, and $[X]_e$ is the equilibrium pesticide concentration. Also, agitation facilitates the settling down of the sediments and thus the separation of dissolved and adsorbed pesticides. Since n molecules of pesticide are associated with a single adsorption site, then [SX_n] is given by:

$$[SX_n] = \ln([X]_i - [X]_e) \dots\dots\dots\dots\dots\dots\dots(9)$$

$$[SX_n] = \ln[X]_{ads} \dots\dots\dots\dots\dots\dots\dots\dots\dots(10)$$

Nomura and Hilton (1977) and later Zaranyika et. al., (1993), demonstrated the existence of a colloidal bound fraction when a pesticide is shaken with water containing sediment. They also showed that the colloidal bound fraction in suspension after settling was significantly small compared to the bound fraction in the sediment thus justifying the assumption made regarding the determination of $[SX_n]$ using $[X]_{ads}$ above. $[SX_n]$ is the concentration of the colloidal bound fraction in suspension at settling equilibrium, since not all the pesticide is adsorbed. Therefore, on modifying equation 10 to show the total adsorbed pesticide we have:

$$[X]_{ads} = nK'([X]_e + [SX_n]_w)^n \dots\dots\dots\dots\dots\dots\dots(11)$$

where K' is the apparent adsorption equilibrium constant and $[SX_n]_w$ is the concentration of the colloidal bound fraction in suspension at settling equilibrium. On taking logarithm equation 11 yields a linear expression:

$$\ln[X]_{ads} = \ln(nK') + n\ln([X]_e + [SX_n]_w) \dots\dots\dots\dots\dots\dots(12)$$

Assuming that equilibrium exists between the colloidal bound fraction in the sediment and that in the suspension, then equation 2 becomes:

$$nX + S \leftrightarrow (SX_n)_w \leftrightarrow (SX_n)_{se\,dim\,ent} \dots\dots\dots\dots\dots\dots(13)$$
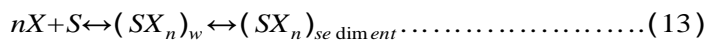
It is apparent from equation 13 that a steady state exists with respect to $[SX_n]_w$ at settling equilibrium. Moreover, a plot of $\ln[X]_{ads}$ versus $\ln([X]_e + [SX_n]_w)$ in equation 12 will not affect the value n in equations 6 and 10, but will affect the value of nK. Therefore, the value of K obtained is not a true equilibrium constant, but rather an apparent equilibrium constant (K').

2.7 Pesticides removal

Various simple home based methods have been studied for pesticides removal. According to Mathew et al., 2000) tamarind water and vinegar are best suited to remove pesticides from vegetables.

The authors used a majority of pesticides available in the market -- rated red (extreme), yellow (high) and blue (moderate) according to toxicity levels, for the tests. "Tamarind water and vinegar have been reported to be effective in removing the pesticide residue (up to 95%), especially in spinach, curry leaves, chillies, lady's finger, snake gourds and brinjals that were contaminated with heavy doses of pesticides." Chemical solutions have also been employed in pesticide residues removal. They include; Acidic, alkaline, ozone and neutral solutions.

Solutions of NaOH, acetic acid, potassium dichromate and soap are used as decontaminating agents. Dipping of fruits in NaOH solution removed 50 to 60 percent surface residues of pyrethroids compared to 40 to 50 percent removal by hydrolytic degradation with NaOH and a detergent solution removed 50 to 60 percent residues (Awasthi et al ., 1983). Ozone because of its powerful oxidizing property is effectively applied in drinking water and waste water treatment. Recently some scientists found that certain pesticides like 2, 4-dichlorophenoxyacetic acid, carbofuran, phorate, chlorophenylurea, can readily be degraded in aqueous solution by ozone (Benitez et al., 2002; Brillas et al., 2003). Ozonation is a safe and promising process for the removal of pesticides from aqueous solution and vegetable surface under domestic conditions. Tap water treatment along with ozonated water treatments significantly reduced the pesticide residues on vegetables, as compared to no-wash treatment (Walter et al., 1998).

Sodium chloride solution is largely used to decontaminate the pesticide residues from different fruits and vegetables. There are several studies (et al., 1999; Powell et al., 1970; Fahey et al., 1969; Zohair et al., 2001) to prove the efficacy of salt water washing for dislodging the pesticides from fruits and vegetable surfaces. In these studies, samples of chopped fruits and vegetables were put in a beaker containing 5 and 10 percent NaCl solution for 15 minutes. The samples were gently rubbed by hand in salt solution and water was decanted. Twenty eight to 93 percent reductions in organochlorines and 100 percent organophoshates removal were achieved by using 5 and 10 percent NaCl solution (Wheeler 2002). The percentage reduction in pesticide residues increases with the gradual increase in concentration of solutions (Ismail et al., 1993; Abou-Arab et al., 1999). NaCl with 2, 4, 6, 8 and 10 percent solution caused 20 to 90 percent reduction in pesticide residues. Similarly 18 to 65 percent loss in pesticide residues was reported by Soliman (2001) by using 2, 4, 6, 8 and 10 percent acetic acid solution.

Soaking of contaminated vegetables in acidic solution like citric acid, ascorbic acid, acetic acid and hydrogen peroxide at a concentration of 5 and 10 percent for 10 minutes indicated significant reduction of pesticide residues (Desmarchelier et al., 1988). Acidic solutions give more pesticide dissipation than neutral and alkaline solutions (Farrow et al., 1966). The acidic solutions of 5 and 10 percent eliminated pesticide residues completely while, citric and ascorbic acid solutions of 5 and 10 percent eliminated pesticide residues up to 80 percent (Wheeler et al., 2002). Some other scientists (Soliman et al., 1999; Powell et al., 1970; Fahey et al., 1969) also reported that partial removal of residues was affected by the washing operation (water and/or acetic acid, sodium chloride).

The current study was focused on determination of various levels of pesticides residues in vegetables and other crops grown by organic container gardening, adsorption of chlorpyrifos by loam soil, washing contaminated vegetables with potassium permanganate, hydrogen peroxide, sodium chloride, sodium hydrogen carbonate and acetic acid and photo-degradation of PCP, chlorothalonil, chlorpyrifos and lambda cyhalothrin by sunlight, 40w, 60w, 75w and 100w bulbs.

CHAPTER THREE

3.0   METHODOLOGY AND INSTRUMENTATION

Analysis of pesticide residues in crop, soil adsorption study, residues removal and photo-degradation phenomenon involved the use of the following:

3.1   Reagents

Pesticides standard (lambda cyhalothrin, chlorothalonil, chlorpyrifos and pentachlorophenol) were obtained from Dr. Esterphester, Germany.

Acetone, Ethyl acetate, 1% Acetic Acid, Acetonitrile from sigma Adrich and were used as received.

Distilled water, Sodium Acetate, Anhydrous Magnesium Sulfate, Concentrated nitric acid, Sulphuric acid, Potassium permanganate, Sodium hydrogen carbonate, Sodium chloride were from Kobian chemical distributers, Nairobi and were used as received.

Ms excel 2007, Libre calc, and Minitab 16 software was used for data analysis.

3.2   Instrumentation

UV-Visible spectroscopy, High pressure liquid chromatography instruments were from shimadzu Kyoto in Japan

Centrifuge, Blender (Eleketa) and Analytical balance were also used in this work.

3.3   Organic container gardening Data collection

Organic container garden data was collected by means of structured questionnaire (appendix 2) for information on crop grown, type of containers used, pest diseases, pesticides used and washing methods and consumers. Data was collected in Kikuyu, Kibera and KARI which was representative of organic farming in the country. Collected data was then analyzed using Minitab 16 and Microsoft office excel 2007 and presented using charts, tables and graphs.

3.4   Soil Fertility Analysis

1. Available nutrient elements (P, K, Na, Ca, Mg and Mn): Mehlich Double Acid Method (Tran, T. S. et al,., 1993, Mehlich, A. 1953)

The oven - dry soil samples were extracted in a 1:5 ratio (w/v) with a mixture of 0.1 N HCl from Kobian distributors and 0.025 N H_2SO_4 (Simard et al,. 1993).

Elements such as Na, Ca and K were determined with a flame photometer and P, Mg and Mn were analysed using calorimetrically method (Mehlich,. 1953).

2. Total organic carbon: Calorimetric method (Gislason et al., 2005)

All organic C in the soil sample was oxidized by acidified dichromate at 150^0C for 30minutes to ensure complete oxidation. Barium chloride was added to the cool digests. After mixing thoroughly digests are allowed to stand overnight. The concentrations were directly read on the spectrophotometer at 600 nm.

3. Total nitrogen: Kjeldahl method (Persson et al,. 2008)

Soil samples were digested with concentrated sulphuric acid containing potassium sulphate, selenium and copper sulphate hydrated at approximately 350^0C. Total N is determined by distillation followed by titration with H_2SO_4.

4. Soil pH (1:1 soil-water)

Soil pH was determined in a 1:1 (w/v) soil-water suspension using a pH meter.

5. Available trace elements (Fe, Zn & Cu): Extraction with 0.1 M HCl (Yang et al,.,2005)

The oven - dry soil samples are extracted in a 1:10 ratio (w/v) with 0.1 M HCl. The elements were determined using an atomic absorption flame emission spectrophotometer (AAS).

6. Cation Exchange Capacity (CEC) pH 7.0 and Exchangeable Ca, Mg, K and Na

The soil sample was leached with 1N ammonium acetate buffered at pH 7. The leachate was analyzed for exchangeable Ca, Mg, K and Na. The sample was further leached with 1N KCl, and the leachate is used for the determination of the CEC. Elements such as Na and K were are determined with a flame

photometer and Ca and Mg with AAS (atomic absorption spectrophotometer). CEC is determined by distillation followed by titration with 0.01MHCl (Carroll et al,.1959,Turner et al,.1966).

3.5   Organic Container Gardening

Recommended seeds (Kales, spinach, tomatoes, cabbages, carrots, beans, peas and potatoes) were obtained from the dealers. They were planted in different plastic basins in a pattern shown in figure 3.2 to a fully treated manure soil whose pesticide residues content was known. Drip irrigation was administered daily. Measures were put in place so that the crops would not be interfered with. Pesticides were sprayed as per plant specialist advice. A control organic garden was also set up, where no pesticide was administered. Figure 3.1 illustrates the organic garden plan.
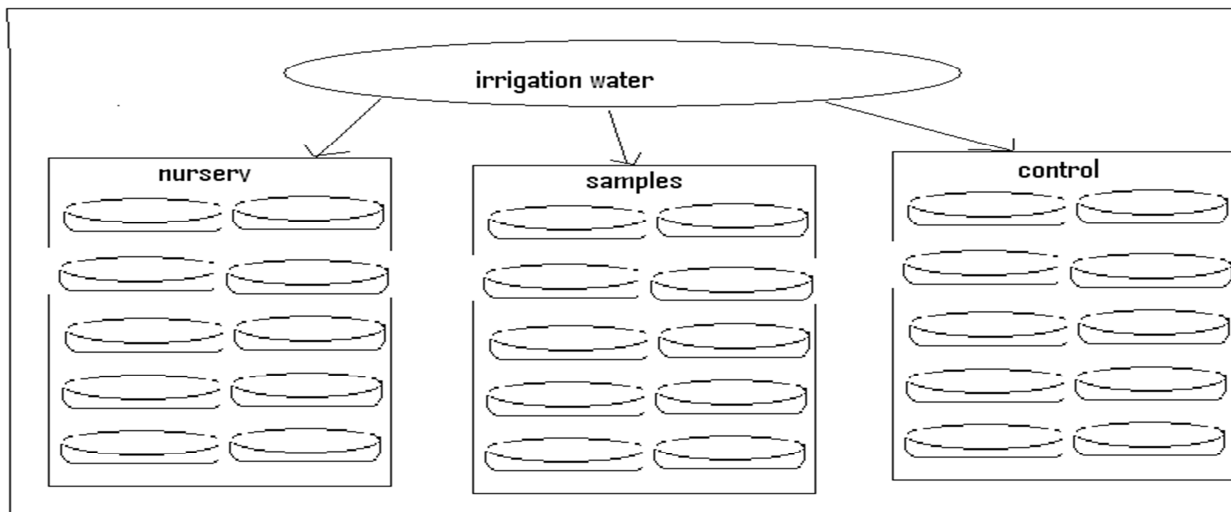
Figure 3.1: Organic container garden plan

In the figures 3.2 below, the pictures were taken at two levels of plant growth. Crops were planted in containers, cement bags and sacks and place on elevated stands (figure 3.2).

(a)   (b)

Figure 3.2: Pictures of organic garden showing crops at different levels of growth.

3.6   Sampling and pretreatment

The level of pesticide residues was assessed in spinach, potatoes and tomatoes 14 days after pesticides application. The samples to be analyzed were harvested, packed in well ventilated and labeled plastic bags, taken to the laboratory and stored at 4^0C before being extracted for analysis.

3.7   Pesticides Residue Analysis

3.7.1   Solutions and Standards preparation

Standard pesticide mix of 10 ppm stock solutions was prepared in 0.1 % acetic acid in acetonitrile. Calibration curve standard solutions (0.2, 0.4, 0.8, 1, 2, 4, 8 and 10 ppm) were prepared from 2 and 10 µg/mL solutions in acetonitrile containing 0.1 % acetic acid by serial dilution. System suitability was tested by running a 10 and 100ppm standard solution. Lambda cyhalothrin, pentachlorophenol, chlorpyrifos and chlorothalonil were used as internal standards.

3.7.2 HPLC conditions

The residues levels were determined using Shimadzu Corporation Kyoto Japan HPLC: Pcbm-20A prominence bus module fitted with spd-20A prominence UV visible detector, lc-20at prominence LC and cto-10-AS Vp Shimadzu column oven was used for identification and quantification of pesticide residues in crop. Separation was performed on reverse phase Luna C18 column. Samples were injected manually through Rheodyne injector. The detector was connected to a computer for data processing. The working conditions were; 20µl injection volume. The mobile phase was acetonitrile: water (80:20) ; flow rate was 0.5-1 ml per minute and the wavelength of the UV-VIS detector was fixed at 254 nm for residual analysis for all the pentachlorophenol, chlorpyrifos, chlorothalonil and lambda cyhalothrin. The run time was 20 minutes.

3.7.3 Recovery analysis

Pesticide free samples of spinach, potatoes and tomatoes were harvested from the organic container garden where no pesticide residue had been applied. The samples were spiked with known concentration of standard solutions of 10, 40, and 100 ppm for pentachlorophenol, chlorpyrifos, chlorothalonil and lambda cyhalothrin. The samples were extracted using QUECHERS AOAC 2007 method (Anastassiades et al., 2007) without the cleanup part and detection made to determine the percentage recovery.

Tomatoes, potatoes and spinach were chopped into 1-3 cm pieces, homogenized with a kitchen blender and placed into a zip-lock bag, and stored in a -4°C freezer before analysis.15 g of pretreated sample was weighed in a 50 mL centrifuge tube. Three sets of samples were spiked at 10ppm, 40ppm and 100 ppm stock solution using 1ml of stock solution. An aliquot of 15 mL of 1 % acetic acid in ACN was added to the samples and 1ml of pentachlorophenol, chlorothalonil, lambda cyhalothrin and chlorpyrifos were added as internal standards.6.0 g MgSO4 and 1.5 g NaOAc was dispensed into each tube. The tubes were first shaken by hand for 1 minute and then centrifuged at 3500 rpm for 2 minutes. The aliquot was filtered through A42 Whatman filter paper and analyzed with HPLC with UV-Visible detector at 254nm.

3.8   Adsorption study

Solutions of standard pesticides standards in acetone in the concentration range 0-100 ppm were prepared. Each of the 20, 40, 60, 80, 100 ppm solutions prepared was scanned using the UV-Vis spectrophotometer on a wavelength range 200-800nm. The resultant absorbance curves was made and further used to determine the levels of adsorbed pesticides.

In order to demonstrate the existence of the adsorption/desorption equilibrium, 0.1, 0.5, 1.0, 1.5 and 2.0g of the dried sediment were shaken with 10ml of 2mg of pesticide aqueous solution for 60 minutes in an orbital shaker. The soil samples were then allowed to settle for 72 hrs, after which the water phase was decanted, and then filtered through Whatman A40 filter paper. The concentration of pesticides in the clear aqueous solution was determined by UV-Visible spectrophotometer. In order to determine the values of n and, 0.5g of the dried sediment was shaken with 10ml distilled water spiked with 10, 20, 30, 40 and 50mg/ml level of pesticides. Each of the samples in quadruplicate was shaken for 15, 30, 45 and 60 minutes using an orbital shaker. The concentration of the pesticide in clear solution was determined with UV-Visible by reading the absorbance and using calibration curve to determine the concentration. The apparent thermodynamic properties were determined by making regression line using SSPS or Minitab 15/16 software.

3.9   Removing pesticide residues

Washing of pesticides contaminated residues was carried out as follows:

3.9.1   Washing solutions preparation

All washing solution treatments were prepared from the ingredients available in common household kitchen. These consisted of 0.9% $NaCl$, 0.1% $NaHCO_3$, 0.001% $KMnO_4$ and 0.1% acetic acid (5% Distilled vinegar), distilled water was used as control and diluents for all the solution treatments. All washing solutions were freshly prepared. The reagents were obtained from school equipment and chemical supplies in Nairobi.

3.9.2 Studies on degradation of pentachlorophenol, chlorothalonil, lambda cyhalothrin and chlorpyrifos in washing solutions

The standard pesticides were diluted with distilled water according to the product label recommendation to the concentration of 100ppm active ingredient. The pesticides were mixed with the washing solutions in 1:9 ratios and allowed to stand for 15 min. Then 0.5 ml of the mixture was taken and extracted immediately. The concentration of the pesticides was determined as outlined above to determine the effect of the washing solutions on the pesticide degradation.

3.9.3 Studies on reduction and dissolution of pentachlorophenol, chlorothalonil, lambda cyhalothrin and chlorpyrifos in washing solutions

Vegetable samples were harvested from Organic container garden. The samples were equally divided into 20 sub samples of about 2.0g by hand and each was soaked in 100ppm pentachlorophenol, chlorothalonil, lambda cyhalothrin and chlorpyrifos in washing solution for 5 min to simulate the deposition of pesticides on them. The treated samples were then air-dried for 1 hour in the shade. Samples from each pesticide treated produce were analyzed for the pesticides. Each of the samples left was then divided into five groups assigned for the specific washing solution tests. The pesticide-treated samples were soaked in the washing solutions for 15 min, with the initial 15s gentle rotation by hand. This is believed to mimic actual household vegetable washing procedure. Following the washing process, the vegetable samples were picked up and air-dried for 1 hr.

3.9.4 Sample extraction

The pesticides were extracted from the treated-samples and after-wash sample solutions using the procedure of QUECHERS AOAC 2007.01 method without clean up described above and the extracts analyzed using UV-visible spectrophotometer.

3.10 Photo-degradation

Five set of spinach leaves and tomatoes were placed in a petri dish. 0.01g each of lambda cyhalothrin, chlorothalonil, chlorpyrifos and pentachlorophenol were dissolved in analytical grade acetone to make 1000ppm solution each. 2ml of each pesticide standard solution was spread on the

spinach and tomatoes surface. Acetone was allowed to evaporate for 1 minute. The set was then exposed to sunlight, 40w, 60w, 75w and 100w bulbs which were enclosed in a container to prevent light loss for 4 hours. An empty petri dish which had been spiked with the above standards was also set in each case. Temperature from each container was also recorded.

After four hours, the samples were allowed to stabilize for 24 hours before washing with 10ml acetone for chlorothalonil, lambda cyhalothrin, chlorpyrifos, and pentachlorophenol. The extracts were then analyzed for the pesticide levels using UV-Visible spectrometer at 340nm for chlorothaloni, chlorpyrifos and pentachlorophenol and 254 nm for lambda cyhalothrin. The amount of residue left after exposure was determined.

To study the effect of time on the rate of degradation of these pesticide residues, 5cm by 5cm of spinach leaf was cut and dipped in 100ppm standard solution of chlorothaloni, chlorpyrifos, pentachlorophenol and lambda cyhalothrin prepared in acetone for 2 minutes. Figures 3.3 indicate the experimental setup for the photo-degradation experiments.

Figure 3.3: Schematic illustration of photo-degradation experiment setup.

The leaves were placed in a petridish and acetone allowed to evaporate in air for 1 minute. The set was then placed in a plastic basin where the setups were exposed to sunlight, 40w, 60w, 75w and 100w bulbs for 10, 20, 30 and 60 minutes. The set up was removed and washed with 5ml acetone and then residue concentration analyzed with UV-Visible spectrophotometer.

CHAPTER FOUR

4.0 RESULTS AND DISCUSSION

The results obtained for organic farmer's survey, adsorption of chlorpyrifos by loam soil photo-degradation of pesticide residues, analysis of pesticides level and methods of removal are discussed.

4.1 Organic farming survey

A survey was carried out among organic farmers in KARI, Kibera and Kikuyu areas of Nairobi city as a representative of organic farming to determine the extent of organic farming in the city and whether, how and which pesticides are used in these areas. Kibera is a slum area and therefore less land is available for growing vegetables, KARI is source of information for organic farmers and therefore it was the reference point while Kikuyu has the largest number of recently trained organic farmers. The survey was to give an overview on what is happening in the field. This was conducted using structured questionnaire, attached in the appendixA2. The results are given below: twenty seven organic farmers from Kikuyu and 3 from Kibera were interviewed. Organic farming specialist from Kenya agricultural research institute was interviewed to give guidance on organic farming. When the farmers were asked on the crop they grew in their organic gardens, 56% grew spinach while 57% grew kales. The graph in figure 4.1 shows different crops usually grown by farmer in their organic gardens.
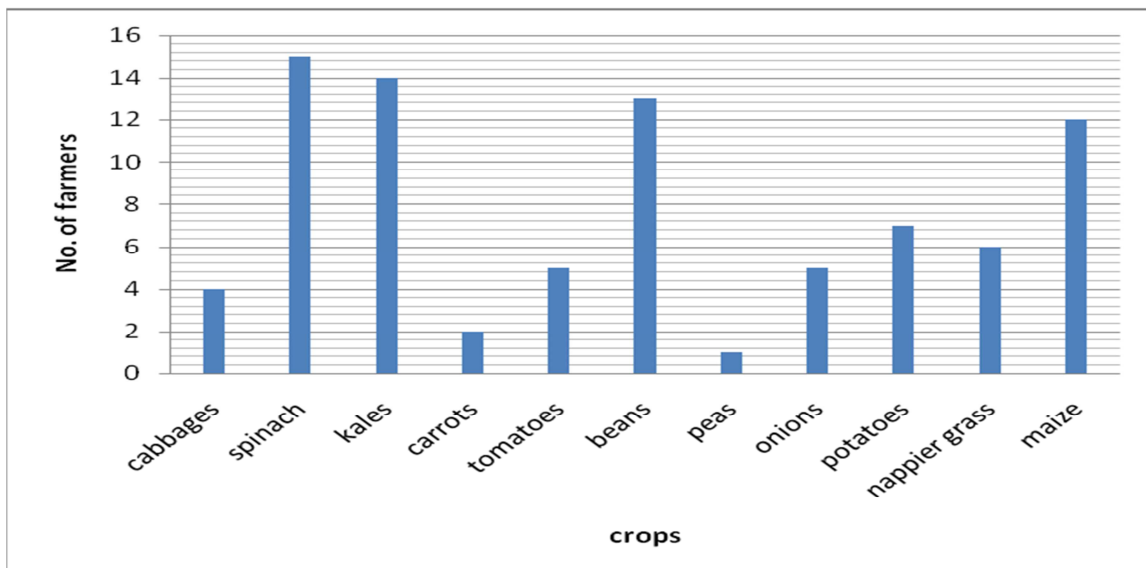
Figure 4.1: A graph of no. of farmers versus type of crop grown.

Spinach and kales grow fast and have ready market. This is the reason they are highly grown. Farmers also grow nappier grass in their organic garden since it can be irrigated with any type of water including soapy water.

Organic farmers grow their crops in different type of containers as shown in the graph below (Figure 4.2) including; plastic bags, sacks, flower beds, plastic buckets among others:
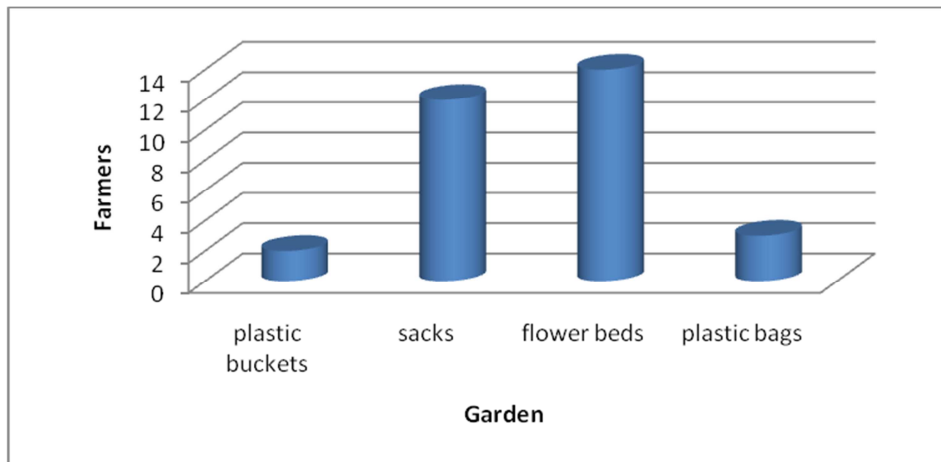
Figure 4.2: A graph of the number of farmers versus type of garden.

Flower beds are cheap to construct and hold more crops compared to others. Sacks are cheap and readily available since most of the interviewed farmers also practice livestock farming.
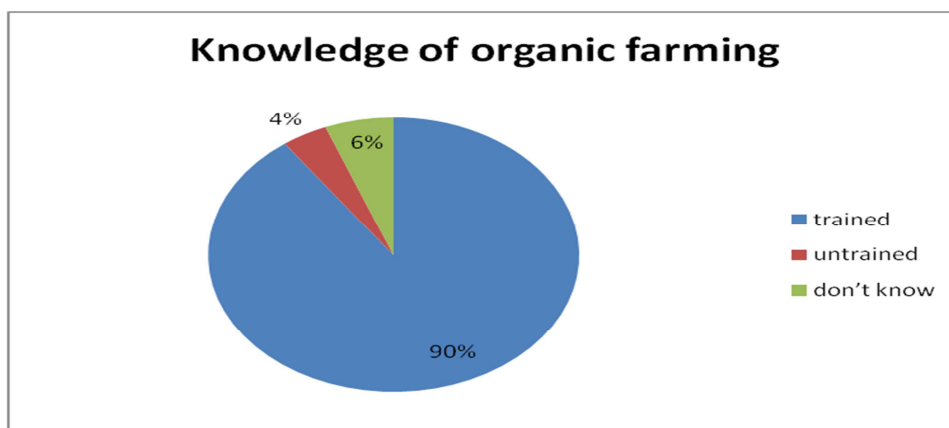
Figure 4.3: A pie-chart of farmer's knowledge on organic farming

90% of the interviewed farmers know what organic container gardening is and have prior knowledge on this farming method (figure 4.3). 4% practice organic container gardening with no prior knowledge. Most of the interviewed farmers are members of the group which is being trained by the government on this gardening method.

The crops are often attacked by pests e.g. cutworms, moths and spider mites. Among the diseases that affect these crops include wilting diseases. Most farmers reported that they do not use pesticides since organic farming doesn't support chemical usage. Some farmers reported use of dursban,radozim, perl mancizebs, metalaxyl, benalaxy, radomil, karate, master galvanized, sulcop, culprit, caffaro, tata master and daconil. Pesticides use is widely used in cabbages and tomatoes in green house farming. Those who use these chemicals reported to harvest the crops after hours, days and others as recommended by plant specialist.

The graph below (figure 4.4) indicates where the products harvested from organic container garden are used:
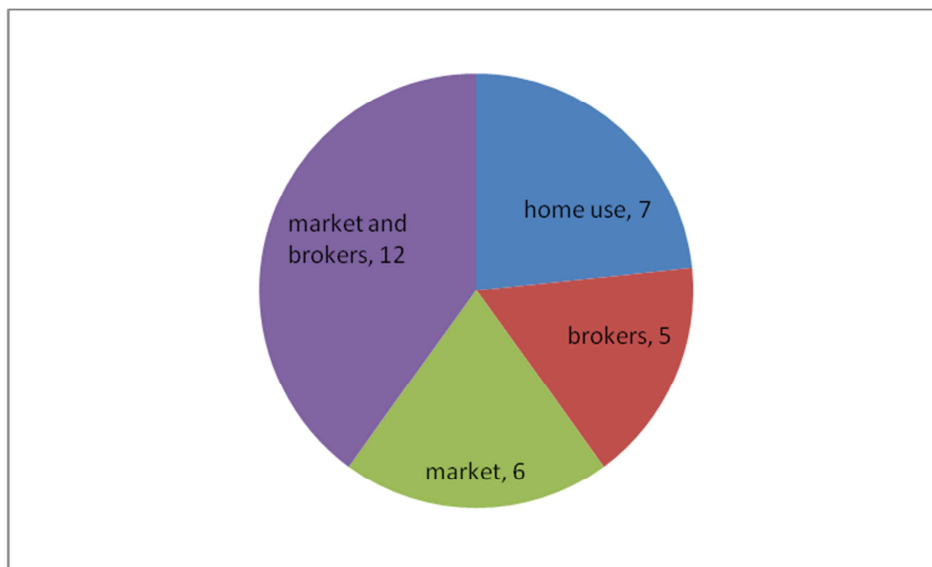
Figure 4.4: A chart of where organic produce are used.

After harvest, washing the produce before use or even offering to the market was surveyed. 98% said they wash the produce while 2% said they do not wash. Those who said yes; wash their produce in

water. 98% said they don't think most consumers know how the produce are grown while 2% said they think they know how the produce are grown and even get to the market.

The farmers gave the following advantages of organic farming: easy to manage, little space required, less labor, no chemical use, more yield per unit area and healthy produce.

4.2   Soil analysis

The properties of Limuru loam soil where the plants used in this study were grown are shown in the table 4.1 below:

Table 4.1: Properties of loam soil where plants were grown.

Profile	Properties	Profile	Properties
Soil depth cm	Top	Calcium milli-equivalent(me)%	44.4
Soil pH-H$_2$O (1:2.5)	6.5	Magnesium me%	3.1
Elect. Cond. ms/cm	0.3	Potassium me%	1.5
Carbon %	2.7	Sodium me%	3.6
Sand %	40	Sum me%	52.6
Silt %	40	Base %	100+
Clay %	20	ESP	14.4
Texture Class	L	Total nitrogen %	0.25
Cat. Exch. Capacity. me%	24.8	Phosphorus ppm	44
Zinc ppm	62.9	Iron ppm	96.2
Copper ppm	1.22	*me is milli-equivalent*	

4.3 ADSORPTION

The adsorption of chlorpyrifos by loam soil used for organic container gardening was studied and the results analyzed by using various adsorption isotherm models. The results are discussed below:

4.3.1 Calibration curve

Standard solutions were prepared using 99.9% standard chlorpyrifos in analytical grade acetone. Shimadzu UV-Vis spectrophotometer was used to obtain the absorbance from which calibration curve was plot. The standard solutions were scanned from 250nm to 400nm and figure 4.5 obtained.
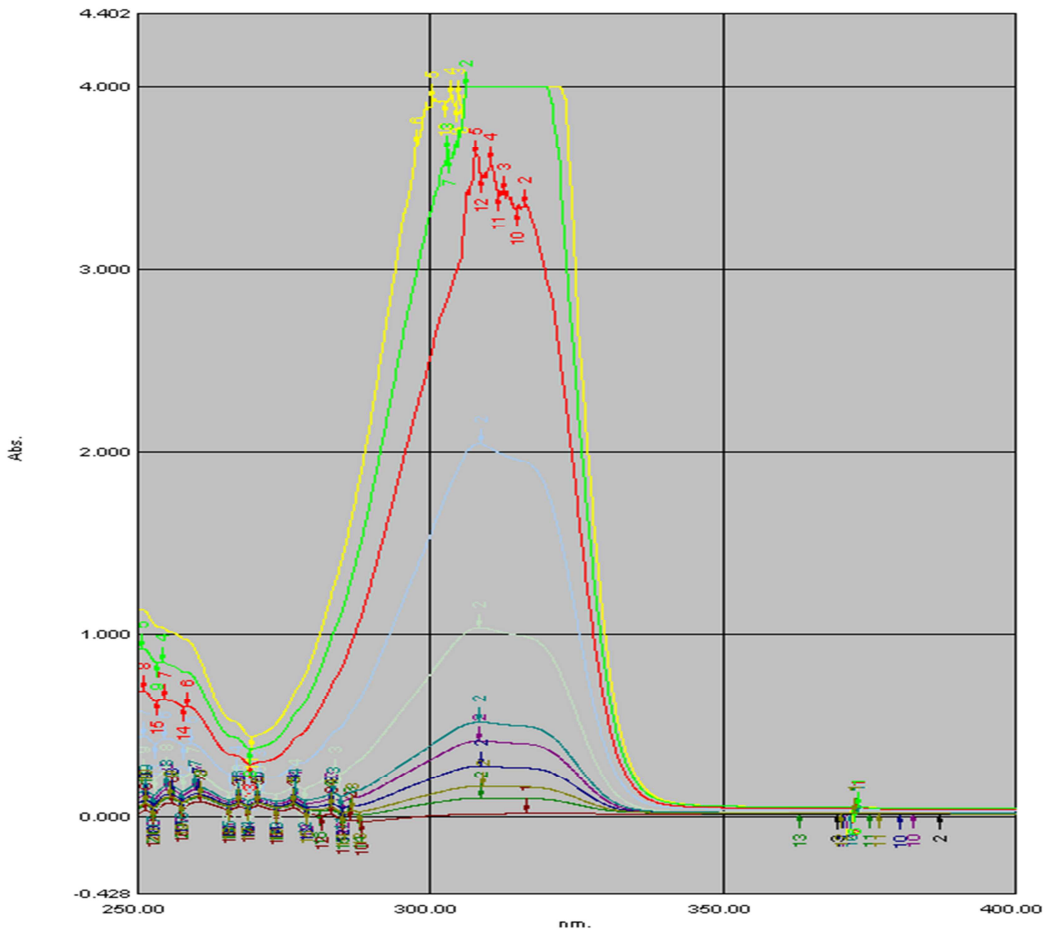
Figure 4.5: UV scans for chlorpyrifos pesticide

Concentration scans using UV-Visible at wavelength range of 250 to 400nm yielded a lambda maximum at 308nm. When the photometric scan was done at this wavelength; the results obtained were

used to plot the calibration curve in a plot of absorbance versus concentration. The curve obeyed Beer's law in the investigated range of 1 to 10ppm (low concentrations). The deviations from Beer's law at high concentrations can be attributed to chemical effects (At high concentrations, chemical species associates and dissociates). The nature of the curves from figure 4.6 below and figure 4.5 above, is explained by both chemical and physical effects (instrumental and samples reparation errors) leading to positive and negative deviation from Beer's law.
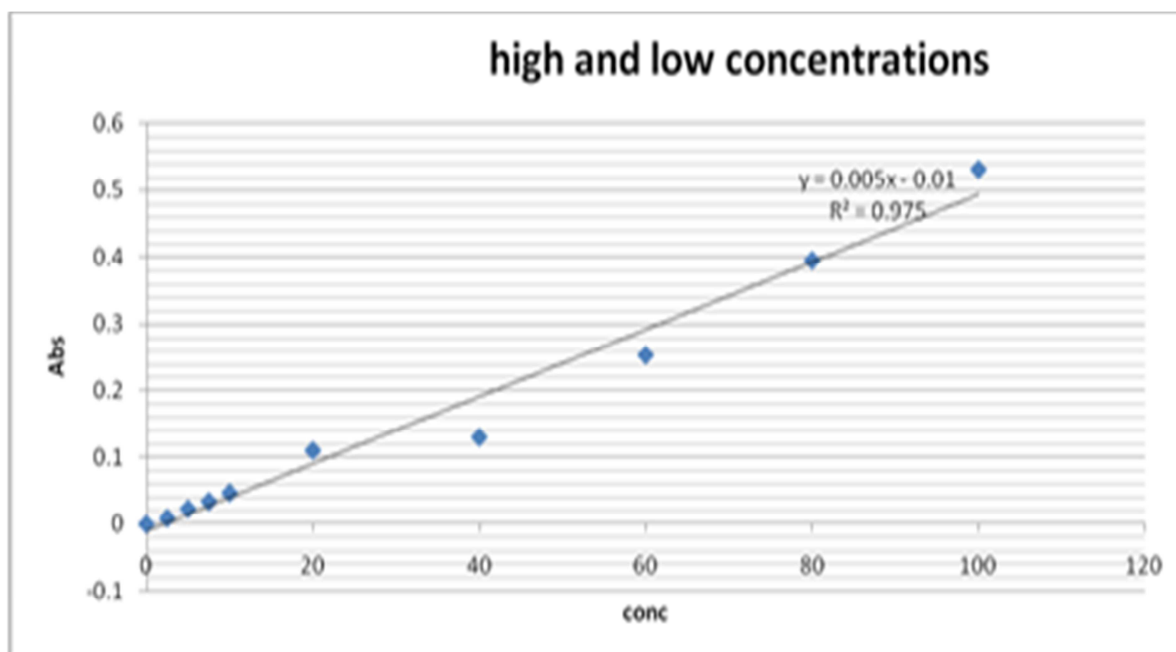
Figure 4.6: A plot of absorbance versus concentration for standard chlorpyrifos.

Varying amounts (0.1-2g) of loam soil were equilibrated in aqueous solutions containing same amount of pesticide residue (2mg) in the experiment for determination of the effect of different mass of soil on adsorption of chlorpyrifos. The obtained data is recorded and used to plot figure 4.7 below.
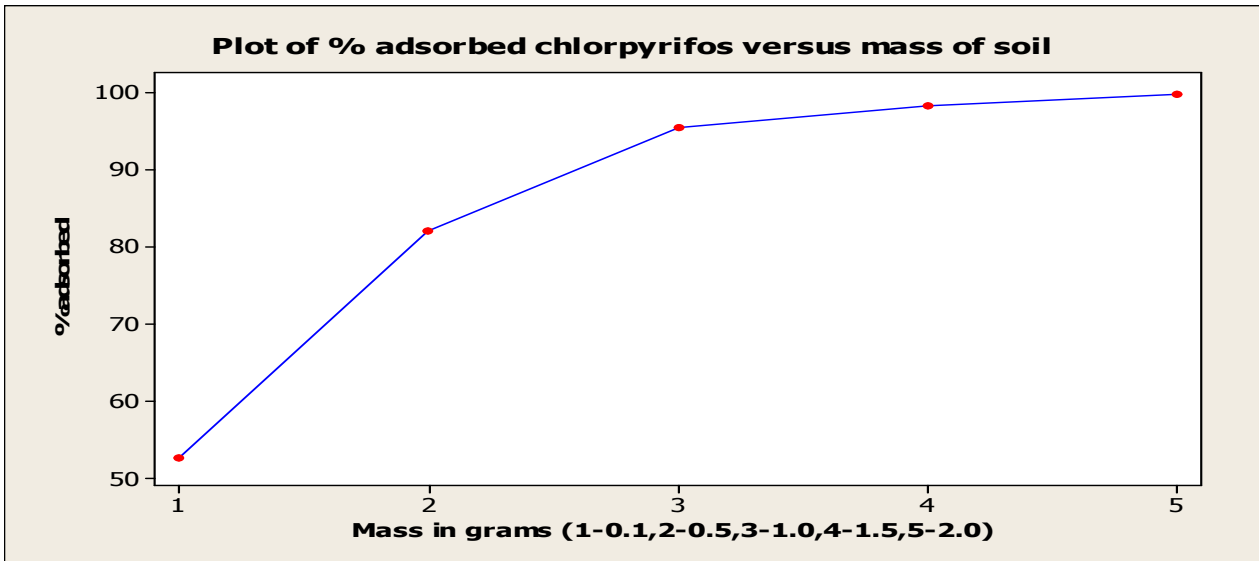
Figure 4.7: Plot of % adsorbed chlorpyrifos versus mass of soil in grams.

Figure 4.7 shows that when a 20 µg/ml chlorpyrifos solution is equilibrated with increasing amounts of sediment, the amount of the chlorpyrifos remaining in solution and/or suspension decreases exponentially as the amount of soil increases. This is consistent with equation 11 above, and confirms:

a) The existence of an adsorption/desorption equilibrium in the system.

b) The predictions of the adsorption/desorption equilibrium model presented above.

An elaborated picture is shown in figure 4.8 when the data obtained is plot against different mass of soil
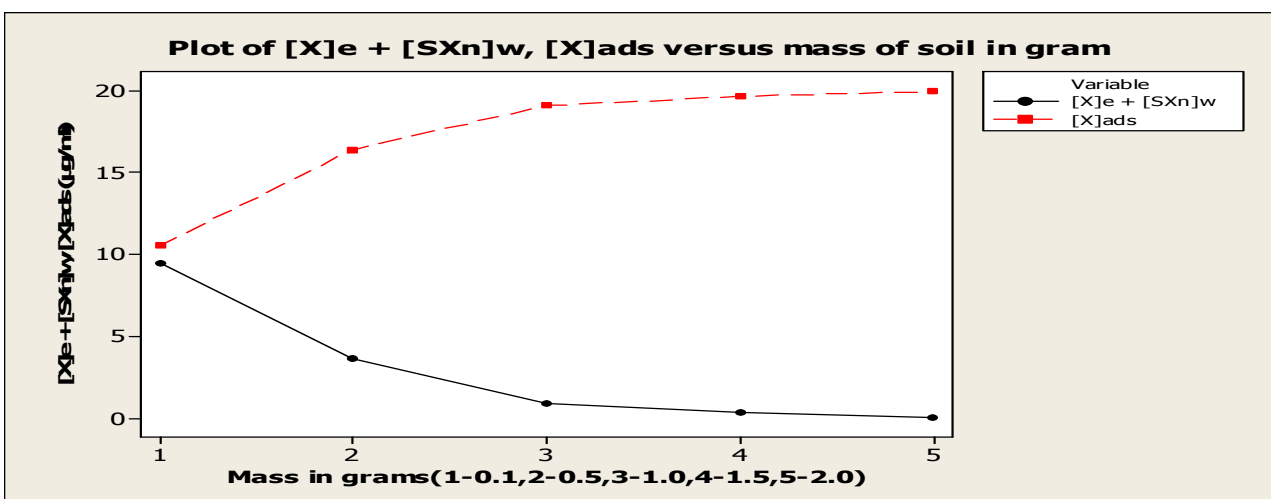
Figure 4.8: Combined graph of $[X]_e + [SX_n]_{w)}$ and $[X]_{ads}$ versus mass of soil sample in grams

To illustrate a more clear picture of adsorbed chlorpyrifos and amount in the suspension/desorbed, a plot of $[X]_e + [SX_n]_w$ and $[X]_{ads}$ against mass was made (figure 4.8). From the figure, we deduce that the amount desorbed decreases with increase in mass as the amount adsorbed increase with increase in mass. This is expected because as mass increases, the adsorption site increases. At around 1.0g any increase in mass doesn't translate to increased adsorption. This can be explained by the limited number of chlorpyrifos molecules. 0.5-1.0g of loam soil seems to have the maximum adsorption site for 20µg/ml solution.

The next experiment involved equilibrating 0.5 g of different samples of soil and spiking the resulting solutions with different concentrations of chlorpyrifos (tableA2 in appendix). The aim of this experiment was to determine the concentrations of chlorpyrifos in dissolved, suspension and adsorbed forms.

The amount of time the pesticide and soil are in contact is an important parameter in adsorption kinetics of an adsorbate at a given initial concentration (H. Babazadeh et al., 2011). Therefore the effect of contact time on adsorption of chlorpyrifos by loam soil was investigated for 60 minutes (figure 4.8). The kinetic studies were carried at different spike levels of 10, 20, 30, 40, 50µg/ml at room temperature, 25^oC. Figures 4.8 illustrate the amount of percentage chlorpyrifos adsorbed against concentration and contact time. The soil adsorbed up to 25% of chlorpyrifos. From the plots, for lower concentrations, maximum adsorption was obtained in 2 minutes. This indicates that the soil readily adsorbs chlorpyrifos which may indicate that with random spraying, a significant amount of residue is left in the soil. This should spark concern to relevant authorities since it indicates that even after a particular pesticide stops being used for any reason (policy, harmful indications or availability of alternative) chlorpyrifos would remain in the soil and still cause environmental concerns. On the other hand, it shows that the soil can be deliberately incorporated in a waste water treatment unit with very positive results. It can also be incorporated on the side of storm water ways to arrest pollutants before the water gets into other sources.
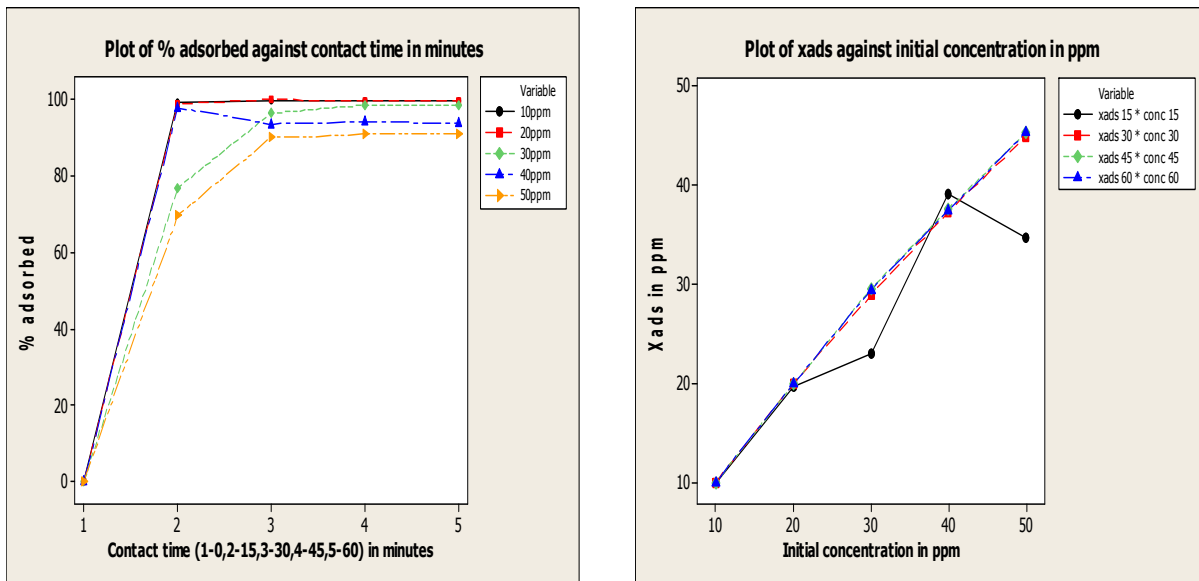
Figure 4.9: Amount of chlorpyrifos adsorbed versus (a) contact time in minutes and (b) initial concentration.

4.4   Adsorption isotherm models

These are models that describe the distribution of the adsorbate species among liquid and solid phases, based on the assumptions related to heterogeneity or homogeneity of the solid surface, the type of coverage and possibility of interaction between adsorbate specie. In the present work of adsorption of chlorpyrifos by loam soil, equilibrium data were analyzed using Freundlich, Temkin, and Langmuir and Quasi Langmuir isotherms expressions.

4.4.1   Freundlich Equation

The Freundlich (1906) equation is an empirical equation based on adsorption on a heterogeneous surface. The equation is commonly represented as:

$$q^e = K^F C e^{1/n} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 4.1$$

Where C_e (mg/L) is the equilibrium concentration and q_e (mg/g) is the amount adsorbed pesticide molecule per unit mass of the adsorbent. The constant *n (measure of adsorption non-linearity between solution solute concentration and adsorption)* is the Freundlich equation exponent that represents the parameter characterizing quasi-Gaussian energetic heterogeneity of the adsorption surface (Bansal and

Goyal, 2005). K_F (L/g) is the Freundlich constant indicative of the relative adsorption capacity of the adsorbent.

Taking the logarithm on both sides

$$\ln q^e = \ln K^F + 1/n \ln C^e \quad\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\mathbf{4.2}$$

This means that a plot of ln q^e against ln C^e is linear with slope of 1/n and is shown in figure 4.10
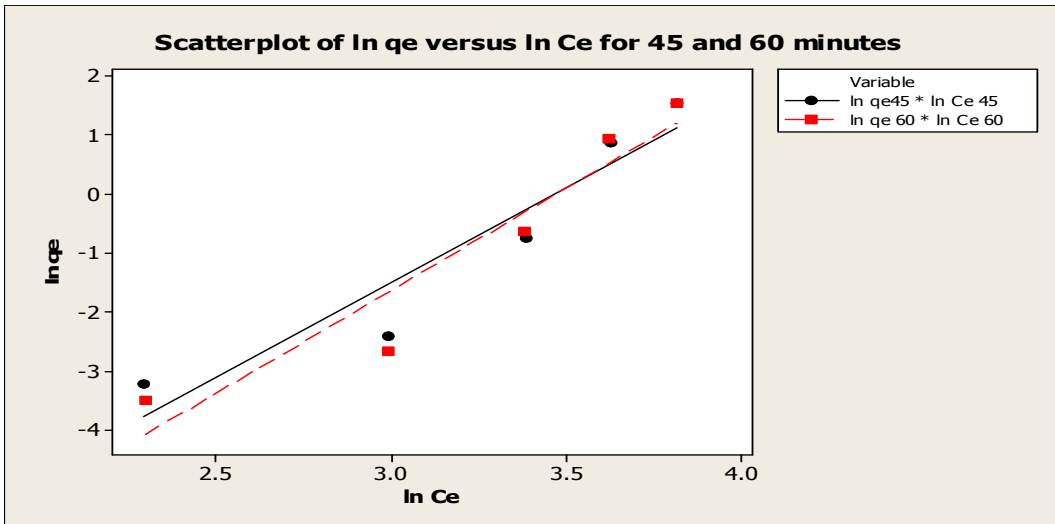
Figure 4.10: Scatter plot of ln q$_e$ versus ln C$_e$

The data in table 4.2 below shows the Freundlich equilibrium constant values from the plots. The regression value ranged from 0.701 to 0.912. The value of n increases with increase in shaking time from 0.1998 to 0.2914, Zaranyika et al., 2003 had observed that as shaking time increases, more adsorption sites are exposed. This was also observed by Kamau et al., 2012 for the adsorption of chlorothalonil.

Table 4.2: Freundlich isotherm parameters

Time in minute	n	ln K^F	R^2
15	0.1998	2.964	0.858
30	0.2022	3.447	0.701
45	0.2805	3.449	0.904
60	0.2914	3.469	0.912

From the R^2 values, the Freundlich isotherm is best obeyed at higher contact time (45 and 60 minutes). This is most probably because at higher contact times, sorption equilibration is achieved and thus adherence to the model.

4.4.2 Langmuir Model

The Langmuir (Langmuir, 1918) model assumes that uptake of pesticide molecule occurs on a homogenous surface by monolayer adsorption without any interaction between adsorbed molecules. The

Langmuir equation $\qquad q_e = \frac{q_m K_L C_e}{1 + K_L C_e}$ …………………………………………….4.3

where qe is the amount adsorbed (mg/g), Ce is the equilibrium concentration of the pesticide molecule (mg/L), qm (mg/g) is the maximum amount of adsorbed molecules per unit mass of sorbent corresponding to complete coverage of the adsorptive sites, K_L (L/mg) is the Langmuir constant related to the energy of adsorption. This can further be written as:

$C_e/q_e = 1/ K Q^0 + C_e/ Q^0$……………………………………………………..4.4

A plot of C_e/q_e versus C_e gives a straight line with intercept of $1/ K Q^0$ and slope of $1/ Q^0$ (figure 4.10) Assumption made is that the adsorbed chemical species do not react with one another.
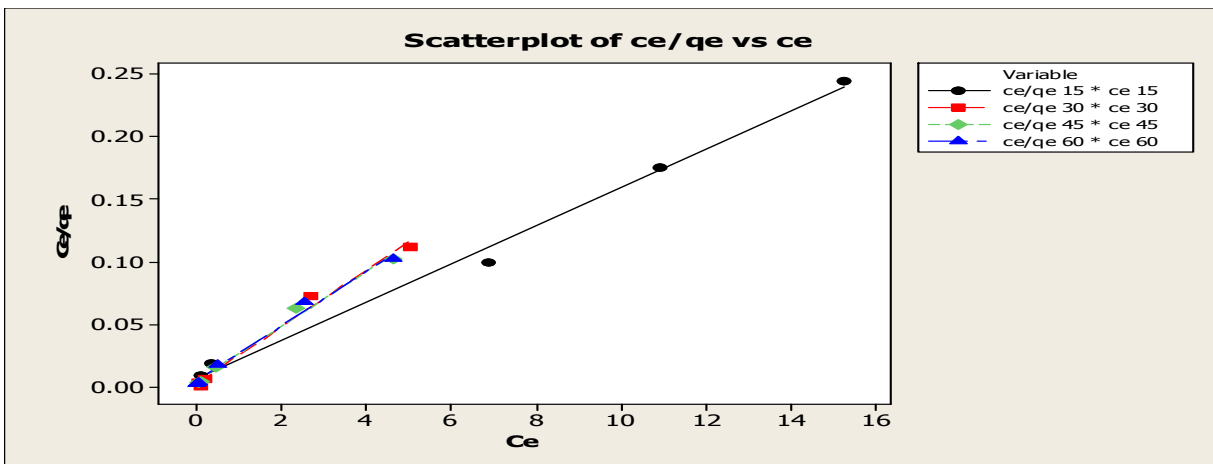
Figure 4.11: Scatter plot of C_e/q_e versus C_e

From the scatter plots above, the obtained values are presented below (table 4.3) with regression values, ranging from 0.908 to 0.990.

Table 4.3: Langmuir isotherm parameters

Time in minute	$1/Q^0$	$1/KQ^0$	R^2
15	0.019000	0.01557	0.908
30	0.022172	0.004877	0.991
45	0.022470	0.003286	0.990
60	0.029820	0.002838	0.953

The Langmuir isotherm model is seen to fit strongly in the adsorption of pesticides in the soil at all contact times investigated ($R^2 \geq 0.9$). This is indicative of monolayer adsorption and also points at physisorption of the pesticide molecules onto the soil particles. This would be encouraging if soil used in the waste water treatment unit, because it may be possible to desorbs the pesticides from the soil and reuse the soil. The pesticide molecules then recovered can be tested for re-use.

4.4.3   Temkin Isotherm Equation

The Temkin isotherm equation assumes that the heat of adsorption of all the molecules in layer decreases linearly with coverage due to adsorbent-adsorbate interactions, and that the adsorption is characterized by a uniform distribution of the bonding energies, up to some maximum binding energy (Temkin, 1940). The Temkin isotherm is represented by the following equation:

$$q_e = \frac{RT}{b} Ln(K_T C_e)$$ ……………………………………………………4.5

Where, T is the absolute temperature (K), R is the universal gas constant (8.314J/mol. K), K_T is the equilibrium binding constant (L/mg), and bT is the variation of adsorption energy (kJ/mol). B_T is Temkin constant related to the heat of adsorption (kJ/mol).This can be rearranged linearly as

$$q_e = B_T ln K_T + B_T Ln C_e$$

Therefore a plot of q_e against ln C_e is linear (figure 4.11). From the plots, the data in table 4.4 was obtained
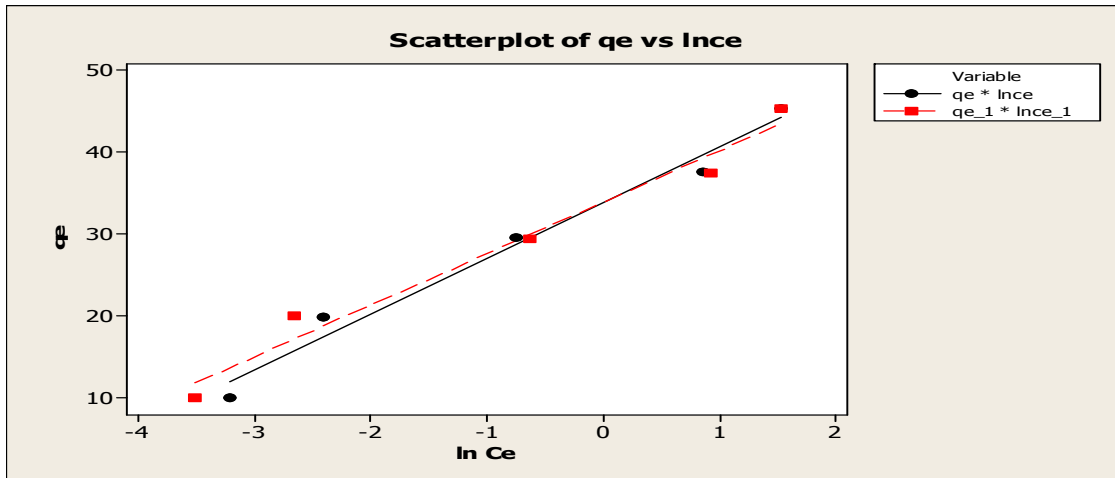
Figure 4.12: Scatter plot of q_e against $\ln C_e$.

The obtained values from the plots of the adsorption data obtained subject to Langmuir equation are recorded in table 4.4 below:

Table 4.4: Temkin isotherm parameters

Time in minute	B^T	$B_T \ln K_T$	R^2
15	4.624	21.91	0.811
30	5.171	34.63	0.852
45	6.803	33.90	0.979
60	6.298	33.90	0.975

Like in Freundlich isotherm, the curve fits better at higher contact times. This is expected since at higher contact times, equilibration is achieved and thus the adsorbents interaction has equilibrated, i.e., the rate of forward and backward reactions are equal. At lower contact times, this has not been achieved and therefore the points are more diverse.

4.4.4 Redlich Peterson (Quasi Langmuir) Model

Quasi Langmuir model is used as a compromise between Langmuir and Freundlich models, which can be written as (Redlich and Peterson, 1959):

$$q_e = \frac{K_{RP} C_e}{1 + \alpha_{RP} C_e^{\beta}}$$ ………………………………..4.6

This can be expressed in its linear form as:

$$\frac{C_e}{q_e} = \frac{1}{K_{RP}} + \frac{\alpha_{RP}}{K_{RP}} C_e^{\beta}$$ 4.7

Where *KRP* (L/g), α_{RP}(L/mmol) and *β* are Redlich-Peterson constants. The value of *β* lies between 0 and 1. The Redlich–Peterson isotherm constants can be predicted from the plot between C_e/q_e versus Ce^{β}. A special case of Langmuir would give the same linear equation as follows

$1/q_e = (1/K_aq_m)\ 1/C_e +$ **$1/q_m$**..**4.8**

This means a plot of **$1/q_e$** versus **$1/C_e$** is linear with **$1/K_aq_m$** as the slope and intercept as **$1/q_m$** and is shown by figure 4.13
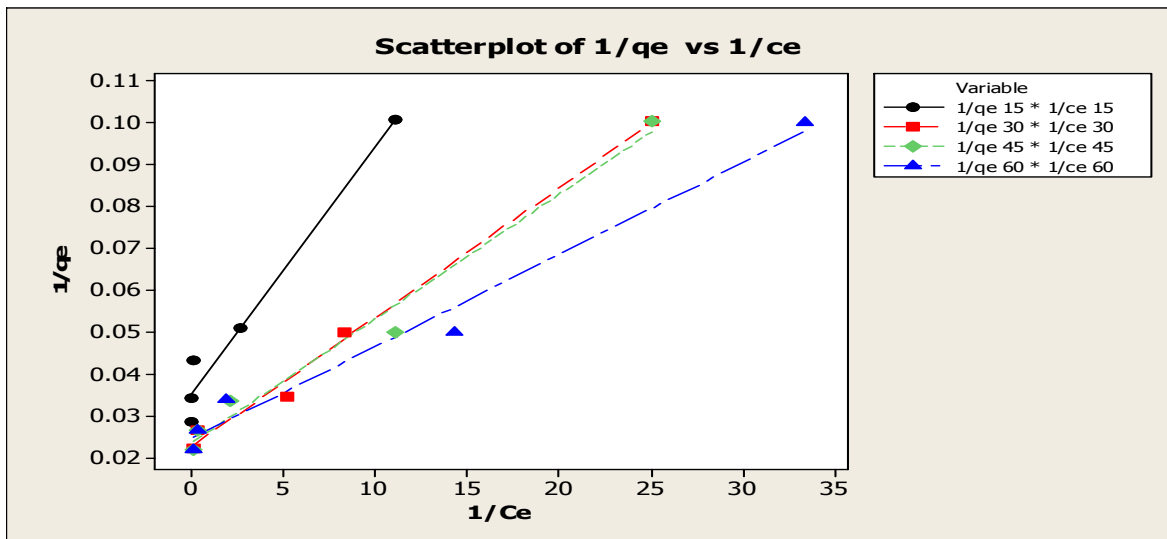
Figure 4.13: Scatterplot of $1/q_e$ versus $1/C_e$.

The parameters of Quasi Langmuir adsorption isotherm are stipulated in table 4.5 below

Table 4.5: Quasi-Langmuir isotherm parameters

Time in minute	$1/K_aq_m$	$1/q^m$	R^2
15	0.005945	0.03490	0.969
30	0.003105	0.02249	0.992
45	0.002980	0.02343	0.983
60	0.002207	0.02451	0.981

The data for all contact times fitted well into the Quasi-Langmuir isotherm model ($R^\geq 0.98$), table 4.5. This model was therefore used to determine the various thermodynamic parameters.

4.4.5   Dubinin- Radushkevich (D-R) Isotherm

Dubinin- Radushkevich (D-R) isotherm was applied to the obtained data to deduce the heterogeneity of the apparent adsorption energy on the adsorption site (Akpomie et al,. 2012). The equation linear form is given as

$$lnq_e = ln\ q_D -B_D\ \acute{\varepsilon}^2 \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots.4.9$$

$$\acute{\varepsilon} = RTln[1+1/C_e]\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots..4.10$$

Where q_D is adsorption capacity of the adsorbent, B_D is the D-R isotherm constant related to energy, $\acute{\varepsilon}$ is the Polanyi potential. The plot of ln qe against $\acute{\varepsilon}^2$ is shown in figure 4.14 below,
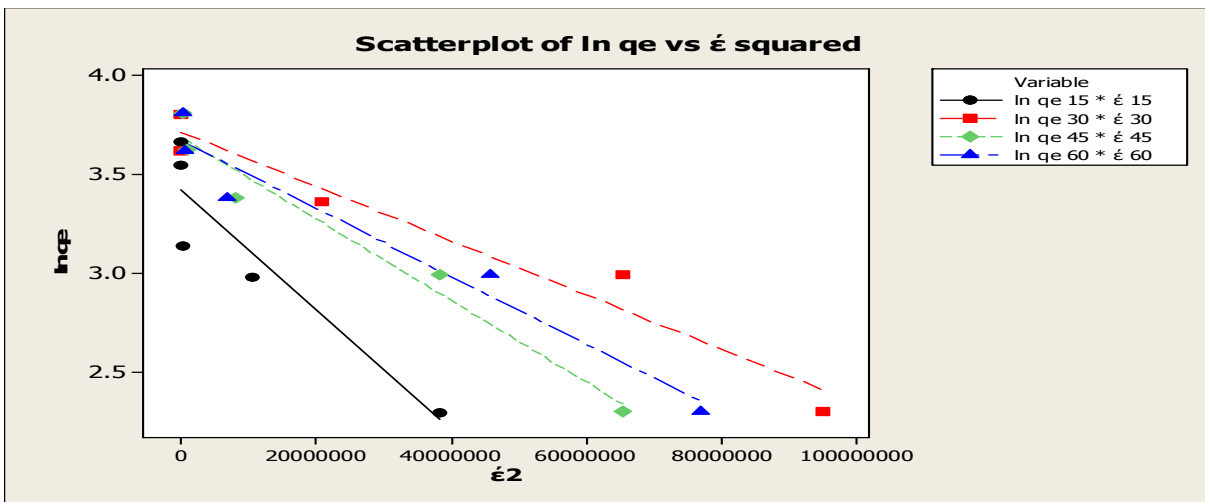
Figure 4.14: Scatterplots of lnq versus $\acute{\varepsilon}^2$

The D-R isotherms parameters are given in table 4.6 below. The mean adsorption energy E (kj/mol) can be obtained from the value of B_D by using the formula

$$E=1/\ [2\ B_D]^{1/2}\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots.4.11$$

Table 4.6: D-R isotherm parameters

Time	Ln q_D	B_D	R^2	E(kj/mol)
15	3.422	0.000001	89.3	0.707
30	3.715	0.00000001	95.4	7.071
45	3.689	0.000000002	96.6	5.000
60	3.671	0.000000002	95.4	7.000

When the adsorption energy is less than 8kj/mol the sorption process is said to be dominated by physisorption(physical attachment of pesticide molecule to the soil surface), if E is between 8 and 16kj/mol, the process is dominated by chemical ion exchange mechanism and if the value of E is greater than 16kj.mol the process is dominated by chemical particle diffusion (Dubinin et al,.1972). The value of E obtained in this work is 4.4445kj/mol which indicates that the adsorption of chlorpyrifos is dominated by physisorption.

4.4.6 Scatchard plot analysis

The scatchard plot analysis is applied to obtain comprehensive information on the affinity of of binding sites and to analyze the result of the adsorption isotherms (Anirudhan et al ., 2012). The equation is given below

Q_e/C_e=Qb-q_eb…………………………………………………………4.12

Where Q and b are the Scatchard adsorption isotherm constants, if the plot of qe/Ce versus qe gives a straight line, the adsorbent consist of one type of binding site (homogeneous surface). However, if the plot deviates from linearity, then the adsorbent consists of more than one type of binding site. The regression value obtained is 0.744 which show some deviation from linearity implying that the loam soil used in this experiment is made up of many sites which are responsible for the adsorption process.
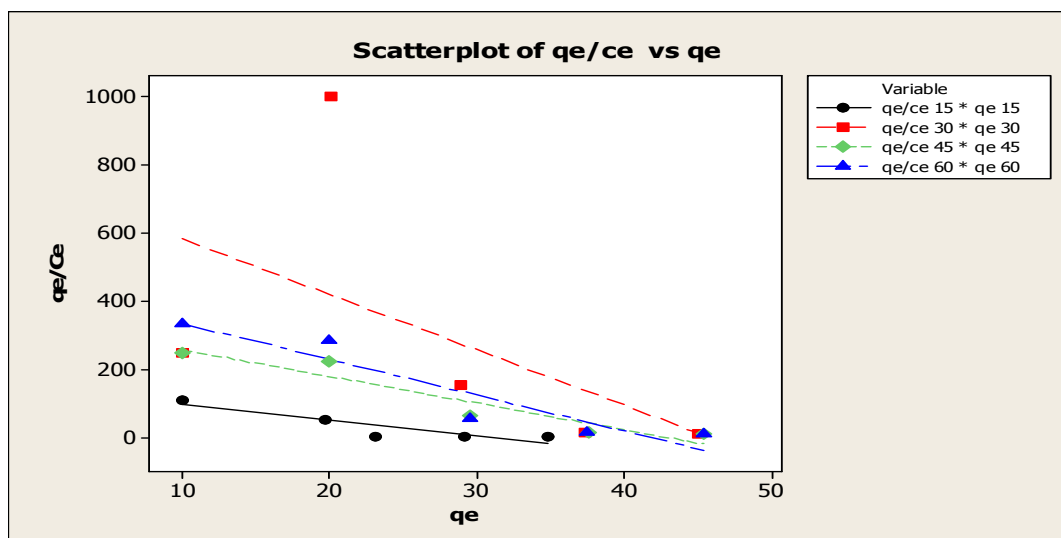
Figure 4.15: Scatterplots of qe/Ce versus qe

The isotherm parameters obtained from the plots in figure 4.14 are shown in table 4.7 below whereby the regression ranges from 0.893 to 0.966.

Table 4.7: Scatchard plot analysis parameter

Time	Q	b	R^2
15	30.825	4.545	89.3
30	45.805	16.21	95.4
45	42.814	7.794	96.6
60	41.756	10.48	95.4

Based on the higher regression values in Quasi-Langmuir isotherms, the experiment was found to follow this model. Freundlich isotherms scatter plots were used to calculate the apparent thermodynamic values of Gibbs free energy, equilibrium constant and *n*. The result from the table in appendixA2 for different shaking time is illustrated logarithmically in figures 4.15 which is a plot of *In[x]$_{ads}$ versus In ([X]$_e$ + [SX$_n$]$_w$)*. The obtained scatter plots have regressions (R^2) ranging from 0.71-

0.91. This confirms that adsorption of chlorpyrifos adheres to Freundlich adsorption model to some extent. The obtained plots parameters were further used to obtain apparent thermodynamic properties.
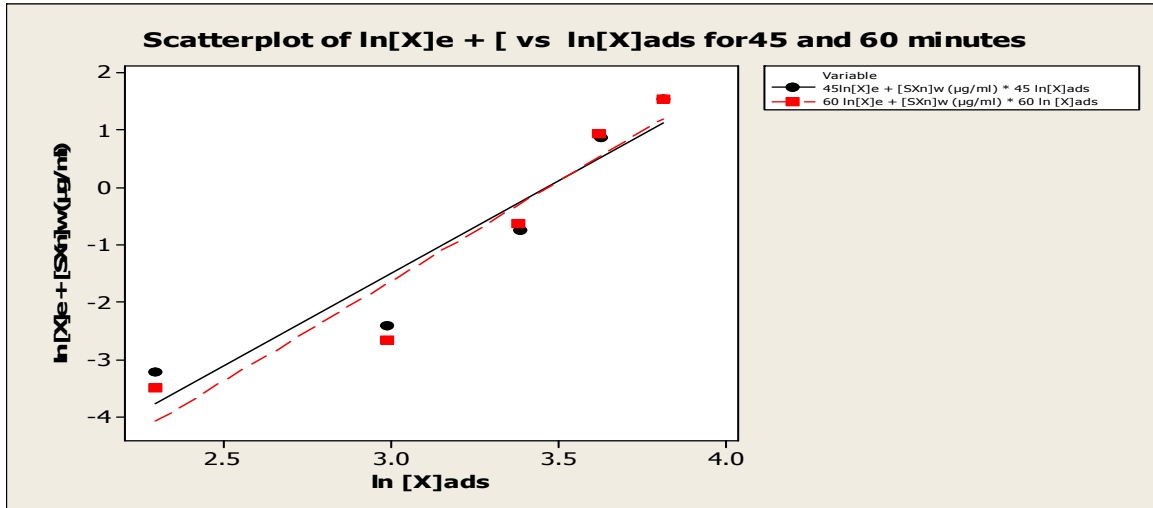
Figure 4.16: Adsorption of chlorpyrifos by loam soil samples: $In[x]_{ads}$ versus $In [X]_e + [SX_n]_w$.

Table 4.8 shows the equation obtained when the plots $In [X]_e + [SX_n]_w$ *against* $In[x]_{ads}$ were made with their linear regression values.

Table 4.8: Freundlich equation for different shaking times

Shaking time(minutes)	Equation	regression
15	Y=2.964+0.1998x	0.858
30	Y=3.447+0.2022x	0.701
45	Y=3.449+0.2805x	0.904
60	Y=3.469+0.2914	0.912

From the linear plots in figures 4.16 and figure 4.11 above, the intercept and the slope were used to calculate the apparent thermodynamic properties shown in table 4.8.

Table 4.9: Values for n, K' and ΔG' for the adsorption/desorption of chlorpyrifos by loam soil

Model	Freundlich				Langmuir	
Time (min)	N	LnnK'	K'	ΔG (kj/mol)	Kc	ΔG(kj/mol)
15	0.1998	2.964	96.974	-11.333512	34.289	-8.766590
30	0.2022	3.447	155.322	-12.500591	284.568	-14.01437
45	0.2805	3.449	112.189	-11.694598	111.745	-11.69680
60	0.2914	3.469	110.174	-11.649.695	139.439	-12.24595
Mean	**0.244+0.05**		**118.665+22.311**	**-11.7946+_0.3**	**142.510+_122.365**	**-11.6809+_2.568**

Table 4.9 shows the values of the apparent thermodynamic properties calculated from Freundlich and Langmuir adsorption isotherms. Adsorption/desorption equilibrium constant, K' of **118.665**, was obtained from the log plots (figures 4.10 and 4.15). Langmuir constant of 142.510 was obtained from $K_c = C_{Ae}/ C_e$ where C_e is the concentration at equilibrium and C_{Ae} is the amount adsorbed on solids at equilibrium. This illustrate that despite the model used, the apparent thermodynamic properties obtained are almost the same. The mean value of n is: **0.244**and the mean ΔG' for the adsorption of chlorpyrifos is **-11.7946Kj/mol** and -**11.6809Kj/mol** for Freundlich and Langmuir isotherms respectively for the loam soil where the plants were grown. The negative value for ΔG' confirms the adsorption reaction occurs spontaneously, as expected. Desorption is a special case of thermal dissociation, therefore we can use transition state theory to obtain that apparent desorption rate constant, K_d, in terms of the apparent adsorption/desorption equilibrium constant, K', thus:

$K_d = kT/hK'$. . ... (13)

Where: k is the Boltzmann distribution constant ($1.3806*10^-23 Kgm^2 s^2/mol/k$), T is the absolute temperature (298K), h is the Planck's constant ($6.626*10^{-34} js^2 mol/K$).

In equation 13, K_d is given by:

$K_d = [X]^n [S]/ [SX_n]$ ....(14)

The mean lifetime of a molecule of adsorbed state, is given by $1/K_d$ (Atkins, 1978).

Substitution of the appropriate values in equation 13 yields a value of $1.916* 10^{-11}$s, for the apparent lifetime of a molecule of chlorpyrifos in the adsorbed state. Such apparent life time of the adsorbed state points to physisorption, rather than chemisorption for which room temperature lifetimes as long as 3000 s have been predicted(Atkins 1990). This agrees with the earlier observation using Langmuir model whereby physisorption was hypothesized.

The exponent **n** is the number of pesticide molecules associated with a single adsorption site, **S**, to give the pesticide-site complex SX_n which is represented graphically as shown below. This indicates that the adsorption site increases with increase in shaking time as expected.

The value of n of **0.244+-0.05** suggests that each molecule of chlorpyrifos is associated with adsorption site. The major adsorption interactions which bind small organic molecules in the soil particles are of colloidal dimensions, i.e., 1nm to 1mm (Burchill et al, 1981). Combining equations 9 and 10 one obtains equation 15 which gives the relationship between the apparent equilibrium constant, K', and the true equilibrium constant, K:

$K' = K[X]_e/[X]_e + [SX_n]_w$ ....(15)

It is apparent that the extent to which K' deviates from K depends on the value of $[SX_n]_w$ and the value of n. The values of K and K_d lead to a value for the rate constant for the adsorption reaction, K_{ad} of 1.912×10^{-11}/s.

4.5 Photo-degradation of pesticides

The degradation of pesticides is currently focused mainly on hydrolysis, photo-degradation and microbial degradation as earlier studied (Pu et al., 2002; Tang et al., 2000; Yang et al.,1999; Zheng et al., 2001). Photo-degradation of pesticides has a significant influence on pesticide residue, efficacy,toxicity and even the environment (Itoh et al., 2005; Abdennour etal., 2005; Li et al., 2008). The photo chemical degradation properties of pesticides have become an important index in ecological environment safety evaluation of pesticide. It is required to provide information of photo-degradation for pesticide registration in many countries. Photo-degradation of pesticides in the environment as an important

process of degradation plays a major role in residue and fate of pesticide in crop surface, atmospheric and water environment (Holmstead et al., 1978; Zheng etal., 2003). On running the standards of pesticides in UV-Vis at different wavelengths, the following calibration curves were obtained and further used for photo-degradation studies (figure 4.17)

(a)   (b)
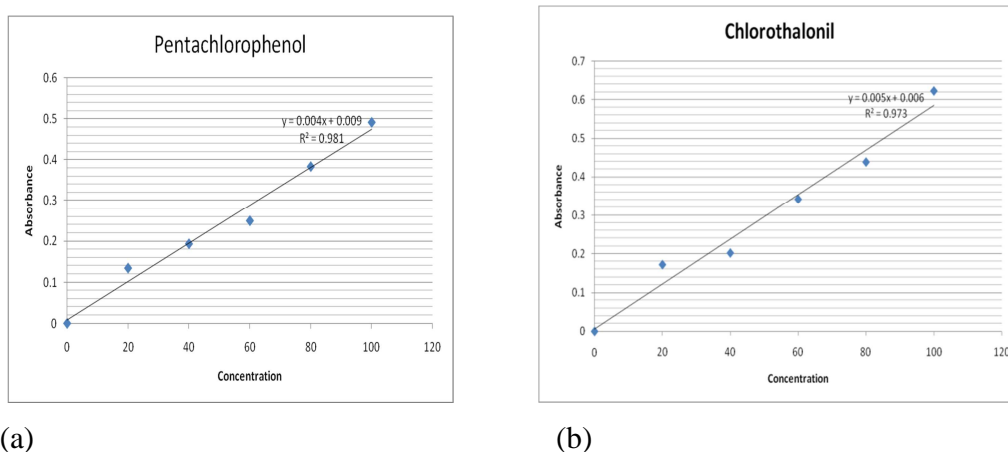
Figure 4.17: Calibration curve of (a) pentachlorophenol (b) chlorothalonil in acetone at 254nm.

Table 4.10 show the equation of standard residues with their regression values on scanning with UV-VIS spectrophotometer

Table 4.10: Calibration curve equations

Pesticide	Equation	Regression
Chlorpyrifos	Y= 0.000x + 0.003	0.992
Pentachlorophenol	Y= 0.004x + 0.009	0.981
Chlorothalonil	Y= 0.005x + 0.006	0.993
Lambda cyhalothrin	Y= 0.010x + 0.015	0.969

Figures 4.16 represent the calibration curves which were used to determine the amount of pesticides residue photo-degraded on the surface of spinach, tomatoes and blank petri dish. Rate of

degradation is assumed to follow first order kinetics. This is attested by Weerasinghee et al., 1992, and the equation they proposed, which were used in this study are as follows:

t$_{0.5}$= ln2/k=0.693/k……………………………………………….4.13

k= 1/Tx.ln a/bx…………………………………..……………4.14

Where: k = Rate of decomposition, T_x = Time in days, a = Initial residue, b_x =Residue at time(x)

4.5.1 Lambda-cyhalothrin

4.5.1.1 Photolysis

Naturally occurring pyrethrins are unstable in light, while the photo stability of recent synthetic pyrethroids has been improved. Photochemical studies with lambda-cyhalothrin had been conducted under UV and sunlight irradiation to understand photo-degradation kinetics, pathways, and products (Fernandez-Alvarez et al. 2007; Ruzo et al. 1987). Exposure of lambda cyhalothrin spiked spinach, tomatoes and blank samples to sunlight, bulb light of 40w, 60w, 75w and 100 W at254 nm) for four hours resulted in nearly complete degradation of cyhalothrin with losses greater than95% of initial amounts applied. The results are indicated in table 4.11 below. The degradation was observed to vary with light intensity and applied surface.

Table 4.11: Photo-degradation of lambda cyhalothrin after four hours.

Light	Temperature(^{0}C)	Spinach		Tomatoes		Blank	
Lambda cyhalothrin		Initial(ppm)	% loss	Initial(ppm)	% loss	Initial(ppm)	% loss
Room	25	1000	--	1000	--	1000	--
Sunlight	26	827	82.7	827	82.7	848	84.8
40w	36	853	85.3	858	85.8	863	86.3
60w	40	862	86.2	865	86.5	864	86.4

75w	47	879	87.9	877	87.7	896	89.6
100w	58	922	92.2	882	88.2	927	92.7

The amount of lambda-cyhalothrin degraded on the spinach and tomato can be represent as shown in the figure 4.18 for light and temperature, respectively.
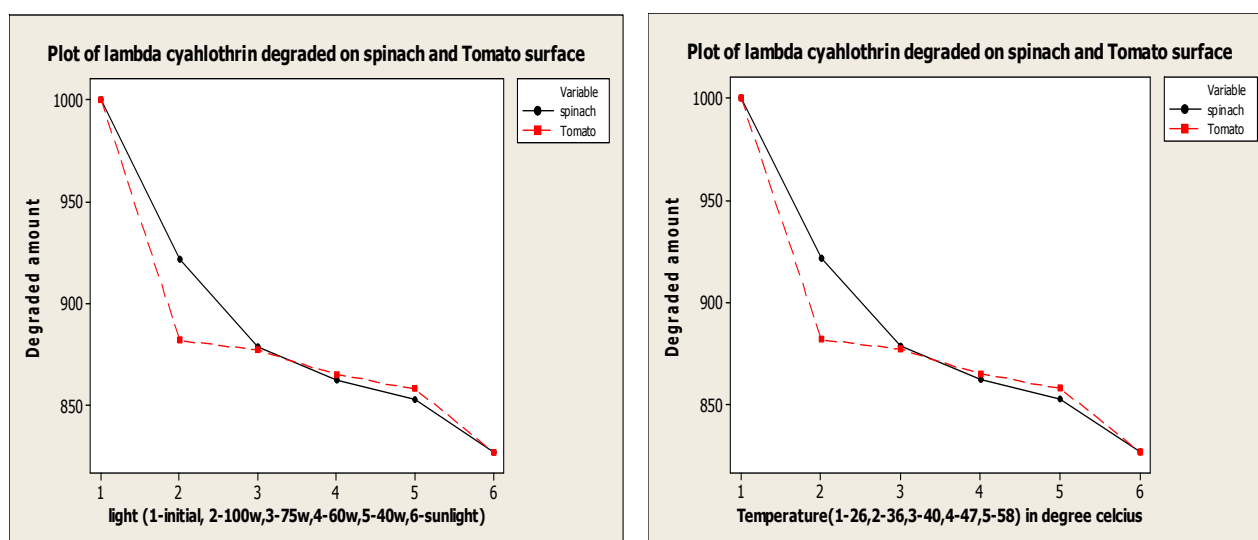
Figure 4.18: Plot of %lambda cyhalothrin degraded on spinach, tomato against (a) light and (b) temperature.

The similarity in figures 4.18 (a) and (b) reflects that as light intensity increases, so does the temperature and therefore confirms the fact that light intensity and temperature are some of the factors which dictates the rate of degradation of pesticide residues.

Figure 4.19 represent the percentage lambda cyhalothrin degraded on the surface of spinach and tomato when exposed to different lights
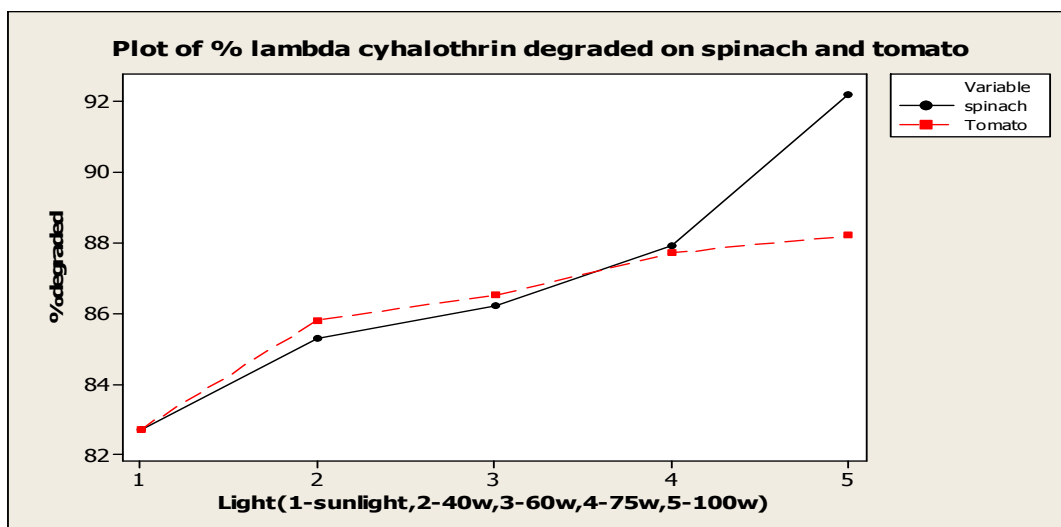
Figure 4.19: % lambda cyhalothrin degraded with respect to light.

Different wattage bulbs emitted different amount of light intensity and heat. This means that photo-degradation of lambda cyhalothrin on the surface of spinach; tomato and blank petri dish resulted from both light intensity and heat. Figure 4.19 illustrate the amount degraded versus temperature in degree Celsius. Lambda cyhalothrin degradation was highest at 58^0C as expected from light and heat emission from 100w bulb. This is in agreement with the Stark Einstein law which stipulates that for every photon absorbed a molecule undergoes photochemical reactions (Atkins 2011). This means that the reaction depends on the number of photons that illuminate a surface (wattage) and the bond being cleaved (substance).

In the two plants investigated the half-life decreases with the strength of radiation which further agrees with Stark Einstein law; the higher the radiant energy, the more the photons, the higher the amount of molecules undergoing reaction and therefore the shorter the amount of time required for half the entities to photo-degrade (figures 4.18 and 4.19).

In the case of 100w, there is significant difference in half-life of spinach and that of tomatoes. This may be due to the fact that tomatoes have a protective layer which keeps the pesticide from rapid degradation and also from high temperatures. Spinach on the other hand is a leafy crop that does not have that protective coat and is degraded at high temperatures. This may account for its relatively low half-life.

Table 4.12: Half-lives of lambda cyhalothrin.

Light	Temperature(^{0}C)	spinach($t_{1/2}$)	tomatoes($t_{1/2}$)	Blank ($t_{1/2}$)
Sunlight	26	0.066	0.066	0.061
40w	36	0.060	0.059	0.058
60w	40	0.058	0.058	0.058
75w	47	0.055	0.055	0.051
100w	58	0.045	0.054	0.044

Except for the 100wattage, the half-lives do not seem to depend on the species of the plant under investigation, which may imply that reaction rate only depends on the radiant energy and the substance being degraded.

4.5.2 Pentachlorophenol (PCP)

When PCP was exposed to sunlight and different energy bulbs, the amount of PCP after 4 hours were recorded and used to plot figures 4.18 below and the trend of the residues degraded against light (figure 4.20 (a) and temperature (b) is shown in the figures below.
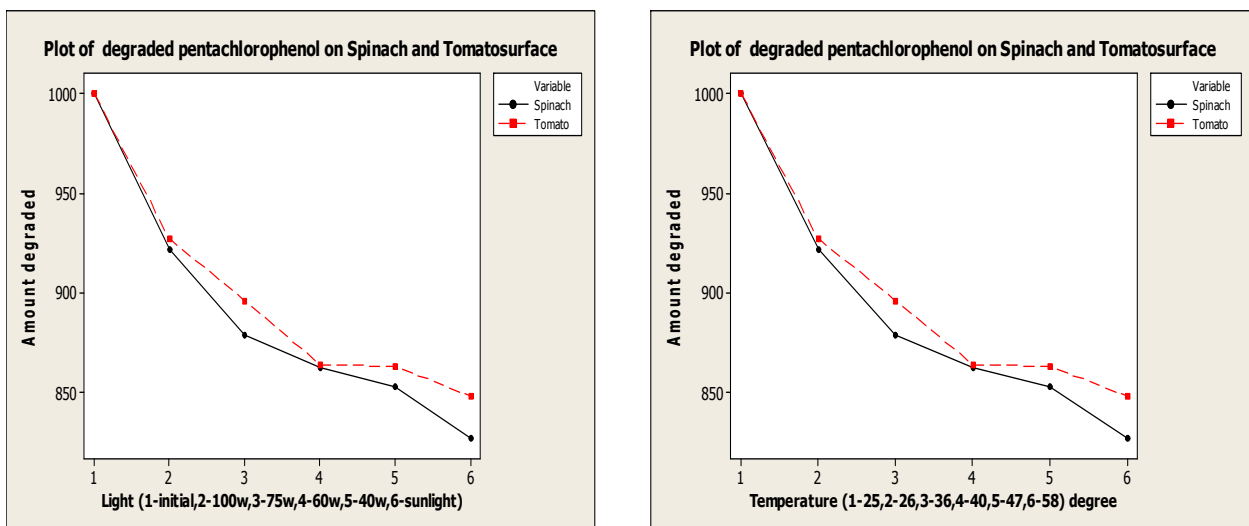
Figure 4.20: Plot of pentachlorophenol degraded against light and temperature.

The % loss degraded from initial concentration of 1000ppm as indicated in figure 4.20 shows that 92.2, 88.2 and 92.7% PCP on the spinach, tomato and blank surfaces, respectively degrade on exposure to 100w. PCP degradation is highly dependent on temperature and light intensity.
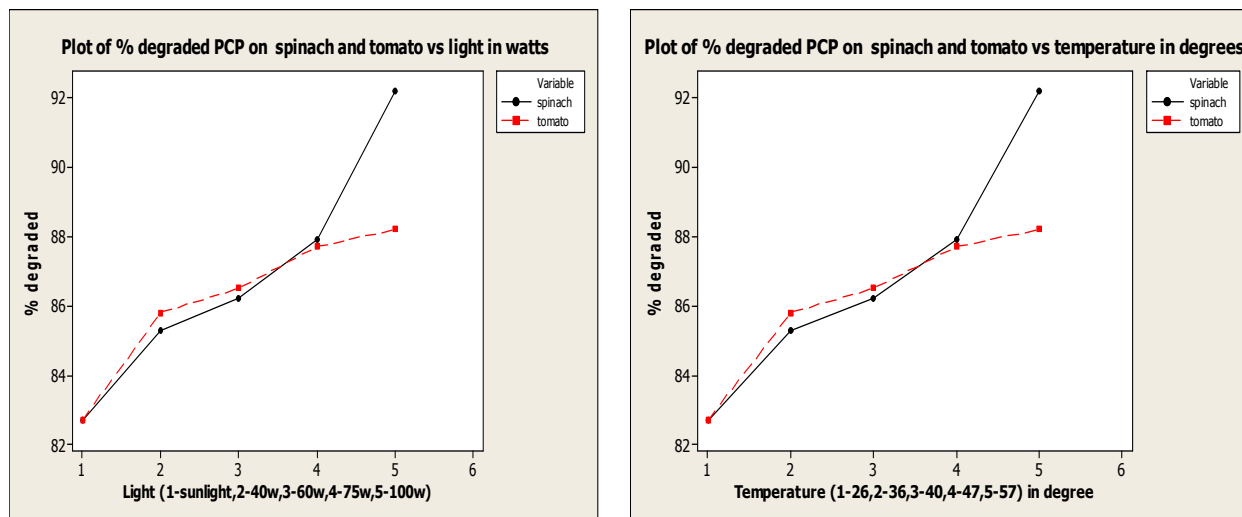
Figure 4.21: % PCP degraded (a) light (b) temperature.

After 4 hours exposure, the, half-life of PCP was calculated and was recorded in table 4.12 for spinach tomatoes and blank dish. The half-lives depend on temperature and the light intensity reaching the residue surface. The half-life on the blank surface is explained by total exposure compared to residue on tomato and spinach. Unlike the case of lambda cyhalothrin, the half-lives obtained upon degradation of PCP seem to depend on wattage, plant surface being analyzed and the residues being photo-degraded.

Table 4.13: Calculated half-lives of PCP.

Light	Temperature(^{0}C)	Spinach($t_{1/2}$)	tomatoes($t_{1/2}$)	Blank ($t_{1/2}$)
Sunlight	26	0.074	0.074	0.043
40w	36	0.141	0.115	0.104
60w	40	0.105	0.096	0.091
75w	47	0.091	0.089	0.089
100w	58	0.060	0.055	0.036

The half-lives obtained for different light intensity depend on the surface of exposure except for the sunlight. PCP degradation is different from the other residues studied which can be explained by the different reactions that occur when degrading the pesticides. The half-lives for spinach are consistently higher than those of tomatoes with all variation apart from the sun. This could be due to the protective coating on tomato fruit and/or interference with chlorophyll at the surface of spinach. In the second case it may mean that the photo-irradiation, other molecules other than PCP are being photo degraded and that activation energy maybe similar to that experienced when PCP is being degraded. It could be that there are two competing reactions which mean that less PCP is degraded per unit time, i.e., the rate of photo-degradation of PCP is lower and thus takes much longer to get to half the initial concentration. The protective coat and lack of chlorophyll in tomato make the half-life less than that of spinach. It is worth noting that half-lives of PCP are much higher than those of lambda cyhalothrin at all instances, which may be due to the structure of PCP and the many products formed up on PCP degradation (table 4.12).

4.5.3 Chlorothalonil

The % loss of chlorothalonil on exposure to different light intensity from the initial concentration of 1000ppm is recorded in figure 4.22
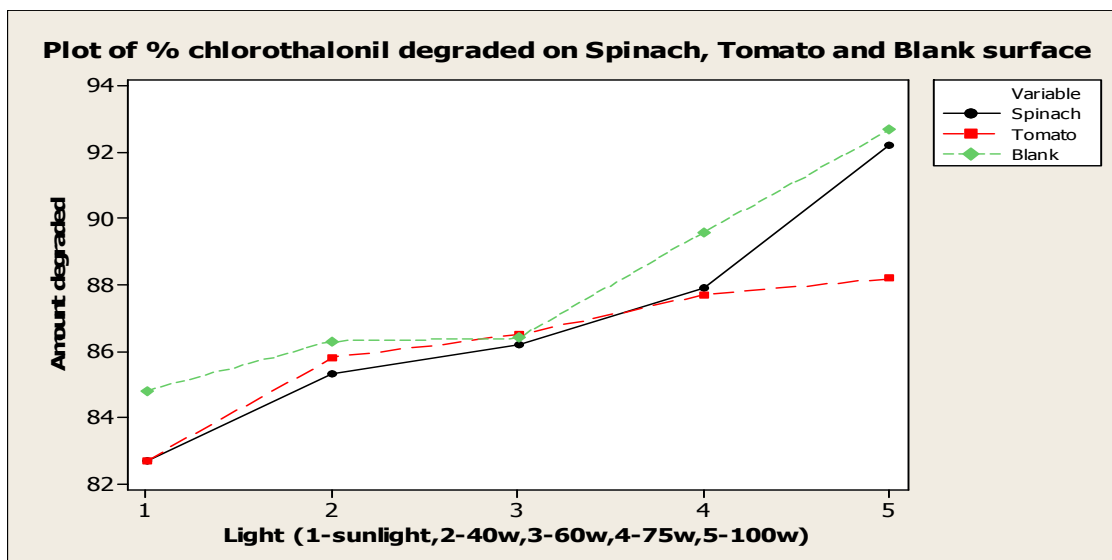
Figure 4.22: % degradation of chlorothalonil after four hours of exposure to different lights (bulbs of different energy).

Plots of percentage degraded on spinach and tomato against wattage and temperature are presented in the figures 4.23 below
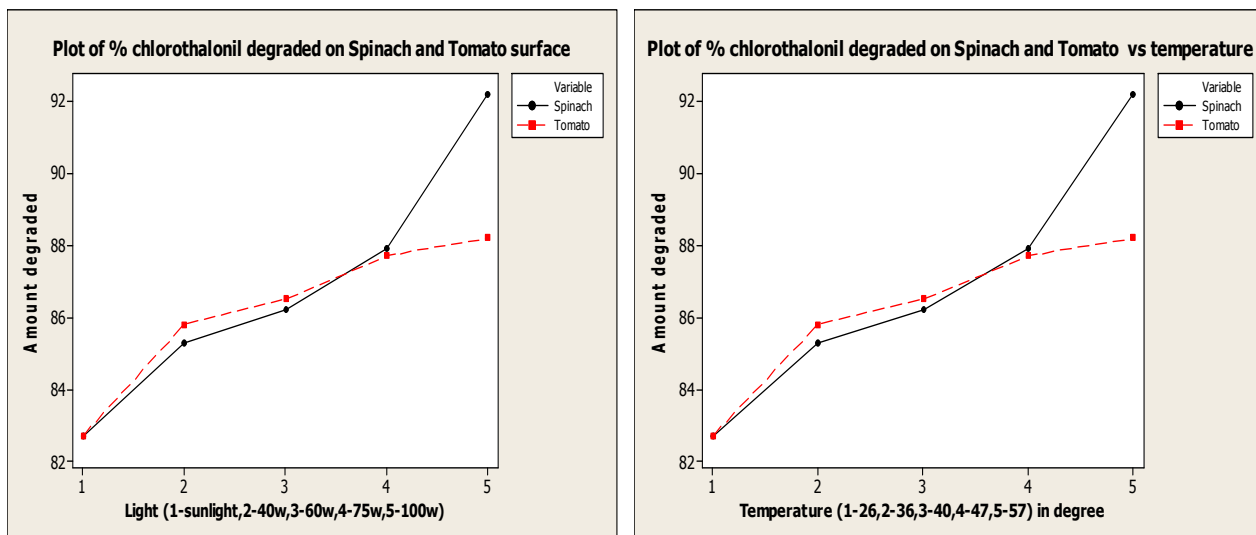
Figure 4.23: Plot of PCP adsorbed on spinach and tomato against light and temperature

Like lambda cyahlothrin the photo degradation of chlorothalonil is found to be independent of species of crop analyzed, but only dependent on wattage which could indicate that they have similar photo-degradation patterns. The presence of cyano group in both species may greatly influence the degradation pattern in the plants in the investigated, and thus the nature of the plant may not influence the degradation.

Despite the fact that the obtained half-lives are comparable to those of lambda cyhalothrin, the amount of chlorothalonil degraded by each of the radiated lights is much lower than that of lambda cyhalothrin (figure 4.19). This can be due to the amount of energy required to breaking of the Cl-C (in benzene) bond; thus eventually these is the degradation of the pesticide even with the same amount of radiation. Once more, the half-life decreases with wattage due to photons degrading more molecules. The rate of degradation in the four hours exposure was calculated and hence the half-life of chlorothalonil on the surface of spinach and tomato as well as on blank dish was obtained (table 4.14).

Table 4.14: Calculated half-lives of chlorothalonil.

Light	Temperature(^{0}C)	Spinach	tomatoes	Blank
Sunlight	26	0.111	0.111	0.111
40w	36	0.079	0.080	0.079
60w	40	0.058	0.058	0.063
75w	47	0.054	0.054	0.058
100w	58	0.041	0.041	0.042

4.5.4   Chlorpyrifos

When 1000mg/L of 99.8% standard of chlorpyrifos on the surface of spinach, tomato and blank petri dish were exposed to sunlight and different watts bulbs, the results are as stipulated in figure 4.24 below.
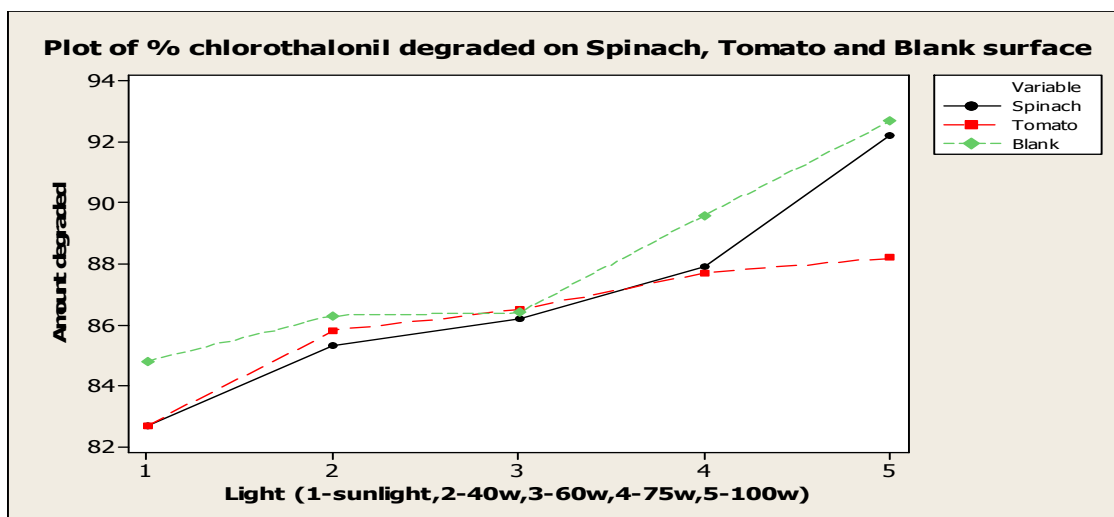
Figure 4.24: Amount of chlorpyrifos lost after four hours of exposure to different lights.

Figures 4.25 indicate that the % chlorpyrifos degraded with respect to light intensity and temperature is the same. This is explained by the fact that different bulbs emit different amount of energy and therefore high bulb wattage translate to higher temperature.
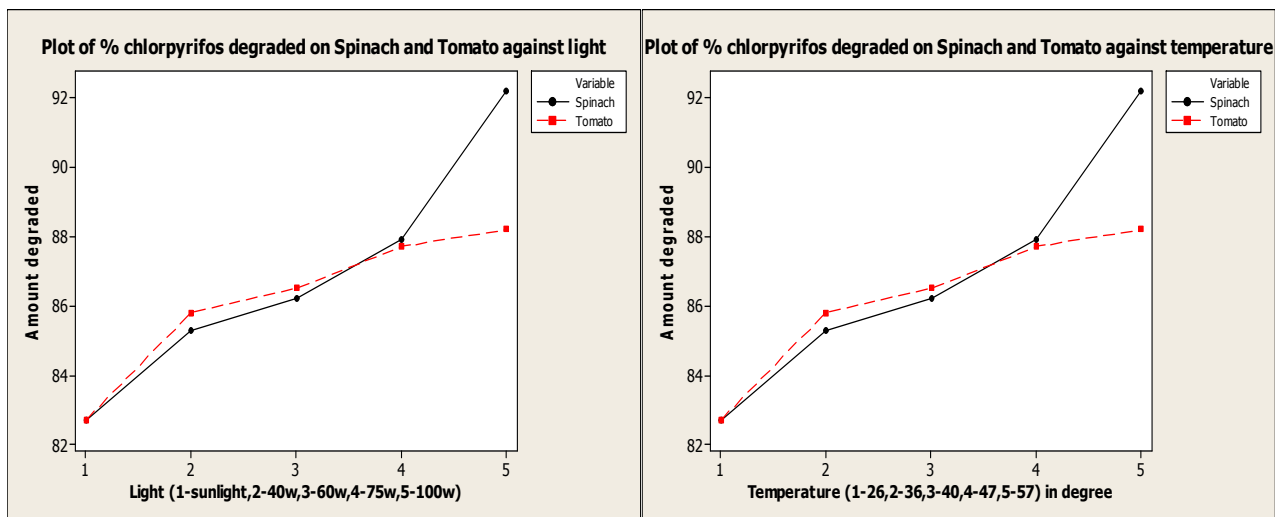
(a)   (b)

Figure 4.25: plot of % chlorpyrifos degraded on spinach and tomato against light and temperature.

Like lambda cyhalothrin and chlorothalonil, photodegradation of chlorpyrifos is independent of species of crops analyzed but dependent on light radiated which indicate that photo-degradation of chlorpyrifos on spinach and tomatoes are similar. Contrary to that, irradiation on blank surface indicates that the half-life of chlorpyrifos is higher than that on the spinach and tomatoes.

Calculated half-lives for chlorpyrifos in spinach, tomato and blank dish are recorded in table 4.15 below. The half-lives decrease with wattages due to increased photons degrading more molecules.

Table 4.15: Calculated half-lives of chlorpyrifos.

Light	Temperature(^{0}C)	spinach($t_{1/2}$))	tomatoes($t_{1/2}$))	Blank ($t_{1/2}$)
Sunlight	26	0.069	0.069	0.069
40w	36	0.065	0.065	0.067

60w	40	0.064	0.064	0.070
75w	47	0.062	0.062	0.064
100w	58	0.042	0.042	0.044

4.5.5 Energy calculations

The total amount of energy absorbed by 5cm by 5cm leaf surface from the sun on a hot summer can be calculated as follows;

Energy= power * time

Power = area * current

Electromagnetic wave from the sun is $1.4kW/m^2$ but only 80% of this reaches the earth surface on a hot summer day, therefore,

$80/100*1.4=1.12kW/m^2$…………………………………………………………………..4.15

Area = 5cm *5cm=25/10000=$0.0025m^2$ of spinach leaf

power=0.0025m2*1.12kW/m2=0.0028kW

Energy = 0.0028kW*14400sec=40.32joules.

This means that the amount of energy absorbed by the spinach and tomato when exposed to 40w, 60w, 75w and 100w bulbs for four hours can be calculated since the area and the wattage is known. The amount of energy responsible for breaking down the pesticide molecules are shown in table 4.16.

Table 4.16: Energy reaching the plant surface

Light	Temperature (^{0}C)	Spinach(joules)	Tomato (joules)
Sunlight	26	40.3200	45.0901
40w	36	1.4400	1.6105
60w	40	2.1600	2.4157
75w	47	2.7000	3.0197
100w	58	3.6000	4.0263

The sun has the highest amount of energy reaching the surface of 0.0025 and 0.002798 m^2 of the spinach and tomato, respectively. From the plots of percentage degradation of the four residues, the sun degraded the least. Several factors account for this degradation trend; the distance from the sun to the molecule surface is 93,000,000 miles meaning the intensity reaching the crop surface is reduced to a large extent unlike for the bulb which is 30cm above the surface. Secondly, as noted earlier by Suett (1979), temperature is a major factor in the breakdown of pesticides whereby he reported doubling of chemical reactions with 10^0 C rises in temperature. Photo-degradation from the sun is influence by light intensity while light intensity and temperature influences breakdown of residues. This explains the pattern of photo-degradation. Clear illustration of the observation is shown by figure 4.26.
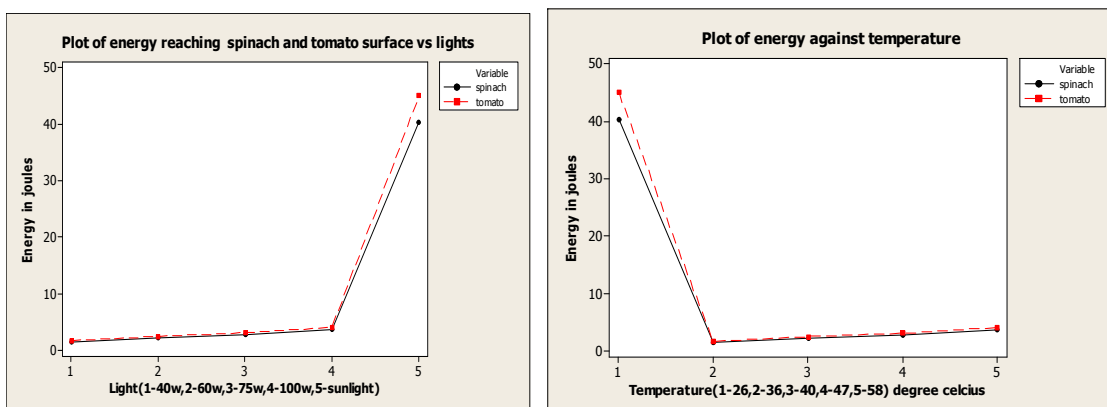
Figure 4.26: Plot of energy in joules versus (a) light and (b) temperature

When the residues photo-degradation was investigated with respect to time, the following results were obtained (figures 4.27):
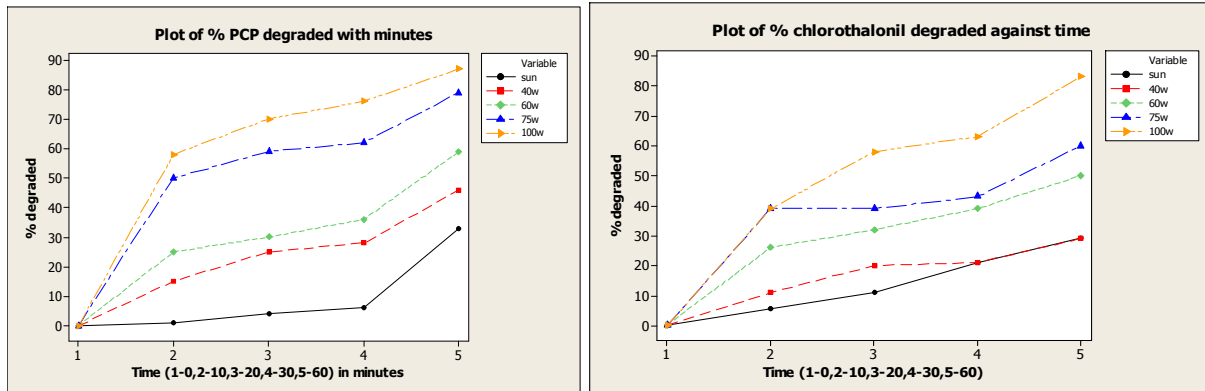
(a)

(b)
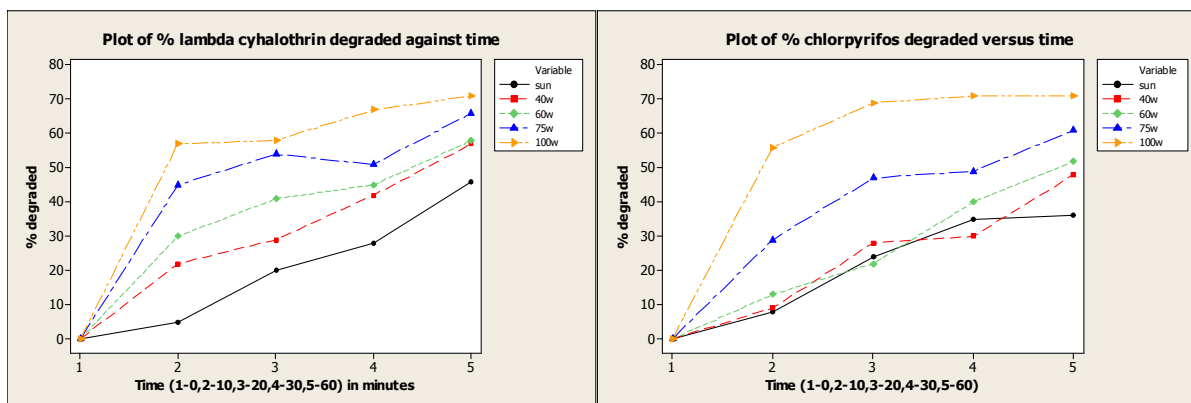
(c)

(d)

Figure 4.27: Plots of % residues degraded against time in minutes (a) PCP, (b) chlorothalonil, (c) lambda cyhalothrin, (d) Chlorpyrifos.

For all the residues studied, photo degradation is dependent on time of exposure, light intensity and temperature. This is consistent with Stark Einstein law. The percentage loss is higher in pentachlorophenol, chlorothaonil with chlorpyrifos and lambda cyhalothrin degrading similarly at 100w on exposure for 60 minutes. The % loss for 100w on exposure for 60 minutes is 87, 83, 71 and 71 for PCP, chlorothalonil, lambda cyhalothrin and chlorpyrifos, respectively

4.6   The rate of degradation

To determine the rate of degradation of pesticide residues with respect to time, plots of natural logarithm of concentration against time were made. The rate of degradation is the slope of the plots. Figure 4.27 illustrate the rate of degradation for the different pesticides residues.
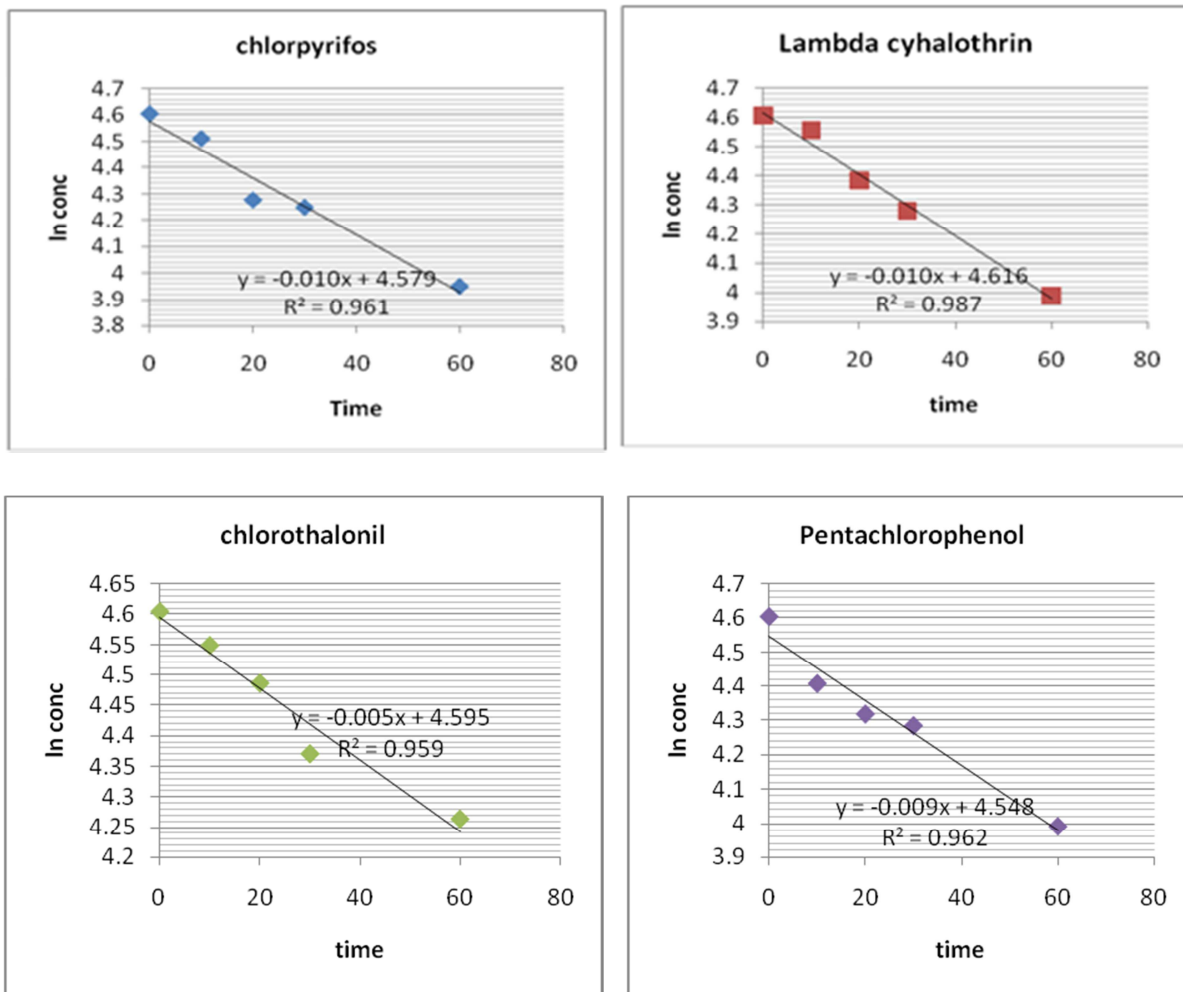
Figure 4.28: Plots of rate constants for pesticide residues.

The rates of degradation of the residues were dependent on: time of exposure, light intensity, particular molecular structure and temperature. As shown in figures 4.28, the rate constant for lambda cyhalothrin and chlorpyrifos were the same while chlorothalonil and PCP rates were 0.005 and 0.009, respectively.

Table 4.17: Rate of degradation plots

Lambda cyhalothrin			
Light	**Equation**	**Rate**	**Regression value**
sunlight	y=0.007x+4.543	0.007	0.781
40w	y=0.010x+4.579	0.010	0.961
60w	y=0.012x+4.579	0.012	0.958
75w	y=0.014x+4.433	0.014	0.855
100w	y=0.016x+4.116	0.016	0.541
Chlorothalonil			
sunlight	y=0.010x+4.616	0.010	0.987
40w	y=0.013x+4.535	0.013	0.968
60w	y=0.013x+4.456	0.013	0.888
75w	y=0.014x+4.329	0.014	0.751
100w	y=0.016x+4.218	0.016	0.671
Pentachlorophenol			
sunlight	y=0.005x+4.595	0.005	0.959
40w	y=0.006x+4.559	0.006	0.945
60w	y=0.010x+4.473	0.010	0.870
75w	y=0.013x+4.408	0.013	0.825
100w	y=0.028x+4.404	0.028	0.957

Chlorpyrifos			
sunlight	y=0.006x+4.664	0.006	0.86
40w	y=0.009x+4.548	0.009	0.962
60w	y=0.013x+4.542	0.013	0.970
75w	y=0.023x+4.334	0.023	0.885
100w	y=0.030x+4.260	0.030	0.886

The rate of pesticide residues degradation from the plots is represented in figure 4.29. The rate was found to decrease in the order of PCP, chlorothalonil, lambda cyhalothrin and chlorpyrifos, respectively apart from the 100w bulb. This was seen to be dependent on molecular structure, wattage and time of exposure. Figure 4.29 below shows the rate of different residues degradation
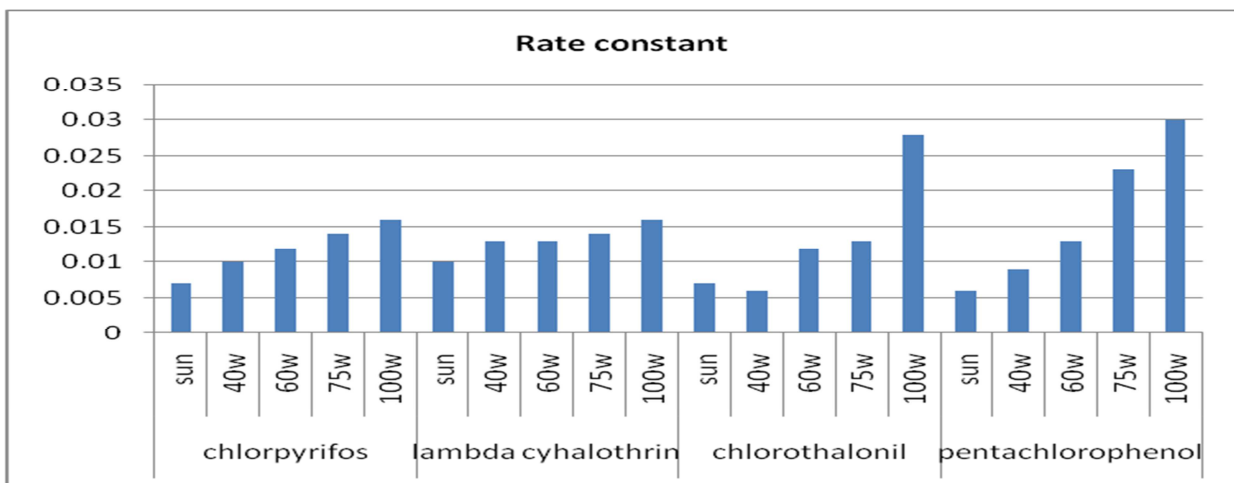
Figure 4.29: Plot of rate constant of pesticide residues.

4.7   Analysis of pesticide residue levels in crops

The occurrence of pentachlorophenol, chlorpyrifos, chlorothalonil and lambda cyhalothrin in tomatoes, potatoes and spinach grown by organic container gardening method was investigated in this work. The plants were chosen to represent fruits, root crop and leafy vegetables. HPLC was used for

identification and quantification of the pesticide residues, according to observation by Pradeep et al (2008). The results obtained are discussed below:

4.7.1 Linearity

From the prepared standard solutions, calibration curves were obtained and their linearity tested by getting their respective regression values. This is shown in the table 4.18 and figure 4.30 below:

Table 4.18: regression equations of pesticide residues

Pesticide coefficient	Linear equation	Regression
Lambda cyahalothrin	y = 125.2x + 19.32	$R^2 = 0.995$
Chlorothalonil	y = 128.5x + 18.94	$R^2 = 0.999$
Pentachlorophenol	y = 147.8x + 3.034	$R^2 = 0.998$
Chlorpyrifos	y = 128.9x + 21.49	$R^2 = 0.998$

The obtained calibration curve when pesticide standard were run on HPLC instrument are shown in figure 4.30 below.
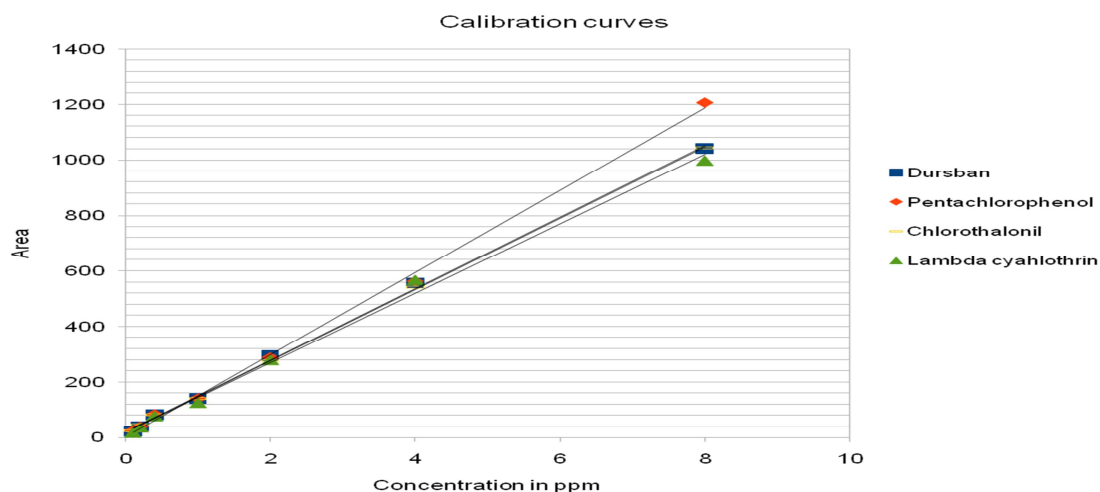
Figure 4.30: Calibration curve of lambda cyhalothrin, Chlorpyrifos, chlorothalonil and PCP using HPLC.

According to figure 4.30, linear relationship was obtained for the four pesticide standards, as expected. The observed calibration curves were used to obtain the concentration of the unknown.

4.7.2 Recovery analysis

Recovery analysis was carried out to determine the efficiency of the HPLC equipment in determining the residues level. The percentage recoveries are recorded in table 5.19 below. The recovery levels of lambda cyhalothrin for 10, 40 and 100ppm spike levels were 18.356, 24.879 and 28.965; 25.236,19.568 and 29.124; 27.568, 21.363 and 29.365 for spinach, tomatoes and potatoes, respectively. Chlorothalonil had the best recovery in all the studied crops. In spinach, the recoveries were 57.239, 76.366 and 78.958 for 10, 40 and 100 ppm spike levels, respectively. The high recovery levels can be attributed to the large surface are of the leaf with the residue adsorbing to the leaf surface. Recovery in potatoes was least compared to spinach and tomatoes.

Table 4.19: % Pesticides recovery in spinach, tomato and potato

Spinach				
Spike level(mg/L)	chlorothalonil	pentachlorophenol	Lambda cyhalothrin	Chlorpyrifos
10	57.239+_10.8	34.935+_5.6	18.356+-1.2	30.236+-5.0
40	76.366+-4.8	43.257+_7.8	24.879+_3.6	44.632+-2.9
100	78.958+_2.3	43.683+-5.2	28.965+_7.0	67.895+_6.2
Tomato				
Spike level(mg/L)	chlorothalonil	pentachlororphenol	Lambda cyhalothrin	Chlorpyrifos
10	41.256+_6.3	54.658+-5.3	25.236+_4.2	41.256+-6.3
40	62.368+_2.8	44.968+_4.7	19.568+_5.4	57.856+_4.6

100	77.968+_11.5	47.425+_6.5	29.124+_5.6	73.235+_8.9
Potato				
Spike level (mg/L)	Chlorothalonil	Pentachlorophenol	Lambda cyhalothrin	Chlorpyrifos
10	48.965+_4.8	38.659+_2.3	27.568+_7.2	47.112+_8.9
40	51.369+_4.5	38.428+_9.2	21.363+_2.5	50.254+_1.3
100	64.457+-4.4	42.545+-8.5	29.365+_10.3	52.634+-6.8

Pentachlorophenol recoveries were almost uniform in all the crops. This indicated constant behavior in different surfaces. This is different for chlorpyrifos whose percentage recoveries in potatoes are shown in table 5.19. The general % recoveries of up to 86.17% have been reported in spinach and tomatoes (Pradeep et al 2008).

4.7.3 Maximum residue limits

The contamination level of tomatoes, spinach and potatoes by pentachlorophenol, chlorpyrifos, chlorothalonil and lambda cyhalothrin in organic container gardening was also studied by applying the recommended levels of each residues in the garden. Pesticide residues concentration was determined when the above crops were harvested. These are recorded in table 4.20.

Table 4.20: Pesticide residue levels in spinach, tomato and potato

Pesticide	Spinach	MRL(mg/kg)	Tomato	MRL(mg/kg)	Potato	MRL(mg/kg)
Chlorothalonil	0.12	0.04	0.03	0.1	ND	0.1
Pentachlorophenol	0.68	0.50	0.92	0.1	0.09	0.05
Chlorpyrifos	0.07	0.02	0.03	0.5	ND	0.05
Lambda cyahlothrin	0.04	0.10	ND	0.02	ND	0.02
ND=Not Detected MRL=Maximum Residue Level						

It was found from the results that spinach adsorbed the four residues at different levels with pentachlorophenol having the highest concentration of 0.68µg/l followed by chlorothalonil, chlorpyrifos and lambdyahlothrin at 0.12, 0.07 and 0.04, respectively. In tomatoes, lambda cyhalothrin was not detected. 0.92, 0.03 and 0.03 were the levels of PCP, chlorothalonil and chlorpyrifos in tomatoes, respectively. In potatoes, only pentachlorophenol was detected. Being a root crop, the leaching level of the residues may take place slowly and therefore not reaching the surface of the tuber. Pentachlorophenol is the least soluble and may be adsorbed to the soil and tuber surface. It may also be collected during harvest. The low residues obtained can be attributed principally to growth dilution occurring between application and sampling, as well as to the volatilization associated with application, removal by weathering, heat decomposition, sunlight UV radiation, microbial breakdown or other complex conditions.

Figure 4.31 below illustrates the level of pesticide residues on spinach, tomato and potato from the organic container garden
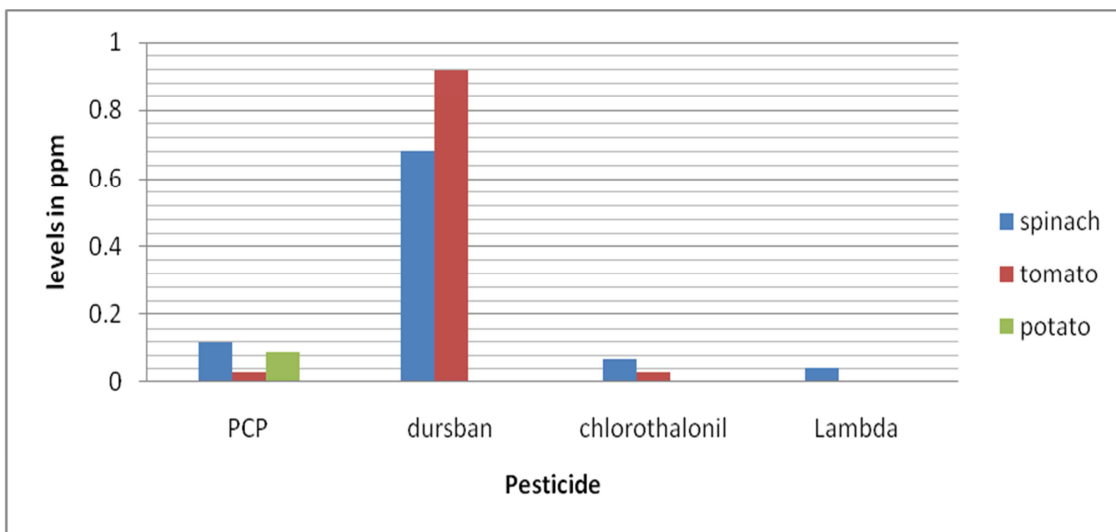
Figure 4.31: Pesticide residues level in plants.

As shown in figure 4.30 and table 4.20, some of the crops contain residues at, below or above the maximum residue limits established by either the World Health Organization or European Union.

From table 4.21 below, the percentage in excess of some pesticides was calculated and recorded in table 4.21 below.

Table 4.21: % in excess of residue compared to CODEX limit

Pesticide	Spinach	Tomato	Potato
Chlorothalonil	20.00	Below	ND
Pentachlorophenol	26.47	89.13	44.44
Chlorpyrifos	28.57	Below	ND
Lambda cyahlothrin	Below	ND	ND
ND=Not Detected			
CODEX-International body for standardization of food and other related products			

The in excess pesticide levels in various crops is shown in table 4.21. From the results, spinach level of contamination is the highest with contamination levels exceeding the set standards by 20, 26.47 and 28.57 % for chlorothalonil, PCP and chlorpyrifos, respectively. These kinds of results are of public concerns since most of the users do not wash spinach before cooking and are short-time cooked and yet the pesticide level may exceed the allowable daily intake. PCP low solubility and mobility in the soil and soil surface plays a role in exceeding the MRL. The high levels in tomatoes are of concern since most people take tomatoes when raw. The indicated levels of photo-degradation of PCP in tomatoes by sunlight may not play a big role in reducing its contamination. Its degradation products are equally hazardous.

4.8 Produce residues washing

The data in table 4.22 shows the initial pesticide residues in spinach, tomatoes and potatoes after immersing the plants in 100ppm pesticide standard solutions of the individual pesticides. Pentachlorophenol adsorption on the surface of these crops was higher compared to the others; this is most probably due to its low solubility in water. Lamda cyhalothrin is the most soluble in water of the four pesticides and hence much of the residues go to the water indicating that little is adsorbed on the crop surface.

To illustrate the effect of washing solutions on the degradation of these residues during washing, when the pesticides solution standard was mixed with the washing agent in the ratio of 1:9 volume/volume and the setup allowed for 15 minutes, all pesticides showed different degrees of degradations. This is indicated in table 4.22 and the results further represented in figure 4.31 below

Table 4.22: Effects of washing solutions on PCP, lambda cyhalothrin, chlorothalonil and chlorpyrifos degradation

Pesticide/ Solution	PCP	Chlorpyrifos	Lambda cyahlothrin	Chlorothalonil
Tap water	66.70+_2	68.70+_1	88.68+_5	85.30+_1
0.9% NaCl	66.00+_1	81.30+_2	83.30+_1	84.40+_2
0.1% NaHCO3	78.60+_3	82.62+_2	82.62+_3	82.63+_2
0.001%KMnO4	88.70+_2	85.65+_1	89.65+_2	92.30+_1
0.1% Acetic acid	76.60+_4	56.10+_1	84.10+_2	86.32+_2

When the data in table 4.22 was plotted, figure 4.32 is obtained which shows that all pesticides residues degraded in all the washing solutions with lambda cyhalothrin having the highest degradation.
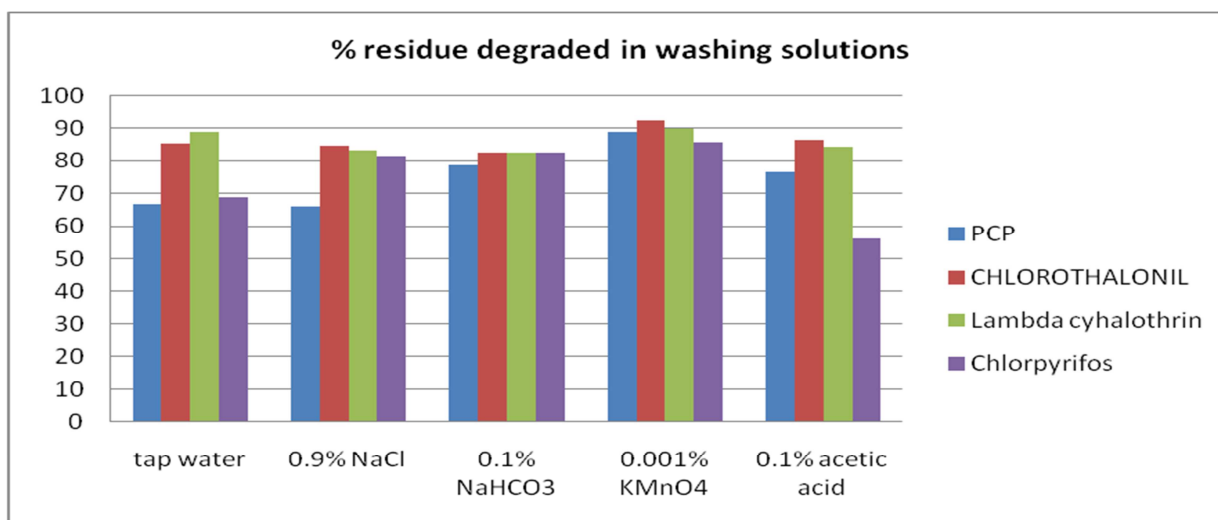
Figure 4.32:% pesticide degraded in washing solutions

0.001% potassium permanganate registered highest degradation value of 85.65-92.3% while the other washing solutions showed no significance difference. This could mean that the pesticides were less stable in potassium permanganate compared to the other washing solutions. The difference in the degradation is due to the differences in chemical properties of the residues. From table 4.20 above, a plot of initial concentration minus what was degraded is illustrated in figure 4.31. The percentage reduction of chlorpyrifos, PCP, chlorothalonil and lambda cyhalothrin in spinach, tomatoes and potatoes are presented in table 4.20 below. To determine the % of pesticide reductions, treated sample concentration was compared to the non-wash treated sample concentration. After the washing process, the reduction of pesticides in lambda cyhalothrin treated samples was shown to be superior to the reduction in PCP, chlorothalonil and chlorpyrifos treated samples. According to Gouri Satpathy et al., 2012, the reduction levels of chlorpyrifos in okra are consistent with the findings of this study. As shown in figure 4.32, lower degree of degradation was observed for PCP, chlorothalonil and chlorpyrifos in all washing solution and explains the low washing solutions efficiency for these compounds. The lower degree of degradation of PCP, chlorothalonil and chlorpyrifos on the samples surface as indicated earlier in this work may be another reason for the difficulty in their removal.

In table 4.23, the percentage pesticide loss in spinach, tomato and potato in washing solutions are stipulated:

Table 4.23: % Reduction of pesticide residues in spinach, tomato and potato

Spinach									
Solutions/Pesticide	0.001% KMnO$_4$		Tap water		0.1% NaCl		0.1% NaHCO$_3$		0.1% acetic acid	
	Initial (ppm)	% Loss	Initial (ppm)	% Loss	Initial (ppm)	% Loss	Initial (ppm)	% Loss	Initial(ppm)	% Loss
Pentachloro phenol	58.5+_3	58.738+_3	58.5+_3	35.221+_2	58.5+_3	60.046+_4	58.5+_3	59.885+_2	58.5+_3	49.609+_0.6
Chlorpyrifos	20.7+_3	78.797+_2	20.7+_3	20.826+_0.5	20.7+_3	54.725+_4	20.7+_3	47.855+_0.9	20.7+_3	35.295+_1

Lambda Cyhalothrin	18.5+_2	87.189+_1	18.5+_2	46.324+_2	18.5+_2	73.331+_2	18.5+_2	68.659+_2	18.5+_2	62.216+_3
Chlorothalonil	24.0+_1	69.283+_4	24.0+_1	10.875+-3	24.0+_1	19.275+_1	24.0+_1	16.954+_5	24.0+_1	52.625+_1
Tomato										
Pentachlorophenol	70.0+_3	78.03+_2	70.0+_3	15.276+_2	70.0+_3	48.011+_2	70.0+_3	50.104+_2	70.0+_3	70.094+_2
Chlorpyrifos	28.5+_0.9	84.959+_2	28.5+_0.9	14.397+_2	28.5+_0.9	49.488+_1	28.5+_0.9	11.706+_0.2	28.5+_0.9	28.456+_3
Lambda Cyhalothrin	19.7+_3	93.401+_1	19.7+_3	92.437+_3	19.7+_3	66.127+_0.9	19.7+_3	90.335+_5	19.7+_3	80.030+_1
Chlorothalonil	24.6+_2	62.246+_4	24.6+_2	21.508+_2	24.6+_2	33.622+_4	24.6+_2	14.671+_3	24.6+_2	13.033+_2
Potato										
Pentachlorophenol	72.3+_2	73.195+_1	72.3+_2	15.520+_2	72.3+_2	32.762+_2	72.3+_2	46.140+_2	72.3+_2	62.136+_4
Chlorpyrifos	24.8+_4	93.168+_2	24.8+_4	45.831+_2	24.8+_4	68.049+_4	24.8+_4	63.976+_3	24.8+_4	63.682+_1
Lambda Cyhalothrin	38.3+_1	94.846+_2	38.3+_1	87.136+_1	38.3+_1	85.136+_1	38.3+_1	79.285+_3	38.3+_1	76.527+_2
Chlorothalonil	55.5+_5	74.500+_1	55.5+_5	56.894+_4	55.5+_5	65.083+_0.6	55.5+_5	56.142+_4	55.5+_5	70.467+_2

Lambda cyhalothrin reduction by all the washing solutions was the highest with 87-62%, 93-66% and 94-76% in spinach, tomatoes and potatoes, respectively. This implies that on average total reduction of lambda cyhalothrin is more than 80% irrespective of the crop and washing solutions as earlier observed in photo-degradation.

The low solubility of chlorothalonil, chlorpyrifos and PCP explains the obtained % reduction. PCP chlorothalonil, chlorpyrifos and PCP are systemic pesticides and therefore are adsorbed on the crop surface and hence are easier to remove. Examination of the obtained data clearly indicated that the initial residues of PCP in all samples were higher in all produce than other residues. An earlier study by Hanafi *et al* 2010 found that boscalid initial deposit in spring onion was approximately 7 times higher than in green beans, as the surface area in spring onion is much higher than in green beans.

0.001% potassium permanganate was on average the most effective pesticide residue washing solutions. This is indicated by the percentage reduction for all the residues under investigation. Tap water was the most effective in reduction of lambda cyhalothrin in spinach, tomatoes and potatoes.This is further corroborated byCabras *et al*. (1999) who reported that home washing with water removed about 50% of imazalil residues and 90% of thiabendazole's from oranges.

The variation in each pesticide reduction depended upon the specification of washing solution. In lambda cyhalothrin the 0.001% $KMnO_4$ had the greatest effect on residue reduction of 94.846%. This could be partially be explained by the degradation effect of this solution. Other studied pesticides were also found highly degraded in the 0.001% KMnO4 solution (Table 4.21) because $KMnO_4$ is a strong oxidizing agent and the solution resulted in a high redox potential when used as the active ingredient for a given concentration. Oxidative compound such as hypochloric acid in strong acids electrolyzed water has also been reported for its most effectiveness in reducing dimethoate concentrations by oxidation (Zhang *et al*., 2007). Thus, the oxidative property of $KMnO_4$ could also have a significant effect on degradation of studied pesticides. 0.1% acetic acid also registered substantial degradation which is explained by the relatively high acidity and/or high redox potential.

CHAPTER FIVE

5.0   CONCLUSION AND RECOMMENDATIONS

From this research work, the following conclusion and recommendations are made:

5.1   CONCLUSION

Adsorption of chlorpyrifos decreases with increase in mass of loam soil. The longer the contacts time the higher the adsorption with an equilibration time of 30 minutes. Increase in concentration results in decreased percentage (%) adsorption. This is because at high initial concentration the number of moles of chlorpyrifos available to the surface area were high, so functional adsorption becomes dependent on initial concentration. Adsorption of chlorpyrifos followed Redlich-peterson isotherm model with regression values ranging from 0.954 to 0.992. As shaking time increased from 15 minutes to 60 minutes, the value of n increased from 0.1998 to 0.2914. The value of ΔG was 11.7946+_0.3kjol/mol which indicates that adsorption of chorpyrifos by loam soil is spontaneous.

Photo-degradation of residues on the surface of spinach leaf by different light intensity followed first order kinetics. The degradation rate was in sequence of 100w>75w>60 > 40>sun. The rate of degradation heavily relied on temperature, exposure time and light intensity. The half-life ranged from 0.069 to 0.141 for spinach and 0.074-0.105 for tomatoes.

The results of monitoring the four residues under investigation indicated significant levels of chlorothalonil, pentachlorophenol and chlorpyrifos in spinach and high levels of PCP in both tomatoes and potatoes. PCP levels exceeded CODEX limits by 26.47, 89.13 and 44.44 % in spinach, tomatoes and potatoes, respectively, while chlorothalonil and chlorpyrifos in spinach exceeded levels by 20.00 and 28.57 % respectively.

Washing solutions showed significant efficiency in removing the residues to be below the recommended MRL. Factors such as physical and chemical property of pesticide, the type of vegetable and the washing solutions affected the removal of pesticide residues. Among the washing solution treatments, 0.001 % KMnO4 washing solution was the most effective in reducing the pesticide residues which was consistent to high degree in the pesticide degradation.

5.2 RECOMMENDATION

Based on the findings, results and discussions of this research project, the following recommendations are highly proposed;

- The government and agricultural experts should promote organic container farming in slums, arid and residential areas.

- Organic farming should be organic farming i.e. farmers should avoid residues in their farms. Biological pest and weed control measures should be used.

- Whenever organic garden produce are offered to the market, farmers should indicate so and the residue levels clearly indicated in the package.

- Environmentalist and scientist should come up with more efficient and effective ways of disposing residues and residues packaging materials.

- Thorough washing of produce is encouraged with running water as well as peeling of fruits before consumption.

- KEPHIS, KARLO and Pesticide board should come up with a Kenyan database containing residues in particular area with their disposal mechanisms

- The government should ensure banned residues are not present in the market in any formulation. Pesticides adulteration should be dealt with more strictly.

5.3 RECOMMENDATIONS FOR FURTHER WORK

Further research work is highly recommended to:

- Further survey on farmers praising organic container farming in slums and other areas, those using pesticides and marketing of produce.

- Produce should be sampled from the market and pesticide residues level determined. Information should be disseminated to the general public

- Determine the mechanism of pesticide residues degradation in organic container garden.

- Further work on adsorption behavior of these residues with respect to change in temperature should be done. This is because of the different weather conditions under which different farmer use these residues.

- A database should be put in place on how farmers are using different classes of residues, how they dispose them and more so how they dispose the containers holding these residues.

Different washing methods should be researched. They should be efficient, easy and practical in most areas e.g. market, roads and homes.

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APPENDIX A1

Table 1: Results of tap water rinsing in reducing residues across all commodities

Pesticides	Pairs of Data	Significantly Reduced	Water Solubility (mg/L @ 20 ° C)
Insecticides			
Endosulfan	60	Yes	0.32
Permethrin	37	Yes	0.2
Diazinon	22	Yes	40
DDE	21	Yes	<1
Chlorpyrifos	13	No	2
Methoxychlor	12	Yes	0.1
Malathion	7	Yes	130
Bifenthrin	7	No	0.1
Fungicides			
Captan	34	Yes	3.3
Vinclozolin	23	No	3.4
Iprodione	13	Yes	13
Chlorothalonil	9	Yes	0.6

APPENDIX A2

QUESTIONNARRE

ANALYSIS OF PESTICIDE RESIDUES IN SELECTED CROPS GROWN USING ORGANIC CONTAINER GARDENING METHOD

Area:…………………………………Farmers Name………………………Date………………….

1. Which crops do you normally grow in your organic farm?...

2. Do you grow your crops in plastic buckets, plastic bags, and sacks or in flower beds? ....

3. Do you know what organic gardening is? If yes, do you have any prior training organic garden methods? ....

4. Are your crops often or at times attacked by pest and/or diseases? Which pest and diseases? ....

5. Do you apply any chemicals in your farm? If yes which ones and when do you apply? How often do you apply? ....

6. How much do you apply? After applying these pesticides, how long do you take before harvesting? ....

7. Where do you sell or take your harvest? ....

8. Do you wash your produce before taking to the market or eating? How do you do it? ....

9. Do you think most consumers are aware of how the produce is grown or what chemicals are applied? ....

10. What advantages do you have when you grow the crops by organic gardening over other methods? ....

APPENDIX A3

Table 2: Banned Pesticides in Kenya *(pesticide control board 2014)*

	Common name	Use	Date Banned
1.	2,4,5 T (2,4,5 – Trichloro-phenoxybutyric acid)	Herbicide	1986
2.	Chlordane	Insecticide	1986
3.	Chlordimeform	Insecticide	1986
4.	DDT (Dichlorodiphenyl Trichloroethane)	Agriculture	1986
5.	Dibromochloropropane	Soil Fumigant	1986
6.	Endrin	Insecticide	1986
7.	Ethylene dibromide	Soil Fumigant	1986
8.	Heptachlor	Insecticide	1986
9.	Toxaphene (Camphechlor)	Insecticide	1986
10.	5 Isomers of Hexachlorocyclo-hexane (HCH)	Fungicide	1986
11.	Ethyl Parathion	Insecticide.All formulations banned except for capsule suspensions	1988
12.	Methyl Parathion	Insecticide All formulations banned except for capsule suspensions	1988
13.	Captafol	Fungicide	1989
14.	Aldrin	Insecticide	2004
15.	Benomyl, Carbofuran, Thiram combinations	Dustable powder formulations containing a combination of Benomyl above 7%, Carbofuran above 10% and Thiram above 15%	2004

16.	Binapacryl	Miticide/Fumigant	2004
17.	Chlorobenzilate	Miticide	2004
18.	Dieldrin	Insecticide	2004
19.	Dinoseb and Dinoseb salts	Herbicide	2004
20.	DNOC and its salts (such as Ammonium Salt, Potassium salt & Sodium Salt)	Insecticide, Fungicide, Herbicide	2004
21.	Ethylene Dichloride	Fumigant	2004
22.	Ethylene Oxide	Fumigant	2004
23.	Fluoroacetamide	Rodenticide	2004
24.	Hexachlorobenzene (HCB)	Fungicide	2004
25.	Mercury Compounds	Fungicides, seed treatment	2004
26.	Pentachlorophenol	Herbicide	2004
	Phosphamidon	Insecticide, Soluble liquid formulations of the substance that exceed 1000g active ingredient/L	2004
27.	Monocrotophos	Insecticide/Acaricide	2009

APPENDIX A4

Table 2: Aqueous phase concentration of chlorpyrifos following equilibration of 0.5g of different soil samples for different periods with water, spiked with different concentrations of chlorpyrifos

Shaking time (min)	Spike levels	$[X]e + [SXn]w$	$[X]_{ads}$
15	10	0.09+_0.04	9.91
	20	0.37+_0.23	19.63
	30	6.90+_2.36	23.03
	40	10.92+_3.56	39.08
	50	15.24+_2.96	34.76
30	10	0.04+_0.06	9.96
	20	0.02+_0.008	19.98
	30	0.19+_0.05	28.91
	40	2.72+_1.89	37.38
	50	5.03+_2.57	44.97
45	10	0.04+_0.01	9.96
	20	0.09+_0.63	19.91
	30	0.47+_0.27	29.53
	40	2.37+_1.05	37.63
	50	4.63+_1.96	45.37
60	10	0.03+_0.01	9.97
	20	0.07+_0.02	19.93
	30	0.53+_0.21	29.47
	40	2.54+_1.07	37.46
	50	4.63+_1.96	45.37

APPENDIX A5: Maximum residue levels in some crops (codex database; retrieved on 22nd February, 2014)

PESTICIDE	FOODSTUFF	MAXIMUM RESIDUE LIMIT (MG/KG)	ADI
Lambda-cyhalothrin	Apples, grapes (table), pears and plums Apricots and peaches Beans Cruciferae, groundnuts, potatoes and tomatoes Macadamia nuts, mealies (green) onions and peas Sorghum and wheat	0.2 0.5 0.02 0.05 0.01 0.02	0.007mg/kg bw
Chlorothalonil	Beans, cruciferae, cucurbits Tomatoes, groundnuts and potatoes Peas	3.0 0.1 0.3	0.02 mg/kg bw.
Chlorpyrifos	Apples, apricots, carrots, lettuce, mealies (green), peaches, pears, plums, potatoes and wheat Bananas Grapes and tomatoes Citrus Cruciferae Grapes (wine)	 0.05 1.0 0.5 0.3 0.1 0.5	0.01 mg/kg bw.
Cyhalothrin (sum of isomers)	Apples, grapes, pears and plums Apricots and peaches	0.2	0.01 mg/kg bw

		0.5	
Pentachlorophenol	Apples, grapes, mealies (green), pears and sorghum		0.008mg/kg bw
		0.5	
	Beans, peas and tomatoes	0.1	
	Cereal grains	2.0	
	Cotton seed, potatoes and groundnuts	0.05	
	Soya beans	0.1	

Mg   milligram

Kg   kilogram

BW   body weight   and ADI   average daily intake