UNIVERSITY OF NAIROBI

PHOTO-DEGRADATION OF PENTACHLOROPHENOL AND DIMETHOATE ON THE SURFACE OF LOAM SOIL, NAIROBI RIVER SEDIMENT AND SPINACH FROM NGARA MARKET IN KENYA

BY

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AUGUST 2016

DECLARATION

I declare that this research thesis is my original work and has not been submitted elsewhere for research. Where other people's work or my own work has been used, this has properly been acknowledged and referenced in accordance with the University of Nairobi's requirements.

AJULIU PATRICK KINYUA

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DEDICATION

This work is dedicated to my dear wife, my parents Mr. and Mrs. Ajuliu, my children; Kelvin, Kennedy and Lillian, my brothers, sisters and friends.

ACKNOWLEDGEMENT

I express my sincere gratitude to my supervisors, Prof. G.N. Kamau, Prof. Lydia W. Njenga and Dr. J.G.Kithure for their valuable and generous contribution towards the completion of this work. My heartfelt appreciation also goes to Mr. James K. Mbugua for his generous and technical support throughout my research period.

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Finally, I thank the Teachers Service Commission for granting study leave that made my studies possible. I am greatly indebted to the Almighty God who gave me the strength and wisdom to complete this work through his Son Jesus Christ and Saviour.

ABSTRACT

This research endeavours to investigate the photo-degradation of pentachlorophenol and Dimethoate by incandescent bulbs and fluorescence light on Nairobi river sediment, Limuru loam soil and spinach leaf surface. This is because Most of research done in pesticides show that herbicides, fungicides and insecticides tend to persist in the environment mainly soil, water, or air for a long time.

It is therefore necessary to determine their possible decomposition using different light energies and extent of exposure time, which may lead to possible harmless compound.

The research was done by applying 0.01g of each of the pesticide to 1.0g of the river sediment, loam soil and 5cm by 5cm spinach leaf surface. Then it was shaken thoroughly for five minutes. Thereafter the mixture was exposed to sunlight, 40w, 60w, 75w and 100w incandescent bulbs at 10, 20, 30, 60 and 120 minutes after which the set-up was allowed to stabilize for an hour. The stabilized set-up was washed with 2ml of analytical grade acetone. Then it was analysed for pesticide level using Shimadzu UV-Visible spectrophotometer at 322nm and 229nm for Pentachlorophenol and Dimethoate respectively. This procedure was repeated using 9w, 11w, 15w and 20w fluorescence tubes in place of incandescent bulbs. The procedure was repeated three times to obtain consistence results for statistical purpose. The data obtained was recorded, analysed and interpreted using Minitab 17 and Microsoft Excel statistical software's.

The research revealed that, photo-degradation of both pentachlorophenol and dimethoate depends on the surface of exposure, light intensity, temperature among other factors. The 100W incandescent bulbs and 20w fluorescent tubes degraded both molecules mostly due

to the high number of photons striking the molecules, which causes photochemical reactions.

Spinach leaf surface is flat and well defined thus pesticide molecules are evenly exposed to radiation hence high degradation rate. The lower levels of both pesticides in Limuru loam soil are attributed to adsorption and photo-degradation processes.

In both pesticides, first order kinetics was followed. This is based on the high regression values obtained by the plots of natural logarithms of concentration versus time. The half-lives of both molecules on the three-exposure surface ranged between 0.007306 to 0.076days for PCP in incandescent bulb and 0.078 to 0.093 days for fluorescence light while the range of half-life is 0.037 to 0.00446 and 0.0023 to 0.013 days for DM in incandescent bulb and fluorescence light respectively. This was also dependent on the light intensity, surface of exposure and radiation time.

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LIST OF ABBREVIATIONS

Abbreviation	**Meaning**
ACH	Acetylcholine
BHC	Benzene hexachloride
DM	Dimethoate
BX	residue at time x
ChE	Cholinesterase
Conc.	Concentration
Dev't	Development
EC	European Commission
EU	European Union
FAO	Food and Agricultural Organization
GTZ	German Trade Zone
K	rate of Decomposition
LA	Local authority
Ln	natural Logarithm
MOA	Ministry of Agriculture
MOH	Ministry of Health
PCP	Pentachlorophenol
PH	Hydrogen potential
Ppm	parts per million
Tepp	Tetrathylphosphate
Tx	time in days
T1/2	half-life
WHO	World Health organization

CHAPTER ONE

INTRODUCTION

1.1 Background information

The world human population is anticipated to reach 9.15 billion by 2050. This implies that to feed such a population agricultural production should increase to 70% (GTZ -2010). To produce enough food to meet this rapidly growing population is a big challenge to the third world countries. This is due to unpredictable weather patterns, expensive farming machinery and methods, cost of pesticide and applicability skills.

Since 2008, Kenyan food security steering group has been facing severe food insecurity problem. Over 20 million Kenyan are living under food insecurity, majority relying on relief food. Vegetables and partly fruits make Kenya daily diets a main source of vitamins, minerals for human growth and development. The commonly consumed vegetables are Sukuma wiki, spinach, cabbages, onions, tomatoes, pigweeds among others. These vegetables, fruits and cereals grown in Kenya are heavily destroyed by various diseases and pests hence pesticides usage becoming inevitable. Weeds, fungi and insects rob crops much needed nutrient, they attack them hence reducing the farmer's yields (Helweg 2003).

1.2 Definition of pesticide

Pesticide is defined as an agent intended for prevention, destroying, repelling or mitigation of any pest and diseases. Pesticides classification may be divided into groups such as insecticides, acaricides, nematodes, herbicides, avicides, rodenticides and molluscides depending on the species of the pest (Mathew and August 1975).

According to WHO definitions, Pesticides refers to one substance or mixtures of many substances that destroy pests or prevent pests from interfering with production, processing and storage of food or agricultural commodities (Farrely *et al.,* 1984). During the ancient day's soil, salt of metals, ash, natural oils and tobacco products were used as pesticides (Anderson *et al.,* 1981).

1.3 Brief History of pesticides

Pesticides have been used since 1000 B.C., for example, a Scholar known as Homer used Sulphur to fumigate homes around 900B.C. and the Chinese used arsenic products to prevent garden pests. In Ireland arsenic, mercuric chloride, pyrethrum, lime and sulphur were used to treat potato blight (*Phytopthora infestans*), in the mid-19th century. During the World War II, biological substances and inorganic compounds such as calcium arsenate, lead arsenate, selenium compounds, pyrethrum, copper sulphate, thiram, mercury, and nicotine were used mostly to control pest. However, cultural methods such as tillage rotations, and manipulation of sowing dates were also used to control pests. Today use of pesticide has mushroomed with 1,600 types of pesticides available. About 4.4 million tonnes of pesticide costing more than $20 billion are used annually. Twenty five percent of this pesticide market is consumed in the United States of America (Pimentel *et al.,* 1982).

1.3.1 Older insecticides

The first synthetic insecticide, dichlorodiphenyl-trichloroethane (DDT) was discovered in Switzerland in 1939. It was very effective in controlling body lice, head lice, and agricultural pests, for many years. Today DDT has been banned from the market. Benzene hexachloride (BHC) and chlordane were discovered during World War II. Heptachlor and oxaphene were discovered slightly later. Two organochlorines, aldrin and dieldrin, were discovered followed by isobenzan endosulfan, and endrin (Pimentel *et al.,* 1980). Organophosphate pesticides originated from nerve gases developed by

Germans in 1945. Pesticides developed as insecticides, for example, parathion and tetraethyl pyrophosphate (TEPP) were very toxic to mammals. Other organophosphatessuch as demeton, diazinon, phorate, methylschradan, dimethoate, disulfoton, meviphos and trichlorophon have been registered. Organophosphate pesticides act by inhibiting the enzyme cholinesterase (ChE) in mammals and insects. Cholinesterase acts by breaking down neurotransmitter acetylcholine (ACh) at the nerve synapse. This causes blockage of nerve impulses hence hyperactivity, tetanic paralysis and eventually the death of the insect. Some organophosphate are systemic in animals and plants, although most of them are not persistent thus do not bio-accumulate in animals hence have no significant environmental impacts (US EPA-2007)

1.4 Large scale farming in Kenya

Large-scale farming use aircrafts to apply pesticides to control weeds, fungi and insects that destroy crop proper growth and better yields. This is common in large plantation of cotton, rice wheat among others. Below is an aircraft spraying tea plantation in China (figure: 1.1).

Figure 1.1: Tetradifon pesticide application on a large scale.

Agricultural production has been accompanied by continuous use of agrochemical applications. About 98% of the agrochemicals (pesticides) and 95% herbicides reach different destinations from target species falling in air, water, soil and plants. In most developing countries, farmers employ small-scale farming suggesting manual spray of pesticides (Figure1. 2) (Helweg, 2003)

Figure 1.2: Farmers spraying their crops with pesticides

Synthesis of chemical pesticides has been on increase where today more than fifty classes and about 1500 individual substances have been produced in more than 100,000 formulations (Anderson *et al*., 1981). The immediate weapons against pests are the pesticides . Pesticides are applied during storage and after harvesting. For a farmer to have increased food production to reasonable levels increased pesticides usage is necessary. Therefore, a great need to produce non-toxic pesticides. There is a great need to research thoroughly on safer, more effective and efficient pesticides that are being used. Pesticides are needed in future to help production of adequate food for survival of the humankind (Frejika 1975). Pesticides are of various types for example organochlorines, organophosphate, carbamates and pyrethroids. Large-scale farmers apply more pesticides ending up in environmental contamination. Some of the pesticides used to control weeds, fungi and insects are organochlorines and organophosphates like pentachlorophenol (PCP) and Dimethoate (DM), respectively. Wide spread use of PCP and DM in agriculture to combat diseases, herbs and insects has caused public concern based on human risk that can be caused by the ingestion of PCP or DM contaminated foods (Randhawa *et al.*, 2007).

1.5 Effects of pesticides in the environment

PCP is an organochlorine insecticides while Dimethoate is an organophosphate insecticide used in insect control. This is because of their acute toxicity to insects and short persistence after application. After the pesticide is applied, only 0.1% of it reaches the target site while the rest ends up in environmental contamination (Ardley J., 1999). Various processes such as absorption, breakdown, transfer and degradation affect pesticides in the environment. Transfer of pesticide refers to moving pesticides away from the targeted sites by leaching, spray drift, volatilisation, run off, crop removal and absorption (Ruzo and Casida, 1992).

1.6 Pesticide residue in the environment

Once a pesticide is placed into the environment, several processes take place. Among them, the commonest is the leaching process. Leaching aids the herbicides to reach into the root zone of the plant and this gives a farmer a better control of weeds. The pesticides (chemical) that does not get or reach the target, would be very harmful to people and other organisms in the environment (Harrison, 1990), as illustrated in figure 1.3 below.

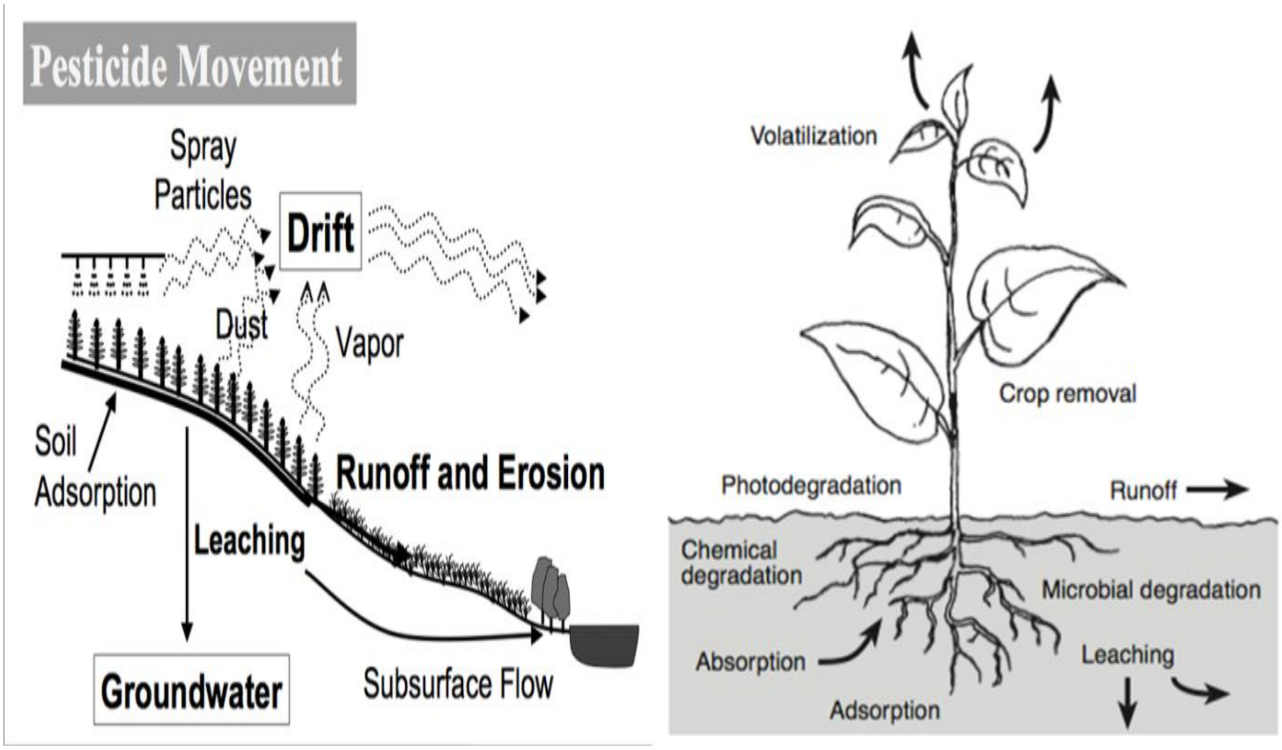


Figure 1.3: Schematic diagram illustrating pesticide residues in the environment.

It is important to note that surface runoff move away the herbicide from targeted weeds. This result in reduced weed control, chemical wastage and possibly pollutes soil and water (Rockets, 2007). Transportation of pesticide is affected by process such as breakdown, transfer, adsorption, and degradation processes as demonstrated by figure 1.3 and 1.4.

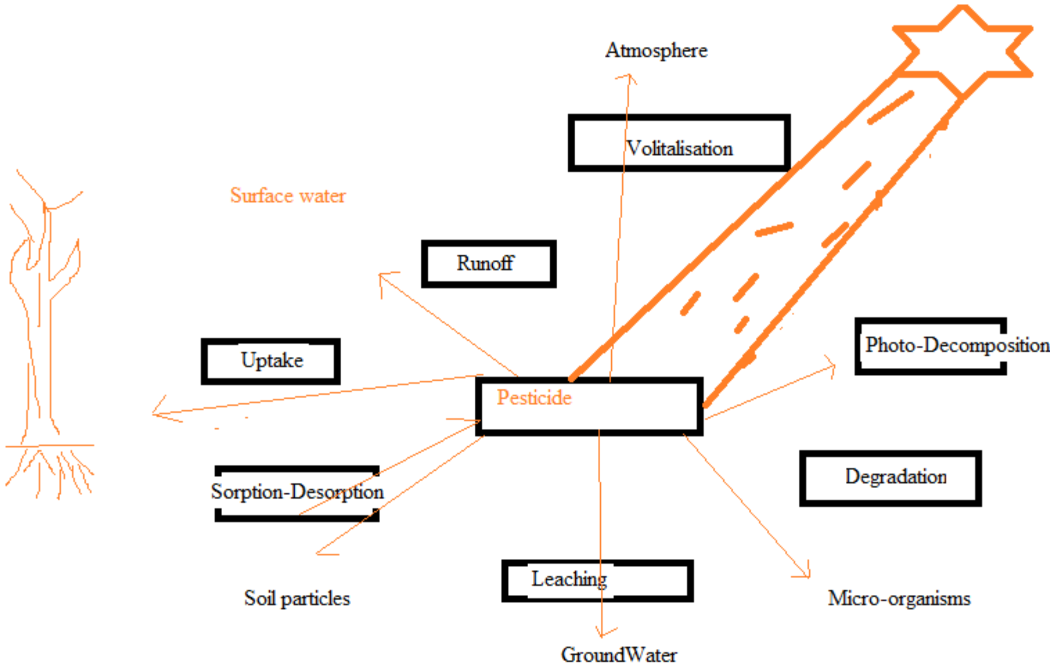


Figure 1.4: **Pesticides Dissipation pathways.**

Adsorption refers to adhesion of pesticides to the surface of the soil particles or it is a phenomenon where molecules attach themselves onto the surface of substances. There are various types of adsorptions for example physio-sorption and chemi-sorption. Physio-sorption is the physical adsorption where the forces of physical nature are relatively weak whereas chemi-sorption is chemical adsorption where the forces of attraction are relatively stronger. The amounts of pesticides adsorbed to the soil surface vary with pesticide types, soil pH, soil moisture contents and texture of the soil (Jong-Hang *et al.*, 1997).

1.7 Statement of the research problem

To meet the large world population food needs, pesticides have to be used to improve food crops yields (Paul, 2005). Dimethoate is a Pesticide, which is a toxic organophosporus insecticide to human beings and poses environmental pollution to air, soil, water and plants (Spiric and Saicic 1998). Wide use of PCP and DM has caused human risks caused by ingestion of pesticides contaminated foods (Randhawa *et al.*, 2007). Some photo-degraded by products are more harmful and toxic than the parent molecule. This may pose great danger to the public. Environmentalist mainly specializes on the movement and removal of the parent molecule as compared to the by-products. The Kenyan government through the pesticide control board has banned several residues with an aim of protecting the environment (See appendix 1). Therefore, urgent need to analyse, know the extent of pollution and how to decompose them is important.

Degradation of pesticides is the breakdown into its simpler by products of pesticides after it has been applied. This is through chemical reactions, microbial activities and light effects or photo-degradation. The rate of degradation process of pesticides varies from one pesticide to the other and from hours to days and to years depending mostly on environmental conditions. Pesticides that are easily degraded provide only a short-term control effects to the farm (Ardley J., 1999). Microbial degradation is effective when environmental temperatures are moderate, moist soil, favourable crop soil pH and oxygen concentration. Chemical breakdown of pesticides especially the organophosphates are mainly influenced by soil temperature, pH level and adsorption of pesticides. Microbial degradation on alkaline soil is faster than on acidic soils (Barcelo *et al.,* 1993).

Photo degradation of pesticide refers to the breakdown of pesticide by sunlight effects. Intensity and duration of exposure to sunlight influences the rate of degradation. Pesticide sprayed on leaf surface shall be exposed to more sunlight than pesticide incorporated into the soil. This study focused on photo degradation of PCP and DM on selected loam soil, spinach leaf surface and Nairobi river sediments using incandescent, sun and fluorescent light. Pesticides in the greenhouse made of glass roof, photodegrades faster than greenhouse made of plastic cover. This is because glass filters out some light (UV light that degrades pesticides) (Weerasinge *et al.,* 1992). Currently there is no detailed information on photodegradation of pesticides.

1.8 General Objective

This work was aimed at evaluating the extent of photo-degradation of pentachlorophenol and dimethoate on Thigio loam soil, Nairobi river sediment and spinach leaf surface relative to exposure time and different energies of light.

1.8.1 Specific objectives

i. To investigate possible photo-degradation of pentachlorophenol and dimethoate on Limuru loam soil, Nairobi river sediment surface and spinach leaf surface using direct sunlight, 40W, 60W, 75W and 100W bulbs and 9w, 11w, 15w and 20w fluorescence tubes.

ii. Determine effect of different light intensities and temperature on photo-degradation of pentachlorophenol and dimethoate using sunlight, 40W, 60W, 75W and 100W bulbs and 9w, 11w, 15w and 20w fluorescence tubes.

iii. Determine rate of photo-degradation of pentachlorophenol and dimethoate on loam soil and Nairobi river sediments and spinach leaf surface using sunlight, 40W, 60W, 75W and 100W bulbs and 9w, 11w, 15w and 20w fluorescence light.

1.9 Justification of the study

Most of research done on pesticides show that herbicides, fungicides and insecticides tend to persist in the environment mainly soil, water, or air, for a long duration of time. There are many scholars trying to review photolysis of pesticides but very little is known due to limited information that is published.

It is therefore necessary to determine pentachlorophenol and dimethoate possible degradation/decomposition using different light energies and extent of exposure time, which may lead to possible harmless compound, thereby lowering their persistence power.

CHAPTER TWO

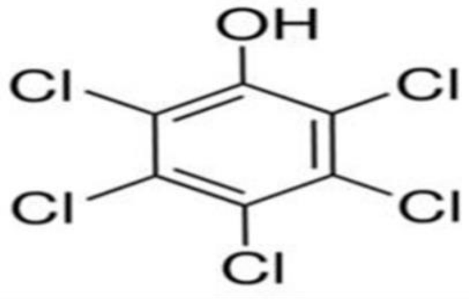
LITERATURE REVIEW

2.1 General overview

Degradation of pesticides may give rise to intermediate compounds that may be more toxic than the original pesticide or herbicide. For example insecticide such as parathion (O,O-diethyl-O-P-nitrophenylphosphorothiate) is extensively used pesticide that undergoes enzymatic hydrolysis to produce p-nitro phenol, which further hydrolysis to produce nitrous acid and hydroquinone(p-hydrophenol) which is metabolic intermediate. 2, 4-dichlorophenoxyacetic acid (2, 4-D) bio-degrade to produce the phenolic acid compounds such as 2, 4-dichlorophenol and 4-chloro-2-hydroxyphenol (Alexander, 1964).

2.2: General properties of pentachlorophenol (PCP) molecule.

Pentachlorophenol is a hydroxy-derivative of benzene and condensed nuclei as demonstrated in figure 2.1 below.



C_6Cl_5OH

Figure 2.1: Structural and molecular formula of pentachlorophenol molecule.

PCP has a molecular weight of 266.33g. It is a white mono clinic crystalline solid. It is slightly soluble in water but very soluble in acetone and ethyl ether. It is non-combustible, non-corrosive in absence of moisture. It has a characteristic odour i.e. benzene-like odour. It has a density of 1.97g/cm$^{3.}$ It has a boiling point p of 309-310^{0}C and melting point of 174^{0}C. It is used as a fungicide, insecticide, herbicide and wood preservative in USA.

2.3 General properties of dimethoate (DM) molecule

Dimethoate is an organophosphate molecule whose structure is shown in figure 2.2 below.

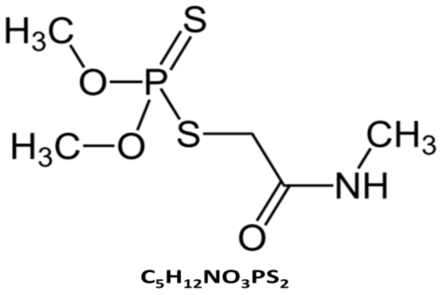


Figure 2.2: The Structural and molecular formula of dimethoate molecule.

The IUPAC name for dimethoate is O, O-dimethyl-carbamoyl methyl phosphorodimethioate. Pure dimethoate is colourless crystalline solid with an odour of mercaptan. DM is highly soluble in ketones, chloroform, methylene chloride, and esters and slightly soluble in water and acids at room temperature. It’s unstable in alkaline media. When DM is heated strongly, it’s converted to O, S-dimethyl phosphorothioate. DM is used commonly as an insecticide. It is toxic and inhibits cholinesterase activities. DM has half-life of 2 to 5 days in moist air. DM degradation in soil depends on soil type, temperature, moisture and pH level. DM has a melting point of 45^0C to 52.2^0C and boiling point of 107^0C at 0.05mmHg and 86^0C at 0.01mmHg. DM has water solubility of 39g/l at pH 2 to 7.

2.4 Overview of pesticides

According to an earlier research (Lorenz, 2009) most pesticides are not easily biodegraded, they persist in soils, leach to the ground water and surface water and hence bio-accumulate in food chains thus influence human health thereby resulting in several negative effects in the environment. Photo-degradation is one of the natural pathways common for pesticides degradation after it is released into the environment.

Photolysis process on soil surfaces is vital when a pesticide is placed directly to the soil. Alternatively, photolysis is not significant especially when plants leaf cover intercept sunlight from reaching the ground soil surface. Different plant species have various foliar interceptions of the pesticides, which increase, with their stage of growth (Linders *et al.*, 2000), As plants mature soil photolysis is lessened. Pesticides reach the soil indirectly through Spray drift or wash off after rainfall.

To clarify the environmental photo degradation profiles of pesticide, many researchers have focused on photolysis in dilute solution or organic solvent solution. Photolysis on soil is made more difficult to understand by the soil heterogeneity, plant surfaces as well as unpredictactabe transmission of sunlight on them. Despite the many scholars trying to review photolysis of pesticides (Roof 1982; Miller and Zepp 1983;Choudhry and Webster 1985; Marcheterre *et al.*, 1988; Parlar 1990; Wolfe *et al.*, 1990; Cessna and Muir 1991; Me´allier 1999; Floesser-Mueller and Schwack 2001; Burrows et al. 2002), very little is known due to limited number of investigations carried out hence limited information is published. Photolysis on plants is based on speculation of plant metabolism studies. Therefore, photodegradation on soil and plant surfaces needs a lot of attention and skilled research to investigate experimentally and theoretically in order to understand the photo-physical mechanism and photochemical processes in pesticides solid phases. Such knowledge if applied the understanding of dissipation profiles will be clear. Thus, the current research aims at adding value to limited data on photo degradation.

T.Katagi (2004) reviewed factors affecting the photo-degradation process by considering the basic photo-physics and photochemistry studies that are relevant to the degradation of the pesticides. T.Katagi also investigated deactivation, molecular excitation and chemical processes for different classes of pesticide residues. T.Katagi (2004) discussed the photo-degradation process as both a photo-physical and photochemical process.

2.4.1 Photo physical processes

The UV absorption profiles of the pesticides, the emission spectrum of sunlight and surrounding medium are the factors that the extent of the sunlight photolysis depends on. This is true because the energy needed to split a chemical bond in any pesticide molecule ranges from 70 to 120 kcal mol^{-1}, which corresponds to light wavelengths of 250–400 nm (Watkins 1974). Therefore, sunlight spectral irradiance detected near the ground somehow becomes paramount in determining the photodegradation of the pesticides. Sunlight intensity decreases to about 10% by passing it through the troposphere; no light is conveyed at a wavelength of less than 295 nm, because UV will be absorbed by ozone layer (Zepp and Cline 1977; Parlar 1990). This result in sunlight near the ground to exhibit a maximum at 440 to 460 nm and at this wavelength the UV becomes responsible for photodegradation of pesticide to approximately 5% to 6% of the total intensity.

Figure 2.3 illustrates the photophysical absorption pathways of sunlight (Turro 1978; Roof 1982; Parlar 1990).

Molecular excitation and interaction occurs when a photon passes very close to a molecule of a pesticide through the electric field of light and dipole moment of a pesticide molecule without change of molecular geometry(Franck–Condon principle). Each photon can only activate a single molecule in the ground stateata time (S_0) with a probability certainty of the excited singlet state (Stark–Einstein rule), where the lowest excited state (S_1) is usually involved in further photo processes. Generally, pesticide molecules which exhibits a UV-Vis absorption spectrum of less than 290 nm have a substituted aromatic segment, that is conjugated with a lone-pair of electrons or the unsaturated bonds like that of carbonyl or carbamoyl group, and thus $\pi \rightarrow \pi^*$ or $n \rightarrow \pi^*$ transition occurs upon irradiation.

The Photo-physical pathways from the S_1 state are emission of fluorescence, non-radiative internal conversion and intersystem crossing of the excited triplet state (T_1) as shown in Figure 2.3 below. Pathway S_1-T_1 is the relaxation from that of higher vibrational levels (˜10^{12} sec-^{1}) in S_1 state. This is followed by a relaxation onto a lower electronic state, which has the same multiplicity (10^{6}–10^{12} sec^{-1}).

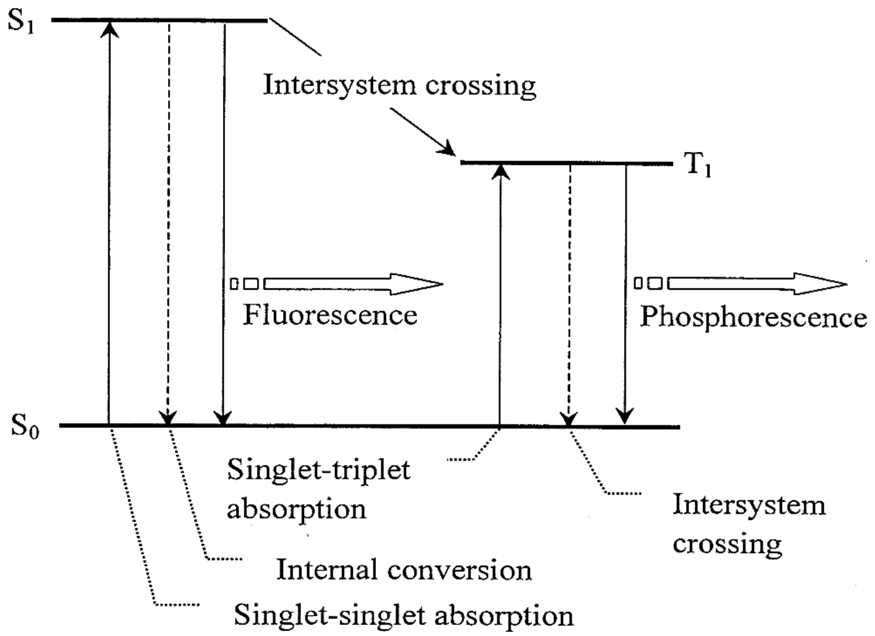


Figure 2.3 : Sketch of energy state diagrams (T. Katagi, 2004).

The pathway T_1-S_1 is radiative deactivation process. Here fluorescence spectrum, which is a close mirror image to that of absorption (due to the Franck–Condon principle), shifted to the red. The fluorescence lifetime is usually very short (microseconds to nanoseconds) because transition between states has a similar multiplicity. The final pathway is a spin-forbidden ($S_1 \rightarrow T_1$) process, which is followed by a slow radiationless deactivation also known as emission of phosphorescence. The $T_1 \rightarrow S_0$ process is spin-forbidden also, and its lifetime of phosphorescence is of order milliseconds to 102 sec. Despite many chemical classes and either temperature difference in measuring spectra or a solvent system, their wavelengths maximum are located in the range of 380 to 530 and 280 to 450nm, respectively. The following equation converts energy level(E) and emission wavelength (λ) (Gould 1989b), where the energy levels of the triplet (Et) and excited singlet (Es) states can be estimated to be 54–75 and 64–102 kcal mol^{-1} for these pesticides, respectively.

$E\ (\text{kcal mol}^{-1})\ 2.864 = 10^4/\ \lambda\ (\text{nm})$ ………………………………… … (PP.1)

The presence of a heavy atom in a molecule facilitates intersystem crossings, and since the fluorescence spectrum of a pesticide is difficult to measure at room temperature, instead phosphorescence can efficiently be detected.

This foregoing argument isalso applicable to molecules of pesticide in the solid phase, where adsorption onto these media may affect the Photophysical processes. Molecular motion if highly restricted and its interactions with heterogeneous surfaces would result in modified electronic states. In such a case, (spectrum of a pesticide) reflectance gives very important information than an absorption spectrum, and this is clearly demonstrated by the relationship of the Schuster and Kubelka-Munk (Parlar 1984) rather than the Beer–Lambert law, equation pp 2.

$F\ (R\infty) = (1 - R\infty)^2/2R\infty = K/S$…………………………………………….. (PP.2)

F (R∞) is the diffuse reflectance, representing the radiation that penetrates into the powder and resembles the usual transmission spectrum. R∞ is representing the ratio of a standard to that of reflectance thus a non-absorbing standard such as MgO compared to F of an infinite thick layer. S and K are the scattering and absorption coefficients, respectively. Adsorption may produce unequal excited and ground state displacement potential curves that result into different vibrionic band shape. Therefore, adsorption spectral changes are characterized by broadening of absorption bands, spectral shift, changes of extinction coefficient and appearance of new bands (Wendlandt and Hecht 1966; Nicholls and Leermakers 1971; Parlar 1984).

2.4.2 Photochemical processes

The cause of the many chemical reactions in an excited molecule is the energy lost as heat in an excited state molecule or emitted as light. There are two main types of photochemical reactions, “indirect” and “direct” photolysis (Roof 1982; Miller and Zepp 1983). Direct photolysis refers to the photoreaction that proceeds by absorbing light energy, while indirect photolysis refer to a reaction of the ground-state molecule and other excited molecule or reactions of the photo-chemically produced reactive species. The indirect photolysis is also known as photosensitization or quenching, and the direct photolysis called photo-induced reaction and proceeds with a reactive oxygen species.

In a well-mixed system, the average rate of direct photolysis can be approximated using the GCSOLAR program that is based on spectral irradiance of sunlight, quantum yield and absorption profiles of pesticide (Leifer 1988). In contrast, if pesticide molecules deposits on plant surfaces and soil, the heterogeneous microenvironment makes such kind of estimation quite difficult. For instant, many researchers have reported enough information on the quantum yield for pesticides photolysis in solution form, but very limited discussions on solid-phase photolysis (Samsonov and Pokrovskii 2001 ;Krieger et al. 2000). In the study of soil photolysis process, Balmer *et al.,* (2000) introduced model function of light reduction in soil diffusion in a pesticide molecule to describe the dissipation profiles in a better way.

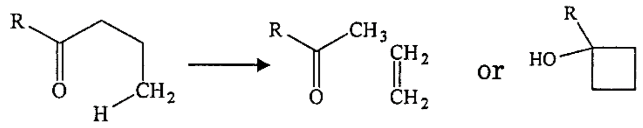
The molecule in the T_1 or S_1 state undergoes different chemical reactions. For example, typical reactions obtained in photolysis of plant and soil surfaces are summarized below in figure 2.4. Amongst the most important photoreactions is the one that is initiated by carbonyl $n \rightarrow \pi^*$excitation.

The breaking of C-C bond produces a ketyl radical or a carbonyl carbon at excited state from akyl groups. When C=C bond or aromatic compounds cleaves, a cis/trans geometric isomerization results. Photo-degradation reactions have been known to break homolytic bonds which is the main mechanism for photolysis.

Photo-induced breakdown of pesticide/organic molecules is illustrated by the chemical equations shown in figure 2.4 below. According to the figure 2.4, esters/ketone photo-chemically breaks via decarboxylation or de-carbonylation, which takes place to the hydrolysed molecule with the extent depending on stability and structure of the solvent. Some proposed mechanisms of Dimethoate and PCP photodegradation pathways are shown in appendix 2 and 3 respectively.

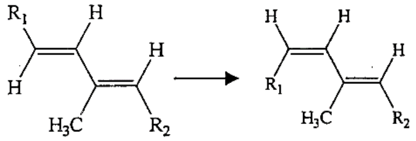
1. Norrish type-I reaction

2. Norrish type-II reaction

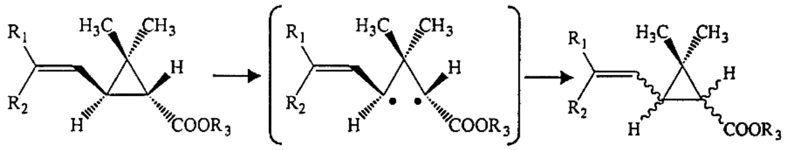


3. Isomerization (geometrical or optical)

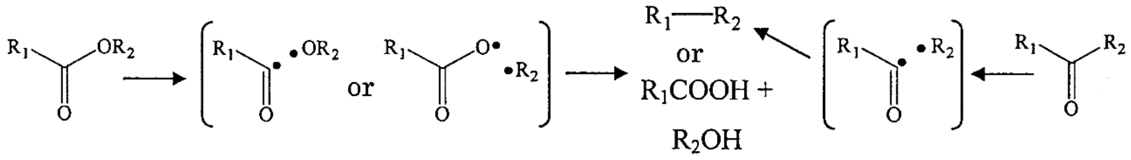
(a)



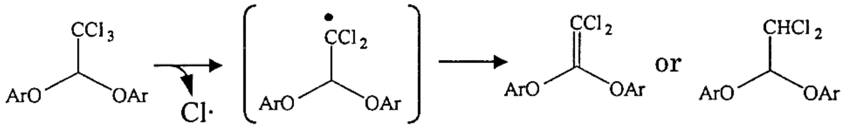
(b)



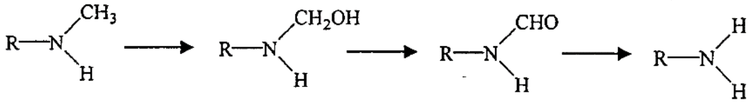
4. Ester cleavage, decarboxylation, decarbonylation



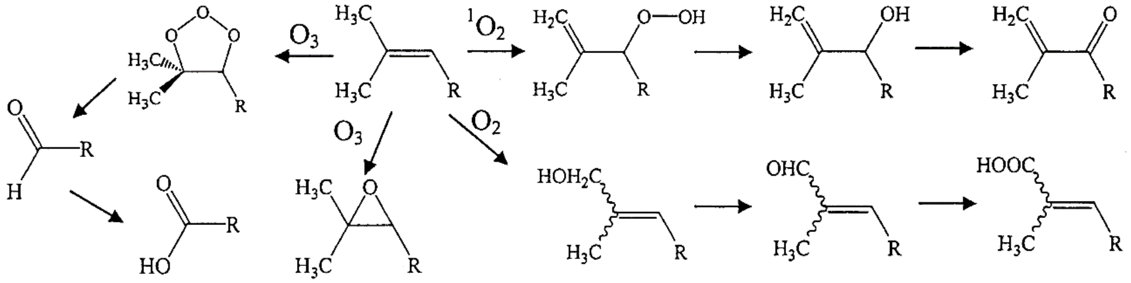
5. Dehalogenation

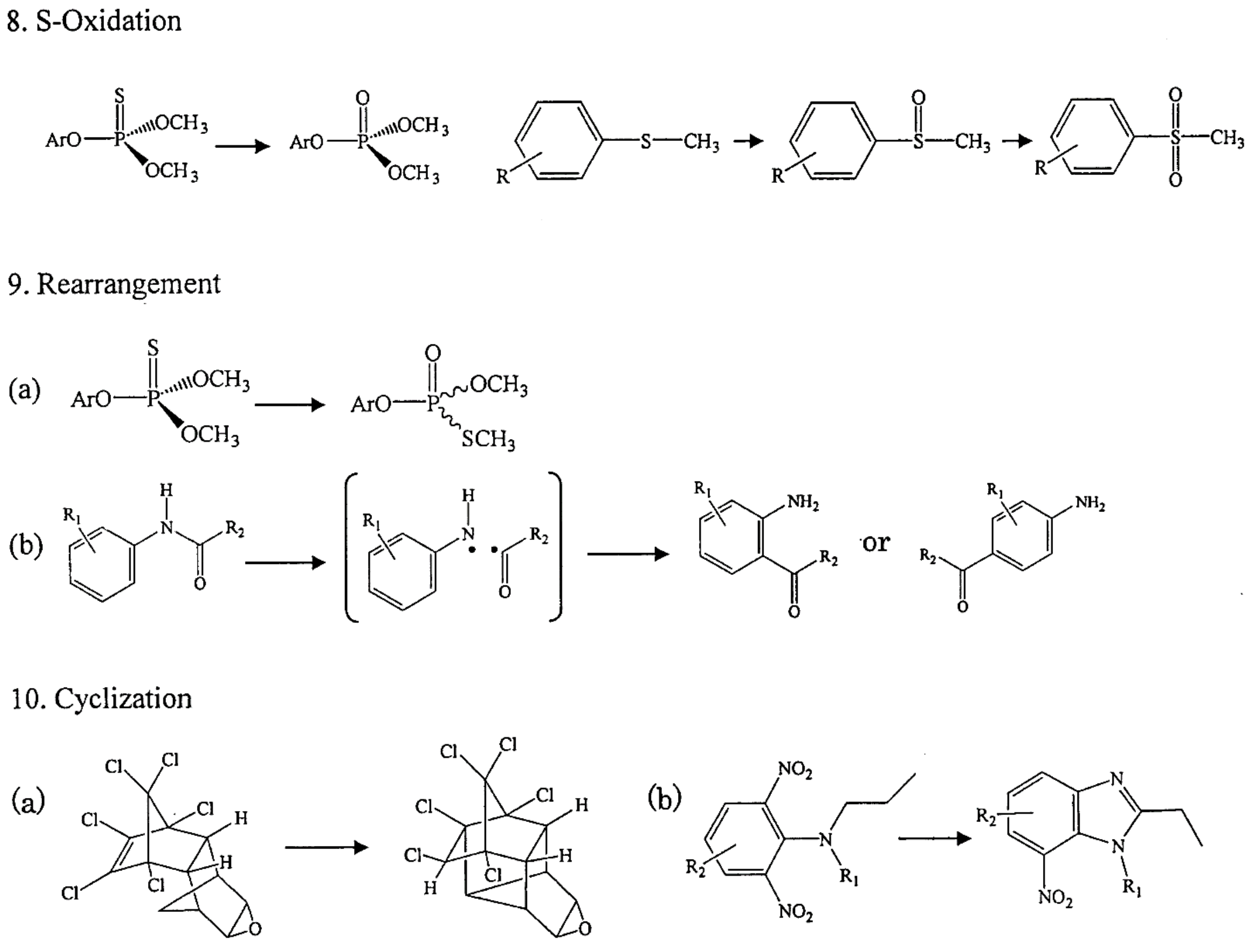


6. Dealkylation



7. C-Oxidation





8. S-Oxidation

9. Rearrangement

10. Cyclization

Figure 2. 4: Typical photochemical reactions.

2.5 Factors controlling photolysis on plant surfaces

Among the factors that influences photolysis of pesticide residues are environmental conditions, formula, mode of application and the affinity to different surfaces (Willis and McDowell (1987), Zongmao and Haibin (1997).

2.5.1 Environmental factors

Dissipation of pesticide molecules in the environment is highly influenced by photodegradation and not elution by rainfall and evaporation (Rodriguez *et al*. 2001).

For instance, Garau *et al.,* (2002) did a study on loss of pesticide from cellulose membrane resulting from co-distillation and evaporation in water. He observed that evaporation, co-distillation and photolysis influence the degradation of pyrimethanil and cyprodinil. In tomatoes for example, the wax layer slowed down evaporation and co-distillation of many pesticides while displaying the screening effect. Further, molecules with high vapor pressure and less photo reactivity like chloropyrifos volatilization loss was the dominating factor (Meikle *et al*., 1983).

2.5.2 Illumination conditions

The glass like material used in green houses absorbs high amount of light at a wavelength range of 280-320nm. The filtering effect significantly reduce the solar emission spectrum and near-UV absorption spectrum overlap for many pesticides (Kleier 1994). In an experiment mimicking the actual greenhouse situation, the rate of molecular degradation by light reduces measurably once a petri dish is covered with a polythine bag (Garau *et al*. 2002). In another experiment, Fukushima *et al*. (2003) examined the photolysis of ^{14}C-fenitrothion on tomato fruit in a greenhouse with a ceiling made of quartz or borosilicate glass as illustrated in figure 2.5 below.

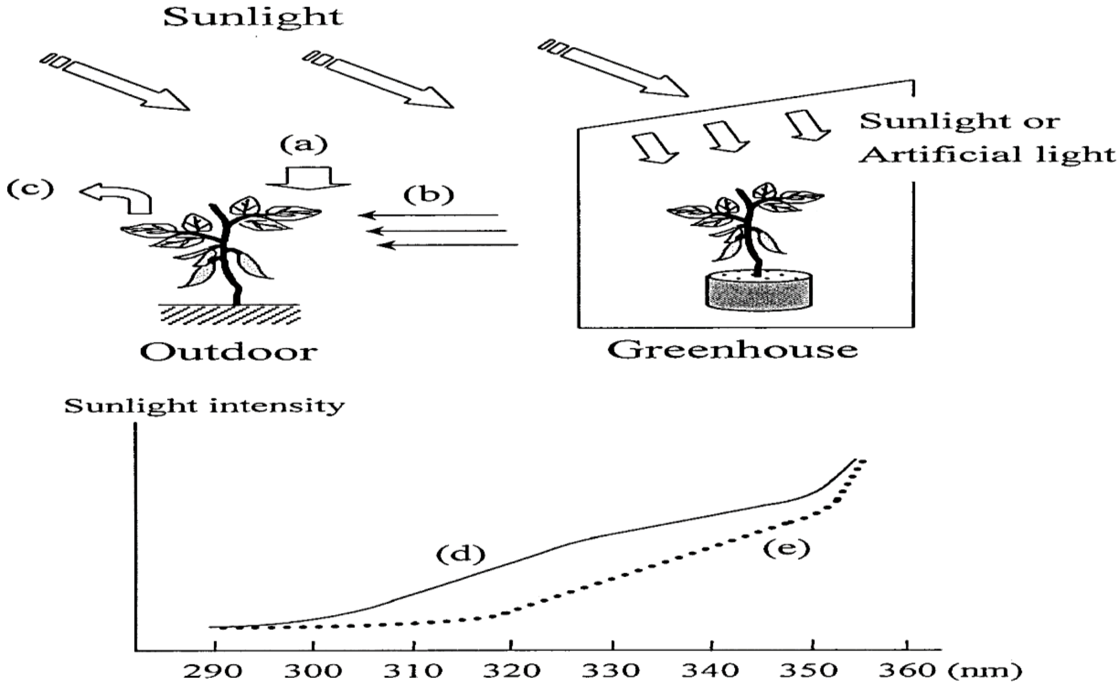


Figure 2.5: Photo-degradation of pesticide on plant (a), precipitation (b), wind (c), volatilization (d), sunlight outdoors (e) and sunlight in the borosilicate glass greenhouse (Hoerger and Kenaga , (1972)).

He observed that for light with less than 360nm was reduced by borosilicate glass greenhouse. It was also observed that the transmission is reduced by glass pollution (Van Koot and Dijkhuizen 1968).

Among other factors that influence photochemical degradation is the crop and season (Martı´nez Vidal *et al.* 1998) with similar results being observed for fenpropathrin (Martı´nez Galera *et al*. 1997), with degradation of methomyl highly depending on greenhouse effects (Gil Garcia *et al*. 1997).

2.5.3 Effect of formulation

The active ingredients in a given pesticide molecule such as surfactants, clay, humectant and crop oil determine its behaviour in the environment. For instance, the additives like hydrophobic and hydrophilic provides a medium for photolysis while their aromatic properties has been known to be photo-sensitizer or quencher (Nutahara and Murai 1984 ;).

2.5.4 Anatomy of the leaf

Many leaves have protective cuticles that decrease water loss as well as protect plant from infections by pathogens as shown by figure 2.6. Cuticle is a structure made up of pectin layer which holds together the epidermal cell walls and epicuticular wax which is unique for every plant McFarlane 1995; Bianchi 1995). The leaf structure is indicated by figure 2.6 below;

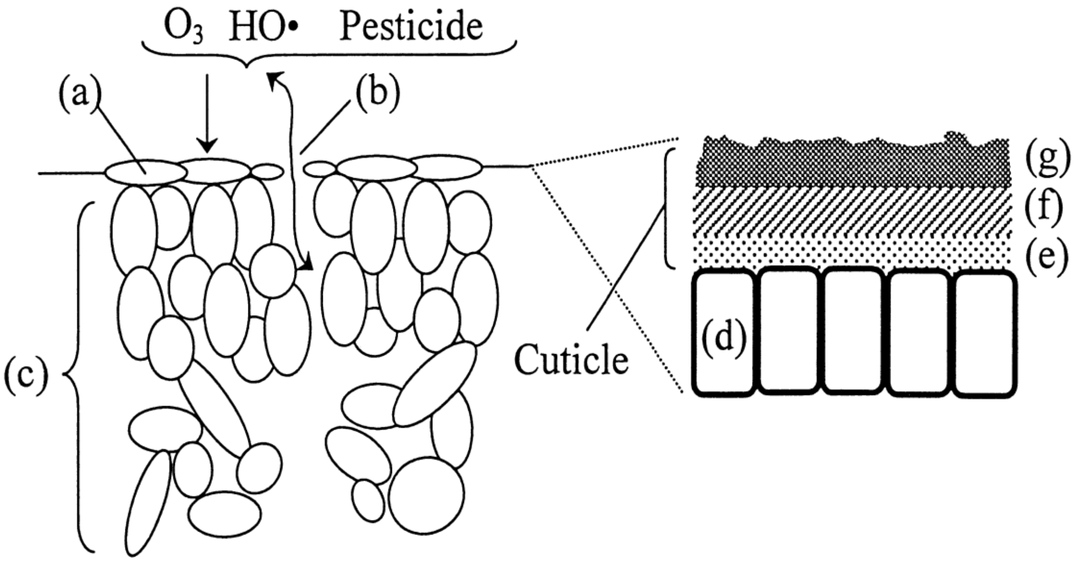


Figure 2.6: Transverse view of the typical surface structure of plant foliage (a, d) epidermal cell, (b) stoma, (c) mesophyll, (e) pectin, (f) cutin and embedded waxes, (g) epicuticular waxes (Fletcher *et al*. (1994), Robert Wright., (1993).

Leaves absorb radiant energy from sunlight. During sunny days, radiation from the sun is reflected and scattered by leaf hairs, leaf pubescence with some light entering the leaf (Robberecht and Caldwell 1980; Holmes and Keiller 2002). The light that enters the leaf is reflected inside the intercellular space of the cell wall due to different refractive index between air and water (Gates *et al*. 1965). Pesticides that are applied by foliar means can be distributed on the epicuticular wax layer while some get into the plant via stomata or diffusion. This portion is considered during photo-degradation experiments with the rate being determined by the radiation reaching the surface and the anatomy of the leaf.

2.5.5 Wax chemistry

Most fruits and crops consist epicuticular waxes, which are aliphatic compounds that readily dissolve in organic solvents. For example, a 1:1 v/v chloroform and diethyl ether can be used to isolate waxes of cyclic compounds Baker 1982). The wax content of fruits especially tomatoes has been observed to influence absorbed pesticide molecules. The wax coating protects the molecule from the radiated light as observed by Mbugua *et al.*, 2014.

2.6 Factors controlling photolysis on soil surfaces

Photo-degradation of the pesticide molecules is not only influenced by molecular properties but also by some external factors. In this section, we shall discuss the soil surface factors:

2.6.1 Soil components

Soil comprises of different levels of minerals, carbon matter and moisture which support life of different crops (Manahan 1994). Five percent of organic matter comes from plant decay while 95% is inorganic matter. Different soil types have different aeration and texture. This means that different soils would exhibit different water retention capability and therefore influence other factors like how sunlight radiation enters the soils.

2.6.2 Environmental factors affecting soil properties

Soil photolysis is highly influenced by basic soil properties especially moisture (Misra et al. 1997; Frank et al. 2002). The penetration of light into the soil is approximately 0.5cm. In a given environment, different soil properties affect the capillarity properties. Miller et al. (1989 carried out some simulation on a diurnal variation of temperature on 0.2cm soil surface with temperature increase up to 400C for 20 days. This review showed that change in temperature varied the moisture content of the soil, which was translated to drying of soil during day and subsequent raise of moisture content during the night. The fluctuation in moisture content affects activities from microbes. Reichman et al. (2000) proposed a model which was one-dimensional non-isothermal model which explain the dynamic behaviour of applied pesticides.

2.6.3 Mass transport in soil

Fick’s law explains the diffusion of pesticide molecule in soils. Soil characteristics makes the explanation more complicated as different soils have different properties(Graham-Bryce 1969), as illustrated in figure 2.7.

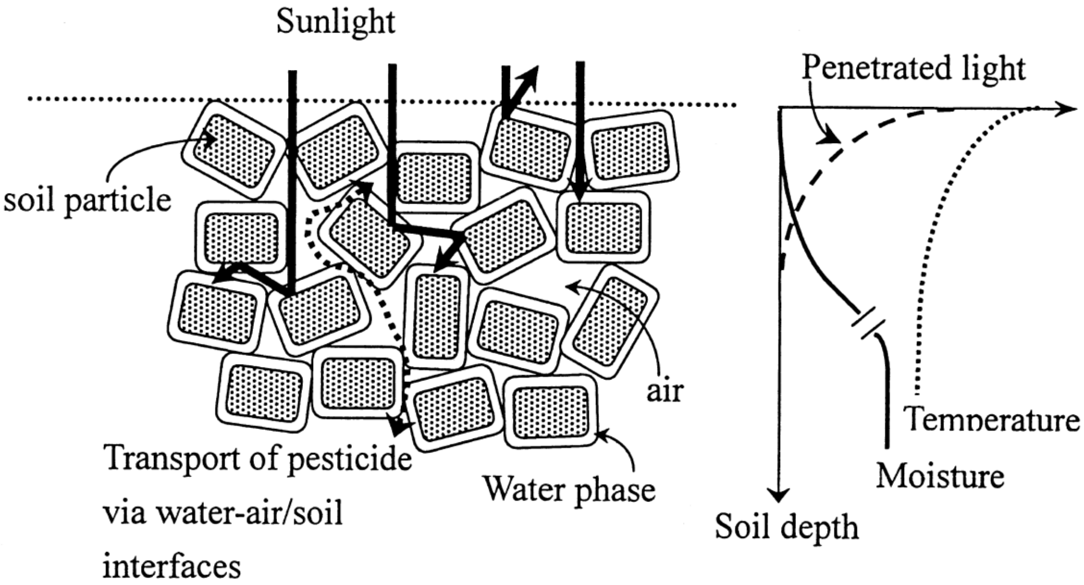


Figure 2.7: Structure of soil surface.

When the pesticide residues are homogeneously distributed in a given solution in soil, their diffusion at a given time t is given by (2Δt) ½ where Δt is time. This means that in a study by Graham-Bycre it would take 2.4hours for parathion molecule to move through 1-mm thick soil and 1 to 2.5days for trifluralin molecule. Mass movement is not the only factor influencing movement of molecule in the soil; other factors are involved as well. According to Walker and Crawford (1970) an observation was made that diffusion constant has an inverse relationship to soil adsorption coefficient. Further smaller diffusion has been observed with higher water content for dinitroaniline herbicides (Jacques and Harvey 1979). An opposite relationship for triazines was observed (Scott and Phillips 1972). Ehlers *et al.* (1969). Among other factors influencing molecule diffusion in soils are depth of the water table and molecular properties (Mahnken and Weber 1988).

2.6.4 Photic depth in soil

High heterogeneity and unmixed soil means that illumination would take place in indefinable surfaces as observed by Wolfe et al. 1990 and Senesi and Loffredo 1997). In such situations, the photic depth has to be estimated. For soils with 0.17mm thickness, radiation from the UV-light was observed to have more than 90% attenuation (Herbert and Miller 1990). Frank *et al.* (2002).

Herbert and Miller carried out experiments to investigate the transmittance of UV light in soil and observed that 0.5mm thickness has the ability to block 95% of the incident light with little light penetrating 1.5mm thickness.

2.6.5 Chemical effects:

Deviation from Beer's law is observed when the analyte concentration is higher than 10mM. This results from solvent solute interaction and to some extent from hydrogen bonding. For example;

1. When more solutes are present in a given solution, they cause charge distribution differences in the solution, which translate to shift in wavelength of the chemical species of interest.

2. The refractive index (η) is altered by high solute concentration. Therefore, the Beer's Law has to be corrected accordingly as shown in equation pp.3 $A = \varepsilon bc\,(\eta^2 + 2)^2$………………………………………………….. (PP.3) below 10mM, the correction was not necessary.

2.6.6 Physical effects

2.6.6.1 Polychromatic radiation

The law of absorbance of analyte is followed only when the radiation is monochromatic. More often than not, polychromatic radiation is observed. Let us consider for example an analyte whose molar absorptivity is ε' and ε" at a given wavelength of λ' and λ". For such a molecule, the absorbance is given by equation pp.4

$$A_m = \log \frac{(I_0' + I_0'')}{(I_0' 10^{-\varepsilon' bc} + I_0'' 10^{-\varepsilon'' bc})} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(PP.4)}$$

Equation pp.4 above is for polychromatic radiation where ε' = ε". An increase in deviation is observed in cases where ε' and ε" changes are significantly increased.

2.6.6.2 Presence of Stray radiation

When the light is outside the nominal wavelength selected, it said to be stray radiated. This is very different from the required wavelength. When analyte absorbance results from reflection from lenses, mirrors windows and filters then this results in deviation from Beer's Law.

2.6.6.3 Mismatched cells or cuvettes

Cuvettes with different path lengths and unequal optical properties lead to sample of interest deviating from Beers Law. It is important to scan the sample using same properties cuvettes. In cases where the cuvettes are mismatching, a plot of calibration curve will have an intercept at k as indicated by equation pp5 below;

$A = \varepsilon bc + k$ …………………………………………………………………… (PP.5)

2.7 Photo-degradation of pesticides

Pesticide breakdown in the environment results from hydrolysis by ground water, degradation by microorganisms and light as well as heat from the sun (Pu et al., 2002; Tang *et al*., 2000; Yang *et al*., 1999; Zheng et al., 2001; Itoh *et al*., 2005; Abdennour et al., 2005; Li *et al*., 2008). The by-products of photo degradation of parent molecules significantly influence the toxicity and adsorption/desorption behavior in the environment. The photolysis of pesticide molecules is an important index especially in ecological safety evaluation of residues (Holmstead *et al*., 1978; Zheng *et al*., 2003).

2.7.1 Rate of degradation of pesticides

The rate at which pesticide residues degrade on exposure to light, water or any other degradation agent can be derived by considering the following:

$$A \rightarrow Products \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots. (R.1)$$

Where A is the molecule of interest,

$$Rate = -\frac{\Delta[A]}{\Delta T} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.. (R.2)$$

Where Δ [A] is change in concentration of A, and ΔT is change in time.

From the rate law, $Rate = k[A] \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.... (R.3)$

Where k is rate of decay constant. When the two equations are combined, then

$$Rate = -\frac{\Delta[A]}{\Delta T} = k[A] \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.... (R.4)$$

Using calculus $\frac{Ln\,[A]t}{[A]0} = -kt$.. (R.5)

This on rearranging gives:

$$Ln[A]t = -kt + Ln[A]0 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.. (R.6)$$

This means that a plot of ln [A] $_t$ against time will be linear with slope as the rate of degradation. The rate constant was calculated using the following formula,

$t_{\frac{1}{2}} = \frac{ln2}{k}$ (Weerasinghee *et al*., 1992).

Therefore;

$$k = \frac{1}{t_x \times \frac{lna}{b_x}} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots. (R.7)$$

$$t_{\frac{1}{2}} = \frac{ln2}{k} = \frac{0.693}{k} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.. (R.8)$$

Where: k the Rate of decomposition,

t_x is time in days**,**

a is the Initial residue,

b_x is the residue at time(x).

2.7.2 Degradation of pesticide by incandescent and fluorescent light.

Photo-chemical reaction from incandescent bulbs result from heat and light energy. Mbugua *et al*.,2014 observed that degradation of pentachlorophenol when exposed to incandescent bulbs is highly dictated by the light intensity, duration of exposure and temperature. When pesticide molecules are exposed to fluorescence light, the rate of degradation is lower compared to when they are exposed to incandescent bulbs. This is explained by the fact that the amount of heat emanating from the fluorescence tubes is less. This means that in fluorescence light, photo-degradation results from light intensity and not a combination of both light and heat (Mbugua, *et al.,* 2014).

CHAPTER THREE

3.0: MATERIALS AND METHODOLOGY

3.1 The area of study

The Nairobi river sediment sample was collected 200m from the Department of Chemistry, University of Nairobi along the Nairobi-Nakuru highway at the coordinates of 1°16'18.1"S and 36°48'28.1"E as shown in figure 3.1 of the Google map below;

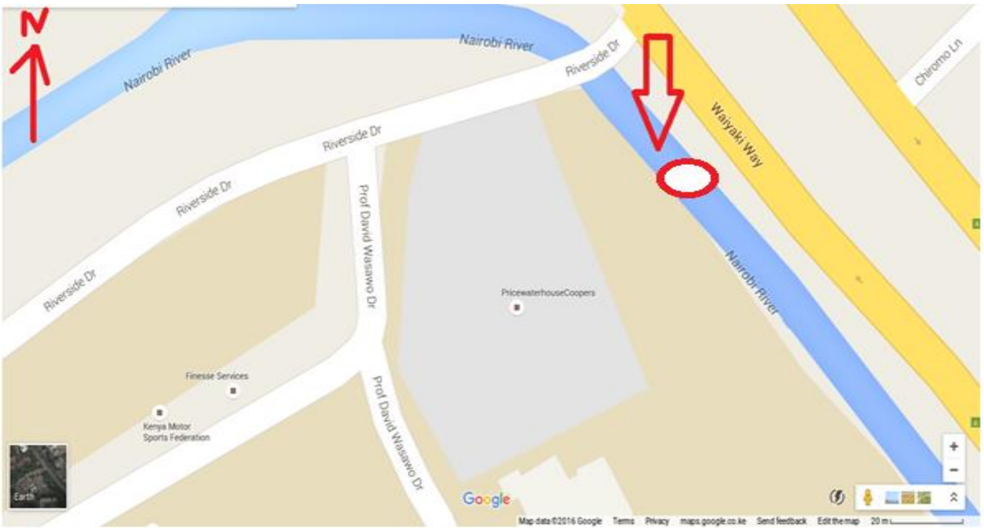


Figure 3.1: Map of Nairobi River where the sediments were collected.

The Thigio loam soil sample was collected from Kiambu County, Limuru-Sub County Thigio location, Gichagi village along Kaberi road at a coordinate of 1°12'25.5"S 36°36'06.7"E as shown in figure 3.2 below;

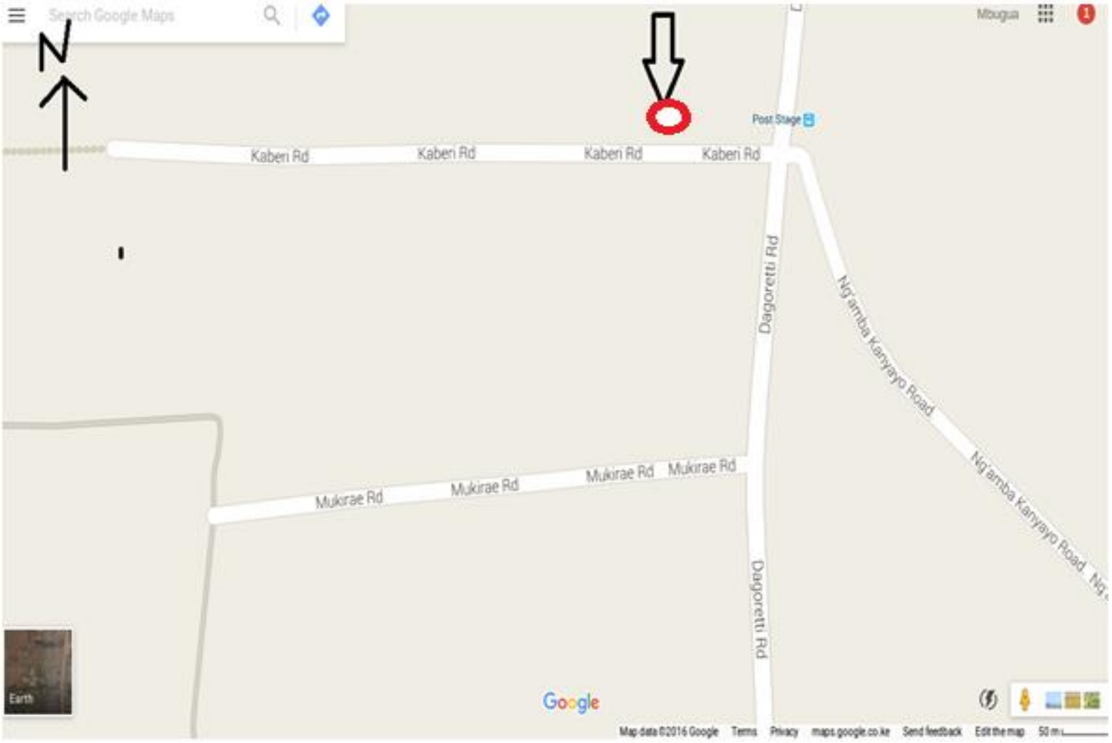


Figure 3.2: Map of Thigio sub location where fresh loam soil was collected.

3.2 Sampling

The sediment samples used in this research study were obtained from Nairobi River next to Chiromo mortuary (Figure 3.1) five centimetres from the flowing water and fresh loam soil (top soil layer) was collected from Thigio, Limuru Sub County (figure 3.2). The spinach sample was bought from the Ngara market, Nairobi, Kenya. These samples were collected in aluminium foil paper sealed in sealing bags and taken to Chiromo Campus, Department of Chemistry laboratory for analysis. The spinach samples were stored in plastic bags under -4^{0}C at Chiromo Campus, Department of Chemistry laboratory for analysis. The analysis of photo-degradation of pentachlorophenol and dimethoate pesticide residues involved the use of the following reagents and apparatus:

3.3 Reagents and apparatus

- 99.9% dimethoate from Schuchart Company in Munchen, Germany.
- 98.9% Pentachlorophenolfrom Schuchart Company in Munchen, Germany.
- Mini Pipette were bought from school labs and suppliers, Nairobi.
- Bulb holders were bought from Tuskys supermarket, Nairobi.
- Distilled water was bought from school laboratory and suppliers, Nairobi.
- Incandescent bulbs 100w, 75w, 60w, 40w (Philips) were bought from Tuskys supermarket.
- Fluorescence tubes- 9w, 11w, 15w, 20w (Philips) were bought from Tuskys supermarket.
- Fresh loam soil (Collected from Limuru, Thigio Division).
- Glass Cage constructed from science workshop.
- Spinach Bought from Ngara Open Market.
- 98% Acetone was supplied by Alpha Chemika Mumbai, India.
- Acetonitrile was supplied by Mahir Technologies Inc. Kandivali West, Mumbai.
- 2.5mm electrical cable was bought from Jonnah Electrical, Nairobi.
- Nairobi River sediments were collected near Chiromo Mortuary .
- Glass Bottles were obtained from School laboratories and Suppliers, Nairobi.
- Aluminium foilwas obtained from school laboratories and suppliers, Nairobi.
- Labels and stickers were obtained from school laboratory and suppliers, Nairobi.
- 1cm quartz cuvettes were gotten from Advalue Technology, USA.
- Sealing bags were obtained from school laboratory and suppliers, Nairobi.

Instrumentation

- U.V vis. (UV-VIS NIR-spectrophotometer, Shimadzu,Japan)
- Analytical Balance- (Model Fisher scientific A 160).
- Oven- (Model Mammoth oven)

3.3 Cleaning of glass-ware

All glassware including mini pipettes, glass bottles, measuring cylinders, volumetric flasks, conical flasks, Beakers were soaked for 12 hours in freshly prepared chromic acid. They were then rinsed in distilled water and after they were soaked in distilled water for 6 hours to leach off any adsorbed chromic acid ions. They were dried in open racks after rinsing with distilled water.

3.4 Loam soil and Nairobi river sediment analysis

3.4.1 Procedure

3.4.1.1 Available nutrient elements

The nutrient elements available in Nairobi river sediment and Limuru loam soil e.g.

Potassium, phosphorus, sodium, calcium, magnesium and Manganese were determined using Mehlich No. 1(Double Acid Method Tran, T. S. *et al*., (1993). The hot dry soil samples from the oven were extracted in a ratio of 1:5 where 1g of the soil sample was mixed with 5cm^{3}of a mixture of (1:1) 0.1M dilute Hydrochloric acid and 0.025 dilute sulphuric (VI) acid. Elements such us sodium, calcium and potassium were determined using a flame photometer while phosphorous and manganese were determined calorimetrically.

3.4.1.2 **Total organic carbon**

Calorimetric method used to obtain the total organic carbon (gislason, E.A *et al.*, 2005). Complete oxidation was ensured by oxidizing all organic carbon samlpe in the soil using acidified $Cr_2O_{7(aq)}$. To the cool digests $BaCl_2$ was added. Thereafter they were mixed thoroughly and the digests allowed to stand for 24 hours. Then the concentration was read at wavelenght of 600nm on the spectrophotometer.

3.4.1.3 Total nitrogen or Kjeldahl method: (jan-åke persson *et al*, 2008).

Here the Soil samples were digested using a mixer of concentrated H_2SO_4 containing K_2SO_4 Selenium and hydrated $CuSO_4$in ratio 1:1 at 350^0C. Distillation was used to determine total nitrogen followed by titration with H_2SO_4.The following were the chemical equations used:

a) Degradation:

$Sample+H_2SO_4 \rightarrow (NH_4)_2SO_4(aq)+CO_2(g)+SO_2(g)+H_2O(g)$..(3.1)

b) Liberation of ammonia:

$(NH_4)_2SO_4(aq) + 2NaOH \rightarrow Na_2SO_4(aq) + 2H_2O(l) + NH3(g)$....................................(3.2)

c) Capture of ammonia:

$B(OH)_3 + H_2O + NH_3 \rightarrow NH_4^+ + B(OH)_4^-$..(3.3)

d) Back-titration:

$B(OH)_3 + H_2O + Na_2CO_3 \rightarrow NaHCO_3(aq) + NaB(OH)_4(aq) + CO_2(g) + H2O(l)$ ......(3.4)

3.4.1.4 Soil pH (1:1 Water ,soil ratio)

Soil sample pH was determined by mixing soil-water in the ratio 1:1 (w/v). The soil-water mixture was shaken thoroughly and the suspension allowed to settle for five minutes.The pH was read using the digital pH meter.

3.4.1.5 Available trace elements

The following procedure was carried out to determine the trace elements like Fe, Zn & Cu. They were extracted using 0.1 M HCl where 1g of hot dry soil samples from the oven were extracted using $10cm^3$ of 0.1M hydrochloric acid. The elements present were obtained using an atomic absorption spectroscopy (AAS).

3.4.1.6 Cation Exchange Capacity (CEC).

The exchangeable cations such as Ca^{2+}, Mg^{2+}, K^+ and Na^+ from the soil sample were leached with 1M ammonium acetate buffered at pH 7. Then the leachate was analysed for exchangeable Cations. The sample was further leached using 1M KCl to determine CEC.Na and K were as certained by use of flame photometer. Ca and Mg were determined using AAS (atomic absorption spectrophotometer).

3.4.2 Preparation of stock solution

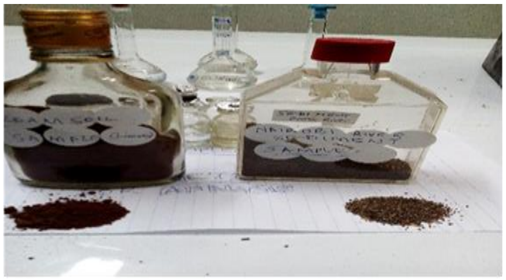
100-ppm of the stock solution for pentachlorophenol and dimethoate was prepared in analytical grade acetone (99.8%). Serial dilution method was used to prepare 2, 4, 6, 8, 10, 20, 40, 60, 80 and 100-ppm solutions. The solutions were photometrically scanned using Shimadzu UV-visible spectrophotometer model at 200 to 900nm wavelength range to obtain the lambda maximum for each of the pesticide.

A plot of absorbance versus concentration for each pesticide standard was made and further used in the degradation study to obtain the concentration decrease.

3.4.3 Photo-degradation

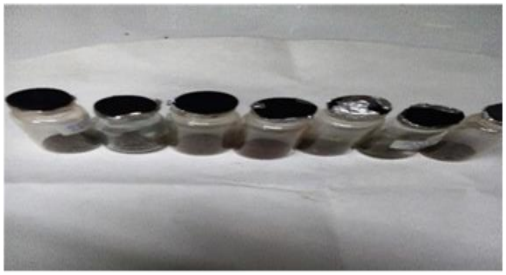
Five sets of 0.1g of Limuru loam soil and Nairobi River sediment samples were weighed into clean dried glass bottles. 1.0ml of 100-ppm standard solution of pentachlorophenol and dimethoate prepared in analytical grade acetone was added to each of the samples and shook for five minutes. Acetone was allowed to evaporate for 2 minutes. The samples were then exposed to sunlight, 40W, 60W, 75W and 100W bulbs. The samples were removed after 10, 20, 30, 60 and 120 minutes, allowed to stabilize for 1 hour after which they were decanted carefully and analysed using Shimadzu UV-Vis spectrophotometer. Some of the set up used to investigate photo degradation work are shown in figure 3.3a and figure 3.3b below.

Figure 3.3a: Lighted fluorescent tubes before being exposed to samples.

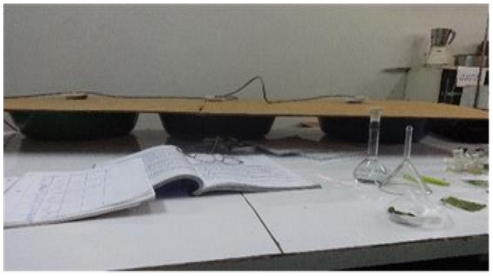


Soil and sediment samples to be weighed

Spinach samples from Ngara market



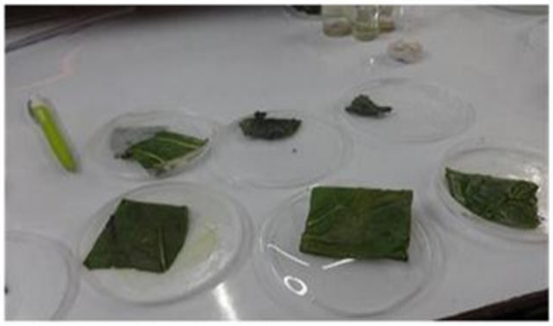
Soil samples awaiting addition of pesticide.



Exposing samples to light bulbs.

Timing for 10, 20, 30, 60 and 120 mins

Lighted incandescence bulbs exposed to the extracts.



Spinach products obtained after exposure to light intensities

Figure 3.3b: Photodegradation experiments.

The above experimental procedures were repeated with fluorescence tubes of 9, 11, 15 and 20 watts. This was done for both Thigio loam soil and Nairobi river sediment. Temperature in each case was recorded after the setup had stabilized. Each set was done in triplicate.

3.4.4 Photo degradation on spinach surface

Six sets of 5cm by 5cm spinach leaves were placed in a petri dish. 2 ml of 100ppm of pentachlorophenol and dimethoate were prepared in acetone. Acetone was allowed to evaporate for 1 minute. The set was then exposed to sunlight, 40w, 60w, 75w and 100w incandescent bulbs, which were enclosed in a container to prevent light loss or external interference. The sets were exposed for 10, 20, 30, 60 and 120 minutes. Temperature from each container was also recorded.

The above experimental procedures were repeated with fluorescence tubes of 9, 11, 15 and 20 watts. This was done for both Limuru loam soil and Nairobi river sediment. Temperature in each case was recorded when the setup had stabilized. Each set was done in triplicate.

3.5 Methods of analysis

Microsoft Excel 2013 and Minitab 17 Statistical analysis software was used to analyse the data, plot the photo-degradation figures and calculate the rate of pesticide degradation.

3.6 Rate of degradation

To obtain the order of the reaction of PCP and DM, plots of natural logarithms of concentrations versus time were plotted. Half-life($t_{1/2}$) was calculated using the equation below (Weerasinge *et al*., 1992):

$$\boldsymbol{t_{\frac{1}{2}} = \frac{ln2}{k} = \frac{0.693}{k}} \text{ ………………………………………………………….. } \mathbf{(3.1)}$$

$$\boldsymbol{t_{\frac{1}{2}} = \frac{1}{T_x \times ln\frac{a}{b_x}}} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \mathbf{(3.2)}$$

Where k = Rate constant for decomposition,

T_x= time in days,

a= initial residue,

b_x= residue at time (x).

CHAPTER FOUR

RESULTS AND DISCUSSION

In this chapter, obtained results were interpreted and discussed using graphs, tables and charts. Minitab 17 and MS excel Statistical software's were used for data analysis.

4.1 Loam soil and river sediment properties

Properties of the Limuru loam soil and Nairobi river sediment used in this study are as shown in the table 4.1 below.

Table 4.1: Nairobi river sediment and Limuru loam soil properties.

Profile	Limuru loam soil	Nairobi river sediment
Soil depth cm	Top	Top
Soil pH-H_2O (1:2.5)	6.50	7.2
Elect. Cond. mS/cm	0.3	0.18
Carbon %	2.7	0.3
Sand %	40	80
Silt %	40	14
Clay %	20	6
C.E.C. me%	24.8	6.8
Calcium me%	44.4	8.9
Magnesium me%	3.1	3.1
Potassium me%	1.5	0.6
Sodium me%	3.6	0.8
Total nitrogen %	0.25	-
Phosphorus ppm	44	-
Zinc ppm	62.9	-
Copper ppm	1.22	-
Iron ppm	96.2	-

NB: me stands for miliequivalent.

From the table 4.1 above its evident that quantity of carbon in Limuru soil was higher than the quantity from Nairobi river sediments; this is because farmers in Limuru applied organic humus in their farms whereas none was applied in Nairobi river sediments. The pH of Nairobi river sediments was almost neutral compared to the slightly acidic pH in Limuru soil due to application of manure, and acidic fertilizers used by the farmers in Thigio in Limuru farms. The usage of nitrogenous fertilizers in Limuru was the possible cause of detection of 0.25% nitrogen in Limuru compared to zero detection in Nairobi river sediment.

4.2 Calibration curve

A set of standard solutions of PCP and DM for working were prepared by diluting portions of the stock solutions with 98.9% acetone (analytical grade) to give concentrations ranging from 1.0 to 100.0 ppm and scanned photometrically. The UV-VIS spectrum obtained for each pesticide residues are shown in the figures 4.1 and 4.2 below:

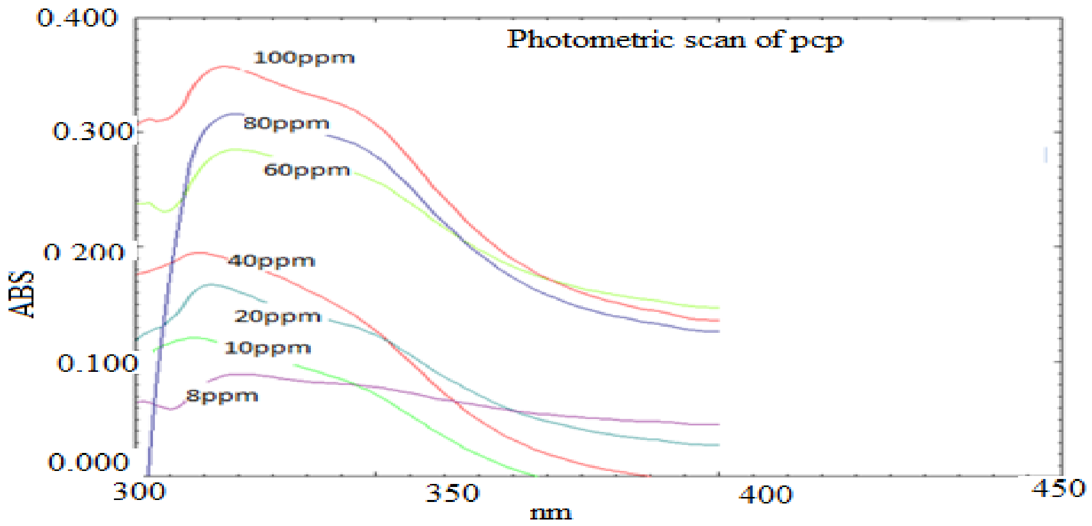


Figure 4.1: Pentachlorophenol UV-VIS spectra.

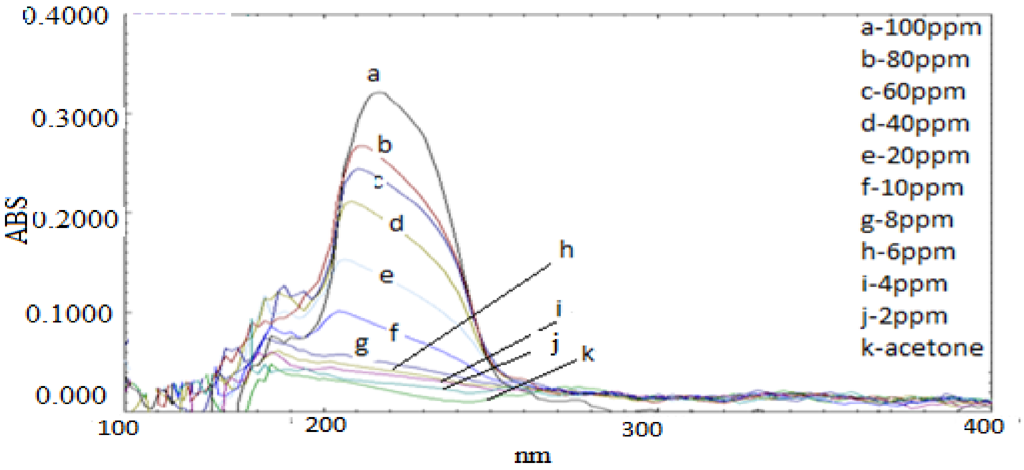


Figure 4.2: Photometric scan of dimethoate.

From the photometric scans of pentachlorophenol and dimethoate obtained in the figures 4.1 and 4.2 above, the absorption maxima (wavelength of maximum absorption) for pentachlorophenol and dimethoate were found to be 322nm and 229nm, respectively. Further analysis for the residues determination were done at these wavelengths. Photometric scan results were used to plot the calibration curve. The calibration curves for each pesticide residue were constructed by plotting the absorbance versus concentration and are shown in the figures 4.3 and 4.4 below.

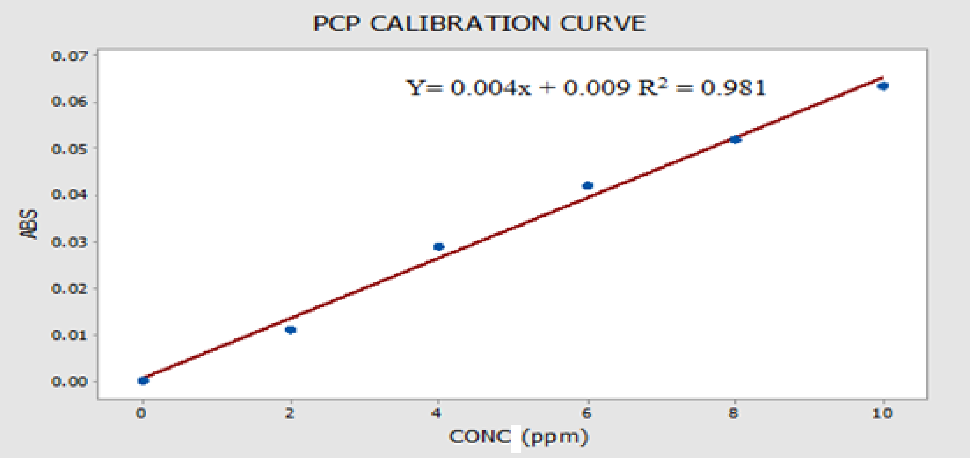


Figure 4.3: Pentachlorophenol absorbance-concentration calibrations.

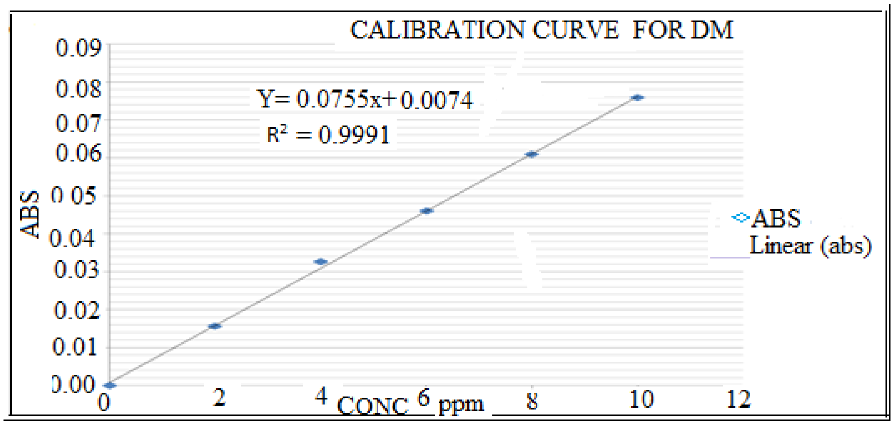


Figure 4.4: Dimethoate absorbance –concentration calibration curve.

The calibration curve for both pesticides obeyed Beer's law at concentrations range of 1.0 to 10ppm (low concentrations) which is attributed to chemical and physical effects as discussed in literature review. Beer's Law is the relationship between concentration and absorbance.

For example, the calculations of molar absorptivity for PCP from the curves are:

A= εbc where A is absorbance, ε =molar absorptivity (1/mol cm), b= path wavelength in cm, c= concentration (in mol/l).

So 0.01= ε x1x1.8

ε =0.005 l/mol cm

DM absorptivity (ε) is O.01= ε x1x2

ε=0.01/2, therefore ε =0.005 l/mol cm

4.3 PCP degradation using incandescent bulbs

Photo-degradation of pentachlorophenol in Limuru loam soil, Nairobi river sediment and spinach leaves surfaces were achieved by use of different wattage bulbs, fluorescent tubes and sunlight. The fluorescence tubes used had 9w, 11w, 15w,20w while incandescent bulbs had 40w, 60w, 75w and 100w. The results obtained for different radiation exposure are discussed below.

When PCP was exposed to sunlight and incandescent bulbs of 40, 60, 75, 100 wattages for 10, 20, 30, and 60 and 120 minutes, the amount of pesticide residue degraded with time as shown in figures 4.5, 4.6 and 4.7 below.

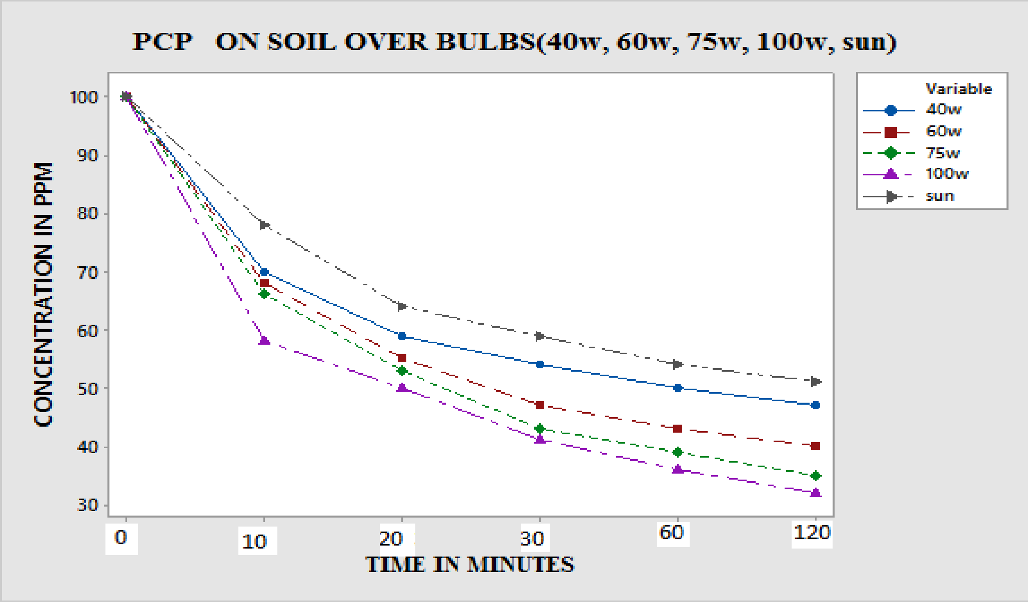


Figure 4.5: Plot of concentration of PCP on soil versus time using incandescent bulbs.

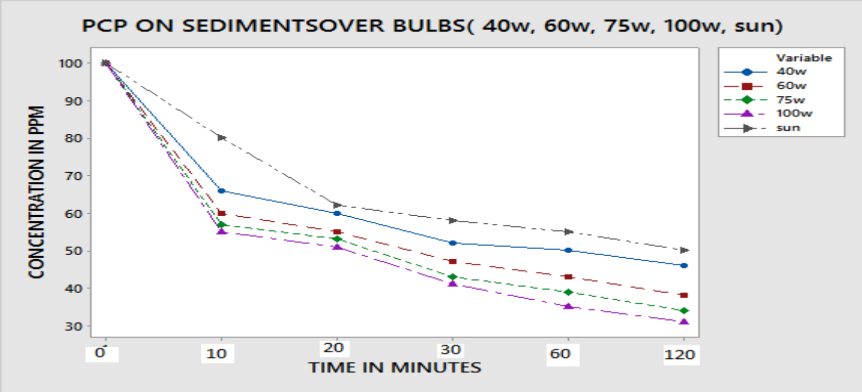


Figure 4.6: Plot of concentration of PCP on sediment versus time using different incandescent bulbs.

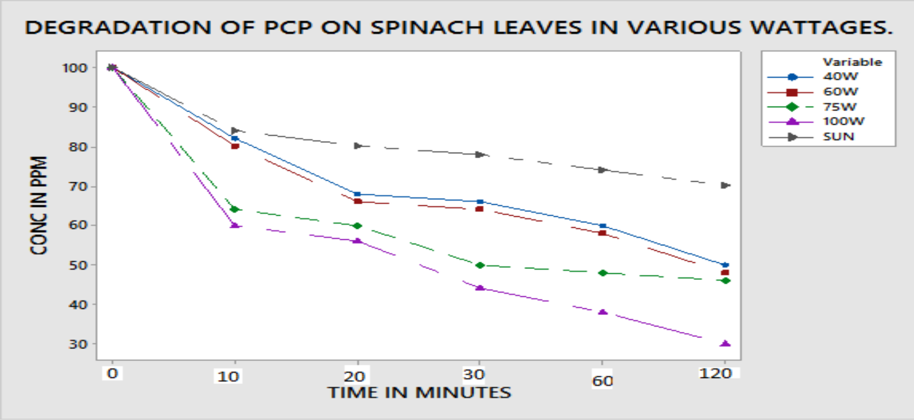


Figure 4.7: Plot of conc. of PCP on spinach vs time using incandescent bulbs.

When 100ppm of PCP was applied on different surfaces and exposed to different power bulb and sunlight, the results obtained are as shown in the figures 4.5 to figure 4.7 above. According to these figures, sunlight degradation of PCP was the least at all-time intervals while 100w bulb degraded the pesticide residue most. This can be attributed to both high light intensity and high temperature. According to Stark Einstein law, each molecule causing the main photochemical process absorbs one photon. This means that for 100w bulb absorbs more photons hence triggering the photochemical degradation of the pesticide molecule. This further means that since the photons reaching the pesticide molecule are less, the photodegradation on exposure to sun is relatively low.

The trend observed is sunlight < 40w<60w< 75w<100w in incandescent bulbs. The trend observed for fluorescent light is sunlight <9w <11w <15w <20w. The results obtained further indicate that the surface area of exposure influenced the amount of PCP degraded. On the river sediment surface, the amount of residue degraded was higher compared to soil.

This is attributed to less adsorption on the sediment thereby translating to higher exposure of individual molecules. On the loam soil surface, the higher amount of organic carbon attracts the organic molecules of the pesticide making it unavailable for degradation as fast as the others. This causes less degradation on soil surface. On spinach leaf, the surface is well spread and this translates to large exposure surfaces, which further translate to the highest degradation of PCP.

The half-life for PCP 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 photochemical reaction and therefore the shorter the amount of time required for half the entities to photo-degrade. The trend is observed for all the investigated exposure time. The table below indicates the calculated half-lives for PCP by different power bulbs and sunlight on different exposure surfaces. The equation below was used to demonstrate or calculation of the half-lives as shown on the table 4.2 below: $t\frac{1}{2} = \frac{ln2}{k} = \frac{0.693}{k}$

Therefore $\boldsymbol{t\frac{1}{2} = \frac{1}{Tx \times \frac{lna}{bx}}}$

$$But\ k = \frac{1}{Tx \times \frac{lna}{bx}}$$

k is rate of decomposition/ decay ,

$t\frac{1}{2}$ = half-life.

T_x= time in days,

a= initial residue,

bx =residue at time x.

For example, half-life of PCP in 10 minutes in 40W. So $k = \frac{1}{tx \times \ln\frac{a}{bx}}$

Time	Hrs	tx(days)	Observed	100/observed	ln(a/bx)	$tx \times \ln\frac{a}{bx}$	1/k
10mins	0.166667	0.003968	34	2.941	1.078809	0.00428	233.605

But $t_{1/2}$=ln2/k ,therefore$t_{1/2}$= 0.011584

Table 4.2 calculated half-life values of PCP on loam soil, river sediment and spinach leaf using incandescent bulbs.

10 Minutes					
EXPOSURE ENVIRONMENT	**40W**	**60W**	**75W**	**100W**	**SUNLIGHT**
Nairobi River Sediment	0.011584	0.009423	0.008563	0.008052	0.021571
Limuru Loam Soil	0.013496	0.012481	0.011584	0.008837	0.019373
Spinach Leaf	0.010581	0.009328	0.007568	0.006605	0.020461
20 Minutes					
Nairobi River Sediment	0.020139	0.016103	0.015164	0.014297	0.020139
Limuru Loam Soil	0.018246	0.017100	0.015578	0.015112	0.021571
Spinach Leaf	0.010446	0.009200	0.007510	0.006142	0.020119
30 Minutes					
Nairobi River Sediment	0.022083	0.019126	0.01711	0.016186	0.02651
Limuru Loam Soil	0.023435	0.019133	0.01782	0.016199	0.02736
Spinach Leaf	0.010208	0.009126	0.007412	0.006060	0.020105
60 Minutes					
Nairobi River Sediment	0.041667	0.03422	0.030672	0.02751	0.048309
Limuru Loam Soil	0.040678	0.03212	0.030571	0.028269	0.046871
Spinach Leaf	0.010166	0.009020	0.007306	0.005275	0.020083
120 Minutes					
Nairobi River Sediment	0.074385	0.059697	0.053542	0.049319	0.083333
Limuru Loam Soil	0.076504	0.063039	0.055021	0.050694	0.085784
Spinach Leaf	0.010043	0.008896	0.007354	0.004919	0.020012

The following figures 4.8, 4.9, 4.10 are showing plot PCP half- life versus bulb capacities for Nairobi river sediment , Limuru loam soil, and spinach respectively, using the incandescent bulbs of 40w ,60w, 75w , 100w and sunlight.

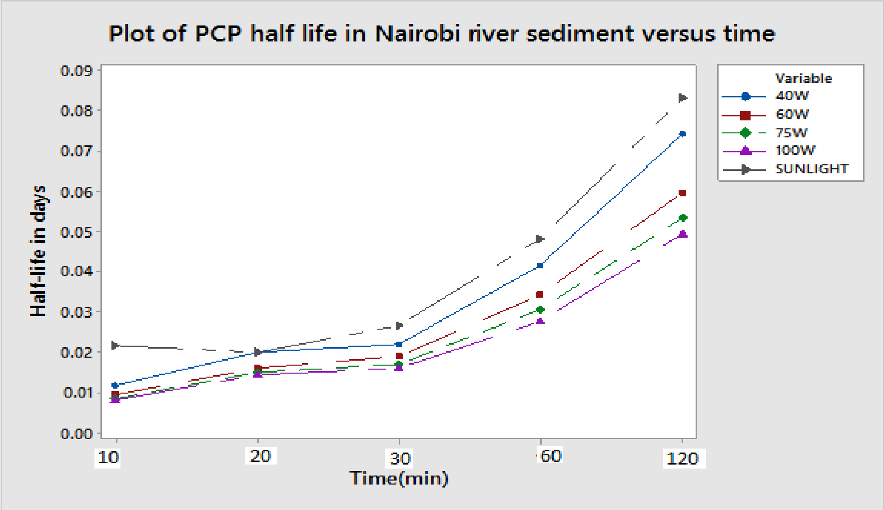


Figure 4.8: Plot of PCP half -life vs bulb capacity for Nairobi river sediment.

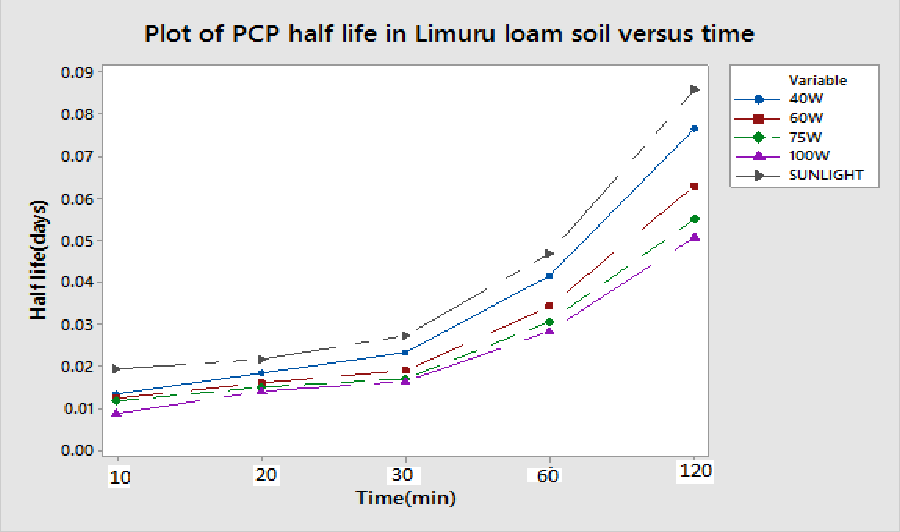


Figure 4.9: Plot of PCP half- life vs bulb capacity for Limuru loam soil.

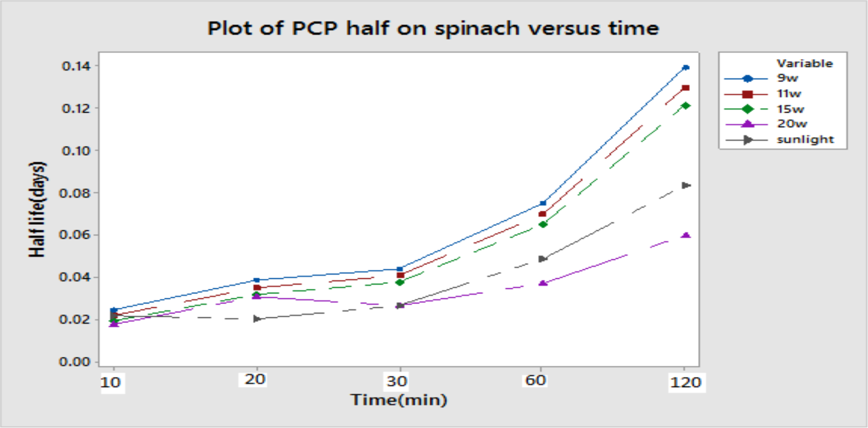


Figure 4.10: Plot of PCP half- life vs bulb capacity for spinach.

4.3.1 PCP degradation using fluorescent tubes

In this case PCP on Thigio loam soil, Nairobi river sediment and spinach leaf surface was exposed to different intensities of fluorescence light tubes. The amount of PCP degraded is shown in figures 4.11, 4.12 and 4.13;

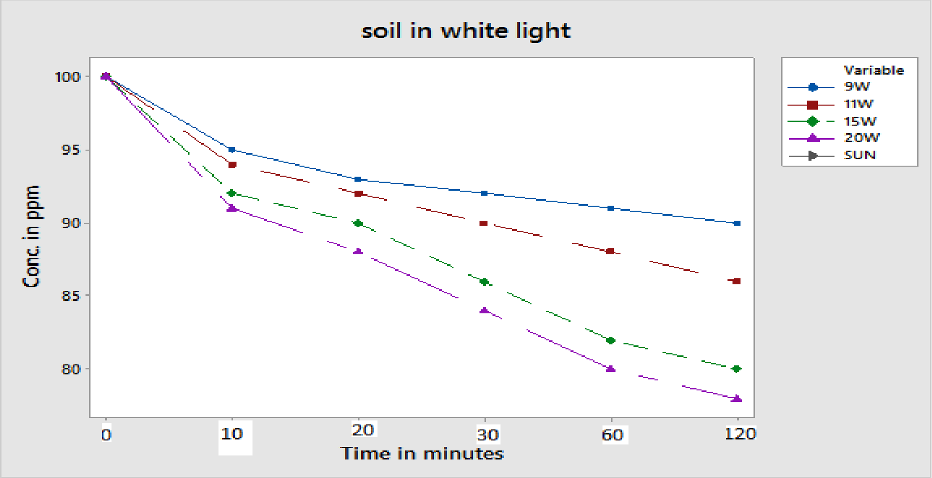


Figure 4.11 : Degradation of PCP on loam soil subjected to fluorescent light.

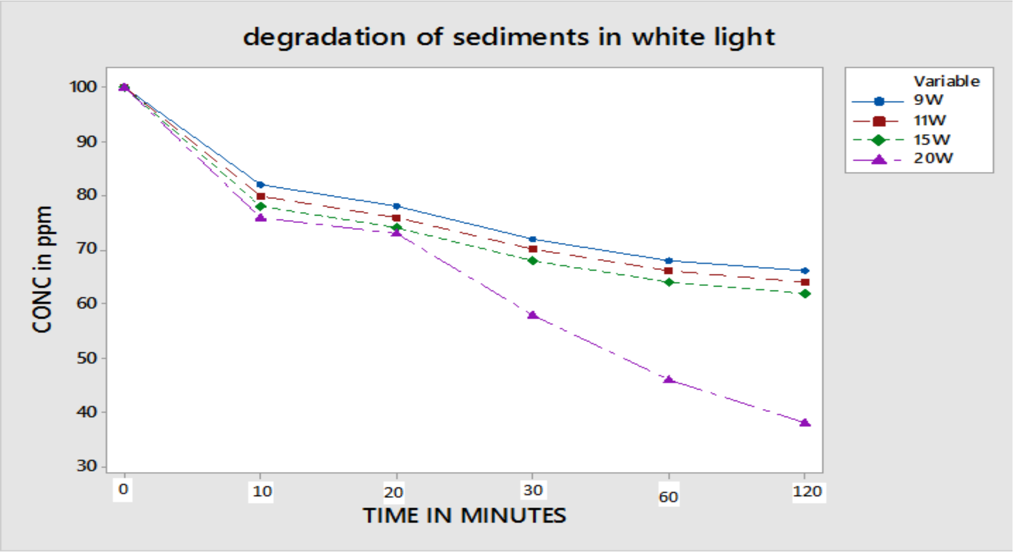


Figure 4.12 : Degradation of PCP on sediments soil subjected to fluorescent light.

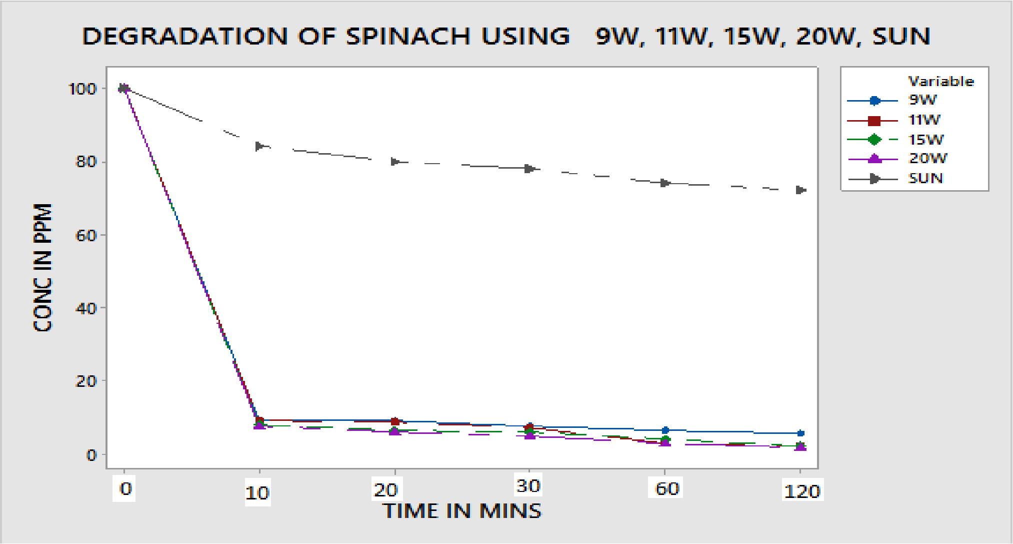


Figure 4.13: Degradation of PCP in spinach using fluorescent light.

From the results obtained above, PCP photodegradation was dependent on the surface of exposure, light intensity and time of exposure (figure 4.11, 4.12, 4.13). This is in agreement with the Stark Einstein law. More photons are present in the 20W tubes meaning higher chemical degradation. The spinach leaf surface is flat meaning that the amount of pesticide applied is fully exposed to radiation from the bulb. As a result, this translates to higher degradation (figure 4.13). According to figure 4.13 the curves level off from 10th minute to 120 minutes, which can be explained by the fact that the intensity difference between 9w and 20w is not significance to exhibit variation in degradation pattern. The half-life calculated for the PCP degradation on fluorescent light on different surfaces is shown in the table 4.3 below.

According to the data obtained; the half- life is depended on time of exposure and the wattage reaching the pesticide surface.

Table 4.3: calculated half-life of PCP on Limuru loam soil, Nairobi river sediment and spinach leaf using fluorescent tubes

10 Minutes					
EXPOSURE ENVIRONMENT	**9W**	**11W**	**15W**	**20W**	**SUNLIGHT**
Nairobi River Sediment	0.024255	0.021571	0.019373	0.018373	0.027608
Limuru Loam Soil	0.093843	0.077794	0.067729	0.051039	0.021098
Spinach Leaf	0.021425	0.021404	0.021437	0.021424	0.021077
20 Minutes					
Nairobi River Sediment	0.038747	0.035079	0.031972	0.03059	0.021071
Limuru Loam Soil	0.093266	0.075457	0.065372	0.051020	0.021083
Spinach Leaf	0.021412	0.021401	0.021398	0.02394	0.021031
30 Minutes					
Nairobi River Sediment	0.037958	0.034048	0.031968	0.03056	0.021067
Limuru Loam Soil	0.093256	0.075445	0.065245	0.050823	0.021069
Spinach Leaf	0.021409	0.021396	0.021393	0.021390	0.021027
60 Minute					
Nairobi River Sediment	0.037947	0.034015	0.031871	0.030444	0.021062
Limuru Loam Soil	0.054823	0.048298	0.045885	0.042324	0.021065
Spinach Leaf	0.021405	0.021389	0.021383	0.021279	0.021011
120 Minutes					
Nairobi River Sediment	0.037901	0.034011	0.031867	0.030415	0.021059
Limuru Loam Soil	0.053623	0.053559	0.053515	0.053510	0.021047
Spinach Leaf	0.021401	0.021379	0.021371	0.021355	0.021343

The figures 4.14, 4.15 and 4.16 below shows how half –life of PCP varies with time using the fluorescent light.

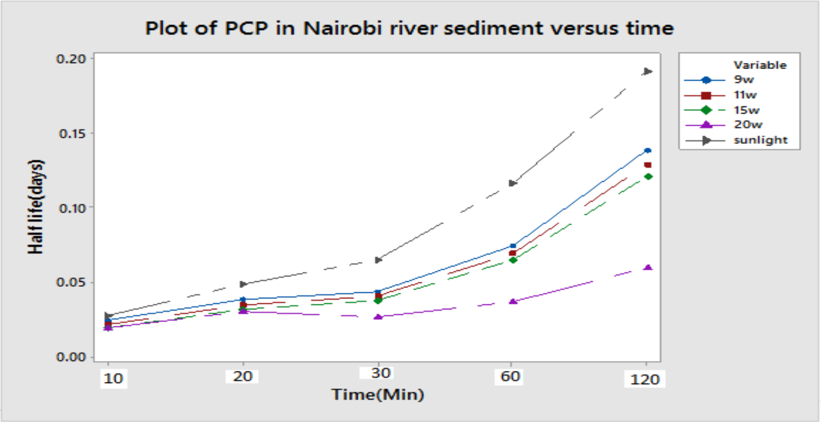


Figure 4.14 : plot of PCP half- life vs sediment over sediment.

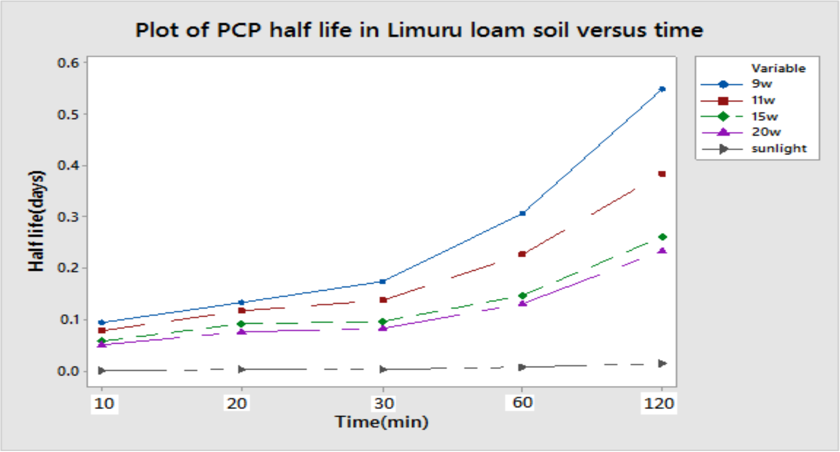


Figure 4.15 :plot of half -life of pcp vs bulb capacity over Limuru loam soil.

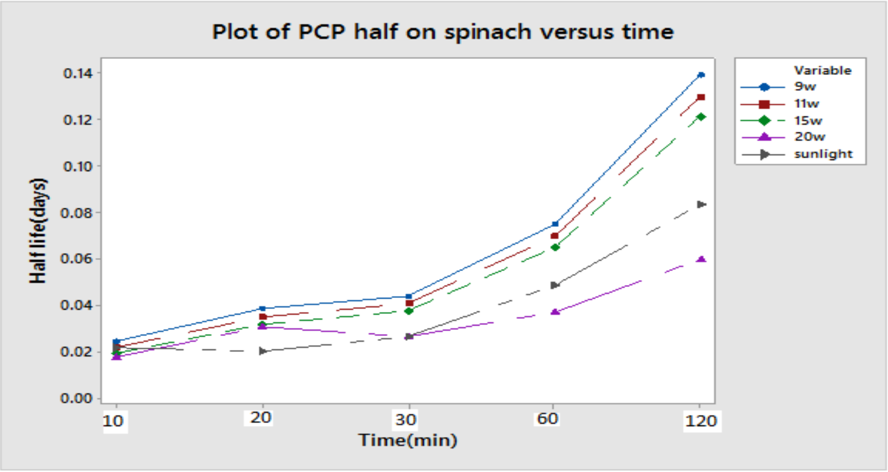


Figure 4.16 : plot of half -life of pcp vs bulb capacity over Limuru loam soil

4.4 Dimethoate (DM) degradation by incandescent bulb

When loam soil mixed with DM was subjected to incandescent bulbs and run in UV-VIS spectrophotometre for absorbance, the data obtained was plotted as shown in figure 4.17 using Minitab soft ware. Then Nairobi river sediment and spinach experiment were repeated as in the case of the loam soil and data obtained plotted in figures 4.18 and 4.19 respectively.

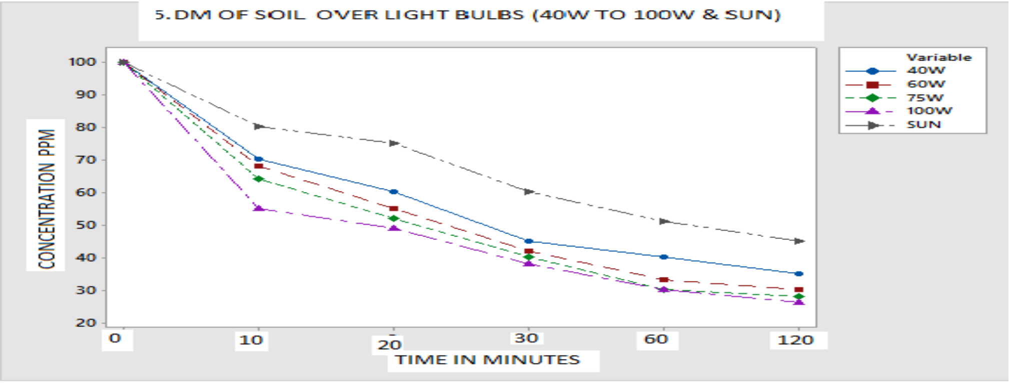


Figure 4.17: DM on soils subjected to incandescence bulbs.

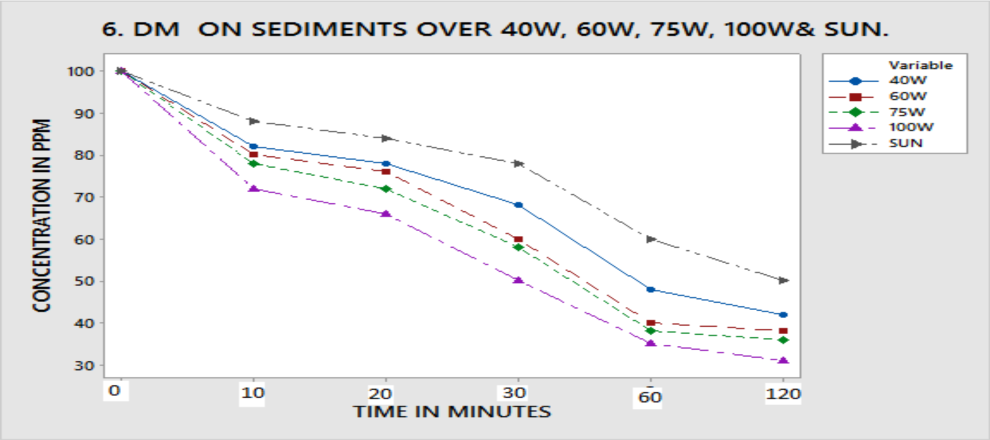


Figure 4.18: DM on sediments and exposed to incandescence bulbs.

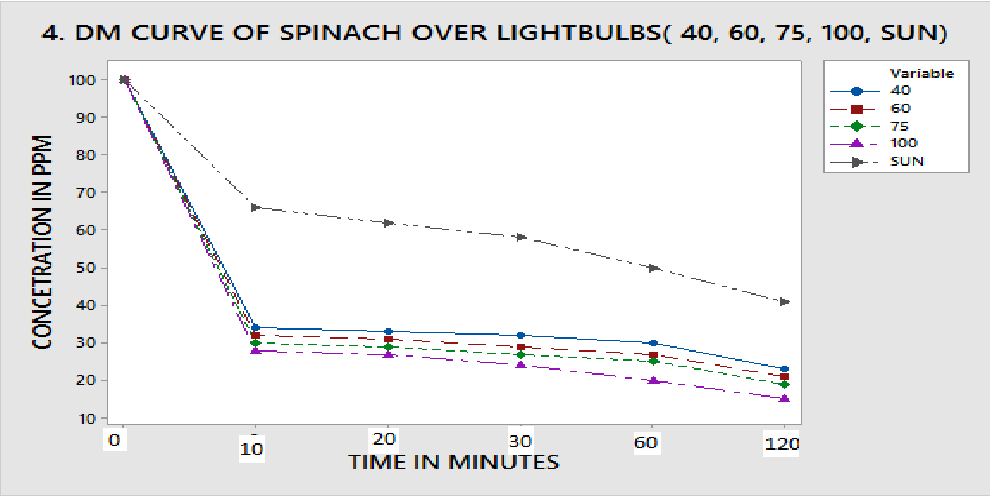


Figure 4.19: DM on spinach exposed to incandescence bulbs.

From the figures 4.17, 4.18 and 4.19 above, it is evident that the amount of dimethoate degraded depends on power applied, time of exposure and surface onto which the pesticide is applied on. In Limuru loam soil, the higher degradation is explained by the fact that dimethoate is adsorbed by the loam soil largely compared to the river sediment. This is because of the higher organic carbon content in loam soil (table4.1). This means that some residues are adsorbed while others are degraded. On spinach leaf surface, the degradation is the same for all the bulbs regardless of the exposure time. This is explained by the fact that the flat exposure surface experience light intensity similarly. This result in degradation of residues during the first few minutes of exposure is fast but slows down as molecules to be degraded are exhausted. On calculating the half-lives at different exposure time, the half-lives obtained are dependent on time of exposure, light intensity and on the type of surface used. The half-lives are tabulated in table 4.4;

Table 4.4: calculated half-life of dimethoate on Limuru loam soil, Nairobi river sediment and spinach leaf on incandescent bulbs.

10 MINUTES					
EXPOSURE ENVIRONMENT	**40W**	**60W**	**75W**	**100W**	**SUNLIGHT**
Nairobi River Sediment	0.024255	0.021571	0.019373	0.014653	0.037655
Limuru Loam Soil	0.018846	0.016103	0.014722	0.013116	0.028034
Spinach Leaf	0.004462	0.004342	0.004283	0.004110	0.009423
20 Minutes					
Nairobi River Sediment	0.038747	0.035079	0.029306	0.023169	0.055216
Limuru Loam Soil	0.018976	0.019910	0.015911	0.014116	0.029306
Spinach Leaf	0.008683	0.008449	0.00822	0.007353	0.013889
30 Minutes					
Nairobi River Sediment	0.037443	0.028269	0.02651	0.020833	0.028269
Limuru Loam Soil	0.018084	0.01711	0.01711	0.01576	0.029443
Spinach Leaf	0.012673	0.11666	0.011029	0.010417	0.013719
60 Minutes					
Nairobi River Sediment	0.039349	0.03152	0.029849	0.02751	0.027381
Limuru Loam Soil	0.030672	0.02605	0.02466	0.023331	0.026041
Spinach Leaf	0.023988	0.022058	0.020833	0.017945	0.0136771
120 Minutes					
Nairobi River Sediment	0.074385	0.059697	0.056538	0.052101	0.027333
Limuru Loam Soil	0.055021	0.047976	0.046662	0.037012	0.106039
Spinach Leaf	0.034781	0.032598	0.03152	0.030447	0.0136478

The figure 4.20, 4.21, 4.22 below shows the plots of half –life of DM with incandescent bulbs capacity .

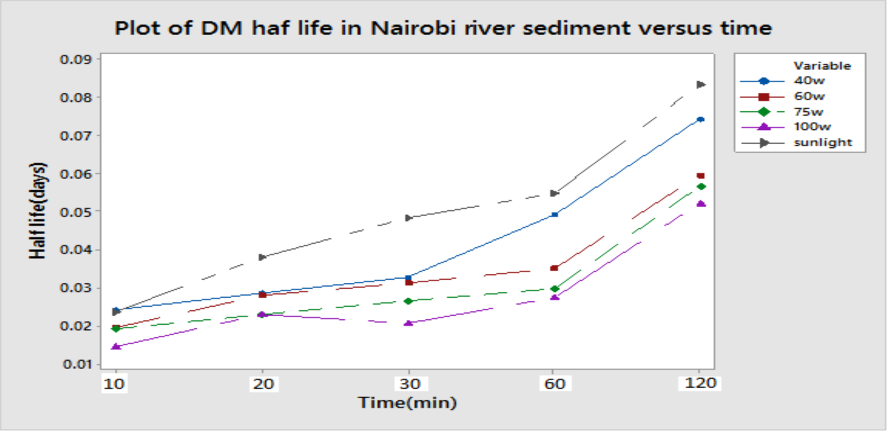


Figure 4.20 : Plot of half-life vs bulb capacity over Nairobi river sediment.

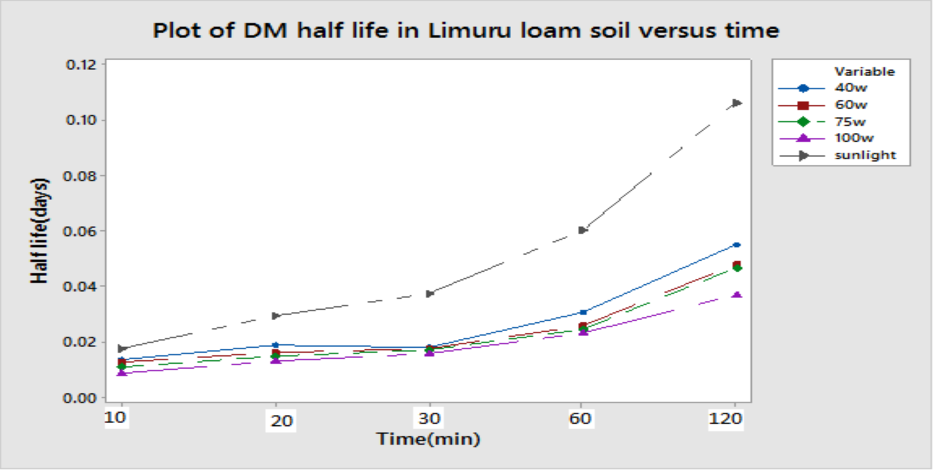


Figure 4.21: Plot of half-life vs bulb capacity over Limuru loam soil.

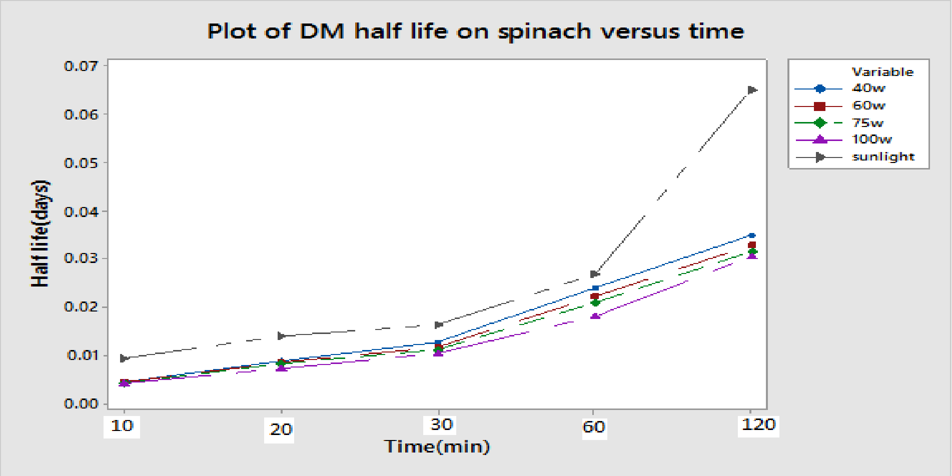


Figure 4.22: Plot of half-life vs bulb capacity over spinach leaf surface.

4.4.1 Dimethoate degradation by fluorescent light

Photo degradation of dimethoate on Limuru loam soil, Nairobi river sediment and on spinach leaf surface results from the impact of light rather than combined light intensity and temperature as observed in incandescent light. When dimethoate pesticide was exposed to different applied power of fluorescence tubes, the results obtained are depicted in the figures 4.23 below

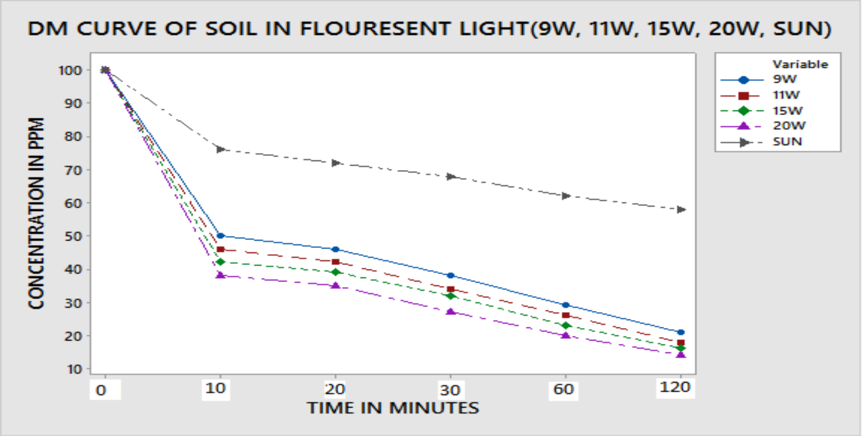


Figure 4.23: DM exposed to loam soil on fluorescent light.

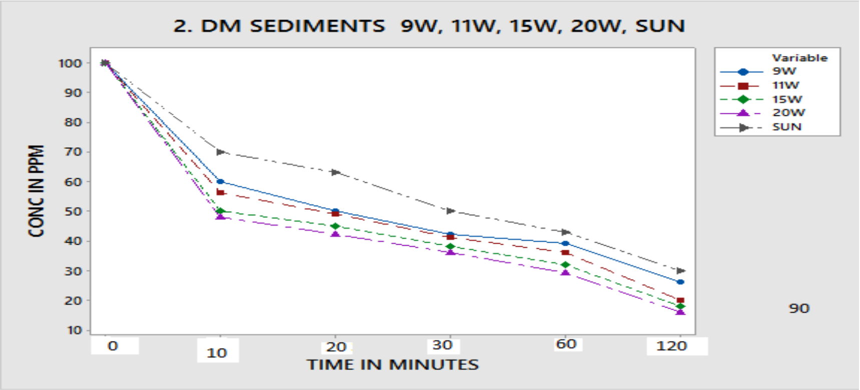


Figure 4.24: DM on sediment soil subjected to fluorescent light.

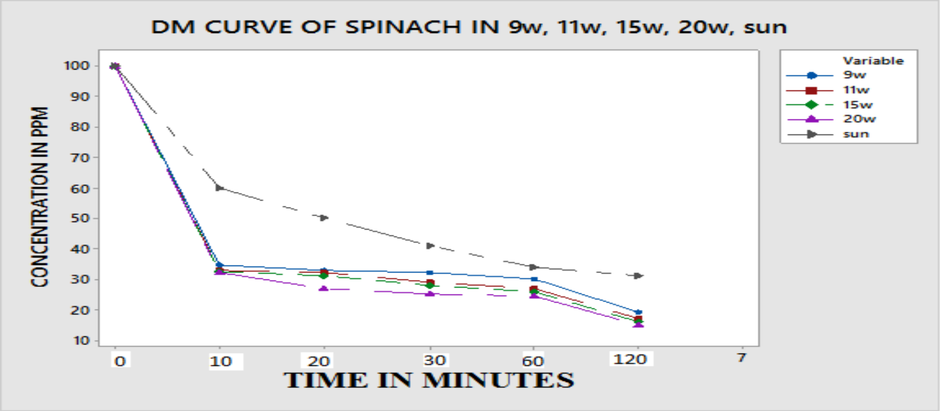


Figure 4.25: DM on spinach exposed to florescent light

According to figure 4.25 above, the photodegradation of dimethoate is in agreement with of Sterk Einstein law, which stipulates that for every photon absorbed by a molecule, it result in photochemical reaction. Photodegradation of dimethoate is higher in 20w exposure since the number of photons is higher compared to sunlight, 9w, 11w and 15w. Just like in PCP, the amount degraded is highly dependent on time of exposure, surface and amount of light intensity.

The calculated half-lives depend on the applied voltage of the fluorescent bulbs and time of exposure among other factors like the molecular structure. The half-lives are tabulated in the table 4.5.

Table 4.5: Calculated half-life of dimethoate on Limuru loam soil, Nairobi river sediment and spinach leaf on white light.

10 minutes					
exposure environment	**9W**	**11W**	**15W**	**20W**	**Sunlight**
Nairobi River Sediment	0.009423	0.008302	0.007944	0.006558	0.013496
Limuru Loam Soil	0.006944	0.006199	0.005549	0.004975	0.01754
Spinach Leaf	0.004841	0.004711	0.004462	0.004342	0.0027608
20 Minutes					
Nairobi River Sediment	0.0093889	0.008296	0.007805	0.0065483	0.0133083
Limuru Loam Soil	0.0068397	0.006140	0.0054022	0.0054017	0.017510
Spinach Leaf	0.004799	0.004709	0.004456	0.004441	0.0024314
30 Minutes					
Nairobi River Sediment	0.0091859	0.008161	0.0071492	0.006537	0.0132081
Limuru Loam Soil	0.0064924	0.006133	0.054016	0.0054015	0.017443
Spinach Leaf	0.004666	0.004602	0.004434	0.004437	0.002312
60 Minutes					
Nairobi River Sediment	0.0090672	0.008082	0.0071307	0.006499	0.0132079
Limuru Loam Soil	0.0062339	0.006128	0.053965	0.0052794	0.017324
Spinach Leaf	0.0044083	0.004196	0.004144	0.004098	0.002307
120 Minutes					
Nairobi River Sediment	0.0090588	0.008058	0.0071278	0.0062724	0.0131864
Limuru Loam Soil	0.0062201	0.006033	0.0053258	0.0051044	0.017320
Spinach Leaf	0.0044062	0.004033	0.0040315	0.004047	0.004038s

Figures 4.26, 4.27 and 4.28 below represents plot of DM half-life versus fluorescent tubes; 9w, 11w, 15w, 20w and sunlight.

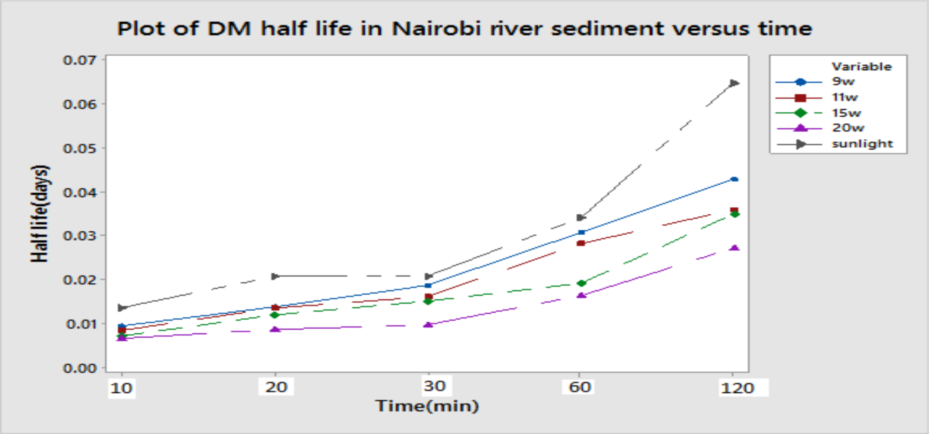


Figure 4.26: Plot of DM half –life versus bulb capacity over Nairobi river sediment.

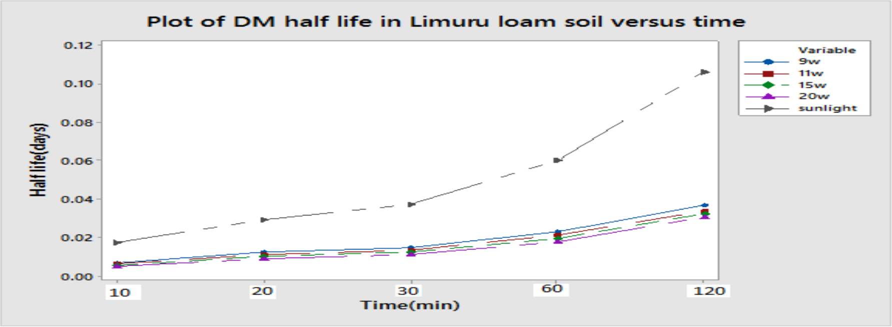


Figure 4.27: Plot of DM half –life versus bulb capacity over Limuru sediment

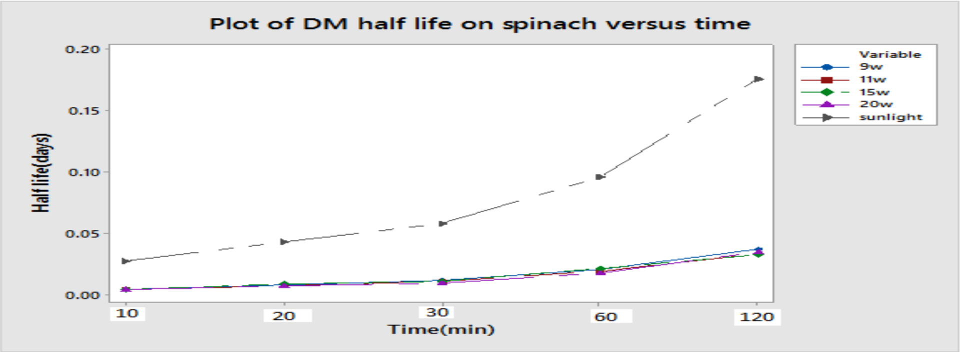


Figure 4.28: plot of DM half –life versus bulb capacity over spinach leaf

4.5 Rate of degradation of PCP and DM

Using calculus for the rate equation:

Rate of degradation is given by equation: $\frac{\ln[A]t}{ln[A]0} = -kt$ … …………..… (R1)

On rearranging equation, R1 becomes $\ln[A] = -kt + \ln[A]o$……….…..(R2)

Where [A] is concentration of pesticide molecule at time t, t is the exposure time, k is rate constant of degradation and $[A]_0$ is the initial concentration. This means that a plot of ln $[A]_t$ against time will be linear with slope as the rate constant of degradation. The graphs below represent the rate of degradation of pesticide residues under investigation. 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. For example, the plots below represent the slope of PCP and DM.

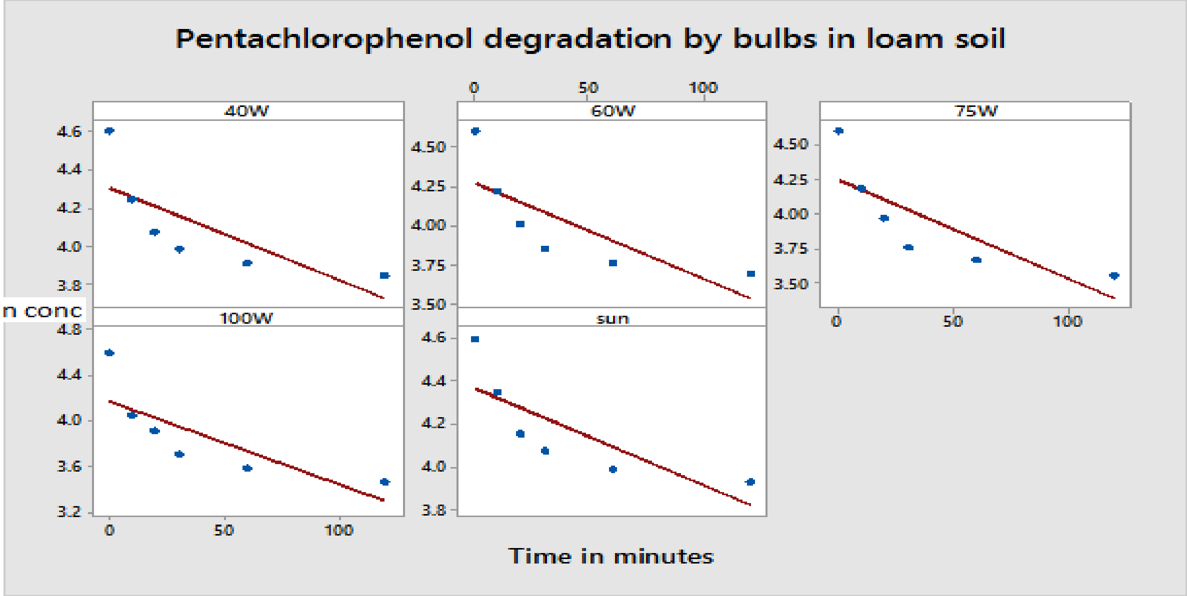


Figure 4.29: PCP degradation on loam soil subjected to incandescent bulbs.

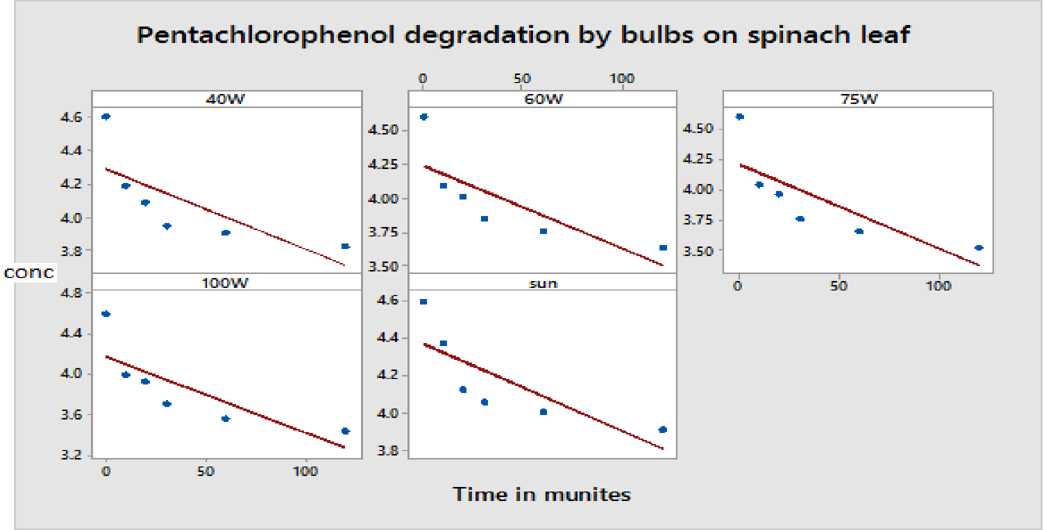


Figure 4.30: PCP degradation on spinach leaf surface subjected to incandescent bulbs.

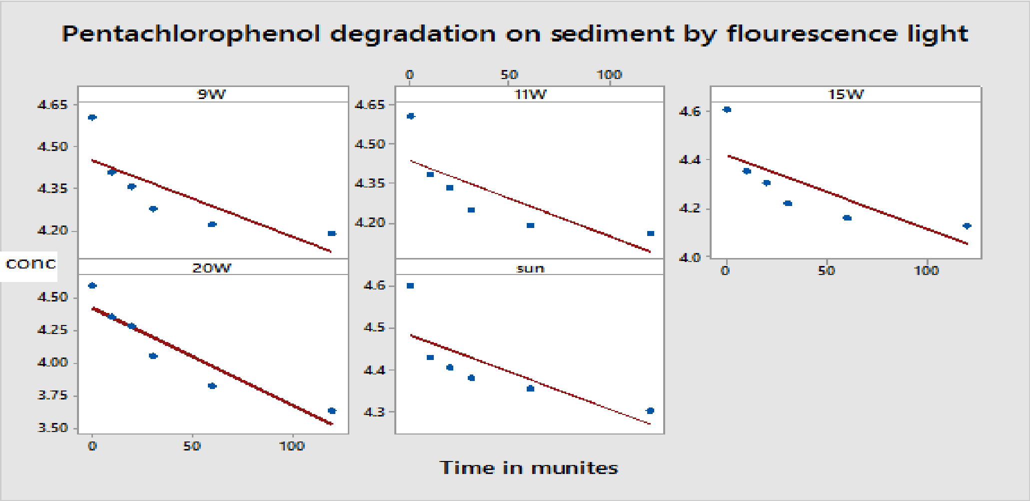


Figure 4.31:PCP degradation on sediment soil subjected to fluorescent light.

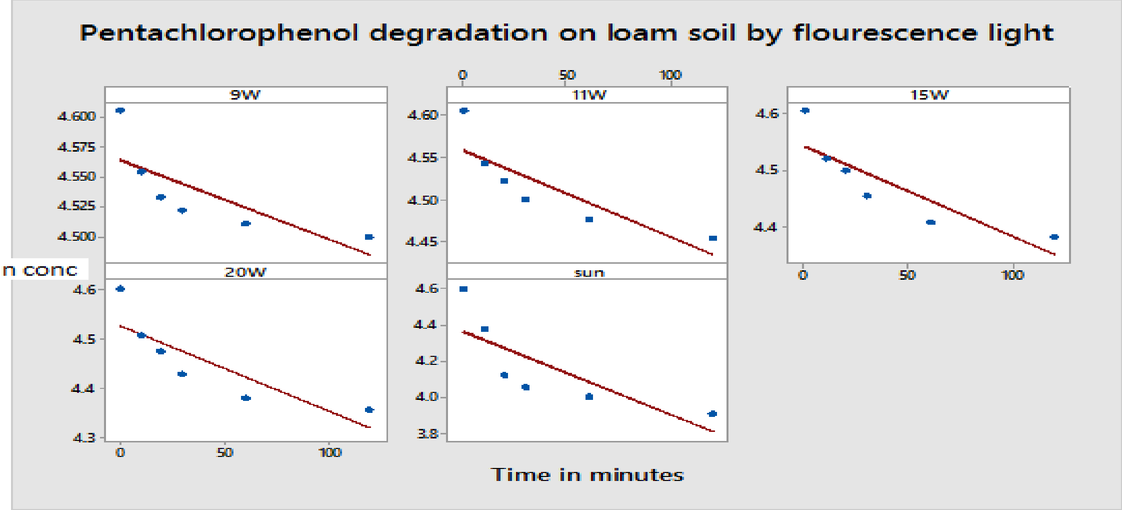


Figure 4.32 : PCP degradation on loam soil subjected to fluorescent light.

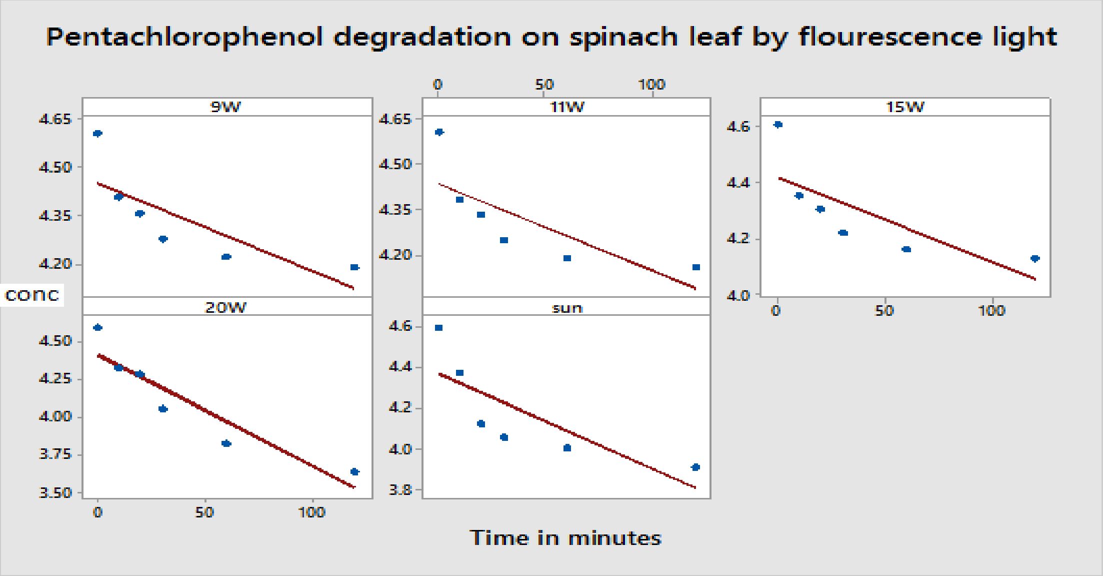


Figure 4.33 : PCP degradation of spinach leaf subjected to fluorescent light.

The equation fitted the first order kinetics providing the nearly linear relationship. However, a fit of zero order to the data did not give the expected curve. Similarly, the equation for second order did not fit the data either hence the conclusion of first order kinetics

4.5.1 Rate of degradation of Dimethoate

The plots below were obtained when the rate of decay for DM was calculated.

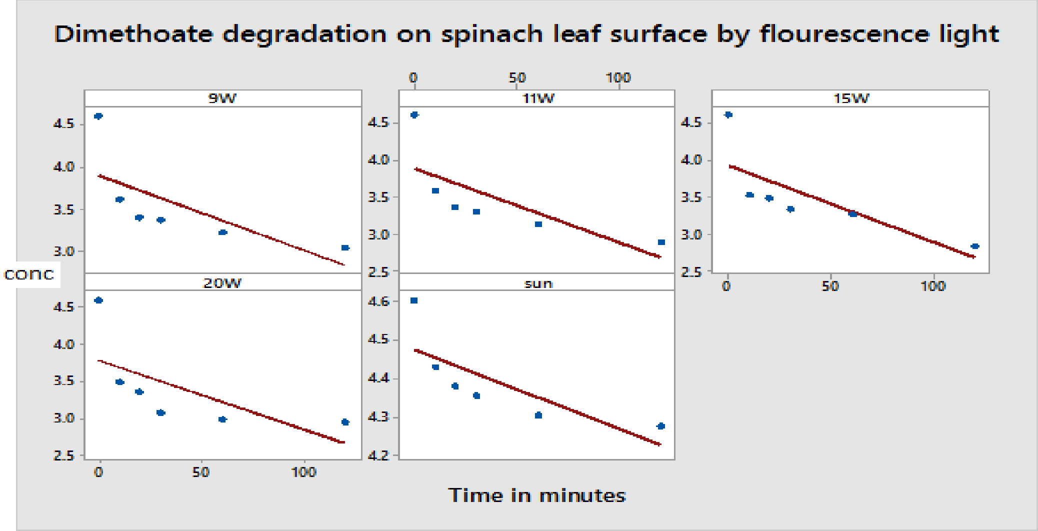


Figure 4.34: DM degradation on spinach leaf surface subjected to fluorescent light.

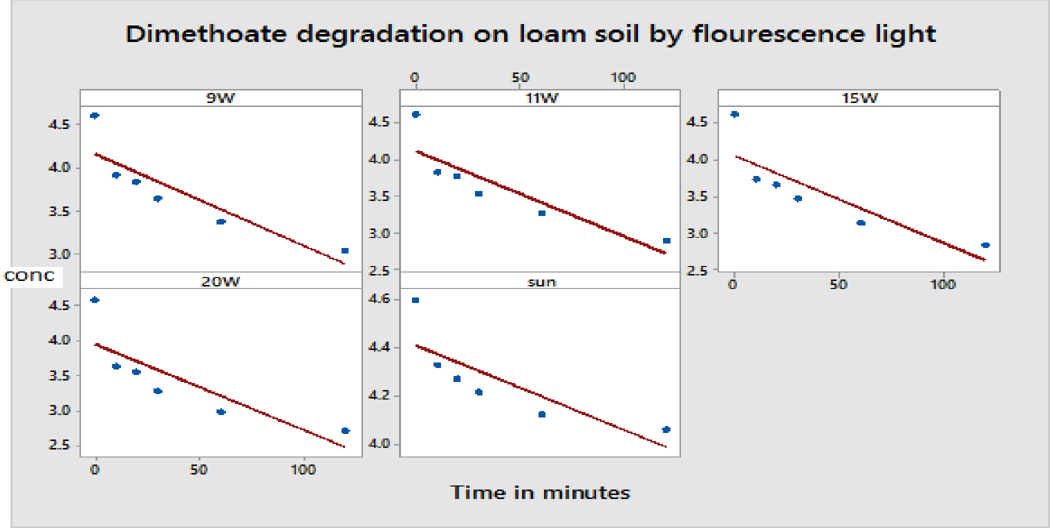


Figure 4.35 : DM degradation on loam soil subjected to fluorescent light.

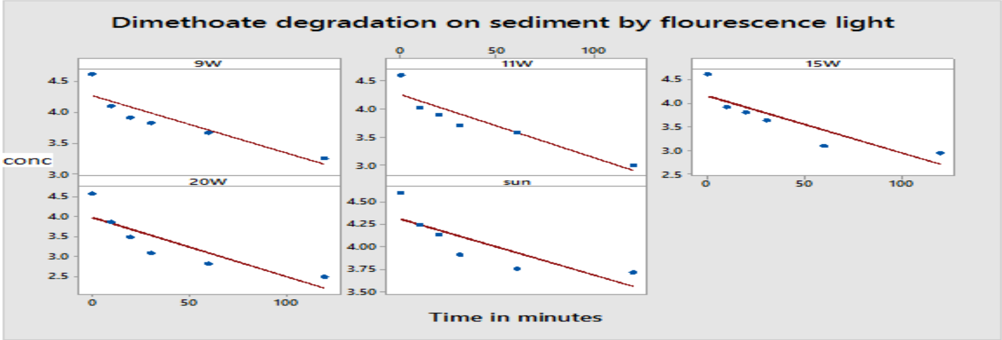


Figure 4.36 : DM degradation on sediment soil subjected to fluorescent light.

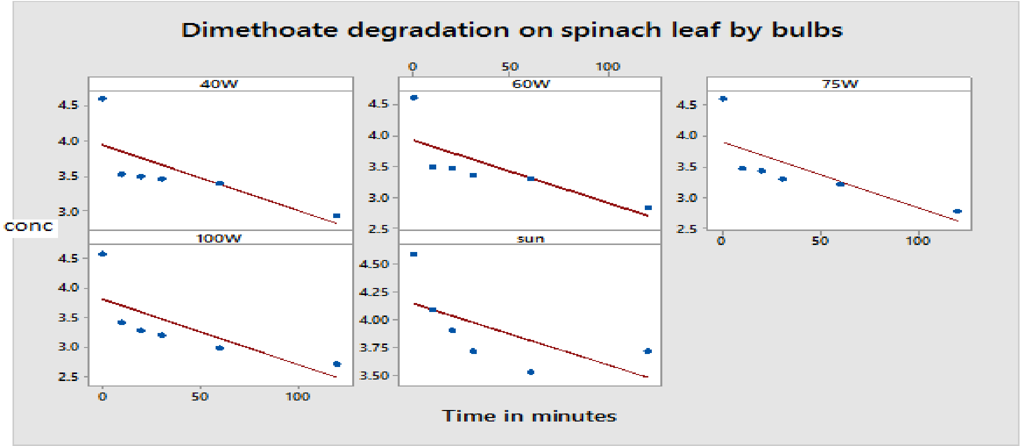


Figure 4.37 : DM degradation on spinach leaf subjected to incandescent light.

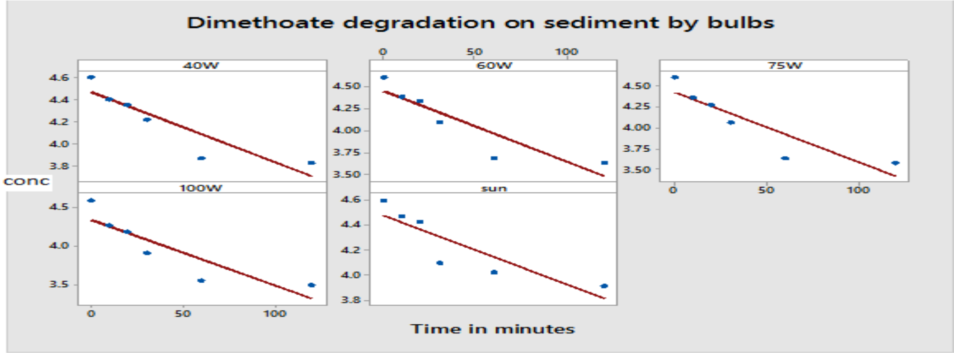


Figure 4.38 : DM degradation on sediment soil subjected to incandescent light.

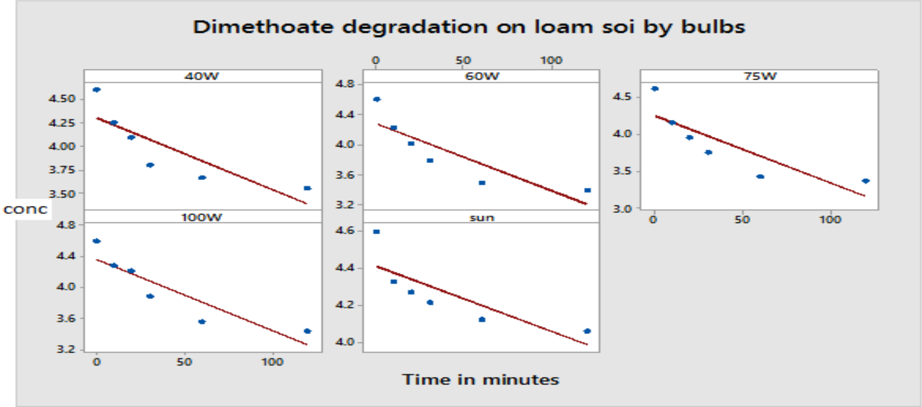


Figure 4.39: DM degradation on loam soil subjected to incandescent light

The rates of degradation of the residues were dependent on time of exposure, light intensity, particular molecular structure and temperature. As shown in figures 4.29 to figure 4.38, the rate constant for PCP and dimethoate is almost the same. The main difference is attributed to the effect of temperature. It’s important to remember that natural degradation of a given substance occurs with time, but this discussed here was accelerated by different exposure to sunlight, incandescent bulbs and fluorescent bulbs. Therefore, the accelerated lights are expected to be much faster than the natural decomposition. The rate of PCP and DM photodegradation can be obtained using equation 3.2. The rate of degradation highly depends on the light intensity hitting the pesticide molecule and the background surface area. The rate of degradation was highest in DM spinach leaf samples. This can be explained by the fact that spinach leaf surface is well spread allowing maximum light reaching the surface. Figure 4.40 below shows the rate of PCP and DM degradation in various surfaces.

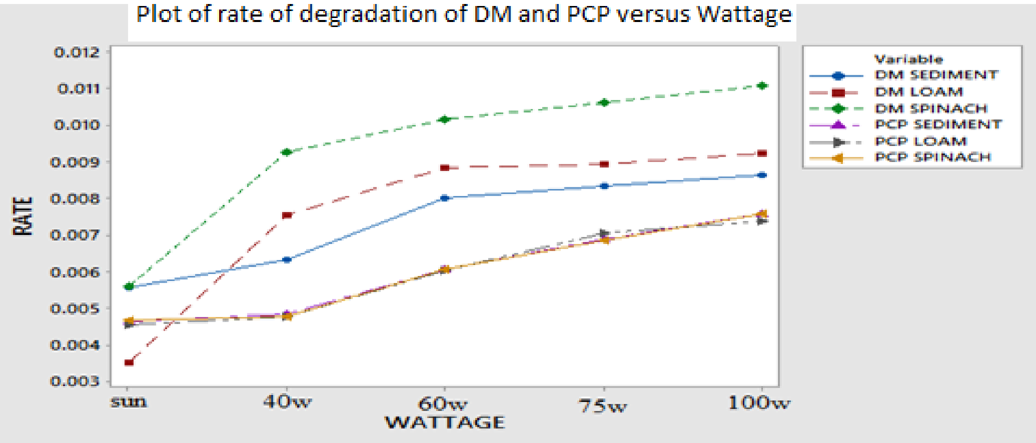


Figure 4.40: plot of degradation rate of DM and PCP VS applied power.

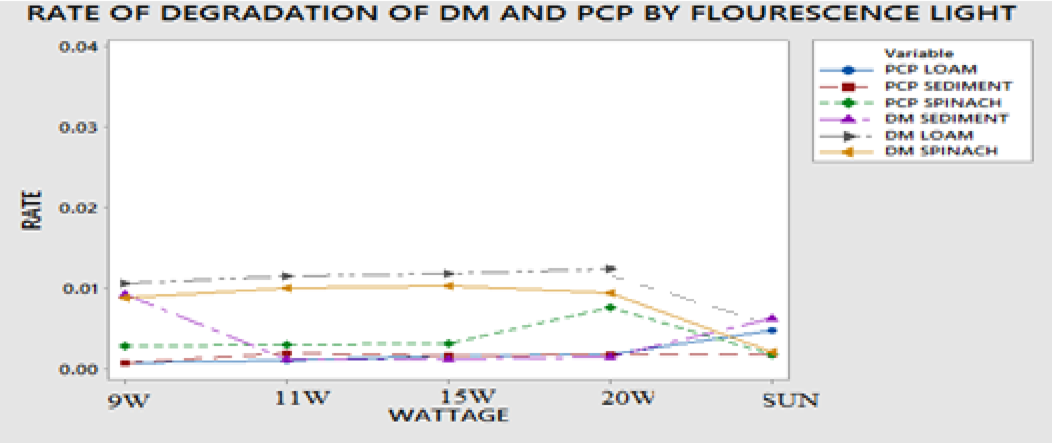


Figure 4.41: Degradation of DM and PCP against fluorescence light.

4.6 Energy calculations

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

Energy= power x time ……………………………………………..................… (4.12)

Energy =hν ....(4.13)

Power = area x current ……………………………………...….................… (4.14)

$\text{current} = \frac{\text{volts}}{\text{resistance}}$ or $\text{current} = \frac{\text{power}}{\text{volts}}$ and $\text{power} = \text{IV}$ ....(4.15)

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, 80/100x1.4=1.12kW/m..................... (4.16)

Area = 5cm x5cm=25/10000=0.0025m^2 of spinach leaf …………………….... .....(4.17)

power=0.0025m^2x1.12kW/m^2= 0.0028kW……………………………............ (4.18)

Energy = 0.0028kWx 2x60x60sec=20.16joules. …………………...……......… (4.19)

This means that the amount of energy absorbed by the spinach when exposed to 40w, 60w, 75w and 100w bulbs for two hours can be calculated since the area and the powerare known. The amount of energy responsible for breaking down the pesticide molecules on spinach leaf surface are shown in table 4.6:

Table 4.6: Energy hitting the pesticide molecule in kilojoules.

	FLOURESCENCE TUBES				**INCANDESCENT BULBS**				
Time	9w	11w	15w	20w	40w	60w	75w	100w	Sunlight
10	0.0135	0.0165	0.0225	0.03	0.06	0.09	0.11	0.15	0.0042
20	0.027	0.033	0.045	0.06	0.12	0.18	0.23	0.3	0.0084
30	0.0405	0.0495	0.0675	0.09	0.18	0.27	0.34	0.45	0.0126
60	0.081	0.099	0.135	0.18	0.36	0.54	0.675	0.9	0.0252
120	0.162	0.198	0.27	0.36	0.72	1.08	1.35	1.8	0.0504

From the table 4.6 above, it is evident that the energy reaching the pesticide molecule of interest is dependent on the bulb capacity and time of exposure. Sunlight energy has the least amount of energy reaching the degradation surface. It is there expected that in both pesticide molecule in this study would be degraded least by the sun light. Figure 4.42 illustrate clearly the amount of energy as a function of time of exposure.

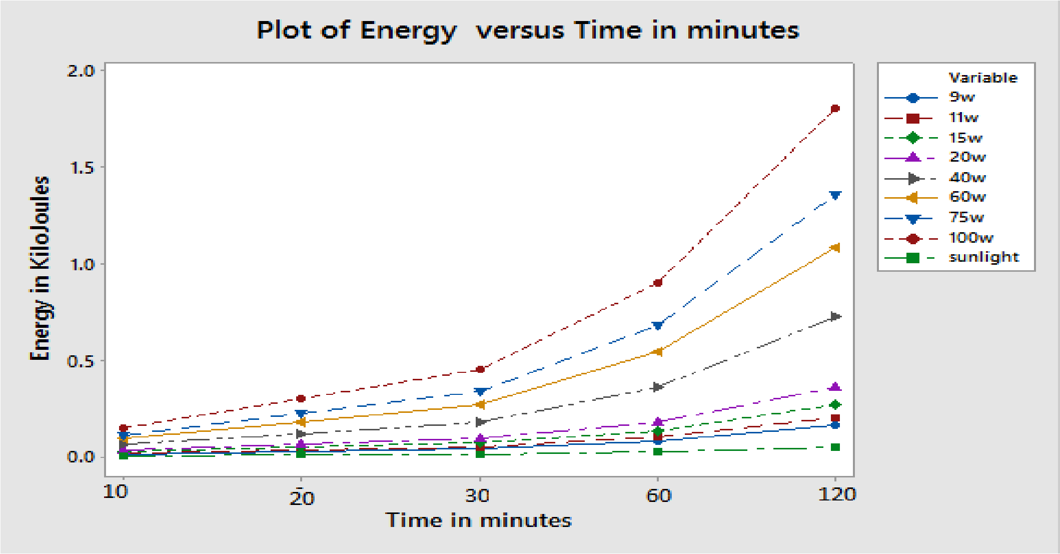


Figure 4.42: Energy in kilo joules versus time in minutes.

4.7 Extending exposure time for PCP and DM

Extending the exposure beyond 120 minutes does not show any additional decrease in degradation. This is well demonstrated in figure 4.41 below. Since the numbers of pesticide molecule undergoing photolysis are depleted, the decomposition rate slows down and eventually plateaus after the 120th minutes. Further increase in exposure time does not result in further degradation. In addition, the by-products formed may need more energy to break further resulting in the trend shown by figure 4.41 and 4.42.

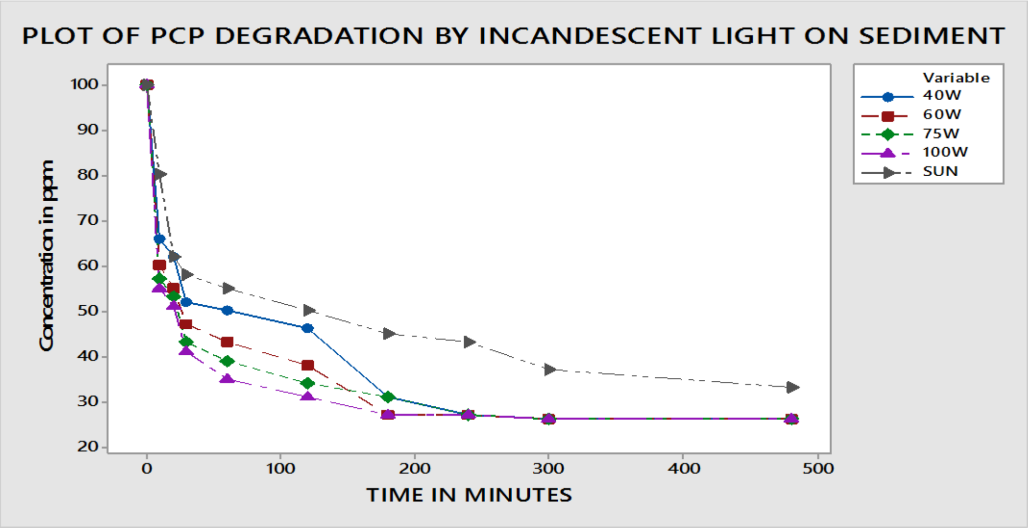


Figure 4.43 : PCP degradation curve on sediment beyond 2hours

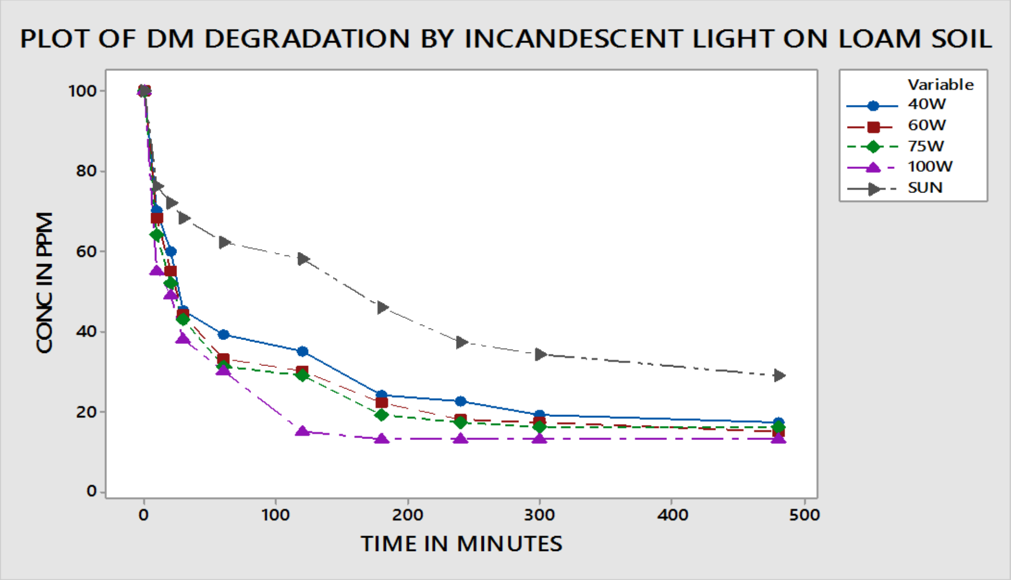


Figure 4.44 : DM degradation curve on loam soil beyond 2 hours

CHAPTER FIVE

CONCLUSIONS AND RECOMMENDATIONS

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

5.1 Conclusions

Photo-degradation of pesticide on the surface of spinach leaf by different light intensity followed first order kinetics. This is because the equation fitted the nearly linear relationship for first order kinetics. A fit of zero order and second order did not give the expected curve for both PCP and DM.

The degradation rate was in sequence of 100w>75w>60 > 40>sun for incandescent light and 20w > 15w > 11w > 9w for fluorescence light. Photo degradation of PCP and dimethoate is highly dependent on light intensity, exposure time, and molecular structure of the pesticide residue and the surface of exposure.

Moreover, the rate of degradation heavily relied on temperature, exposure time and light intensity. The half-lives of both molecules on the three-exposure surface ranged between 0.007306 to 0.076days for PCP in incandescent bulb and 0.078 to 0.093 days for fluorescence light while the range of half-life is 0.037 to 0.00446 and 0.0023 to 0.013 days for DM in incandescent bulb and fluorescence light respectively.

5.2 Recommendations

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

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

ii. The government should ensure banned pesticides are not present in the market in any formulation.

iii. Pesticides adulteration should be dealt with more strictly than what is being done currently.

iv. Other substrates or surfaces need to be considered and extended data bank on degradation be in place.

5.3 Recommendations for further work

Further research work is recommended to:

Determine the mechanism of pesticide residues i.e. Pentachlorophenol and dimethoate degradation in loam soil, river sediments and on plant surface by different electromagnetic radiation.

Carry out detailed study of photo-degradation of pentachlorophenol and dimethoate in different organic solvents, aimed at determining which should be carried out to determine which organic solvent extract these residues fully.

Investigate the pesticide residue levels on vegetables especially spinach offered to the different markets. This is to determine the levels of residues and their different degradation products.

Determination of different techniques and locally available methods of washing/removing pesticides residues from river water and on vegetable surface should be done. This is to ensure that the residue limits are not violated.

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APPENDEX ONE

Banned pesticides in Kenya

Table 5.1: Banned pesticides in Kenya.

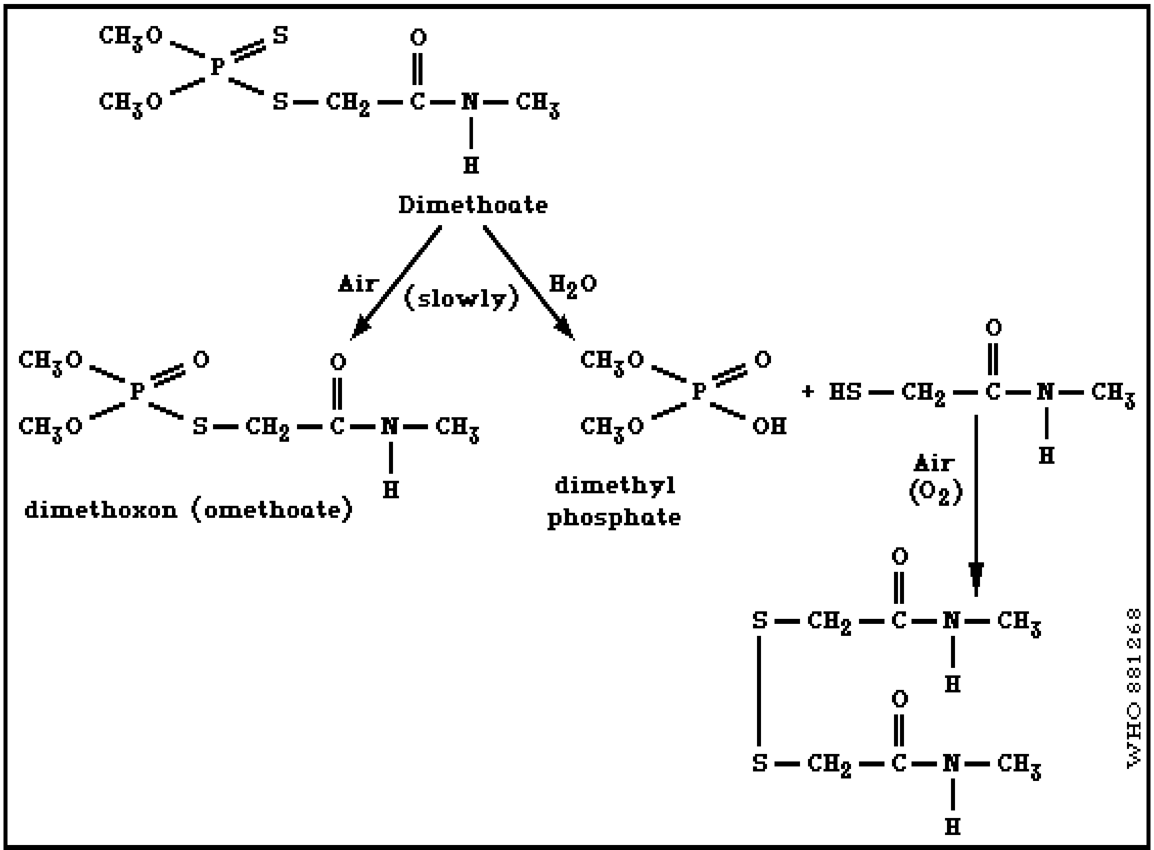
	Common name	Use	Date Banned
1.	2,4,5T(2,4,5–Trichlorophenoxybutyric acid)	Herbicide	1986
2.	Chlordane	Insecticide	1986
3.	Chlordimeform	Insecticide	1986
4.	DDT(Dichlorodiphenyl Trichloroethane)	Agriculture	1986
5.	Dibromochloropropane	Soil Fumigant	1986
6.	Endrin	Insecticide	1986
7.	Ethylene dibromide	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 except capsuleformulationbanned).	1988
12.	Methyl Parathion	Insecticide(All except capsule formulations banned	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
27.	Phosphamidon	Insecticide, Soluble	2004

		liquid formulations of the substance that exceed 1000g active ingredient/L	
28.	Monocrotophos	Insecticide/Acaricide	2009

APPENDEX TWO

Dimethoate degradation mechanism

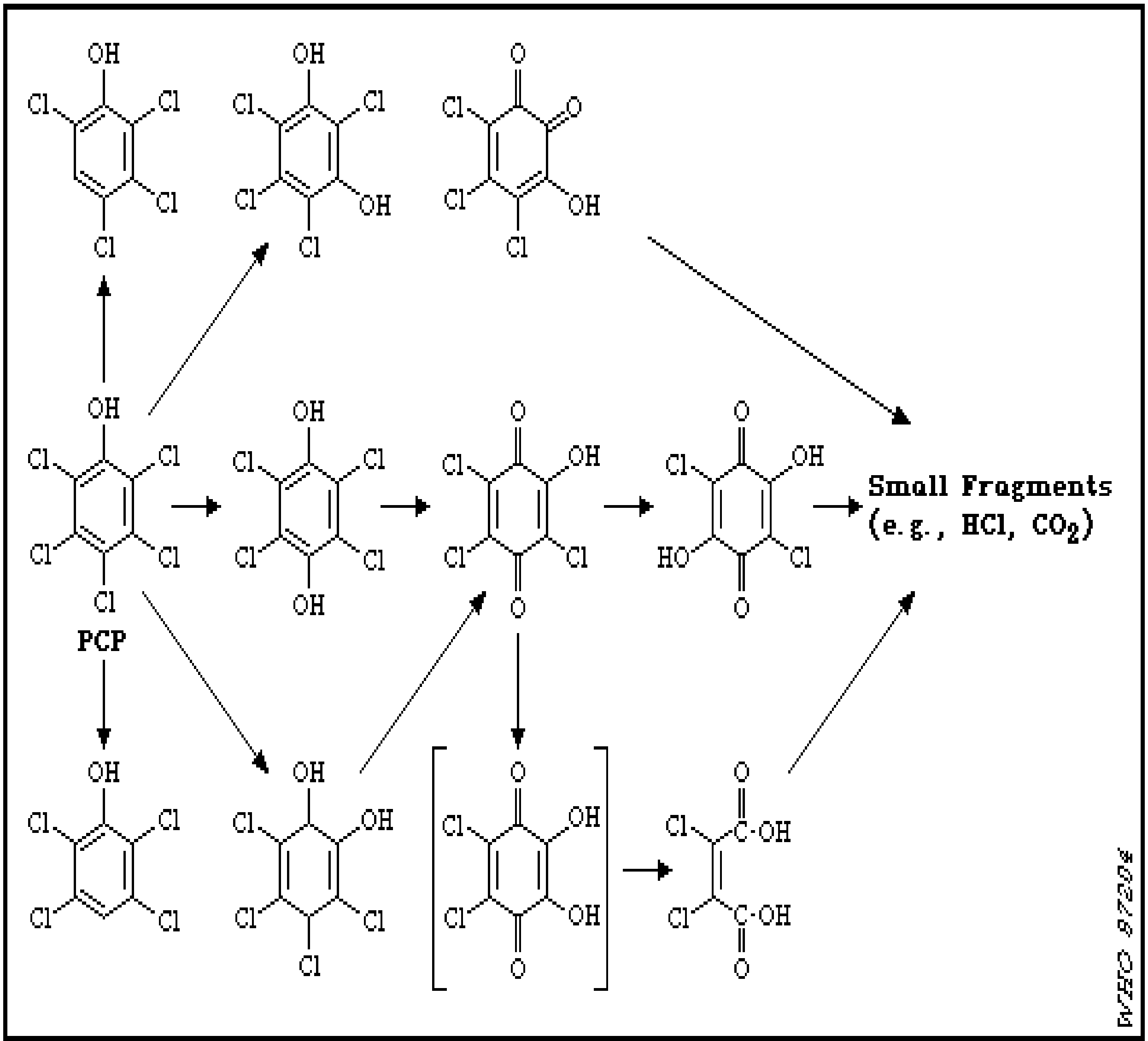


Pathways of dimethoate degradation in air and water.
From: Menzie (1969).

Figure 5.1 : proposed dimethoate degradation mechanism.

APPENDEX THREE

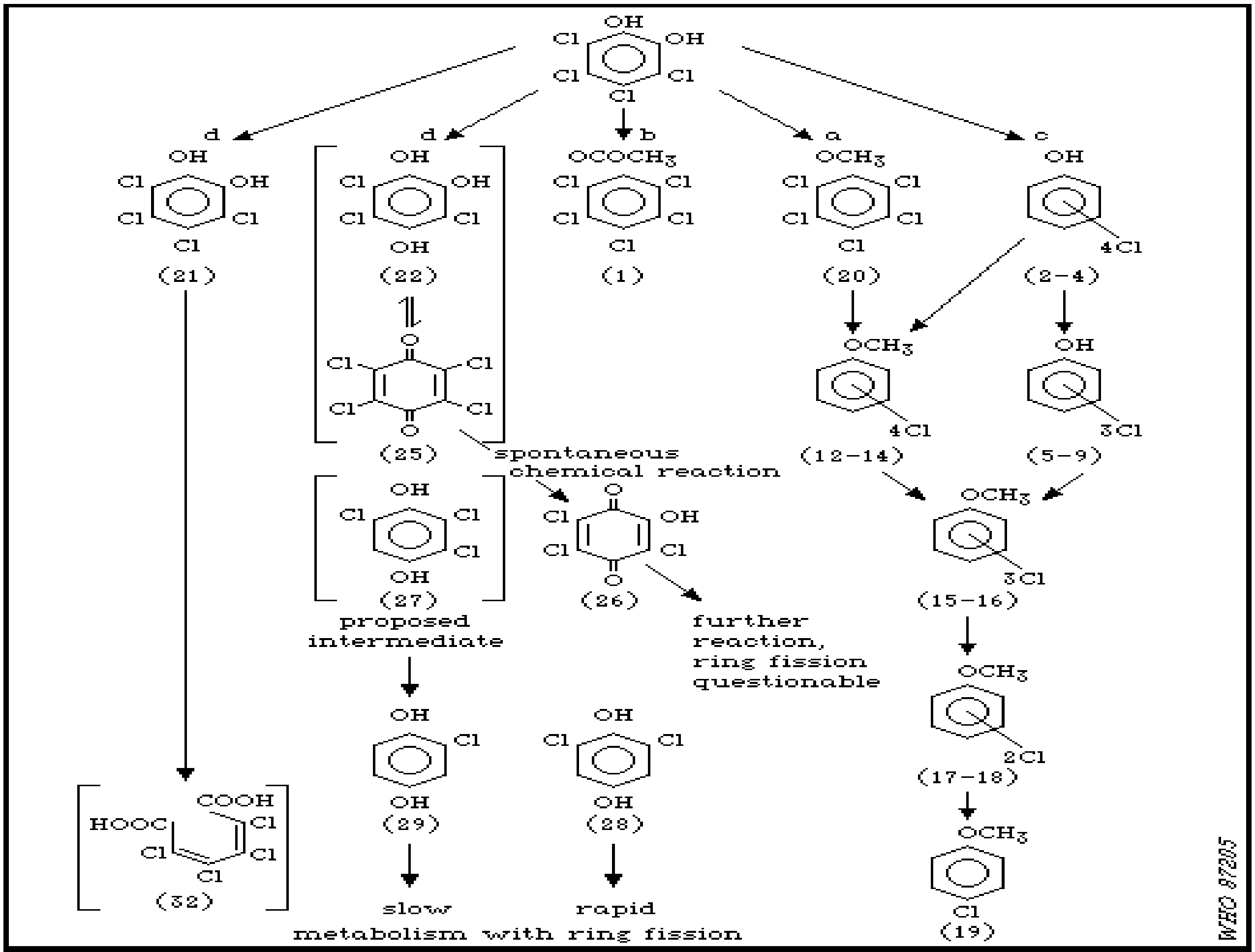
Pentachlorophenol degradation mechanism



Proposed photolysis pathway for PCP. Adapted from: Wong & Crosby (1978).

Figure 5.2: Proposed pentachlorophenol degradation mechanism

PENTACHLOROPHENOL DEGRADATION MECHANISM



Metabolic pathways for the biodegradation of PCP. Adapted from: Kaufmann (1978), Reiner et al. (1978), and Rott et al. (1979). For a list of metabolites (numbers in parentheses), see Table 12.

Figure 5.3: Further pentachlorophenol degradation mechanism.