ADSORPTION OF SELECTED PESTICIDE RESIDUES BY SELECTED SOILS FROM LAKE NAIVASHA REGION IN KENYA: ADSORPTION/DESORPTION PROPERTIES AND RELATED THERMODYNAMIC DATA

By

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DECLARATION:

This Thesis is my original development as a requirement for partial fulfillment of Master of Science in Chemistry and has not been presented as a degree in any other University.

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ABSTRACT

The adsorption/desorption properties of soils in aqueous solution from Lake Naivasha by 1-naphthol N-methylcarbamate (Carbaryl) and N-(3,4-dichlorophenyl)-N,N-dimethyl urea (Diuron) was studied in terms of the first order model of a binary solution expressed as:

$$nX + S \Leftrightarrow SX_n \text{ and } K = [SX_n]/[X]^n[S], \ldots\ldots\ldots\ldots\ldots\ldots(1)$$

X is the chemical species of interest (pesticide) , S is the substrate (soil particles), K is the adsorption/desorption equilibrium constant and SX_n is the particle-pesticide complex. According to this model, the apparent adsorption/desorption equilibrium constant K' is given by equation 2:

$$\ln[x]_{ads} = \ln(nk') + n(\ln[x]_e + [sx_n]_w)\ldots\ldots\ldots\ldots\ldots\ldots(2)$$

where $[X]_{ads}$ is concentration of X in adsorbed state in suspension. $[X]_e$ is the concentration of X in solution at equilibrium. $[SX_n]_w$ is the pesticide adsorption site complex in the suspension at equilibrium.

The significance of the study was to determine the thermodynamic and kinetic properties of these two pesticides in order to ascertain their environmental impact in view of necessary remedies.

The mathematical simplicity of the first order model of a binary solution makes it preferred for this study, since changes in concentration of the pesticide can be used to predict the sorption of the organic compound in the soil. The experimental procedures involved spiking varied masses of the soil with varied concentrations of the pesticides and shaking for different time intervals to attain equilibration. Concentrations of adsorbed pesticide were obtained by analyzing the aqueous phase medium using UV-Visible spectrophotometer and finding the differences from the initial concentrations. Generated plots were used to determine related thermodynamic parameters.

The average values of $K^{'}$ (the apparent adsorption/desorption equilibrium constant), n and $\Delta G^{'}$ (the apparent adsorption/desorption free energy) for Lake Naivasha soils obtained for Carbaryl were 20.56, 0.63 and -7.26 KJ/mol respectively.

The average values of $K^{'}$, n and $\Delta G^{'}$ obtained for Diuron were 18.33, 0.57 and -7.08 KJ/mol respectively.

For both Carbaryl and Diuron, the ΔG values are negative which indicates a spontaneous sorption process. The values of n above obtained for Carbaryl and Diuron are less than unit, suggesting that each molecule of the pesticide is associated with a single adsorption sites.

Lastly, the main difficulty experienced in this adsorption/desorption work with respect to the method and instrumentation used was with regard to the time taken for equilibration to occur. Better equilibration for adsorption experiments are attained over longer shaking times and settling intervals.

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LIST OF ABBREVIATIONS:

ACh -Acetylcholinesterase.

AChE - Acetylcholinesterase Enzyme.

ATP -Adenosine triphosphate.

ATSDR -Agency for Toxic Substances and Disease Registry.

BCF -Bio-Concentration Factor.

CEC -Cation Exchange Capacity.

DDT -Dichloro-diphenyl-trichloroethane.

EC -European Commission.

EPA -Environmental Protection Agency.

EU -European Union.

HPLC -High Powered Liquid Chromatography.

HS -Humic Substances.

LC -Lethal Concentration.

LCh -Liquid Chromatography.

NMR -Nuclear Magnetic Resonance.

OM -Organic Matter.

PAHs -Polycyclic Aromatic Hydrocarbons.

POP -Persistent Organic Pollutants.

SEAD -Strategic Environmental Assessments Division.

SOM -Soil Organic Matter.

USPHS -United States Public Health Services.

UV-Vis. -Ultraviolet visible.

CHAPTER ONE

INTRODUCTION

1.1: Significance of pesticides

Pesticides used in agriculture, public health and agricultural pest control programs can enter the environment in a number of ways depending upon the method and proficiency of application, as a result of accidents or through the unauthorized dumping of unwanted pesticide products or their containers.

Pesticide residues are the deposits of pesticide active ingredient (a.i.), its metabolites or breakdown products present in some component of the environment after its application, spillage or dumping. Residue analysis provides a measure of the nature and level of any chemical contamination within the environment and of its persistence. It is often difficult to correlate pesticide residues in the environment with effects on fauna and/or ecological processes. They can, however, show whether an animal or site has been exposed to chemicals and identify the potential for future problems.

Pesticide soil analysis can be used to:

- investigate residual levels of pesticide in the environment, their movement and their relative rates of degradation.
- identify contaminated areas and/or sources of contamination.
- examine the uptake of pesticide by food chain components.

All pesticides are subject to degradation and/or metabolism once released into the environment. The rates of degradation and dissipation vary greatly from pesticide to pesticide and from situation to situation (e.g the rate of loss for all types of compounds is greater under tropical conditions because of higher temperature as compared to temperate climatic conditions). The purpose of residue analysis is to indicate the residues present at the time of sampling. Knowledge of the properties and characteristics of pesticides is vital in developing a sampling plan for residue analysis [Albanbis et al., 1993].

The following briefly outlines the relevant environmental characteristics of the various pesticide classes:

1.1.1: Organochlorines

Mobility of Organochlorines in soil is generally limited; although it is greater in sandy soil. They tend to be bound in clay soils with limited leaching. Residues of the parent compound or metabolites can be found in soil, sediment, vegetable samples and in vertebrates/invertebrates for extended periods. Their solubility in water is low, although residues can be detected in water where there is extreme contamination and, particularly, on suspended matter in water. Examples includes, lindane (gamma isomer of benzene hexachloride), dieldrin, DDT (p-p' isomer), endosulfan, and heptachlor [Hamaker and Thomson, 1972].

1.1.2: Organophosphates

Organophosphates have a fairly limited environmental persistence and residues in living specimens generally are not detected, or only as metabolites in specific cases. Water solubility is variable but higher than the organochlorine; residues generally break down quite quickly in water (hydrolysis) and are not generally detected except where the contamination or application is quite recent. They include fenitrothion, and fenthion [Stevenson, 1972].

1.1.3: Carbamates

Residues of parent compounds are generally not environmentally persistent; metabolites are rapidly excreted by vertebrates. Water solubility is moderate, but greater for the metabolites.

Most carbamates are relatively stable in water of neutral pH. Stability and mobility in soil varies between compounds. Aldicarb, carbaryl and propoxur form examples of carbamate [Stevenson, 1972].

1.1.4: Pyrethroids

Pyrethroid insecticides are generally non-persistent in the environment, being rapidly degraded in the presence of strong sunlight. Residues are probably only of interest for 5–7 days after spraying, unless in shaded areas and where the concentrations applied are particularly high. Pyrethroid include; cypermethrin, permethrin, and deltamethrin [Hamaker and Thomson, 1972].

1.1.5: Insect growth regulators (IGRs)

Benzoyl urea IGRs generally act by inhibition of chitin synthesis and moulting, thus interfering with the formation of the insect cuticle. They are increasingly used for the control of leaf-eating insects in forestry, ornamentals and fruit. Their low water solubility and adsorption by soil reduces their environmental impact and in general use, residues are only likely to be detected in soil. They include triflumuron, methoprene, and fenoxycarb [Stevenson, 1972].

1.1.6: Herbicides

Although of relatively low acute toxicity to most animals, herbicides can indirectly affect a variety of species through the removal of vegetative cover. Environmental persistence of the herbicides varies; some are readily absorbed by and degraded in soil (e.g. paraquat) whilst others are more persistent and, with relatively high water solubilities, considered to be quite mobile (e.g. triazine materials) [Stevenson, 1972].

1.1.7: Fungicides

Some fungicides can have adverse environmental effects, although they are used extensively in the field for cereal production, their use patterns suggest limited scope for environmental contamination except as the result of disposal (e.g. from large-scale dip treatment operations) or accidental contamination (spillage, etc.). Examples of fungicides are; carbendazim, Chlorothalonil and metalaxyl [Stevenson, 1972].

1.1.8: Soil fumigants

Under controlled use, soil fumigants do not pose a substantial environmental problem unless they are allowed to contaminate watercourses (e.g, methyl bromide is highly soluble in water, 13.4 gl^{-1} at 25 ºC, 1,3- dichloropropene is less soluble, 2 gl^{-1} at 20 ºC).The materials are volatile and dissipate to atmosphere on aeration of the soil.

The method and precision of application (and the purpose of the pest control operation) usually determines the quantity of pesticide applied and its overall distribution. Poor application can result in over-spraying of an area (i.e. an excessive dose), excessive spray drift, or poor targeting with scope for greater non-target contamination.

The types of field treatment used include: Spray operations, Dust treatments, Dip treatments, Granule application, Baits, Fogging and Pour-ons [Hamaker and Thomson, 1972].

1.2: Adsorption mechanisms of pesticides

Adsorption-desorption are dynamic processes in which molecules are continually transferred between the bulk liquid and solid surface. A number of mechanisms have been postulated to be involved in the retention of pesticides. However, it is difficult to isolate a definitive mechanism because most retention arises from an interaction of a variety of forces and factors. In addition, direct experimental evidence for a particular mechanism is quite rare and one is often confined to propose a hypothesis [Calvet, 1989]. Only kinetic, thermodynamic and spectroscopic studies can truly lead to mechanistic interpretations [DiVicenzo and Sparks, 2001] and spectroscopic studies are at times impractical due to the heterogeneous nature of soil.

1.2.1: Hydrophobic sorption

Hydrophobic adsorption is proposed as the main mechanism for the retention of nonpolar pesticides by hydrophobic active sites of humic substances (HS) or clay. The hydrophobic solute is expelled from the water (solvent-motivated adsorption) and this mechanism can also be regarded as a partitioning between a solvent and a nonspecific surface. These sites include aliphatic side-chains or lipid portions and lignin derived moieties with high carbon content of the HS macromolecules [Senesi, 1992].

1.2.2: Van der Waals interactions

Particular adsorption on hydrophobic constituents of organic matter (OM) can be explained either in terms of solute partition between water and organic matter (solvent-motivated sorption, entropy-driven) or in terms of solute adsorption (sorbent-motivated, enthalpy driven). Physical adsorption on OM by van der Waals interactions is probably the more satisfactory explanation, according to Calvet (1989).

1.2.3: H-bonding

H-bonding is an intra- or inter-molecular dipole-dipole interaction that is stronger than van der Waals bonds. It is caused by the electron-withdrawing properties of an electronegative atom (F, N, O) on the electropositive hydrogen nucleus of functional groups such as –OH and –NH. The presence of numerous oxygen and hydroxyl-containing functional groups on HS renders the formation of H-bonding highly probable for pesticides containing suitable complementary groups; although a strong competition with water molecules may be expected for such sites [Senesi, 1992].

1.2.4: Ionic exchange

Ionic exchange is a non-specific electrostatic interaction, which can involve either anionic or cationic pesticide forms.

- *Anion exchange* is the attraction of an anion to a positively charged site on the soil surface, and involves the exchange of one anion for another at the binding site.

- *Cation exchange* is relevant to those pesticides that are in the cationic form in solution or can accept a proton and become cationic (e.g. basic compounds at $pH<pKa$). For these pesticides, it is among the most prevalent sorption mechanism due to the large proportion of negatively charged sites associated with clay and organic matter in soils [Harper, 1994].

1.2.5: Charge transfer

The presence in humic substances of both electron-deficient structures (such as quinones), and electron-rich moieties (such as diphenols), suggests the possible formation of charge-transfer complexes via electron donor-acceptor mechanisms. Pesticides can act as electron donors (amine and/or heterocyclic nitrogen atoms of the s-triazines, pyridines, imidazolinones) or electron acceptors (e.g. deactivated bypyridilium ring of atrazine) [Senesi, 1992].

1.2.6: Ligand exchange

Adsorption by a ligand-exchange mechanism involves the replacement, by suitable adsorbent molecules such as s-triazines and anionic pesticides, of hydration water or other weak ligands that partially hold polyvalent cations associated to soil OM or hydrous oxide surface [Senesi, 1992].

1.2.7: Cation (or water) bridging

Cation bridging arises from the formation of an inner-sphere complex between an exchangeable cation (at a clay or OM surface) and an anionic or polar functional group on a pesticide. As cations are normally surrounded by hydrating water molecules, the organic functional group must be able to either displace the water or it must react in the presence of a dry surface to form an inner-sphere complex. Water bridging occurs when the organic functional group is unable to displace the solvating water molecule.

1.2.8: Bound residues

For most pesticides, it is often assumed that a rapid and reversible equilibrium is established between the chemical in solution and the chemical adsorbed onto the soil surface. However, once adsorbed, many organic chemicals may react further to become covalently and irreversibly bound while others may become physically trapped in the soil matrix [Koskinen and Harper, 1990]. These mechanisms lead to stable, mostly irreversible incorporation of the molecule, mainly into humic substances [Harper, 1994; Scribner et al., 1992; Senesi, 1992].

1.3: The Fate of Organic Pollutants in Soils

Organic pollutants can undergo a number of processes in soils: they can be degraded biotically and abiotically, the low molecular weight organic pollutants have a tendency to volatilize, and they may also be lost by leaching [Semple et al., 2003]. They can be bioaccumulated and adsorbed onto soil minerals and organic matter [Schwarzenbach et al., 1993]. Figure 1.1 shows the fate of organic pollutants in soils.

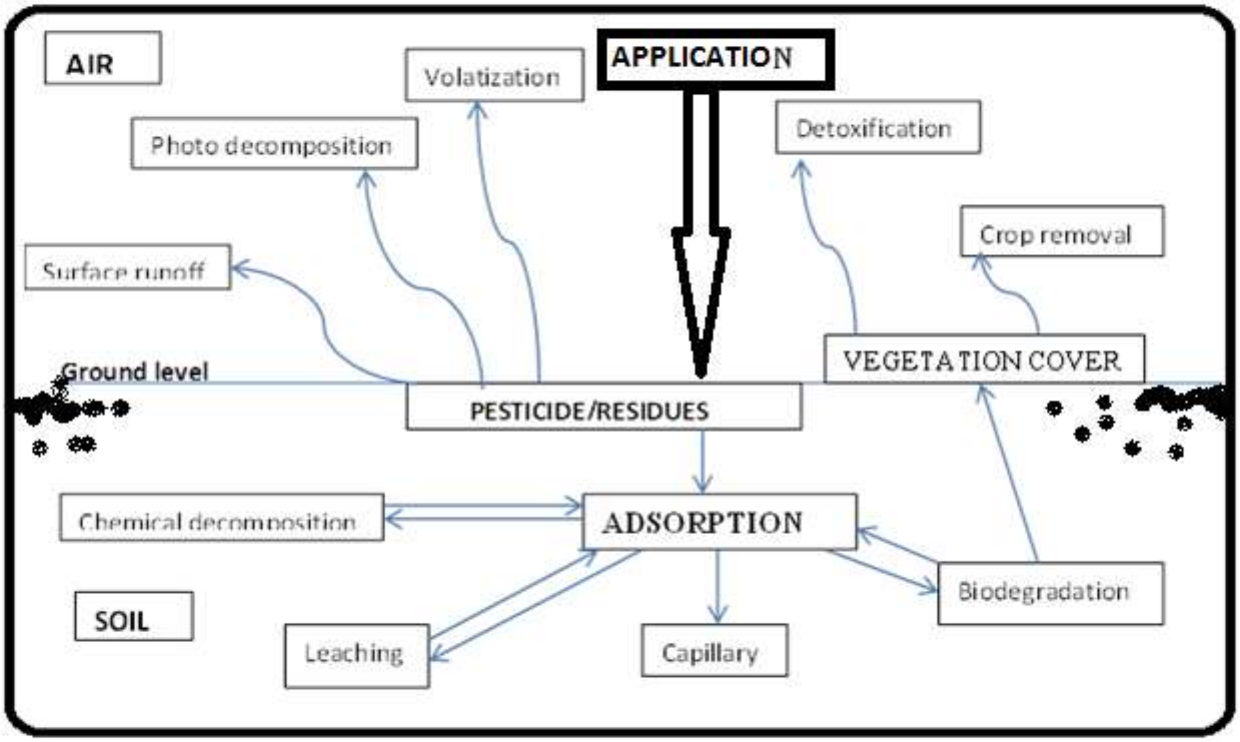


Figure 1.1: Anticipated fate of Organic Pollutants in the soil.

The fate of organic pollutants in a soil is affected by factors such as weather and climate, biological diversity and abundance, the amount and the nature of the soil minerals, and organic matter and pollutant properties such as solubility, polarity, hydrophobicity, and molecular structure [Reid et al., 2000; Semple et al., 2003; Doick et al., 2005].

Sorption is a key process that controls the transformation, transport and distribution of organic pollutants between water, soil and biota. Sorbed organic molecules are generally less reactive, with lower chemical and biological activity. The bioavailability and bioactivity of organic pollutants can be directly influenced by the sorption phenomenon. The effectiveness and efficiency of many remediation technologies are also dependent on sorption. Sorption of organic pollutants by the natural environment and the impact of natural environmental heterogeneity on sorption phenomena are key factors in evaluating risk and choosing between site remediation strategies. Even though numerous studies have found that soil organic matter is the most important soil component for sorption of organic pollutants, soil organic matter is not a single and homogeneous material but a mixture of materials including polysaccharides, lipids, lignin, protein, humic substances, kerogen and black carbon from combustion with different sorption properties. It is not only the soil organic matter that can exert influence on soil sorption properties, but the presence of soil minerals can also influence sorption properties of a soil by reducing soil sorption affinity via blocking organic matter sorption sites or by causing conformational changes in its structure.

1.4: Purpose of this study

To determine the thermodynamic and kinetic properties of the selected pesticides in order to ascertain their environmental impact in view of necessary remedies.

1.4.1: Research problem

Environmental impact of pesticides residues.

1.4.2: Problem statement

Pesticides have been used in various agricultural practices for quite a long time with the main objective of pest control and eradication, which in turn enhance food production. As a consequence, often a significant percentage of the pesticide products or its derivatives/ metabolites are introduced to the environment components like soil, water and air.

This has posed pollution effects to both animals and plants via food chain, depending on the level and state of the pesticide. Thus, there is urgent need to quantify how much pesticide residues are in our environment.

1.4.3: Overall objective

To determine the adsorption/desorption properties of 1- naphthol N-methylcarbamate (Carbaryl) and N-(3,4-dichlorophenyl)-N,N-dimethyl urea (Diuron) pesticide on Lake Naivasha soil and compare their thermodynamic, kinetic and equilibrium data obtained using UV-Visible spectrophotometry technique.

1.4.4: Specific objectives

i). To determine the existence of adsorption/desorption process of the 1- naphthol N-methylcarbamate (Carbaryl) and N-(3,4-dichlorophenyl)-N,N-dimethyl urea (Diuron) pesticide on Lake Naivasha soils.

ii). To obtain equilibrium, thermodynamic and kinetic data of the pesticide under adsorptive/desorptive processes.

iii). To determine factors affecting adsorption/desorption of the Cabaryl and of Diuron pesticide on the soil.

iv). To compare the adsorptive/desorptive data of these two pesticides obtained using UV-Vis. Technique on Lake Naivasha soils as well as other pesticides.

v). To characterize the sediments relative to adsorption properties of the pesticides.

1.4.5: Justification

This investigation of sorption phenomena of pesticide in the soil is of great importance from environmental point of view, as it relates to accumulation/retention nature of the pesticide in the environment.

Pesticide sorption affects other processes like transport, degradation, volatization, bioaccumulation which influence the final fate of these compounds in the soil environment [Gao et al., 1998]. All these processes influence the extent of surface water and ground water contamination. Moreover, soils are heterogeneous mixtures of several components many of which are organic and inorganic compounds of varying composition and surface activity. They can bind pesticide and reduce the bioavailability [Torrents and Jayasandra, 1997]. In addition the adsorbed pesticide may end up in the food chain, thereby affecting the health of human beings and other animals. Thus, the knowledge of pesticide adsorption/desorption characteristics of the soil is necessary for predicting their mobility and fate in the soil environment and also to understand whether bioremediation is a feasible option for the cleanup of the contaminated soil and reduce/eliminate the environmental pollution caused by the chemical pesticide with the focus on flower farming and associated pesticides at/around Lake Naivasha in Kenya.

CHAPTER TWO

LITERATURE REVIEW

2.1: The importance of organic pollutants

Organic pollutant constituents are some of the most important classes of pollutants. Although the highest concentration of organic pollutants is usually associated with human activities e.g in urban areas, they are also widely distributed with some found in substantial concentrations in the most remote areas. Organic pollutants are of concern because of their toxic effects on living organisms. These toxic effects can either be acute or chronic and can include the disruption of the endocrine, reproductive and immune system, neurobehavioral disorder and carcinogenicity. Table 2.1 shows the concentration of pesticide toxicity.

Table 2.1: Concentrations of pesticide toxicity [Helfrich et al., 1996].

Toxicity Classification	Dosage LC_{50} (mg/L)
Super	< 0.01
Extreme	0.01-0.10
High	0.11-1.0
Moderate	1.1-10
Slight	11-100
Minimal	>100
Non-toxic	-

Organic compounds can be introduced into the environment through natural process e.g biomass burning, but most are introduced through human activities, either planned like the use of herbicides and pesticides, or industrial wastes and vehicle emissions.

These issues of organic pollutants first came to wide spread public attention in 1962 with the publication of “Silent Spring” [Carson, 1962] which reported the impact of the synthetic pesticide DDT (dichloro-diphenyl-trichloroethane), used to control malaria-carrying mosquito on the environment. In particular, DDT was found to bio-accumulate in birds and cause thinning of their eggshells and ultimately a lack of reproductive success. Since then, there has been an increased public awareness of the impact of organic chemicals. One of the challenges of dealing with organic pollutants is their vast variety; hence it is clearly not possible to test the fate of each compound individually in every environment where it is likely to occur. Therefore the need for extensive efforts in identifying at a mechanistic level, the key features of organic pollutants and environment, which control the environment fate of organic pollutants.

2.2: The fate of organic pollutants in the soil

2.2.1: Degradation

The ability of soil to degrade organic pollutants depends on soil fertility and health, and most importantly the catabolic activity of the soil micro-organisms. A variety of organisms are able to metabolize organic pollutants.

There are two prerequisites that are needed for biodegradation; pollutants must be bio-available and they must be biodegradable [Reid et al., 2000; Christopher et al., 2002].

The rate of microbial decomposition is affected by several factors [Semple et al., 2003] which includes; the availability of pollutants to micro-organisms with ability to degrade them, the population of the degrading micro-organisms, the activity of the degrading micro-organisms and the nature or structure of the pollutants.

2.2.2: Volatilization

Volatilization is the loss of organic pollutants from the surface of plants, soil and water in the vapor form. For most pesticides, volatization is as important as a dissipation mechanism [Wolters et al., 2004]. The physiochemical properties of the organic pollutant are key determinants of volatilization rates. In particular, Henry's Law constant (H) can be used to predict rates of volatilization from solutions [Schwarzenbach et al., 1993]:

$$H = \left(\frac{C_a}{C_w}\right) RT \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.(2.1)$$

Where C_a is the concentration of the organic compound in air, C_w is the concentration of the organic compound in water, R is the Universal gas constant (8.314 pa/m^3.mol.k), and T is the absolute temperature (K). Values of H greater than 10 indicate very high air affinity, while those less than 10^{-4} indicates very low air affinity.

2.2.3: Leaching

Loss of a chemical through dissolution in a mobile water phase is called leaching. An understanding of organic pollutant mobility is important in evaluating its potential for ground water pollution. Pollutants most susceptible to leaching are those with low sorption and high water solubility [Regitano et al., 1997]. Leaching of low solubility compounds is often mediated by association with other species.

2.2.4: Bioaccumulation

The tendency of chemicals to concentrate in biota generally is expressed as a bio-concentration factor (BCF), defined as the ratio of the chemical concentration in biota to that in its environment at steady state [Hamelink, 1977]. The uptake of hydrophobic or lipophilic organic pollutants by organism is a critical issue because they can accumulate in food chain. BCF data for a given combination of chemical and organism are often not available and are time-consuming and expensive to determine. Therefore, other parameters are used for BCF estimation such as octanol/water partitioning coefficient (K_{ow}), water solubility of compounds and soil adsorption coefficient (K_{oc}) [Lu et al., 2000]. Fish are often used as target for BCF assessment from aquatic environment because of their importance as human food source and the availability of standardized testing protocol [Barron, 1990]. Plants are often used to measure BCF of soil. For example Zang et al. (2004) suggested that leafy vegetables can act as an indicator to human exposure to PAHs.

2.2.5: Sorption

Sorption is a phase distribution process that includes adsorption or accumulation of sorbate at the interphase of an aqueous phase and sorbent as well as absorption or partitioning from the aqueous phase into the sorbent matrix. In other words, sorption describes the transition of molecules from the solution phase to any phased fixed (perhaps temporary) to any of the solid component of the soil. Because the other processes that influence the fate of pollutants (degradation, volatilization, leaching and bioaccumulation) act primarily on the solution phase of the pollutant, sorption plays an over-arching role on the fate of organic pollutant in the soils.

The term ‘sorption’ has gained popularity as it does not imply a mechanism, whereas the terms ‘adsorption’ and ‘absorption’ do. Due to complexity and heterogeneity of the soil, both absorption and adsorption may occur at the same time, and is often impossible to differentiate between the two. Adsorption specifically refers to sorption of molecules to the surface of solid component, whereas absorption refers to the movement of molecules, or partitioning, into a separate phase [Hassett and Banwart, 2002].

Sorption is a key process in aquatic environment that controls the transformation, transport and distribution of organic pollutants between water, sediments and biota [Oliver and Charlton, 1984]. Sorbed organic molecules are generally less reactive, with lower chemical and biological activity. Therefore, they are less toxic to the ecosystem and human health. Sorption can affect the biodegradation of organic pollutants in the environment and make them less available to the degrading organisms. In other words, the bioavailability and bioactivity of organic pollutants can be directly influenced by sorption phenomenon [Baily and White, 1964].

2.3: Factors affecting sorption

Several factors have an effect on organic pollutant sorption to the soil. They can be divided into three categories:

i) The properties of the sorbate (pollutant) which includes solubility, ionization and molecular size.

ii) The properties of the sorbent, which includes organic matter content, surface area, mineral surface area, mineral surface properties and effects of soil lipids.

iii) The Aqueous phase properties, which includes pH, salinity, co-solvents, solid-solution ratio, temperature and solute concentration [Kohl and Rice, 1999; Trembloy et al., 2005b;Chilom et al., 2005; Drori et al., 2006].

2.3.1: Pollutant properties:

2.3.1.1: Solubility

Water solubility of the organic pollutant is the most important determinant of the strength of sorption. Solutes that have lower water solubility have higher equilibrium sorption coefficients [Chiou et al., 1982, 1983]. The solubility of an organic pollutant, in turn depends on its molecular structure as discussed below.

2.3.1.2: Molecular size

The size of organic molecules can affect the sorption process through the molecular surface area and molecular volume of a compound [Calvet, 1989]. The molecular volume is related to water solubility which in turn can affect the sorption process of the organic molecules [Lampert, 1967]. Generally, the larger a molecule or the higher its molecular weight, the less soluble the compound tends to be.

2.3.1.3: Ionization

A permanent electrical charge on a compound increases its water solubility and hence decreases its tendency to sorb. Some neutral organic compounds, particularly those with either a basic or an acidic functional group can be ionized in the soil, depending on the pH as they gain or lose a proton, H^+. The ionization of basic or acidic compounds strongly affects their sorption properties [Kah and Brown, 2006].

2.3.2: Sorbent properties:

2.3.2.1: Organic matter content

Numerous studies have revealed that soil organic matter is the most important soil component for sorption of non-ionic pollutants [Chiou 1989; Wauchope et al., 2002]. This is consistent with organic matter being the most non-polar solid phase in the soil. Most soil minerals are either charged (usually negative) or have a polar surface group. The strong dipole interaction of such surfaces with water (which is strongly polar) results in water 'out-competing' non-polar species for mineral surfaces. As a consequence, soil sorption affinities are often normalized to the organic carbon content of the soil, to decrease the variance in solute affinities between the soils [Hamaker and Thompson, 1972].

2.3.2.2: Mineral surface properties

Two types of charge can be identified in soil minerals, permanent or constant charge and variable or pH dependent charge. Constant charge is a result of isomorphous substitution and is not influenced by pH, but variable charge results from protonation and deprotonation of the SiOH group on the soil surface, and thus it varies with pH. Therefore, the surface charge is variable on soil minerals such as kaolinites, metal oxides, oxyhydroxides, and hydroxides, and layer silicates coated with metal oxides. Some minerals (especially metal oxides) have a point of zero charge (PZC) at environmentally relevant pH. Such uncharged surfaces would be expected to have a higher affinity for non-polar organic molecules than permanently or variably charged mineral surfaces.

2.3.2.3: Surface area

Where sorption is dominated by adsorption (surface sorption) rather than absorption (partitioning), one could expect sorption to increase as surface area increases [Chiou, 2002]. This is indeed the case of sorption of organic pollutants by clay minerals. It has been shown that affinity for organic compounds such as benzene, toluene and xylenes are lower for kaolinite, which has a lower specific surface area, than for montmorillonite and illite, which have higher specific surface areas [Li and Gupta, 1994]. On the other hand, soil surface area is generally a poor predictor of the sorption affinity of organic compounds by soils for a number of reasons. Firstly, much of the surface area of a soil is due to minerals that have low affinities relative to that of organic matter. Secondly, sorption to organic matter is likely to be at least in part an absorption rather than an adsorption process, and hence not dependent on surface area. An exception is sorption with charcoal, which appears to scale with surface area [Bornemman et al., 2007].

2.3.2.4: Soil organic matter (SOM) heterogeneity

SOM is not a single and homogeneous material but a mixture of materials including polysaccharides, lipids, lignins, proteins, humic substances, and black carbon from combustion [Stevenson, 1994], each of which is likely to have differing sorption properties for organic compounds. Different soils will contain different proportions of these components, and this has been identified as a likely cause of variability in K_{oc} between soils [Wauchope et al., 2002].

2.3.2.5: Soil organic matter (SOM) physical conformation

Some studies have shown that conditioning with solvent can change the sorption properties of soil, possibly by altering the physical conformation of SOM [Xia and Pignatello 2001; Lu and

Pignatello 2002; Wang and Xing 2007]. For example, Xia and Pignatello (2001), suggested that a ‘conditioning effect’ led to enhanced sorption of $CHCl_3$ in peat soil in which a high loading of sorbate caused molecules to penetrate the organic polymer matrix and swell its structure.

2.3.2.6: The effect of soil lipid

Lipids can decrease the sorption capacity of natural soil organic matter by reducing the accessibility of sorption sites by competition, steric effect or sorption site deformation [Tremblay et al., 2005b]. It has been reported that lipid removal can increase the sorption affinity of soils for organic compounds by as much as one order of magnitude and at the same time decrease sorption linearity [Kohl and Rice, 1999].

2.3.2.7: Soil organic matter (SOM) mineral interaction

A number of studies have reported that soil minerals have an indirect effect on the sorption affinity of SOM. For example, Njoroge et al. (1998), found out that K_d for 1,2,4-trichlobenzene and tetrachloethene decreased by about 100 fold down a soil profile. This decrease was much greater than could be explained on the basis of SOM content of the lower horizons. They attributed the decrease in K_{oc} with soil depth to the association of SOM with the clay minerals of the soils, and the possible effect of this association on SOM accessibility, sorptivity or both.

2.3.3: Aqueous phase properties:

2.3.3.1: pH

As discussed above, some organic pollutants have soil-dependent charge, and the charge of both organic matter and mineral sorbent phases vary with pH. Because the charge of both sorbent and sorbate affect sorption affinity, the pH of the solution phase (which is in equilibrium with the pH of the solid phase) is an important factor controlling sorption. When the pH of the solution is higher than the pK_a of an organic compound, the conjugate base (which has a negative charge) is the dominant species. As a consequence, sorption affinity for such molecules rapidly decreases with pH above the pKa value. In contrast, for basic compounds, an increase in pH decreases the sorption of charged molecules, therefore increasing sorption affinity [Karickhoff, 1984; Delle Site, 2001].

2.3.3.2: Solid-solution ratio

Although sorption of non-ionic compounds on soils is generally considered as partitioning between two phases and independent of sorbent concentration, in several instances an inverse relationship between sorbent concentration and partitioning coefficient has been reported [Grover and Hance, 1970]. It has been demonstrated that sorption can be affected by the soil to water ratio. For example, a five-fold increase in the sorption of linuron was found on decreasing the soil to water ratio from 4:1 to 1:10 [Grover and Hance, 1970].

2.3.3.3: Co-solvents

Co-solvents, such as methanol and acetone, can decrease the sorption of organic pollutant by virtue of increasing their solution solubility. For hydrophobic organic chemicals, solubility has a long-linear dependence on the volume fraction of organic co-solvent [Rao et al., 1985; Lee and Rao, 1996].

$$\log K_m = \log K_w - \alpha\beta f_c \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(2.2)$$

where K_m is the linear sorption coefficient in mixed solvents, K_w is the linear sorption coefficient in water, α is a chemical constant that reflects solvent-sorbent interaction, β is the co-solvency power and f_c is the co-solvent volume fraction.

2.3.3.4: Salinity

The water solubility of hydrophobic compounds decreases with increasing ionic strength. This effect is called ‘Salting-out’ [Tremblay et al., 2005a]. As a result, sorption affinity increases with increasing salinity [Karickhoff et al., 1979]. For example, from Karickhoff report, an increase in salinity from 0 to 0.34M sodium chloride causes 15% decrease in pyrene sorption.

2.3.3.5: Temperature

Where sorption is an exothermic process, the equilibrium constant should decrease with increasing temperature [Schwarzenbach et al., 1993]. However some studies have demonstrated sorption increased with increasing temperature while others have observed no effect of temperature [Hance, 1980; Hulscher and Cornelissen, 1996].

Sorption of organic pollutants occurs when the free energy of the sorption exchange (ΔG) is negative [Hulscher and Cornelissen, 1996].

$$\Delta G = \Delta H - T\Delta S. \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(2.3)$$

Where ΔG is the change in Gibbs free energy ($KJMol^{-1}$), ΔH is the change in enthalpy ($KJMol^{-1}$), T is the absolute temperature (K) and ΔS is the change in entropy ($KJMol^{-1}K^{-1}$).

The free energy of sorption can be negative because of the entropy or enthalpy terms or both of them. The enthalpy term describes the affinity of a chemical for the absorbing surface relative to its affinity for the solvent. The entropy term is related to the change in randomness or disorder of the system upon sorption [Hassett and Banwart, 1989; Hulscher and Cornelissen, 1996].

2.3.3.6: Solute concentration

One of the most important and widely-studied aspects of sorption of organic pollutant to the soil is the effect of solute concentration on sorption affinity, given that, in theory, this should convey important information about sorption mechanisms. Generally, increase in initial pesticide concentration increases the amount of pesticide molecules uptake per unit mass of the soil. Amount adsorbed increases with increase in spiking levels of the pesticide. The time of reaching equilibration depends on the initial concentration of the pesticide, hence the lower the concentration, the shorter the equilibration time interval due to higher adsorbent surface site ratio to pesticide molecules per unit volume compared to higher concentration. [Grover and Hance, 1970].

2.4: Equilibrium sorption models:

Sorption isotherm models attempt to describe how the concentration of a molecule in the sorbed phase varies as a function of its solution concentration at constant temperature. Sorption isotherm models can provide important information about the physicochemical processes of sorption. Several different equations have been developed to describe sorption isotherms. Some are derived from the consideration of the sorption processes involved, whilst others are empirical. There are several considerations while choosing which equation to use when fitting a sorption isotherm. Clearly it should provide a good fit to the data, but one should also consider the number of fitted parameters and their physical meaning.

2.4.1: The Linear Partitioning Model

In the simplest model of the sorption process, sorption affinity is independent of solution concentration. A number of early studies [Chiou et al., 1979, 1983; Karckhoff et al., 1979; Means et al., 1980, 1982], showed no indication of curvature in the sorption isotherms. This behavior is described by the linear partitioning model, which can be expressed mathematically as:

$$K_d = (x/m)/C_e \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2.4)$$

Where K_d is called the distribution coefficient, x/m is the concentration in the sorbed phase at equilibrium (µg/g), and C_e is the concentration in solution at equilibrium (µg/ml).

As discussed above, for non-polar organic compounds, many studies have found a highly significant relationship between K_d of the compound and the organic carbon content of the soil [Chiou 1979, 1983]. Therefore, Hamaker and Thompson (1972), suggested that to decrease the variance in sorption coefficients, K_d should be divided by the organic carbon concentration (f_{oc}) of the soil to give the organic C normalized soil sorption coefficient (K_{oc}) ;

$$K_{oc} = K_d / f_{oc} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2.5)$$

Chiou et al. (1983), suggested that the linearity of sorption isotherms, is evidence that sorption of non-ionic compounds in soils mainly consists of partitioning of organic compounds into the soil organic matter. Thus, the K_{oc} model for organic compounds sorption is also called the ‘partitioning model’.

The K_{oc} partitioning model is perhaps the most widely-used model to describe sorption of organic pollutants to the soils. A large part of its appeal is its mathematical simplicity- just a single parameter can be used to predict sorption of a given compound to any soil. Furthermore, K_{oc} values for different compounds have been found to closely correlate with the physicochemical properties of organic solutes.

The simplicity of the K_{oc} model is all its short-coming, as its unable to account for more complex sorption behavior. This includes the contribution of minerals to sorption, variability of K_{oc} between soils, non-linear sorption isotherms, sorption-desorption hysteresis and slow sorption kinetics.

2.4.2: The Langmuir Adsorption Model

This model was developed in 1916 to describe the dependence of the surface coverage of an adsorbed gas on the pressure of the gas above the surface at a fixed temperature [Langmuir, 1916]. Even though the model was developed to predict the sorption of gas molecules on a solid phase, it can be used to predict the sorption of aqueous compounds to solid surfaces.

Regarding the assumptions of the model, it seems inappropriate to describe the sorption of organic compounds in soils and sediments. Briefly, the model assumptions are:

i) adsorption takes place at only specific sites.
ii) the adsorbent surface can only be covered by a single layer of molecules.
iii) the surface of the sorbent is energetically homogeneous.
iv) there is no interactions between adsorbed molecules, and
v) there are no phase transitions.

In mathematical terms, the Langmuir Model can be expressed as:

$$q_e = \frac{[Q^0 \beta C_e]}{[1 + bC_e]} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(2.6)$$

where, Q^0 is the monolayer adsorption capacity, β is a parameter related to the net enthalpy of adsorption, and q_e and C_e are the equilibrium solid-phase and aqueous-phase solute concentration, respectively.

2.4.3: The Freundlich model

The Freundlich Model is one of the empirical sorption model used to describe non-linear sorption. The model has the following form:

$$q_{sorb.} = K_f C^{1/n} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(2.7)$$

where $q_{sorb.}$ is the sorbed concentration (mg kg^{-1}), C is the solute concentration, K_f is the Freundlich coefficient (mg kg^{-1}) (L $mg^{-1})^{1/n}$ and n is the isotherm linearity.

Normally the value of n is less than 1, indicating that sorption affinity decreases with increasing solution concentration. Often, experimental data do not fit the linear model, but they can be fitted to the empirical Freundlich Model [Schwarzenbach et al., 1993]. The Freundlich Model can also be rearranged and expressed in a linear form:

$$\log q = 1/n \log C + \log K_f \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(2.8)$$

The plot of log q versus log C has a slope equal to 1/n, and an intercept equal to log K_f.

2.4.4: The Polanyi-Manes Adsorption Model

This model was first used to describe the adsorption of gas molecules on energetically heterogeneous solids [Polanyi, 1916.], but in 1969 it was extended by Manes and Hofer for using in liquid phase systems and called the Polanyi-Manes theory [Manes and Hofer, 1969].

In this theory, for any adsorbate molecule in the presence of an adsorbent surface, there is an adsorption potential (ε) between the molecule and the solid surface. The potential (ε) at any location in the adsorption space is defined as the energy level required to remove the molecule from the location outside the attractive force field of the solid surface. The potential (ε) is dependent on the adsorbent surface and the nature of the sorbate.

$$\varepsilon_{sw} = RT\ 1n\ (C_s / C_e) \ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2.9)$$

where ε_{sw} is the adsorption potential (energy required for a volume of a solute (s) to displace a volume (l) in the adsorption process), R is the gas constant, T is the absolute temperature, C_s is the solute concentration and C_e is the equilibrium concentration.

2.4.5: The Distributed Reactivity model and the Dual SOM Model

One of the main difficulties in modeling sorption in natural systems such as soils and sediments is that they typically contain multiple sorptive phases. These will not only have different sorption affinities for organic compounds, but may also represent different sorption mechanisms. The explanation on sorption based on a single sorption reaction may therefore be misleading. In light of this, Weber Jr et al. (1992), introduced a new concept of sorption, considering different distributions of sorption reactions and mechanisms for different solute-solid combination.

In this model, the overall sorption isotherm is the sum of the sorption isotherms of the active parts;

$$q_{er} = \sum_{i=1}^{m} x_i q_{ei} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2.10)$$

where q_{er} is the total solute sorbed per unit mass, x_i is the mass of fraction of soil component i, and q_{ei} is the sorbed phase concentration.

Furthermore, the model assumes there are two types of organic matter; ‘hard carbon’ which has a high sorption capacity and exhibits non-linear isotherms typical of adsorption, and ‘soft carbon’ which is less sorptive and exhibits almost linear isotherms typical of partitioning sorption behavior. Therefore, in the distributed reactivity model (DRM), one can consider that the mechanism of sorption in the soft part of SOM is partitioning, and conversely, the mechanism of of sorption on the hard carbon SOM is considered as an adsorption process with non-linear sorption isotherms which can be described by the Freundlich equation.

2.5: Selected compounds

2.5.1: 1-naphthyl-N-methyl carbamate (Carbaryl)

Carbaryl (figure 2.1) is one of the most frequently used carbamate insecticides for the control of a variety of pests on fruit, vegetables, forage, cotton and many other crops, as well as on poultry, livestock and pets [Mathew et al., 1995]. It is available as wettable powders, pellets, granules, dusts, suspensions and even solutions [U.S. EPA, 1988].

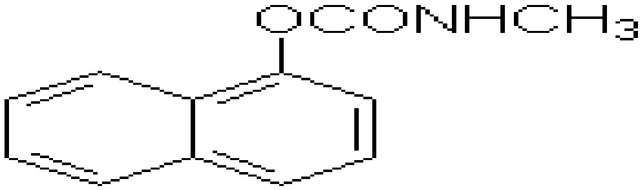


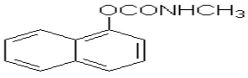
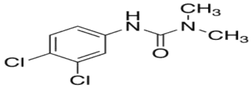
Figure 2.1: Carbaryl (1-naphthyl-N-methyl carbamate).

2.5.1.1: *Mode of action*

Carbaryl is a member of the widely used carbamate pesticides. Like most carbamates, carbaryl acts as an inhibitor to cholinesterase, one of many important enzymes in the nervous systems of humans, vertebrates and insects. A specific cholinesterase enzyme, acetylcholinesterase (AChE), plays an important role in breaking down the acetylcholine (Ach), which is the synaptic mediator of nerve impulses in the nervous systems of mammals and insects [WHO, 1994d]. The presence of cholinesterase inhibiting pesticides, such as carbaryl, prevents AChE from breaking down acetylcholine and results in high concentration of Ach in the nervous system. As a result, the continuous stimulation of the muscle leads to uncontrolled, rapid movement of some muscles, paralysis, convulsions and even death.

The physical and chemical properties of carbaryl are represented in Table 2.2

Table 2.2: Physical and chemical properties of carbaryl and diuron pesticides [DPR Pesticide Chemistry Database, 2003].

	PHYSICAL AND CHEMICAL PROPERTIES	FIRST PESTICIDE	SECOND PESTICIDE
1.	Common name	Carbaryl	Diuron
2.	Chemical name (IUPAC)	1-naphthalenylmethylcarbamate	N-(3,4-dichlophenyl)-N,N-dimethyl urea
3.	Trade names	Arilat, Arylam, Carbacine, Karbaryl, Vioxan.	Direx, Karmex, Krovar etc.
4.	Structural formula		
5.	Empirical formula	$C_{12}H_{11}NO_2$	$C_9H_{10}Cl_2N_2O$
6.	Molecular weight	201.00 gmol^{-1}	233.10 gmol^{-1}
7.	Water solubility	113 ppm (at 22 ^{0}C)	36.4 ppm (at 25 ^{0}C)
8.	Vapor pressure	1.17 x 10^{-6} mmHg (at 25 ^{0}C)	6.90 x 10^{-8} mmHg (at 25 ^{0}C)
9.	Octanol/water partition coefficient	70.8 (logK_{ow}=1.85) (at 25 ^{0}C)	648-747 (at 25 ^{0}C)
10.	Henry's law constant	2.7425 x 10^{-9} atm m^{3}g.mol^{-1} (at 25 ^{0}C)	5.10 x 10^{-10} atm m^{3}g.mol^{-1} (at 25 ^{0}C)
	ENVIRONMENTAL FATE		
11.	Hydrolysis Half-life	>1500 days (pH=5) 12.1 days (pH=7) 3.2 hours (Ph=9)	1490 days (pH=5) 1240-1330 (pH=7) 2020 days (pH=9)
12.	Soil Adsorption Coefficient (K_{oc})	100-600 mlg^{-1}	418-560 mlg^{-1}
13.	Photolysis Half-Life (Soil, Artificial Light)	41 days	173 days
14.	Photolysis Half-Life (Water, Artificial Light, pH=5)	21 days	43.1-2180 days (pH 7at 25 ^{o}C)
15.	Aerobic Soil Half-Life	4-17 days (Sandy loam soil) 21-27 days (Clay loam soil)	372 days
16.	Anaerobic Soil Half-life	78 days	995 days
17.	Field Dissipation Half-life	0.76-10.9 days	99.9-134 days
	TOXICITY AND ECOLOGICAL EFFECTS		
18.	Mallard Duck (oral, acute)	LD$_{50}$ >2179 mg/kg	>2000mg/kg
19.	Japanese Quail (oral, acute)	LD$_{50}$ >2230 mg/kg	8 days LC$_{50}$ 1730ppm
20.	Daphnia Magna (48hrs)	LC$_{50}$ 18.6 ppb	LC$_{50}$ 8 ppm
21.	Rainbow Trout (96hrs)	LC$_{50}$ 4.38 ppm	LC$_{50}$ 190 ppm
22.	Bluegill Sunfish (96hrs)	LC$_{50}$ 6.76 ppm	LC$_{50}$ 5.9 ppm
23.	Honey Bee	LD$_{50}$ 1.54-26.5 µg a.i/bee	LD$_{50}$ 145 µg/bee

2.5.1.2: Environmental fate

2.5.1.2.1:Air

Carbaryl has a low vapor pressure, 1.17 x 10^{-6} mmHg, and is not readily volatilized into the air. A low Henry's law constant, 2.74 x 10^{-9} atm $m^3g.mol^{-1}$, suggests that carbaryl has low potential to volatilize from aqueous solution [Lyman et al., 1982]. It might be found in the atmosphere associated with air-borne particulates or as spray drift but should not be over a large area. If existing in air, carbaryl tends to react with hydroxyl radical in the ambient atmosphere [Kao, 1994].

2.5.1.2.2:Water

Hydrolysis is the primary degradation pathway for carbaryl at pH 7 or above. The compound degrades rapidly at pH 7 and 9 at 25 ^{0}C, with half-lives of approximately 10~17 days and 3 hours, respectively [Aly and El-Dib, 1971; Carpenter, 1990]. In acidic water, carbaryl is rather stable with a half-life of more than 1500 days at 27 ^{0}C [Wolfe et al., 1978]. The identified degradation products are 1-napthol, methylamine and carbon (IV) oxide. [Aly and ElDib, 1971; Larkin and Day, 1986]. Figure 2.2 shows the degradation products of Carbaryl.

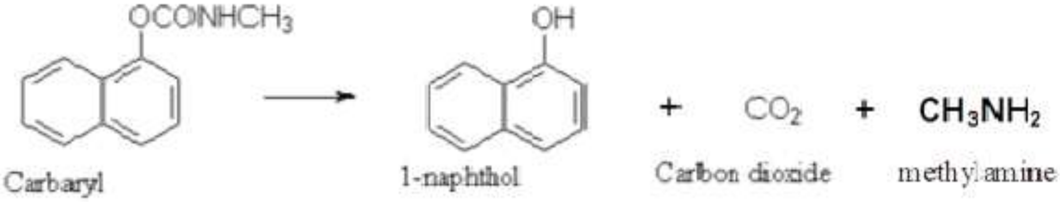


Figure 2.2: Degradation products of Carbaryl [Chapman and Cole 1982, Wolfe et al., 1978].

In natural water, carbaryl is expected to degrade faster due to the presence of microorganisms. The half-lives of carbaryl in streams, rivers and brooks as a result of forest spraying are 25, 28 and 23 hours, respectively [Stanley et al., 1980].

The aqueous photolysis of carbaryl was determined to be 21 days in sterile distilled water under artificial sunlight at a concentration of 10.1 ppm and pH 5 [Das, Y.T., 1990a].

The major photolysis product is 1-naphthol, which will further photo-oxidize to 2-hydroxy-1,4 naphtho-quinone in basic condition [Wauchope and Haque, 1973]. The soil sorption coefficients (K_{oc} = 100 ~ 600), octanol/water partition coefficients ($\log K_{ow}$ = 1.85 – 2.36) and water solubility indicate that carbaryl moderately binds to soils and sediments. Thus, suspended particulates or mud in natural water may remove some carbaryl from the aqueous phase.

2.5.1.2.3:Soil

Overall, carbaryl is not persistent in soil. It can be degraded through hydrolysis, photolysis as well as by microorganisms. The photo-degradation of carbaryl was investigated on soil under artificial sunlight for a total of 30 days [Das, 1990b]. In this case, carbaryl was applied on 1-mm soil layers at a concentration of 9.8 ppm. The estimated half-life was approximately 41 days with no findings of major metabolites. Microbes play a significant role in the degradation of carbaryl in soil. Quite a few bacteria can use carbaryl as their sole source of carbon and nitrogen.

2.5.1.2.4:Biota

The efficacy of carbaryl for the control of pests is attributed to its ability to inhibit acetylcholinesterase (Ache) in the nervous systems [Barabona and Sanchez-Fortun, 1999]. Given the same mode of action, carbaryl also poses risks to other non-target animals, including human beings. Carbaryl can penetrate the skin, mucous membranes, respiratory tract and gastrointestinal tract of mammals. However, it can be rapidly metabolized by various animals, and excreted especially in the urine as glucuronides or sulfates [Dorough and Casida, 1964; Fukuto, 1972]. The following metabolites have also been identified: 1-naphtyl N-hydroxymethylcarbamate, 4 hydroxy-1-naphthyl-Nmethylcarbamate, 5-hydroxyl-1-naphthyl-N-methyl-carbamate and 5,6 dihydroxy-1- naphthylmethylcarbamate.

i)Mammals: Carbaryl is relatively safe to mammals although it can temporarily inhibit AchE. For example, rats given a single oral dose of 560 mg/kg body weight showed a decrease of 42% erythrocyte- and 30% brain-ChE activity within 5 minutes [Carpenter et al., 1961]. However, the activity recovered to normal level after 24 hours.

ii)Fish: Carbaryl is considered moderately to highly toxic to fish with LC_{50} values ranging from 4ppm to 13 ppm [Beyers, et al., 1994; McKim, 1987; Sinha et al., 1991]. The chemical is especially toxic to the aquatic invertebrate *Daphnia magna* with LC_{50} values at 48 hours less than 18.6 ppb [Li and Yang, 2000].

iii)Birds: Carbaryl is slightly or practically non-toxic to birds, with LD_{50} for young mallard ducks, young pheasants and pigeons of >2179, 2000, 1000-3000 mg/kg, respectively.

iv)Plants: The side effects of carbaryl on the growth of plants have been well documented [Murthy and Raghu, 1990; Jones et al, 1991]. For example, undesirable thinning of apples have been observed after paclobutrazol and carbaryl were applied to apple trees within an interval of seven days in a period over 20-30 days after full bloom Carbaryl with a concentration of 2.5ppm in clay and sandy loam soils had no effect on the growth of barley. However, higher concentration of carbaryl, 25 and 100 ppm, demonstrated the inhibitory effects [Murthy and Raghu, 1990]. The phototoxic effects of carbaryl only lasted for a few days after the application of carbaryl in soil.

2.5.2: N-(3,4-dichlorophenyl)-N,N-dimethylurea (Diuron)

Diuron (Figure 2.3) is a systemic substituted phenyl urea herbicide. It is often used in combination with other herbicides such as bromacil, hexazinone, paraquat, thiadiazuron, imazapyr, monosodium, sodium chlorate, sodium metaborate, and copper sulfate [U.S. EPA, 2004a].

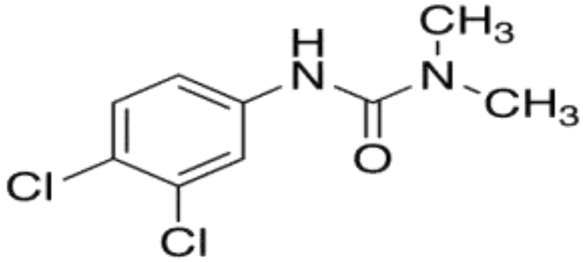


Figure 2.3: Diuron (N-(3,4-dichlorophenyl)-N,N-dimethyl urea).

2.5.2.1: Mode of action

Diuron is easily taken up from soil solution by the root system of plants and rapidly translocated into stems and leaves by the transpiration system, moving primarily via the xylem. Diuron primarily functions by inhibiting the Hill reaction in photosynthesis, limiting the production of high-energy compounds such as adenosine triphosphate (ATP) used for various metabolic processes.

Diuron is available in wettable powder, granular, flowable, pelleted/tableted, liquid suspension, and soluble concentrate formulations. Technical Diuron is a white, crystalline, and odorless solid. Diuron is stable in neutral media at normal temperatures, and is hydrolyzed by acid and alkalis. It is stable towards oxidation and moisture under normal conditions and decomposes at 180-190 ° C [Helliwell et al., 1998].

Diuron is a broad-spectrum residual herbicide registered for pre-emergent and post-emergent control of both broadleaf and annual grassy weeds. When Diuron is used on pre-emergent weeds, it allows seeds to germinate normally, but causes them to lose their green color, after which they soon die of starvation [Ferrell et a., 2004].

Diuron also has widespread use in non-agricultural applications, especially industrial and rights of way uses, where often in combination with other herbicides it provides total vegetation control. These applications include along fence lines, pipelines, power lines, railway lines, roads, footpaths; in timber yards and storage areas; and around commercial, industrial and farm buildings, electrical substations, and petroleum storage tanks. It has some use as an algaecide in ornamental ponds, fountains, and aquaria, but not natural water bodies. It may be used as a mildewicide in paints used on buildings and structures.

The physical and chemical properties of Diuron are represented in Table 2.2 .

Figure 2.4 in the appendix shows the degradation products of Diuron.

2.5.2.2: Environmental fate

2.6.2.2.1:Air

Diuron is applied by broadcast or band spray on soil surface using ground or aerial equipment, suggesting that there is a possibility of drift. However, Diuron is non-volatile, as indicated by its low vapor pressure of $6.90\ \mathrm{x}10^{-8}$ mm Hg (25 ºC), and a low Henry's law constant of 5.10×10^{-10} atm m^3 mol^{-1}. Its low vapor pressure and low Henry's law constant indicate that Diuron is unlikely to be dispersed in air over a large area and has a low tendency to volatilize from water or moist soils. Volatilization is insignificant except when Diuron is exposed on the soil surface for several days or weeks under hot, dry conditions [Hess and Warren, 2002].

2.5.2.2.2:Water

Diuron's relatively low K_{OC} indicates a relatively low tendency to sorb to soils and sediments, while its hydrolysis and aqueous photolysis half-lives are relatively long. Consequently Diuron is both mobile and relatively persistent, and is therefore prone to off-site movement in surface runoff, and migration to ground water [Andrieux et al., 1997].

2.5.2.2.3:Soil

Diuron is moderately to highly persistent in soils. The commonly reported average field dissipation half-life is 90 days, although such half-lives are typically highly variable. Phytotoxic residues generally dissipate within a season when applied at low selective rates. At higher application rates, residues may persist for more than one year [Kidd and James, 1991]. Microbial degradation is the primary means of Diuron dissipation from soil. Photo-degradation is not considered a primary dissipation route, but losses can be significant if Diuron remains on the soil surface for several days or weeks [Hess and Warren, 2002].

Diuron is mobile in soil. Similar to many other pesticides, Diuron sorption is highly correlated with organic matter [Spurlock and Biggar, 1994]. Consequently leaching is greatest in low organic matter soils. Other soil conditions that favor Diuron leaching include high soil permeability to water, such as in coarse soils.

2.5.2.2.4:Biota

i) Mammals: Once Diuron is ingested, it is excreted through feaces and urine of test animals. In a study, cows fed very low doses of Diuron in their diets had small amounts of residues in whole milk. Cattle fed small amounts, accumulated low levels of Diuron in fat, muscle, liver, and kidney. Little tissue storage under field conditions is anticipated [Hess and Warren, 2002].In mammals, metabolism principally occurs through hydroxylation and de-alkylation. The predominant metabolite in dogs is 3,4-dichlorophenyl urea. Breakdown of this compound is similar in animals, plants and soils. The first step is N-demethylation followed by ring cleavage.

ii)Fish and Aquatic Invertebrate: Diuron is toxic to fish and aquatic invertebrates. The LC_{50} (48hr) values for Diuron range from 4.3 to 42 mg/L in fish, and range from 1 to 2.5 mg/L for aquatic invertebrates. The LC_{50} (96hr) is 3.5 mg/L for rainbow trout [Hess and Warren, 2002].Therefore, diuron is moderately toxic to fish and to aquatic invertebrates.

iii)Plants: Diuron is readily absorbed through the root system of plants and less readily through the leaves and stems. Diuron is translocated rapidly from roots to shoots via the xylem. Little to no Diuron moves from the apex downward toward the base of a treated leaf via the phloem. Diuron symptoms of disease are foliar chlorosis concentrated around veins or sometimes interveinal followed by necrosis [Hess and Warren, 2002].

CHAPTER THREE

MATERIALS AND METHOD

3.1:Selected soils

3.1.1:General setting of Lake Naivasha

Lake Naivasha (0.45^0S, 36.26^0E), (Figure 3.1) is a shallow basin lake, 80km northwest of Nairobi, Kenya and is positioned at 1,890m above sea level. It lies on the floor of Africa's Eastern Rift Valley and covers approximately 140Km^2. The lake contains fresh water supporting a rich ecosystem, with hundreds of bird species, papyrus fringes filled with hippos, viparian grass lands where water buck, giraffe, zebra and various antelopes graze, dense patches of viparian acacia forest with buffaloes, bushbuck and other creatures, beautiful swampy areas where waterfowl breed and feed and, at the same time, magnificent views of the nearby volcanoes. Local fishermen depend on the lake for fish and crayfish. Although the lake is situated in a semiarid zone, after the rainy seasons, the fragile soils of the surrounding hills and valley bottom produce grass where pastoral Maasai bring their herds for dry-weather grazing thereby depending on the lake and its various watering points. Amongst other economic activities like fishing and livestock herding, the lake supports extensive flower farming, with the flori-and horticultural increasing as close as 4,000ha since 1980's. Growers now produce at least 25 varieties of flowers (e.g roses, spray, carnations, gypsophila, alstroemeria and eustoma) and vegetables for the export market, all of which are irrigated with lake, river or ground water [Stevenson, 1972].

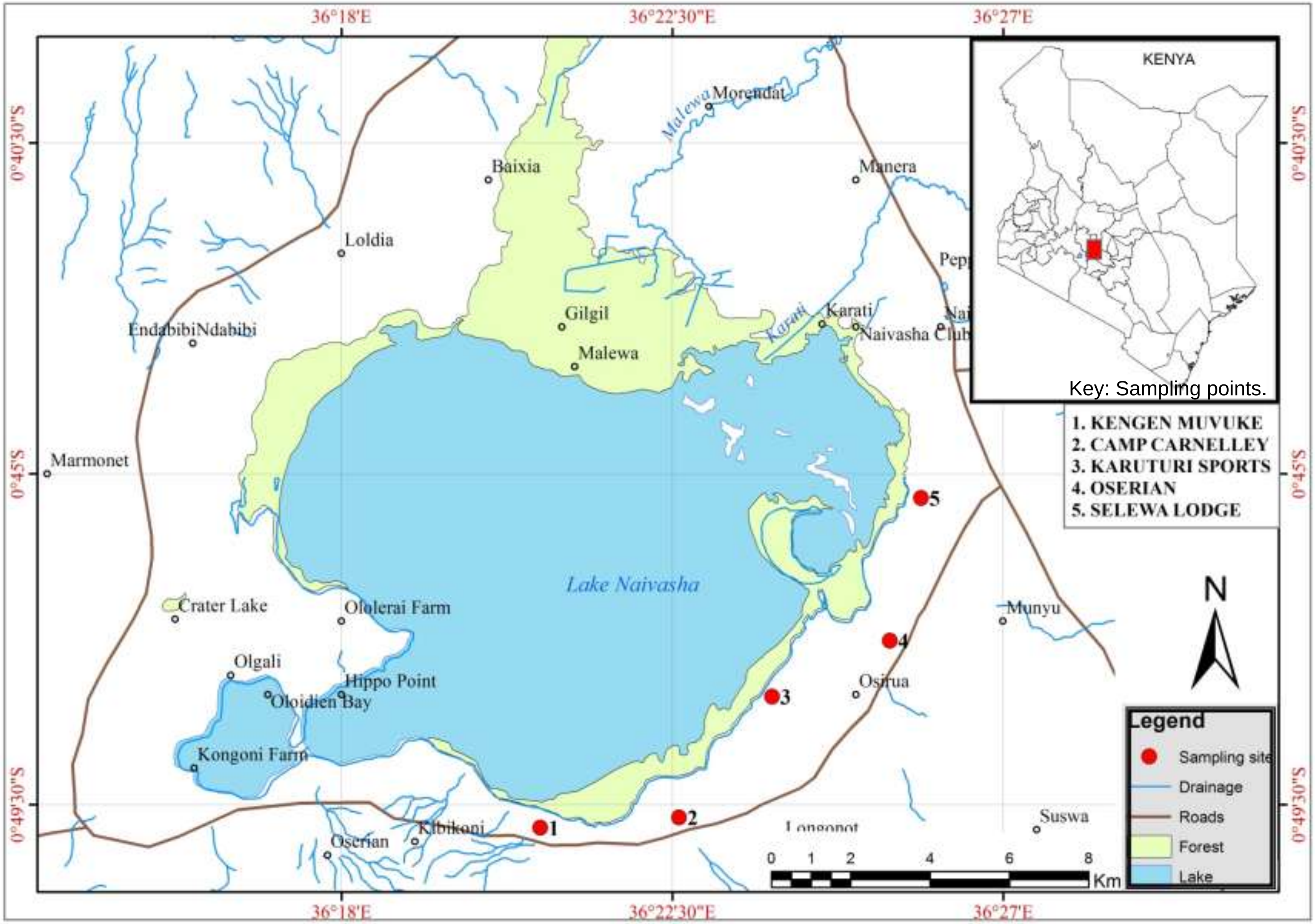


Figure 3.1: Map of Lake Naivasha. (Lake Naivasha Riparian Association).

3.1.2: Soil sampling

The standard sampling method, [M. R. Carter and E. G. Gregorich 2006], involved collecting soils systematically at fixed intervals from the locations. Distance between sampling locations was greater on homogenous fields than on variable fields. Separate soil samples were collected from areas or fields that had different crop history, yield, and fertilizer treatments, or which varied substantially in slope, texture, depth, or soil color.

The field was divided into cells of about 0.5 to 1.0 acre, and collect 3 cores in a zig-zag pattern within each cell to make up the sample (Figure 3.2).This area sampling method provided for fairly complete sampling of the field and a good estimate of the needs for a single uniform application rate that was applied to the entire field.

X	X	X	X	X
X	X	X	X	X
X	X	X	X	X
X	X	X	X	X
X	X	X	X	X

Figure 3.2: Grid Point Sampling Technique - Soil Test Values Represent a Point (Ref: Stratified Systematic Square Grid).

The diagram illustrates an entire sampling location divided into cells of approximately 0.5 to 1.0 acres each. Each sampling cell represented by X had three different samples obtained in a zig-zag pattern and then mixed to make a homogeneous sample. These soil samples were collected to a depth of around 0.25-0.30 meters beneath the surface using a soil auger, each depth increment mixed thoroughly in a large wrapped plastic container and transported as a composite sample.

They were air dried for four days, to prevent nutrient transformation and then sieved using $8.5x10^2$µm and $1.8x10^3$µm sieve particle size. They were then stored into plastic lined soil sampling bags labeled as fine and coarse Lake Naivasha soil sediment samples respectively under airtight conditions.

3.2: Materials and reagents

1- naphthol N-methylcarbamate (Carbaryl) pesticide analytical standard from Kenya Pesticide Control Board.

N-(3,4-dichlorophenyl)-N,N-dimethyl urea (Diuron) pesticide analytical standard from Kenya Pesticide Control Board.

Acetone (pancreac quimica, 95%) from Fisher Chemicals.

Triple distilled water was used for all preparations.

The sediments and soils used were collected from/around Lake Naivasha.

3.3: Instrumentation

All UV-Visible measurements were taken on UV-Visible spectrophotometer (1700 model, Shimadzu Corporation, Kyoto, Japan). A Fischer scientific A-160 analytical balance was used for all weight measurements. An orbital shaker fitted with stop watch was used for all timing purposes.

3.4: Procedure

3.4.1: Soil content analysis.

i). The nutrients (P, K, Na, Ca, Mg and Mn) were analysed using Mehlich Double Acid Method. The oven - dry soil samples were extracted in a 1:5 ratio (w/v) with a mixture of 0.1 M HCl and 0.025 M H_2SO_4 [R. R. Simard et al,.1993].Elements such as Na, Ca and K were then determined with a flame photometer while P, Mg and Mn were analysed calorimetrically [Mehlich, A. 1953].

ii). Total organic carbon (C) was determined by calorimetric method. All organic C in the soil sample was oxidized by acidified dichromate at 150 ℃ for 30 minutes to ensure complete oxidation. Barium chloride was added to the cool digests. After mixing thoroughly digests were allowed to stand overnight. The C concentration was read on the spectrophotometer at 600 nm [Gislason, E.A et al., 2005].

iii). Total amount of nitrogen was determined by Kjeldahl method, where soil samples were digested with concentrated sulphuric acid containing potassium sulphate, selenium and copper sulphate hydrated at approximately 35 ℃. Then nitrogen was determined by distillation followed by titration with H_2SO_4 [Jan-Åke Persson et al,. 2008].

iv). Soil pH was determined in a 1:1 (w/v) soil – water suspension with pH – meter.

v). Available trace elements (Fe, Zn and Cu) were determined by oven drying soil and then extracting in a 1:10 ratio (w/v) with 0.1 M HCl .Then the elements were determined with AAS (Atomic Absorbance Spectrophotometer) [Yang S. et al,.,2005].

vi). To determine Cation Exchange Capacity (CEC) at pH 7.0 and Exchangeable Ca, Mg, K, Na, the soil sample was leached with 1M ammonium acetate buffered at pH 7. The leachate was analyzed for exchangeable Ca, Mg, K and Na. The sample was further leached with 1M KCl, and then the leachate used for the determination of the CEC. Elements such as Na and K were determined with a flame photometer while Ca and Mg were analysed with AAS (Atomic Absorption Spectrophotometer). CEC was determined by distillation followed by titration with 0.01 M HCl. [Carroll et al,.1959,Turner, R.C et al,.1966].

3.4.2: Pesticide analysis.

i). To obtain the standards, solutions of 1- naphthol N-methylcarbamate (Carbaryl) pesticide in acetone in concentration ranges of 1-100ppm were prepared as: 2, 6, 8, 10, 20, 40, 60, 80 and 100ppm.

ii). The prepared solutions above were scanned using UV-Visible Spectrophotometer on a wavelength range of between 200-900nm to obtain the absorbance curves. The linear plots of absorbance versus concentration were used to determine subsequent unknown concentrations at wavelength of 280nm for Carbaryl and 372.5nm for Diuron.

iii). To determine adsorption/desorption in varied masses of the soil sediments, 0.5, 1.0, 1.5, 2.0, 2.5 and 3.0 grams of dried sediments were measured in triplicates. Each of these masses were mixed with 10ml of 3.0mg of the Carbaryl pesticide aqueous solution and shaken using an orbital shaker for about 60 minutes, and then allowed to settle for 24 hours after which decantation of the water phase was done and filtered through Whatman A40 filter paper. The filtrate (aqueous medium) was then analyzed in triplicates using UV-Visible spectrophotometer at wavelength of 280nm for Carbaryl and 372.5 for Diuron to obtain absorbance that was used to determine concentration using the respective linear plot of the standards.

iv). Adsorption/desorption on variable concentrations and shaking time was done by measuring 0.5g of the dried sediment shaken with 10ml distilled water spiked at 10, 20, 30, 40, and 50mg/ml level of the pesticide in triplicates. Each of the samples were shaken for 15, 30, 45 and 60 minutes and left to settle for 24 hours. The filtrate was then analyzed in triplicates using UV-Visible spectrophotometer at wavelength of 280nm for Carbaryl and 372.5 for Diuron to obtain absorbance that was used to determine concentration using the respective linear plot of the standards.

v) In the analysis of N-(3,4-dichlorophenyl)-N,N-dimethyl urea (Diuron) pesticide, a similar procedure "i-iv" was followed using Diuron as the pesticide.

vi). The mean concentrations of the pesticides in water, $[X]_e + [SX_n]_w$ were plotted against the concentration of the chemical pesticides adsorbed to suspended colloidal and/or sediment particles, $[X]_{ads.}$

vii). Determination of the values of apparent adsorption/desorption equilibrium constant k' and the apparent free energy G^o for the adsorption of the pesticides were done using the first order model of a binary solution.

3.5: Selected method for sorption measurement

The theory behind the adsorption process has been reported earlier by Zaranyika et al., 1998. In the present research work, the adsorption kinetics of 1- naphthol N-methylcarbamate (Carbaryl) and of N-(3,4-dichlorophenyl)-N,N-dimethylurea (Diuron) pesticides onto Lake Naivasha sediments is presented based on the adsorption model of a binary dilute solution [Burchill et al., 1981].

The characteristic adsorption of pesticide by soils or sediments can be described by the Freundlich empirical isotherm [Graham-Bryce, 1981]:

$$C_{ads}. = k_F\, C_e^{1/n} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(3.1)$$

Where k_F the Freundlich constant, C_{ads} is concentration (mg/ml) of the pesticide adsorbed by the soil/sediment in a colloidal solution, C_e is the concentration of the pesticide in the solution (mg/ml) at equilibrium and n is the number of adsorbed molecules of the pesticide [Hance, 1965;

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

The adsorption process of pesticides on soils was reviewed by Burchill et al., (1981). Several factors need to be considered in conducting adsorption studies. Firstly is the kinetics involved, particularly the magnitude of the adsorption and desorption rate constants and also the energies involved. Secondly is the initial and equilibrium conditions and how the chemical composition and/or structure of both the adsorbent and the pesticide affect adsorption.

In order to obtain the adsorption/desorption, equilibrium, thermodynamic and kinetic data, there is need to come up with a functional adsorption/desorption equilibrium model, from which the apparent equilibrium constant and kinetic information can be calculated. Assuming that the adsorption of pesticide solute by the colloidal/sediment or both particles occurs during the shaking period, implying when the sediment is in suspension, then the adsorption/desorption equilibrium can be described as follows [Seungman et. al., 2005], equations (3.2 - 3.4):

$$S + X_n \Leftrightarrow SX_n \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(3.2)$$

$$K = [SX_n]/[X]^n[S] \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3.3)$$

On re-arrangement;

$$[SX_n] = K[X]^n[S] \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3.4)$$

where X is the pesticide molecule of interest; S is the adsorbent/substrate or adsorption site on the sediment or colloidal particle in solution and K is the adsorption/desorption equilibrium constant. SX_n is the particle-pesticide adsorption complex. Also, one notes that S is a solid whose mass is very large compared to that of the solute. Therefore, the $[S]$ can customarily be taken to be unity, thereby reducing equation 3.4 to:

$$[SX_n] = K[X]^n \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3.5)$$

And on taking logs we have:

$$\log[SX_n] = \log K + n\log[X] \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3.6)$$

It means, since equation 3.6 is linear, the value of K, the equilibrium constant, and n, the number of pesticide molecules adsorbed, can be obtained from the intercept and slope of the $\log[SX_n]$ versus $\log[X]$ plots, respectively. In addition, the standard Gibbs free energy of activation, ΔG, can be estimated by use of the conventional equation:

$$K = e^{-\Delta G/RT} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3.7)$$

At room temperature of 25^0C,

$$K = e^{-\Delta G/298R} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(3.8)$$

Considering the assumption that the adsorption of Carbaryl and of Diuron pesticides by colloidal and/or sediment particles occurs during the shaking and also that all the adsorbed pesticide goes to the sediment on settling, then the concentration of pesticide adsorbed to the suspended particles $[X]_{ads}$ can be obtained using equation 3.9 :

$$[X]_{ads} = [X]_i - [X]_e \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(3.9)$$

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

$$[SX_n] = {}^{1}\!/_{n}\left([X]_i - [X]_e\right) \ldots\ldots\ldots\ldots\ldots\ldots(3.10)$$

$$[SX_n] = {}^{1}\!/_{n}[X]_{ads} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(3.11)$$

Nomura and Hilton (1977) and later Zaranyika et. al., (1993), demonstrated the existence of a colloidal bound fraction when a pesticide is shaken with water containing sediment. They also showed that the colloidal bound fraction in suspension after settling was significantly small compared to the bound fraction in the sediment thus justifying the assumption made regarding the determination of $[SX_n]$ using $[X]_{ads}$ above. Note that $[SX_n]$ is the concentration of the colloidal bound fraction in suspension at settling equilibrium, since not all the pesticide is adsorbed. Therefore, on modifying equation 3.11 to show the total adsorbed pesticide we have:

From equation 3.5 :

$$[SX_n] = K[X]^n = K'([X]_e + [SX_n]_w)^n \text{ ……………..(3.12)}$$

But:

$$[X]_{ads} = n[SX_n] = nK'([X]_e + [SX_n]_w)^n \text{ …………...(3.13)}$$

where K' is the apparent adsorption equilibrium constant and $[SX_n]_w$ is the concentration of the colloidal bound fraction in suspension at settling equilibrium. On taking the logarithm of equation 3.13 yields a linear expression:

$$\ln[X]_{ads} = \ln(nK') + n\ln([X]_e + [SX_n]_w) \text{....................(3.14)}$$

Assuming that equilibrium exists between the colloidal bound fraction in the sediment and that in the suspension, then equation 3.2 becomes:

$$nX + S \leftrightarrow (SX_n)_w \leftrightarrow (SX_n)_{sediment} \text{........................(3.15)}$$

It is apparent from equation 3.15 that a steady state exists with respect to $[SX_n]_w$ at settling equilibrium. Moreover, a plot of $\ln[X]_{ads}$ versus $\ln([X]_e + [SX_n]_w)$ in equation 3.14 will not affect the value n in equations 3.6 and 3.10 , but will affect the value of nK. Therefore, the value of K obtained is not a true equilibrium constant, but rather an apparent equilibrium constant (K').

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1: Characterization of the soil

The results of characterization of the Lake Naivasha soil with respect to the physical properties and composition of the sediment using the standard methods were obtained as shown in table 4.1.

Table 4.1: Properties of the soil used in adsorption experiment.

Profile	Coarse soil	Fine soil
Soil depth cm	Top	Top
Soil pH-H_2O (1:2.5)	4.68	4.65
Electric Conductivity mS/cm	0.27	0.52
Carbon content %	0.5	2.5
Sand %	78	20
Silt %	36	12
Clay %	10	22
Cation Exchange Capacity %	25.0	5.2
Calcium %	13.1	3.1
Magnesium %	1.7	0.9
Potassium %	0.8	0.8
Sodium %	0.8	1.1

The nature of the soil can greatly influence its adsorption characteristics. According to this table, the texture grade of the soil is sand (78% for coarse and 20% for fine). The pH of the soil approximates weak acidic, whereas the small percentage of organic carbon (0.5% for coarse and

2.5% for fine) may explain the negligible adsorption of organo-pollutant compounds, onto the soil.

4.2: Analysis of the standards

Clear solutions of Carbaryl and Diuron exhibited the expected characteristic UV-Visible spectra. The characteristic absorption band for Carbaryl occurred at λ_{max} of 280 nm, while that of Diuron occurred at λ_{max} of 372.5 nm as indicated by figures 4.1and 4.2, respectively.

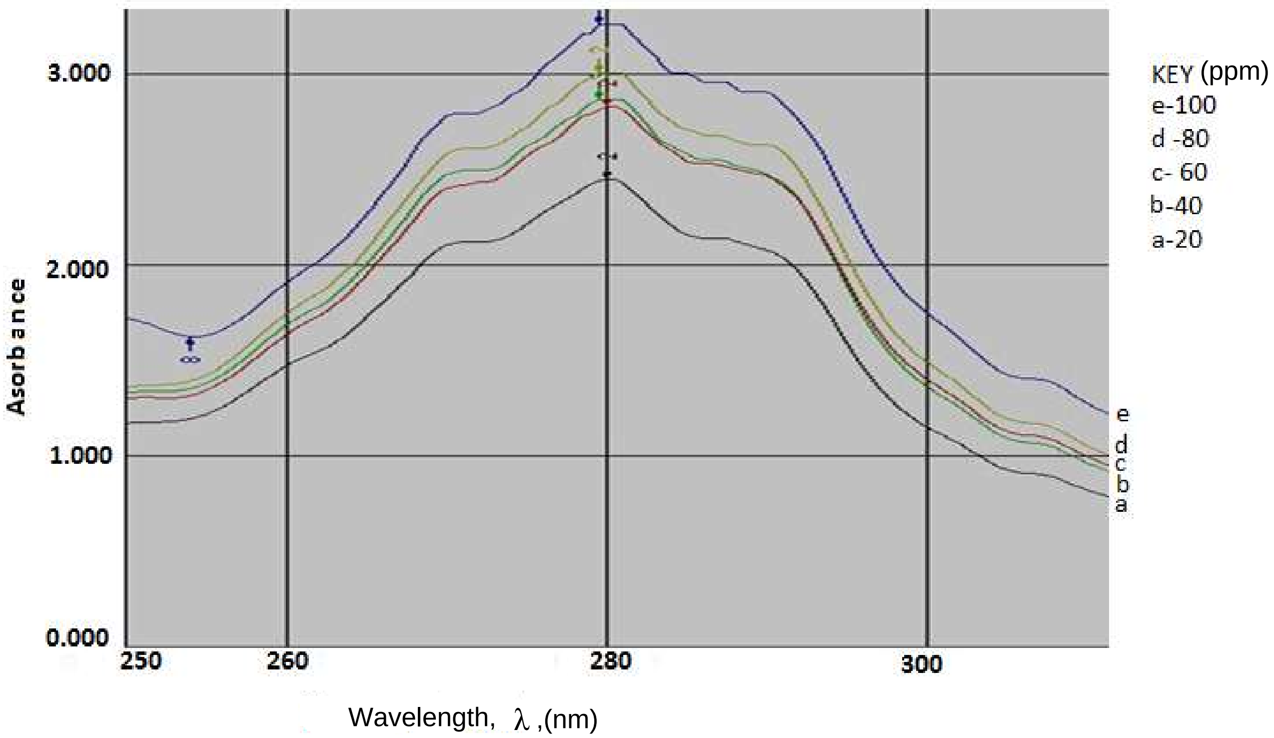


Figure 4.1: Characteristic UV-Visible spectra for Carbaryl, λ_{max} of 280 nm.

The peak heights are proportional to concentration, with the highest peak corresponding to the greatest concentration of 100ppm.

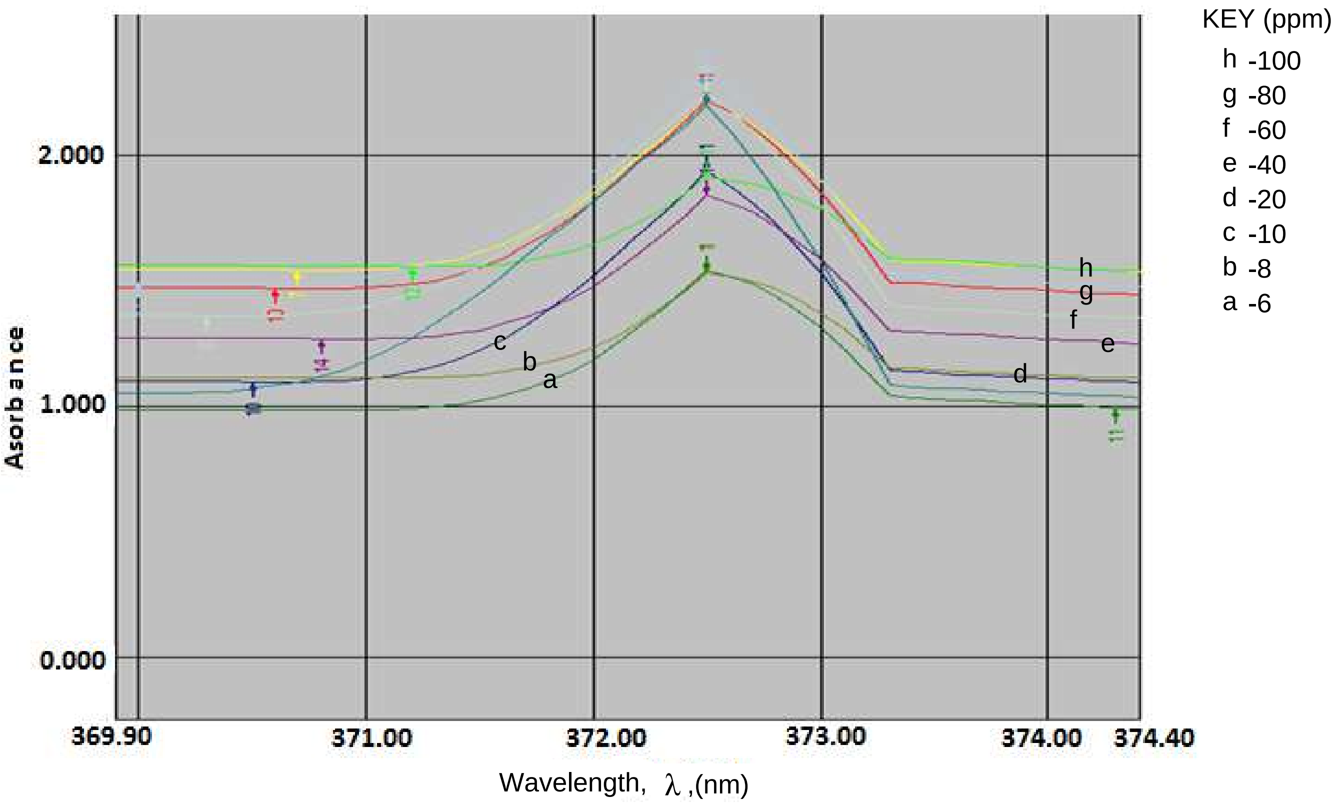


Figure 4.2: Characteristic UV-Visible spectra for Diuron, λ_{max} of 372.5 nm.

Similarly, for diuron the peak heights are proportional to the concentration and the wavelength of maximum absorption (λ_{max}) occurred at 372.5nm as expected.

A plot of the absorbance versus concentration at the lambda maximum (λ_{max}), yielded linear relationship for both Carbaryl (figure 4.3 [i, ii, and iii]) and Diuron (figure 4.4 [i, ii, and iii]). It means the systems adhered to the Beer Lambert's Law, i.e.,

$$A=\acute{\varepsilon}CL \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4.1)$$

where A is absorbance, L is path length, C is concentration and $\acute{\varepsilon}$ is absorption coefficient at the concentration range of 0-100 ppm considered in this research for both Carbaryl and Diuron.

The data for mean absorbance with respective concentration for Carbaryl and Diuron is shown below in tables 4.2 and 4.3 respectively.

Table 4.2: Absorbance against concentration for carbaryl standards at λ = 280nm.

Concentration (ppm)	Mean absorbance.
0	0.0000
2	0.0833
4	0.1709
6	0.2497
8	0.3356
10	0.4129
20	0.6330
40	1.7890
60	2.0350
80	3.4080
100	3.5550

Table 4.3: Absorbance against concentration for Diuron standards at λ = 372.5nm.

Concentration(ppm)	Mean absorbance
0	0.0000
2	0.00198
4	0.00652
6	0.00965
8	0.01047
10	0.0148
20	0.01643
40	0.02753
60	0.04018
80	0.05412
100	0.05909

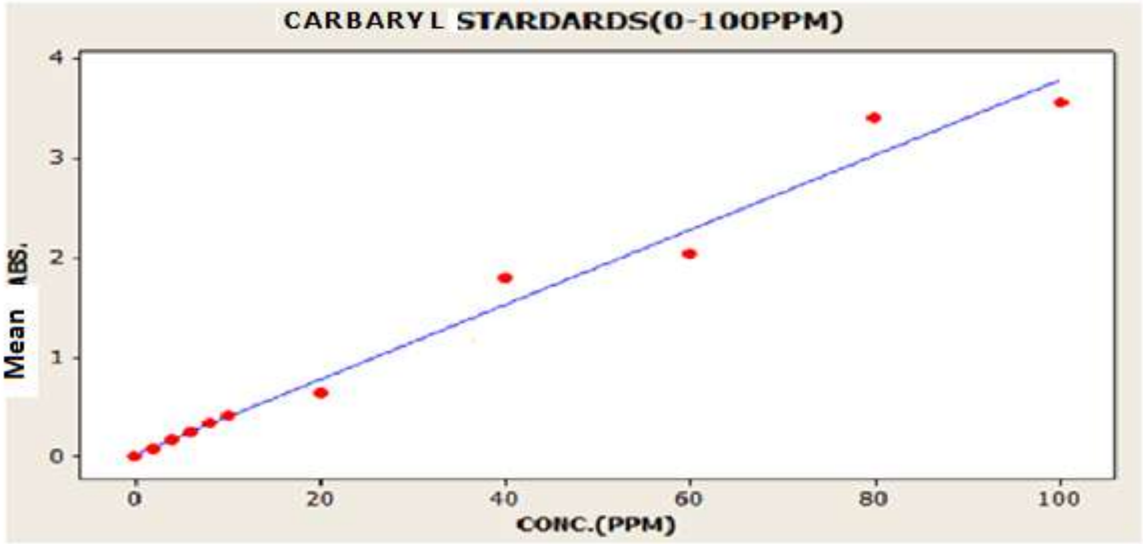


Figure 4.3(i): A plot of the mean Absorbance versus Concentration for Cabaryl at λ_{max} of 280 nm.

In specific, Carbaryl plots for low concentration of 0-10ppm yielded a linear plot of absorbance versus concentration which adhered to Beer Lambert's Law due to higher sensitivity as shown by figure 4.3 (ii) below.

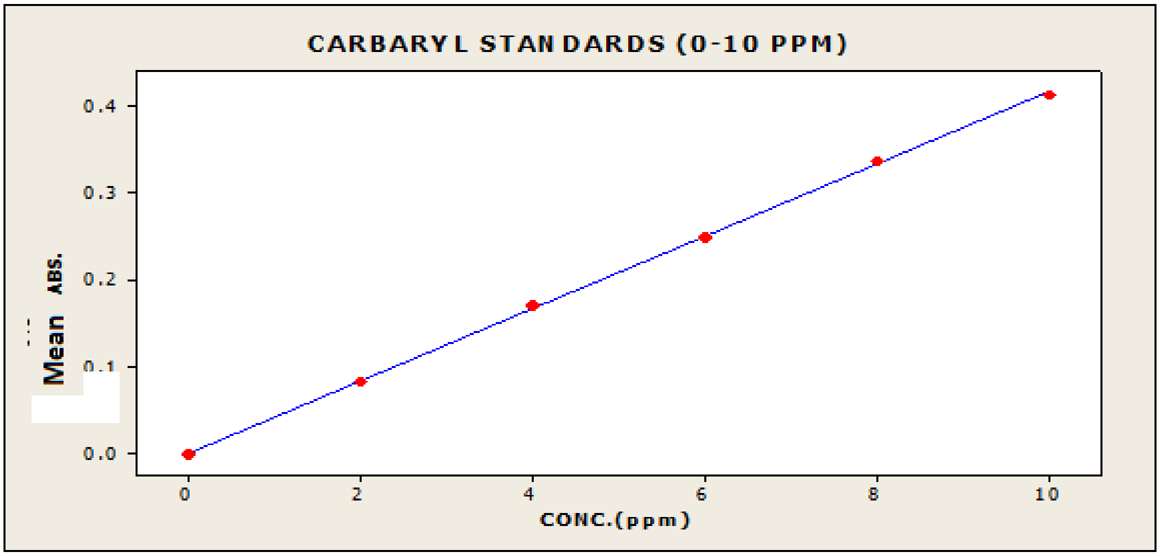


Figure 4.3(ii): A plot of the mean Absorbance versus Concentration for Cabaryl at λ_{max} of 280 nm (0-10ppm).

Deviation from the Beer Lambert's Law at high concentration of 10-100ppm occurred as expected. This is shown by figure 4.3 (iii) below.

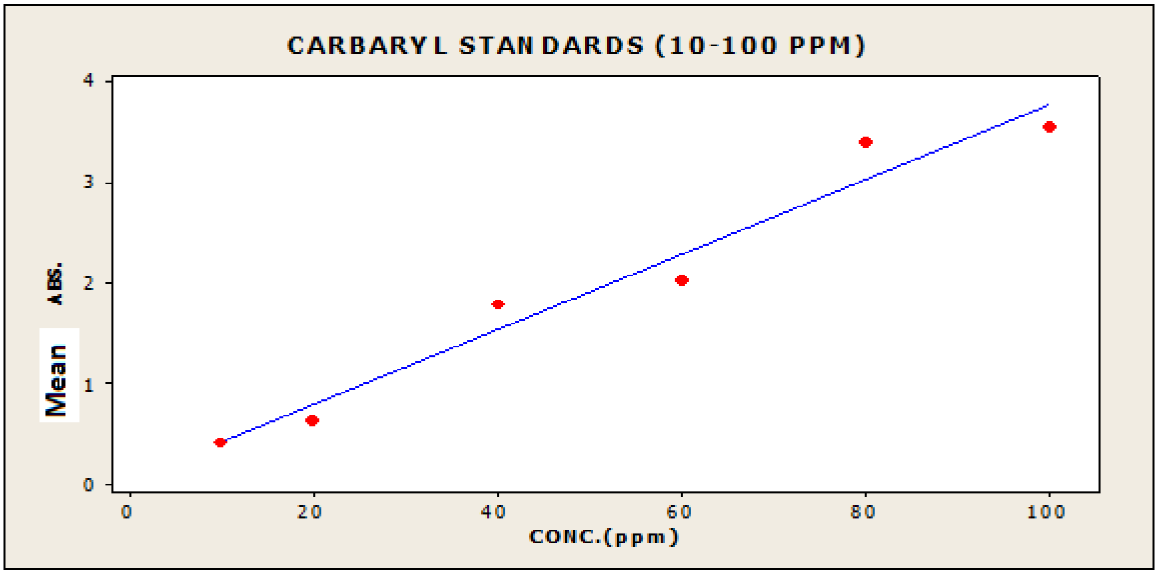


Figure 4.3(iii): A plot of the mean Absorbance versus Concentration for Cabaryl at λ_{max} of 280 nm (10-100ppm).

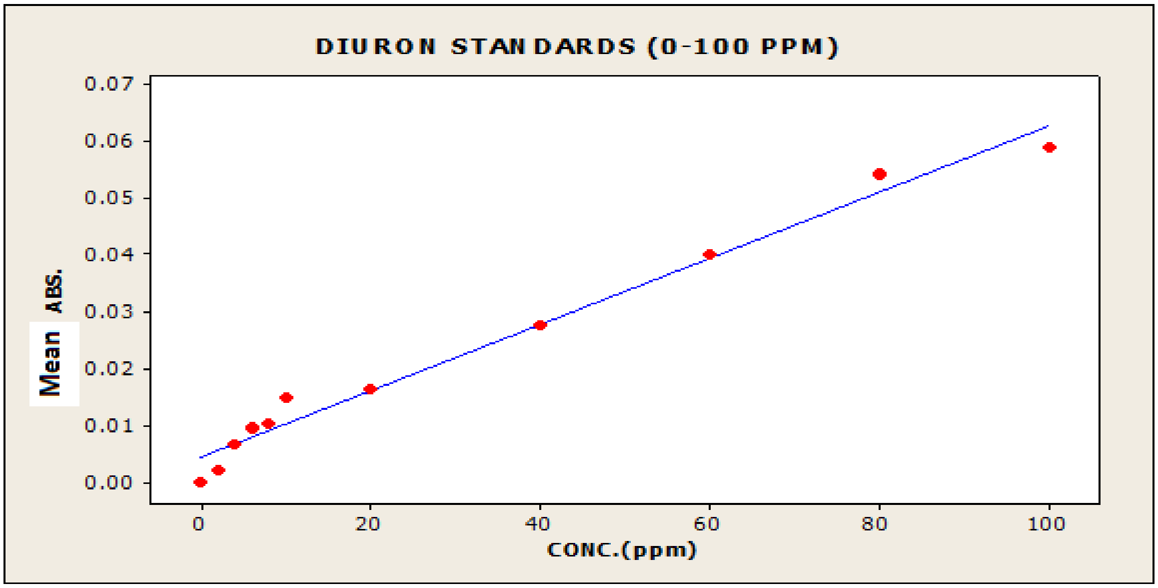


Figure 4.4(i): A plot of the mean Absorbance versus Concentration for Diuron at λ_{max} of 372.5 nm.

For diuron, a plot for low concentration of 0-10ppm indicated greater deviation from Beer Lambert's Law as shown by figure 4.4 (ii) below. This may be as a result of low sensitivity of diuron implying that there was more noise in the instrument at lower concentration.

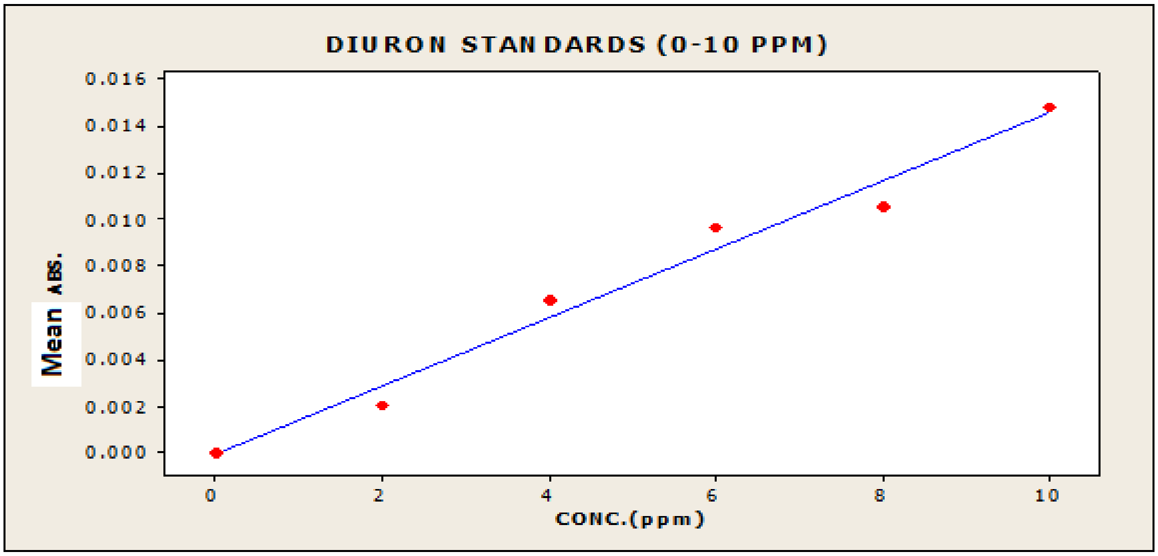


Figure 4.4(ii): A plot of the mean Absorbance versus Concentration for Diuron at λ_{max} of 372.5 nm (0-10ppm).

At higher concentrations of 10-100ppm, Diuron generated greater linearity indicating that plot of absorbance versus concentration adhered to Beer Lambert's Law as expected due to increased sensitivity in the instrument. This is shown by figure 4.4 (iii) below.

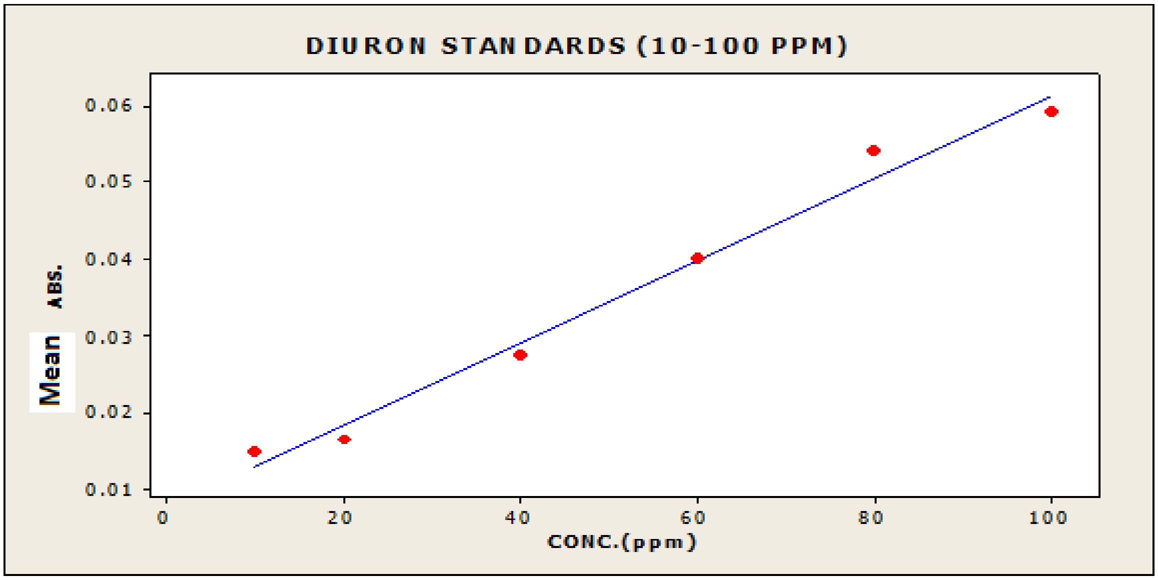


Figure 4.4(iii): A plot of the mean Absorbance versus Concentration for Diuron at λ_{max} of 372.5 nm (10-100ppm).

4.3: Variation of amount of soil

In tables 4.4 and 4.5 shown below, the data of the absorption as a function of variable amount of soil added is presented for Carbaryl and Diuron, respectively. It was found that as the amount of soil in the experimental solutions increased, the concentration of the pesticide in solution ($[X]_e + [SX_n]_w$), (μg/ml) decreased. This was because, the increase in the amount of soil meant increased concentration of the pesticide adsorption sites and thus more and more pesticide being removed from the solution.

These values are recorded as mean (μ) values of the triplicate concentration of the pesticide in solution ($[X]_e + [SX_n]_w$), (μg/ml). The corresponding standard deviation (δ) was calculated.

Table 4.4: Adsorption of carbaryl as a function of variable masses of soil. Initial concentration of carbaryl was 300μg/ml.

Mass of soil (g)	Coarse (Mean values, μ)		Fine (Mean values, μ)	
	$[X]_e + [SX_n]_w$ (μg/ml). (μ ± δ)	$[X]_{ads.}$ (μg/ml).	$[X]_e + [SX_n]_w$ (μg/ml). (μ ± δ)	$[X]_{ads.}$ (μg/ml).
0.5	104.44 ±0.04	195.56	104.28 ±0.02	195.02
1.0	103.60 ±0.06	196.40	104.08 ±0.06	195.72
1.5	101.10 ±0.06	198.90	103.99 ±0.07	196.01
2.0	98.52 ±0.07	201.48	103.52 ±0.02	196.88
2.5	94.93 ±0.11	205.07	102.96 ±0.49	197.74
3.0	89.19 ±0.11	210.81	101.90 ±0.39	198.11

Table 4.5: Adsorption of Diuron as a function of variable masses of soil. Initial concentration of diuron was 300μg/ml.

Mass of soil (g)	Coarse (Mean values, μ)		Fine (Mean values, μ)	
	$[X]_e + [SX_n]_w$ (μg/ml). (μ ± δ)	$[X]_{ads.}$ (μg/ml).	$[X]_e + [SX_n]_w$ (μg/ml). (μ ± δ)	$[X]_{ads.}$ (μg/ml).
0.5	222.00 ±0.57	78.00	215.99 ±0.07	84.01
1.0	198.00 ±0.41	102.00	209.54 ±0.03	90.46
1.5	189.00 ±2.44	111.00	188.96 ±0.29	111.04
2.0	174.00 ±0.33	126.00	170.10 ±0.08	129.90
2.5	140.67 ±0.71	159.34	123.00 ±0.05	177.00
3.0	116.55 ±0.12	183.45	52.05 ±0.04	247.95

The greatest variant value of $[X]_e + [SX_n]_w$ (µg/ml) had a relative standard deviation of 0.11 on coarse, 0.49 on fine for Carbaryl and 2.44 on coarse, 0.29 on fine for Diuron respectively, suggesting relatively good precision of the experiments. Overall, when a 0.3mg/ml of the pesticide solution is equilibrated with increasing amounts of soil, the amount of the Carbaryl and Diuron remaining in solution and/or suspension as expected shows an exponential drop as the amount of soil increases.

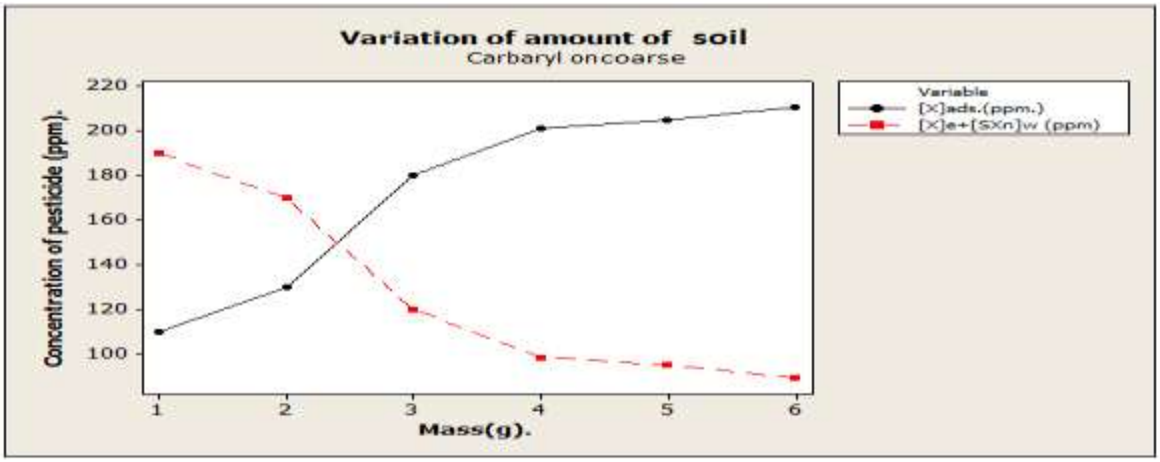


Figure 4.5 (i): Graph of adsorbed Carbaryl [X]ads. Versus variable mass of soil for coarse.

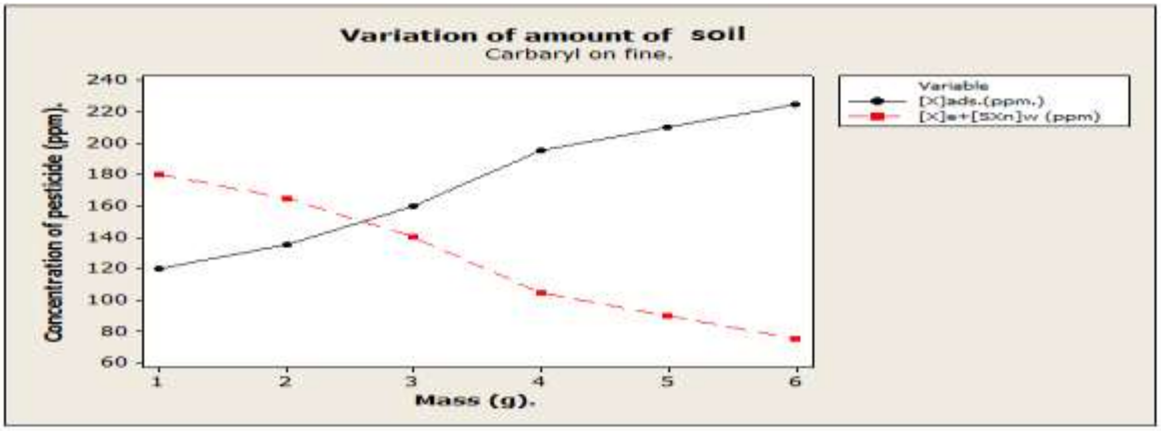


Figure 4.5 (ii): Graph of adsorbed Carbaryl [X]ads. Versus variable mass of soil for fine.

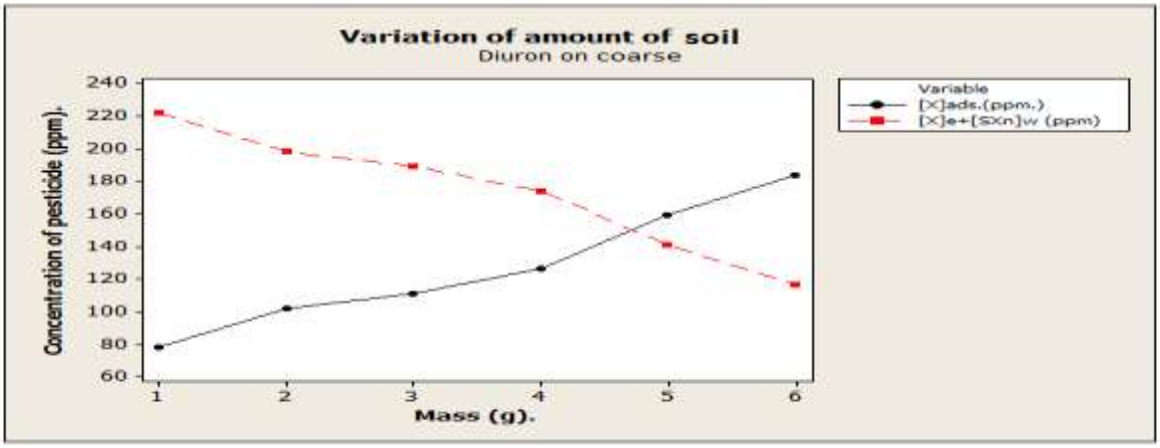


Figure 4.6 (i): Graph of adsorbed Diuron $[X]_{ads}$. Versus variable mass of soil for coarse.

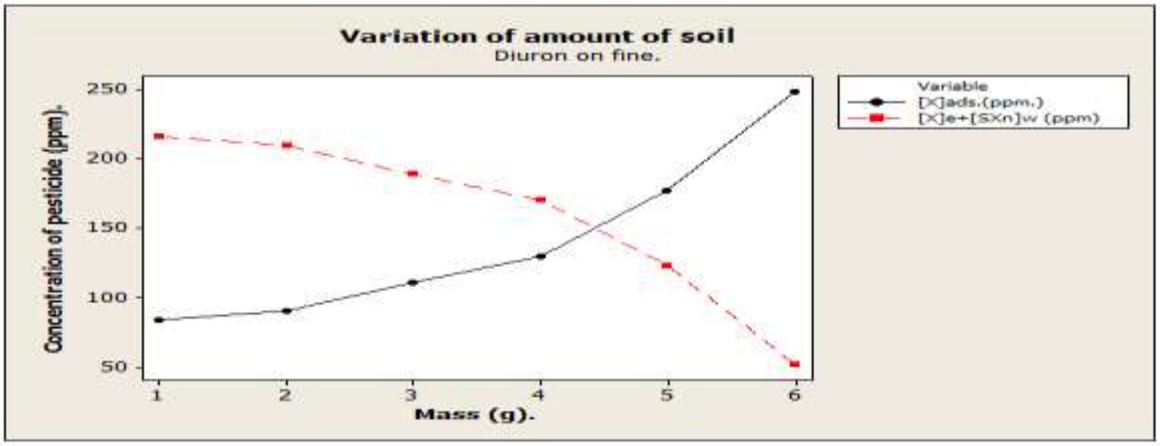


Figure 4.6 (ii): Graph of adsorbed Diuron $[X]_{ads}$. Versus variable mass of soil for fine.

This is consistent with equation 2.24 above, and confirms the presence of adsorption/desorption equilibrium in the systems and agrees with the predictions of adsorption/desorption equilibrium model presented above.

With the increase in the number of adsorption site as the quantities of the soil were increased, the amount of pesticide adsorbed $[X]_{ads}$ is also increased (Figures 4.5 for Carbaryl, and 4.6 for Diuron) above. Tables 4.4 and 4.5 shows that as the mass of the soil increased from 0.5 - 3.0g, the concentration of the Carbaryl and Diuron in the adsorbed state averagely increased from

195.29-204.46 and 81.01-215.70, respectively, a 4.69% for carbaryl and 166.28% for Diuron. This indicates that Diuron is more highly adsorbed than Carbaryl on Lake Naivasha sediments. This can be inferred to factors such as low solubility of Diuron compared to Carbaryl. The lower the solubility, the higher the equilibrium sorption coefficient. The higher molecular weight of Diuron also contributes to its lower solubility. In addition, Diuron has a higher half-life under most conditions as compared to Carbaryl (as shown in Table 2.2) hence it tends to be more stable for longer translating to higher sorption and persistence in the environment.

4.4: Variation of spiking levels and shaking time

Similarly, spiking aqueous solutions, containing 0.5g soil and shaking/equilibration at different times, with Cabaryl and Diuron gave data which were dependent on spiking level and shaking periods as indicted by tables 4.6 and 4.7, shown below. These values are recorded as mean (μ) values of the triplicate concentration of the pesticide in solution ($[X]_e + [SX_n]_w$), (μg/ml), which were determined from their absorbance compared to the standard solutions. Also their corresponding standard deviations (δ) were calculated.

Table 4.6(a): Aqueous phase concentration of Carbaryl following equilibration of 0.5g soil for different time intervals with water spiked with known initial variable concentrations of carbaryl.

Shaking time/Min.	Spike level (µg/ml)	Coarse: (Mean,µ, values)		Fine: (Mean,µ, values)	
		$[X]_e + [SX_n]_w$ (µg/ml). (µ ± δ)	$[X]_{ad.}$ (µg/ml).	$[X]_e + [SX_n]_w$ (µg/ml). (µ ± δ)	$[X]_{ad.}$ (µg/ml).
15	100	66.00 ±0.16	34.00	54.00 ±0.82	46.00
	200	68.50 ±0.24	131.50	79.00 ±0.57	121.00
	300	70.10 ±0.16	229.90	84.00 ±0.82	216.00
	400	74.00 ±0.33	326.00	95.00 ±0.33	305.00
	500	88.00 ±0.65	412.00	102.00 ±0.41	398.00
30	100	72.00 ±0.33	28.00	78.00 ±0.57	22.00
	200	68.00 ±0.73	132.00	90.00 ±0.65	110.0
	300	82.00 ±0.41	218.00	88.00 ±0.16	212.00
	400	82.00 ±0.82	318.00	95.00 ±0.65	305.00
	500	90.00 ±0.33	410.00	95.00 ±0.41	405.00
45	100	68.50 ±0.24	31.50	30.00 ±1.22	70.00
	200	79.00 ±0.16	121.00	88.00 ±0.41	112.00
	300	82.00 ±0.57	218.00	102.00 ±0.82	198.00
	400	90.00 ±1.63	310.00	102.00 ±0.65	298.00
	500	90.00 ±0.41	410.00	102.00 ±0.25	398.00
60	100	74.00 ±0.65	26.00	40.01 ±0.66	59.99
	200	79.00 ±0.41	121.00	74.00 ±0.33	126.00
	300	95.00 ±0.33	205.00	90.00 ±0.41	210.00
	400	82.00 ±0.24	318.00	95.00 ±0.65	305.00
	500	95.00 ±0.16	405.00	102.00 ±0.33	398.00

Table 4.6(b): Natural logarithms (In) of aqueous phase concentration of carbaryl following equilibration of 0.5g soil with different intervals and spike level.

Shaking time/Min.	Spike level (µg/ml)	Coarse		Fine	
		$\ln([X]_e+[SX_n]_w)$	$\ln([X]_{ad.})$	$\ln([X]_e+[SX_n]_w)$	$\ln([X]_{ad.})$
15	100	4.1897	3.5263	3.9890	3.8286
	200	4.2268	4.8752	4.3694	4.7958
	300	4.4067	5.4376	4.4308	5.3553
	400	4.2499	5.7869	4.5539	5.7203
	500	4.4773	5.0210	4.6250	5.9865
30	100	4.2767	3.3322	3.3567	3.0910
	200	4.2195	4.8828	4.4998	4.7004
	300	4.4067	5.3845	4.4773	4.3566
	400	4.4067	5.7621	4.5539	5.6971
	500	4.4998	6.0161	4.5539	6.0039
45	100	4.2268	3.4500	3.4012	4.2485
	200	4.3694	4.7958	4.4773	4.7185
	300	4.4067	5.3845	4.6250	5.2883
	400	4.4998	5.7366	4.6250	5.6971
	500	4.3998	6.0162	4.6250	5.9865
60	100	4.3041	3.2581	3.6891	4.5976
	200	4.3694	4.7958	3.3041	4.8363
	300	4.5599	5.3230	4.4998	5.3471
	400	4.4067	5.7621	4.5539	5.7203
	500	4.5539	6.0039	4..6250	5.9865

From data on table 4.6, graphs of amount adsorbed against the shaking time were obtained as shown below.

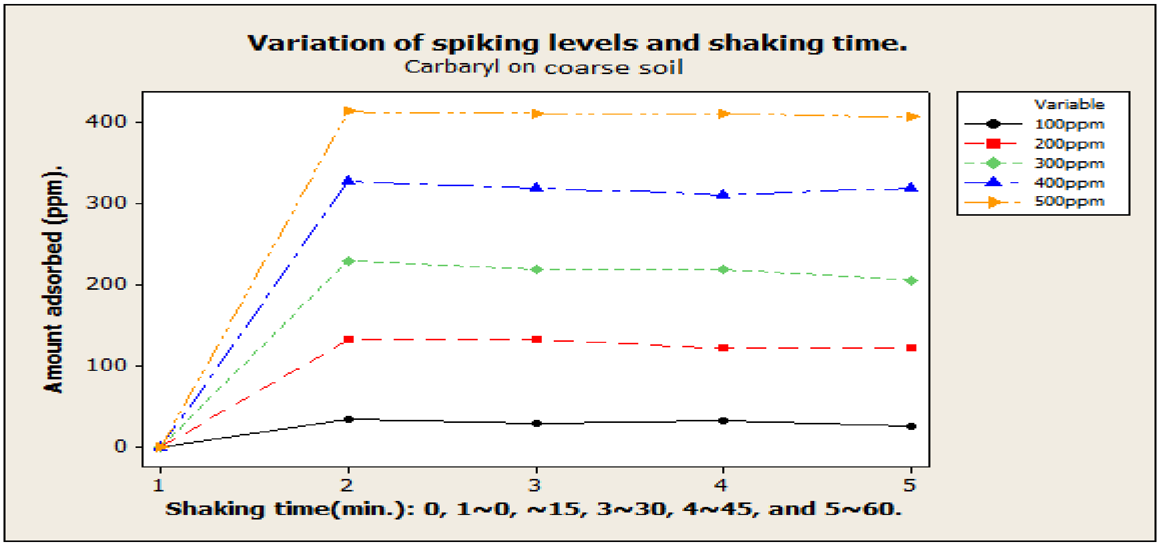


Figure 4.7 (a): Variation of spiking levels and shaking time for carbaryl by Lake Naivasha coarse soil.

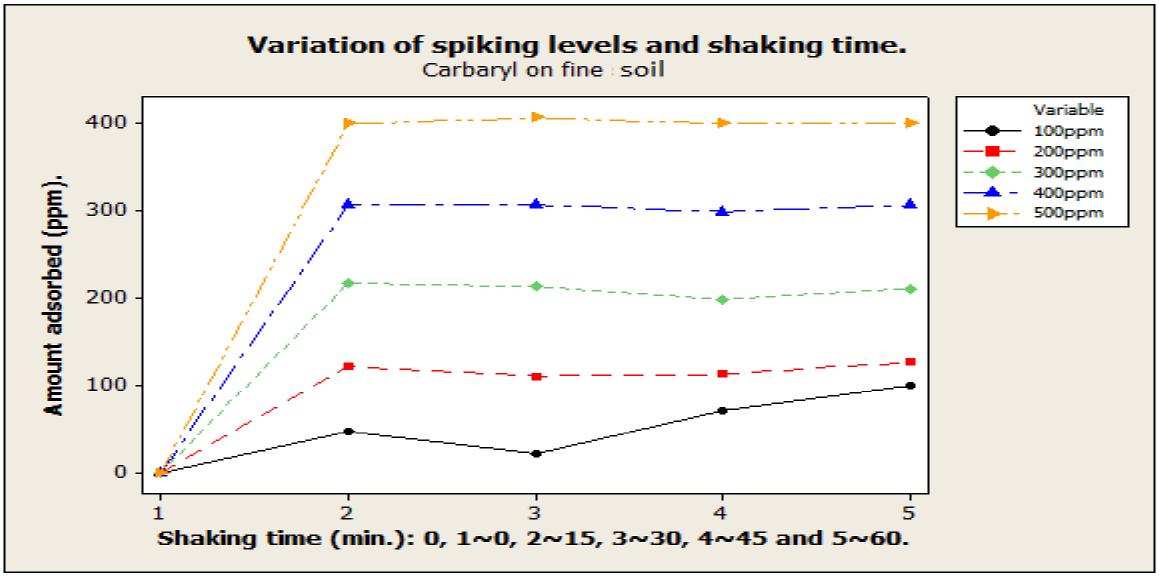


Figure 4.7 (b): Variation of spiking levels and shaking time for carbaryl by Lake Naivasha fine soil.

This indicates that the amount adsorbed increases with increase in spiking levels of the pesticide. The initial rapid phase is due to the presence of large number of vacant adsorption sites, leading to increase in concentration gradient between adsorbate in solution and the adsorbent surface.

The time of reaching equilibration depends on the initial concentration of the pesticide, hence the lower the concentration, the shorter the equilibration time interval due to higher adsorbent surface site ratio to pesticide molecules per unit volume compared to higher concentration. Therefore increase in initial pesticide concentration increased the amount of pesticide molecules uptake per unit mass of the soil.

Generally the plots indicate that the longer the shaking time, the higher the equilibration because of increased pesticide substrate/soil contact adsorption/desorption time.

Table 4.7(a): Aqueous phase concentration of Diuron following equilibration of 0.5g soil for different time intervals with water spiked with known initial variable concentrations of diuron.

Shaking time/Min.	Spike level (µg/ml)	Coarse (Mean,µ, values)		Fine (Mean,µ, values)	
		$([X]_e+[SX_n]_w)$ (µg/ml). (µ ± δ)	$([X]_{ad.})$ (µg/ml).	$([X]_e + [SX_n]_w)$ (µg/ml). (µ ± δ)	$([X]_{ad.})$ (µg/ml).
15	100	41.60 ±1.30	58.40	33.11 ±0.09	66.89
	200	54.27 ±0.06	145.73	122.49 ±0.11	77.52
	300	88.41 ±0.09	211.57	156.18 ±0.15	143.82
	400	135.23±0.03	264.77	208.10 ±0.16	191.90
	500	222.07±0.06	277.93	259.30 ±0.25	240.70
30	100	72.31 ±0.03	27.69	83.51 ±0.17	16.49
	200	98.40 ±0.04	101.60	132.95 ±0.08	67.05
	300	119.94±0.03	180.06	175.04 ±0.19	124.96
	400	213.58±0.10	186.42	238.89 ±0.32	161.11
	500	245.92±0.34	254.08	290.03 ±0.35	209.97
45	100	35.84 ±0.01	64.16	54.98 ±0.07	45.02
	200	55.31 ±0.01	144.69	87.97 ±0.04	112.03
	300	88.85 ±0.09	211.15	170.03 ±0.19	129.97
	400	112.51±0.09	287.50	137.97 ±0.38	262.04
	500	200.14±0.11	299.86	165.01 ±0.09	334.99
60	100	46.67 ±0.18	53.33	38.75 ±0.37	61.25
	200	80.40 ±0.04	119.60	71.02 ±0.41	128.98
	300	139.49±0.12	160.51	140.05 ±0.08	159.95
	400	208.30±0.04	191.70	240.09 ±0.07	159.91
	500	254.17±0.02	245.83	265.07 ±0.10	234.93

Table 4.7(b): Natural logarithms (ln) of aqueous phase concentration of Diuron following equilibration of 0.5g soil with different intervals and spike level.

Shaking time/Min.	Spike level (μg/ml)	Coarse		Fine.	
		$\ln([X]_e+[SX_n]_w)$	$\ln([X]_{ad.})$	$\ln([X]_e+[SX_n]_w)$	$\ln([X]_{ad.})$
15	100	3.7281	4.0673	3.4998	4.2030
	200	3.9940	4.9818	4.8080	4.3505
	300	4.4820	5.3546	5.1510	4.9686
	400	4.9070	5.5789	5.3380	5.2570
	500	5.4030	5.6274	5.5580	5.4836
30	100	4.2810	3.3210	4.4250	2.8028
	200	4.5890	4.6210	4.8900	4.8597
	300	4.4869	5.1933	5.1650	4.8280
	400	5.3640	5.2280	5.4760	5.0821
	500	5.5050	5.5376	5.6700	5.3470
45	100	3.5790	4.1614	4.0070	3.8071
	200	4.0130	4.9746	4.4770	4.7188
	300	4.4870	5.3526	5.1360	4.9673
	400	4.7230	5.6612	4.9270	5.5685
	500	5.2990	5.7033	5.1060	5.8141
60	100	3.8431	3.9765	3.6571	4.1151
	200	4.3870	4.7842	4.2630	4.8597
	300	4.9380	5.0784	4.9420	5.0749
	400	5.3390	5.2560	5.4810	5.0746
	500	5.5380	5.5046	5.5800	5.4464

Similarly, from data on table 4.7, graphs of amount adsorbed against the shaking time were obtained as shown below.

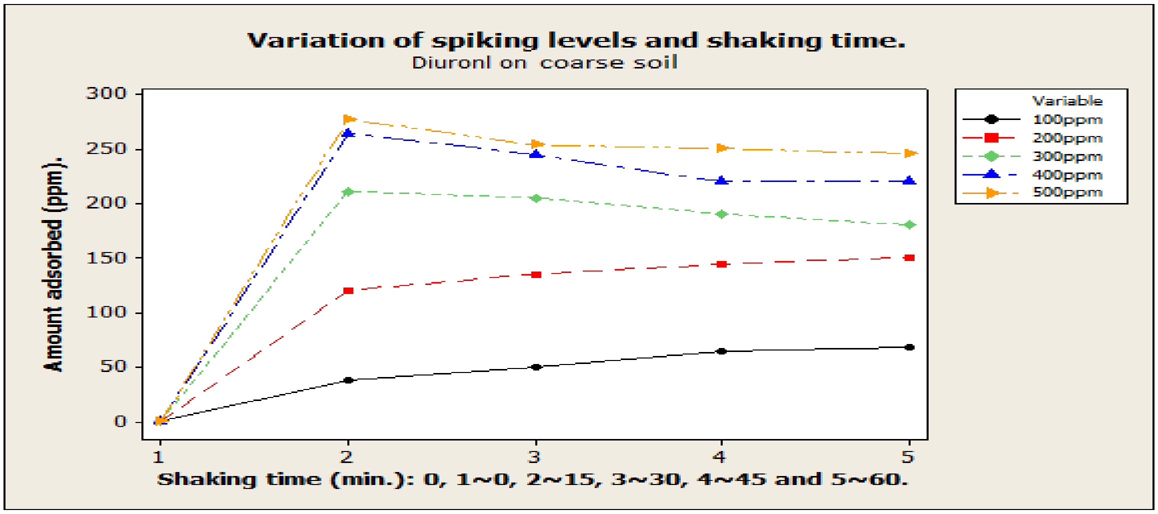


Figure 4.8 (a): Variation of spiking levels and shaking time for carbaryl by Lake Naivasha coarse soil.

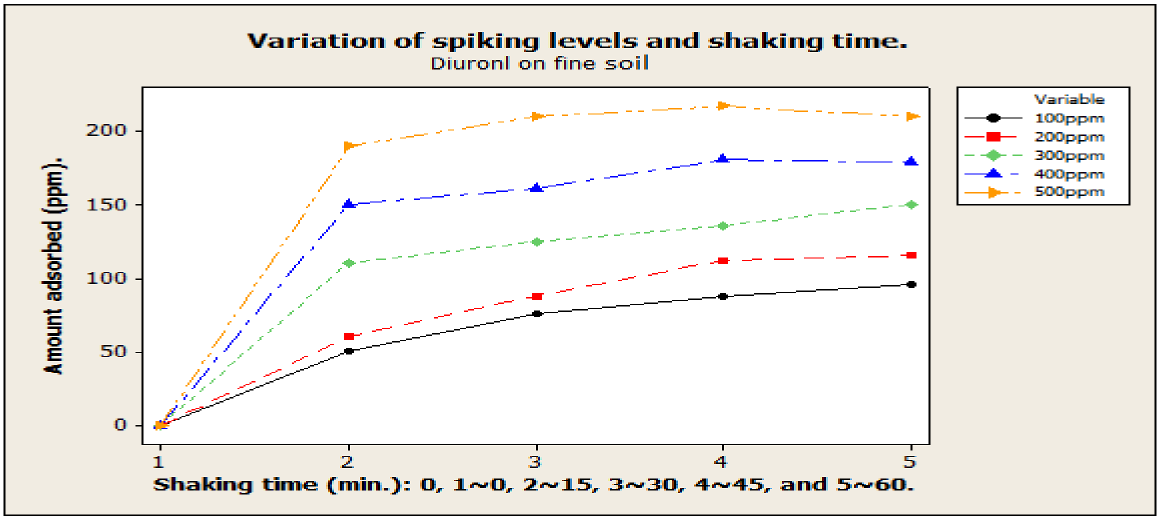


Figure 4.8 (b): Variation of spiking levels and shaking time for carbaryl by Lake Naivasha fine soil.

Plots for diuron also indicate an initial rapid phase, with the amount adsorbed increasing with increase in spiking levels of the pesticide. The equilibration time also depended on the initial concentration of the pesticide with lower concentration having shorter equilibration time interval. Therefore increase in initial pesticide concentration increased the amount of pesticide molecules uptake per unit mass of the soil. Similarly the plots for diuron indicate that the longer the shaking time, the higher the equilibration because of increased pesticide substrate/soil contact adsorption/desorption time.

On considering the assumption that the adsorption of pesticides by colloidal and/or soil particles from a linear model of a binary solution occurs during shaking and that all the adsorbed pesticide goes to the sediment on settling, then the concentration of pesticide adsorbed to the suspended particles $[X]_{ads}$ was obtained by equation 4.2 below:

$$[X]_{ads} = [X]_i - [X]_e \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(4.2)$$

Where $[X]_i$ was the initial pesticide concentration before a known mass of sediment was added and $[X]_e$ was the equilibrium pesticide concentration.

Since not all pesticide was adsorbed, subsequent modification of equation 3.12 for $[X]_{ads}$ becomes:

$$[X]_{ads} = nK'([X]_e + [SX_n]_w)^n \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots..(4.3)$$

from section 2.7 on selected method for sorption measurement.

Hence $[X]_e$ which is the equilibrium pesticide concentration and corresponds to the amount of pesticide not adsorbed or that in aqueous medium is expressed as $[X]_e + [SX_n]_{w.}$ This was determined by only analyzing the concentration of the aqueous /solution layer filtered after the 24 hours equilibration. After analyzing their absorbance, their corresponding respective concentrations were determined from the linear plots of the standards.

On applying equation 3.14 onto the data of Table 4.6 and table 4.7, for 15, 30, 45 and 60 minutes shaking time and a 0.5 g soil quantity, linear relationships were obtained as shown by figure 4.7 for Carbaryl plots and figure 4.8 for Diuron plots.

Generally, greater equilibration occurred under longer shaking times. Increased solute substrate contact time resulted in increased sorption hence for higher concentrations and longer shaking times, more adsorption of the pesticide occurred as expected.

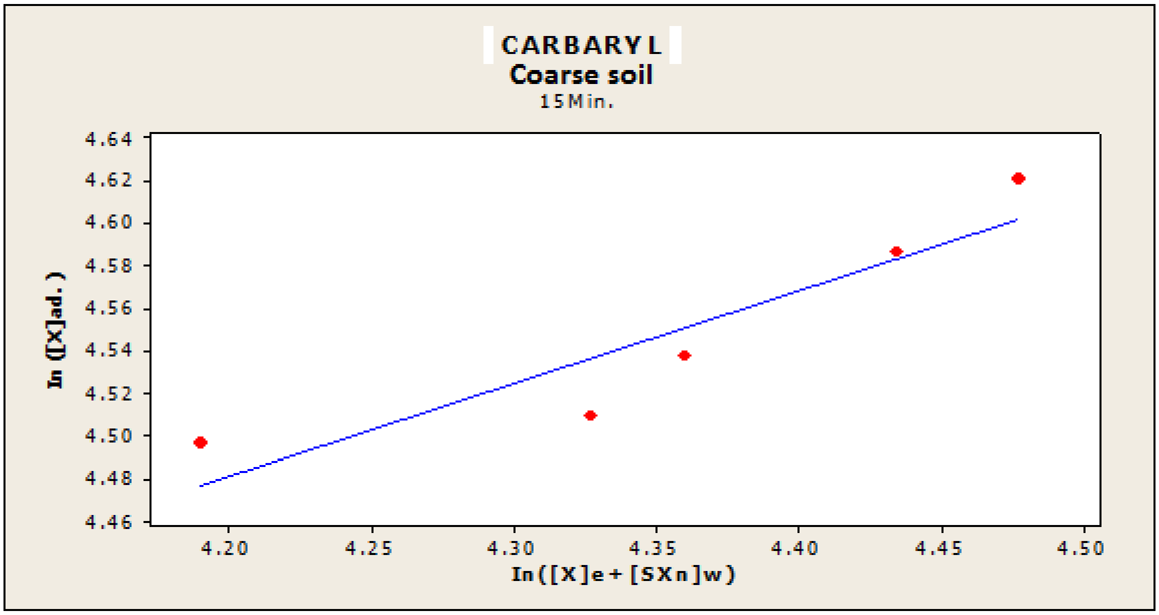


Figure 4.9 (a)i: Adsorption of Carbaryl by Lake Naivasha soil; 15 Minutes, Coarse soil {In($[X]_{ads.}$)=2.224+0.6529 In($[X]_e+[SX_n]_w$)}.

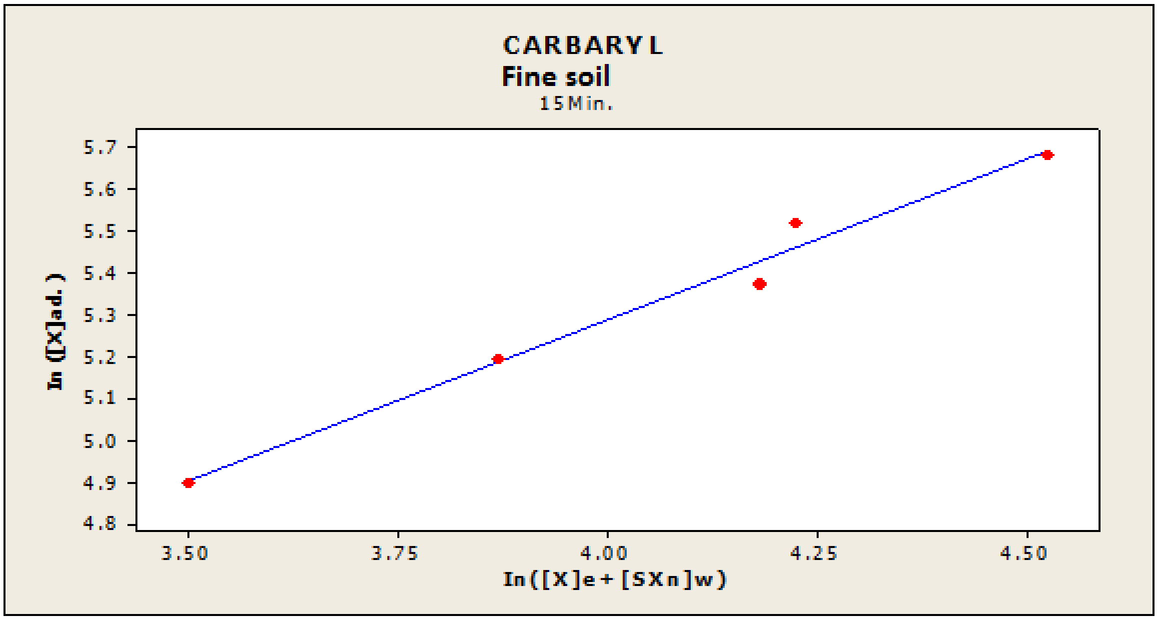


Figure 4.9 (a)ii: Adsorption of Carbaryl by Lake Naivasha soil; 15 Minutes, fine soil {In($[X]_{ads.}$) = 2.198+0.7728 In($[X]_e+[SX_n]_w$)}.

These plots indicated that for 15 minutes, the plot of fine sediment was more linear as compared to coarse soil largely attributed to more adsorption sites on fine sediments leading to better equilibration. This suggests that homogenous sample yields uniform distribution of the adsorbed molecules.

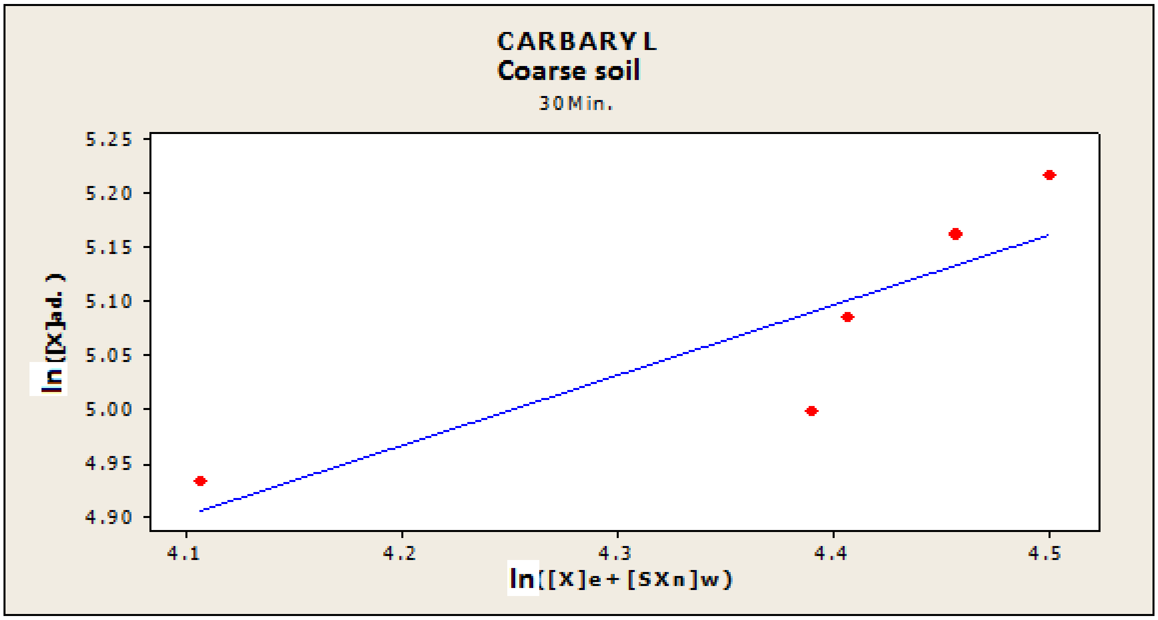


Figure 4.9 (b)i: Adsorption of Carbaryl by Lake Naivasha soil; 30 Minutes, coarse soil {In($[X]_{ads}$.)=2.279+0.585 In($[X]_e$+$[SX_n]_w$)}.

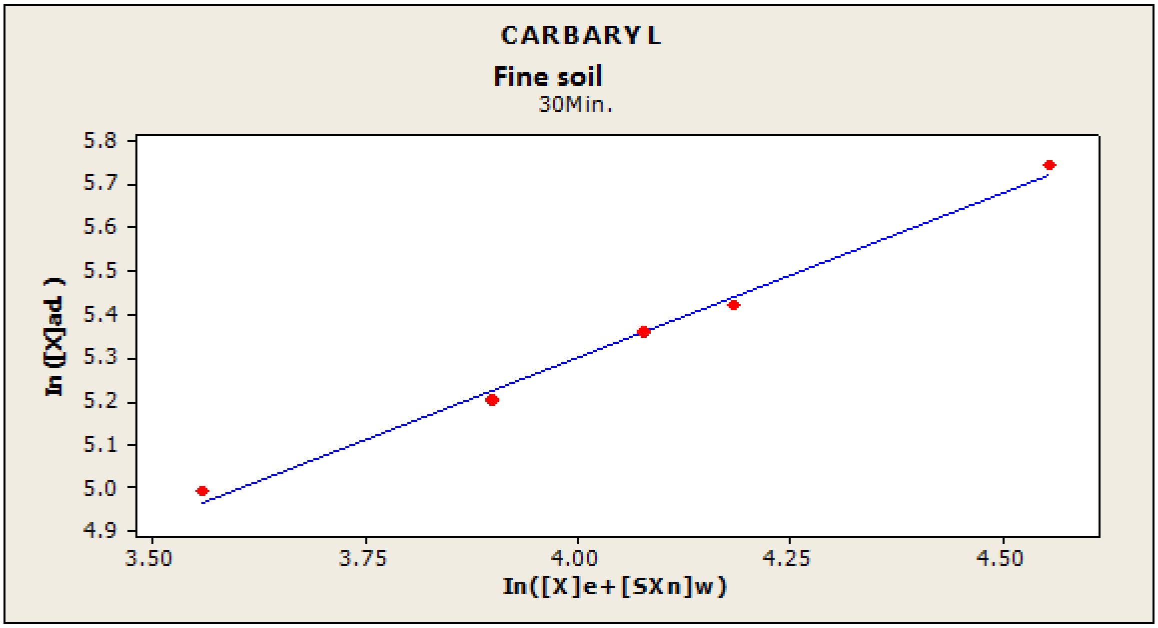


Figure 4.9 (b)ii: Adsorption of Carbaryl by Lake Naivasha soil; 30 Minutes, fine soil {In($[X]_{ads}$.)=2.275+0.756 In($[X]_e$+$[SX_n]_w$)}.

Shaking for 30 minutes indicated that equilibration occurred on the fine soil as indicated from its linear plot.

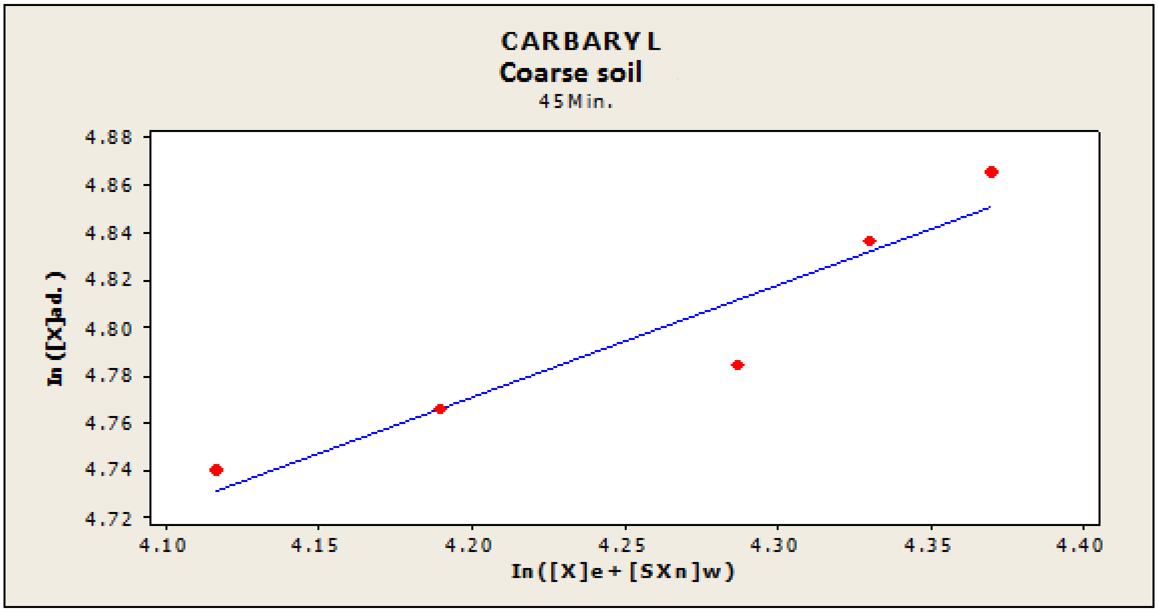


Figure 4.9 (c)i: Adsorption of Carbaryl by Lake Naivasha soil; 45 Minutes, coarse soil {In([X]$_{ads}$.)=2.783+0.4732 In([X]$_e$+[SX$_n$]$_w$)}.

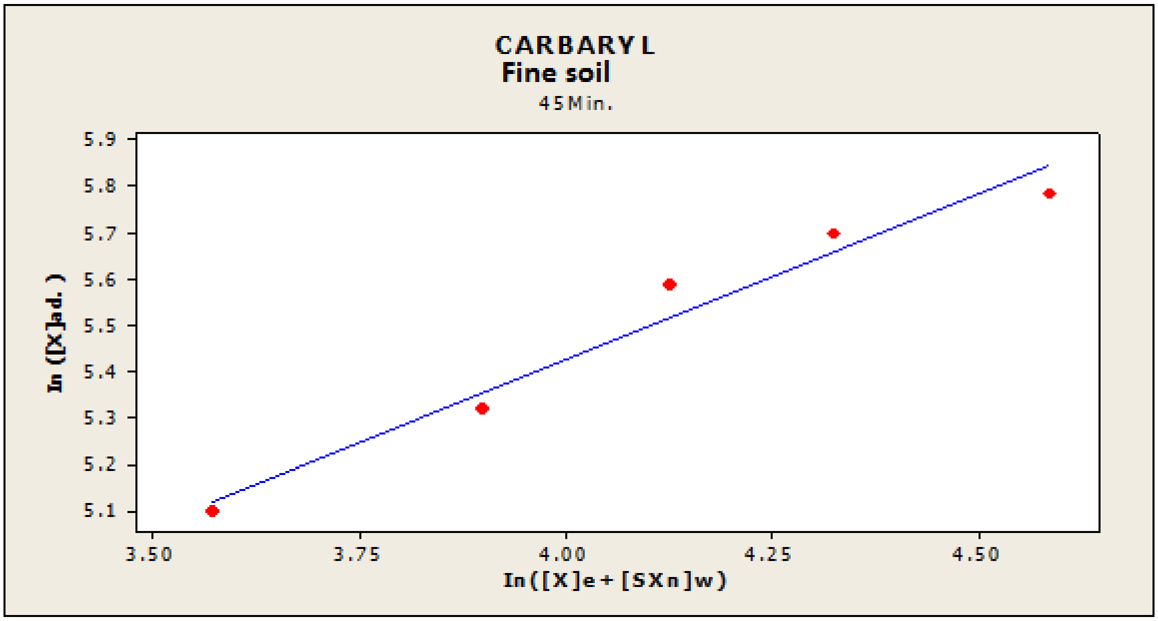


Figure 4.9 (c)ii: Adsorption of Carbaryl by Lake Naivasha soil; 45 Minutes, fine soil {In([X]$_{ads}$.)=2.572+0.7134 In([X]$_e$+[SX$_n$]$_w$)}.

The increased shaking time produced improved linear regression line for both course and fine soil shaken for 45 minutes as compared to shorter durations. More contact time between pesticide and soil and increased contact surface area would account for this as expected, due to effective randomization of the mixture.

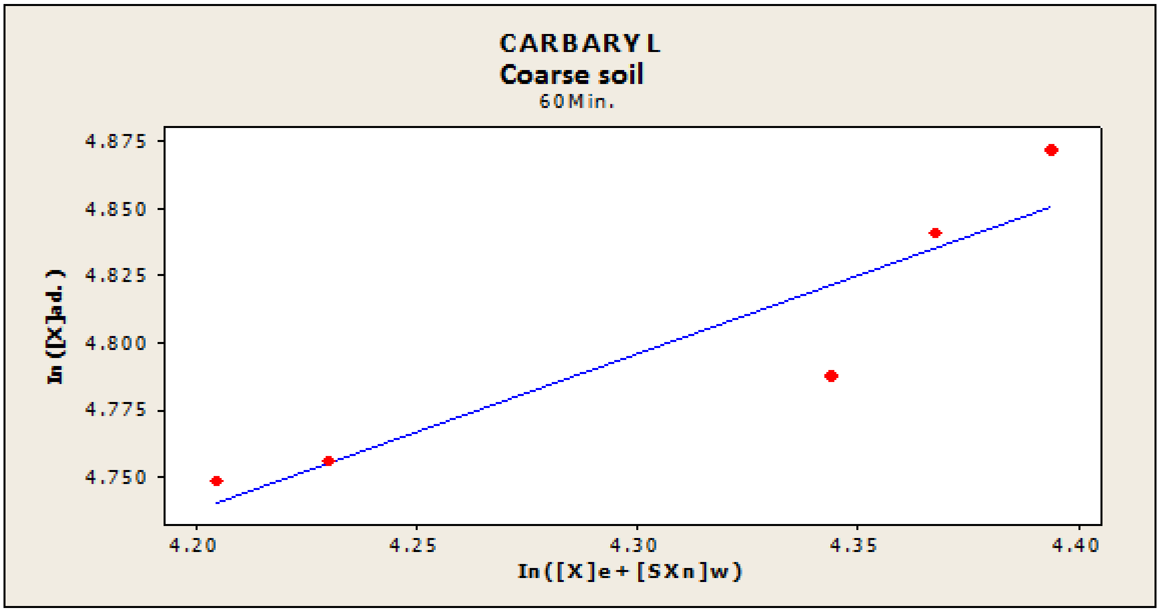


Figure 4.9 (d)i: Adsorption of Carbaryl by Lake Naivasha soil; 60 Minutes, coarse soil $\{In([X]_{ads.})=2.647+0.4367\ In([X]_e+[SX_n]_w)\}$.

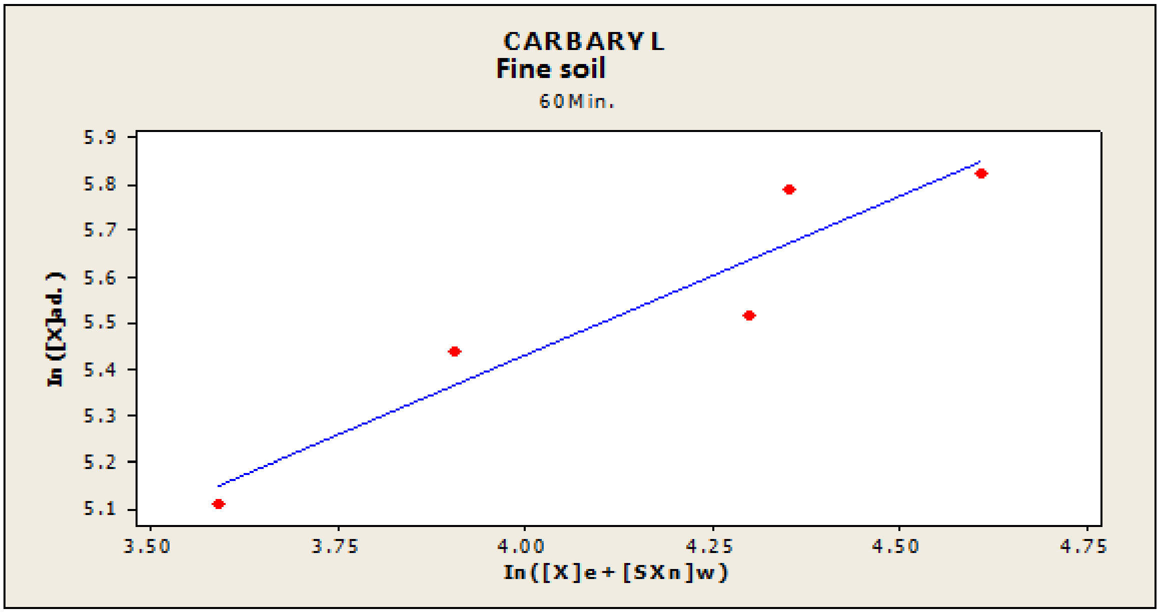


Figure 4.9 (d)ii: Adsorption of Carbaryl by Lake Naivasha soil; 60 Minutes, fine soil $\{In([X]_{ads.})=2.68+0.6862\ In([X]_e+[SX_n]_w)\}$.

The results for the plots obtained after shaking for 60 minutes largely agrees with the expected, keeping all factors constant. Increased shaking time serves to increase the solute substrate contact time which increases equilibration. Still the fine soil plots had a better regression linear plot as expected.

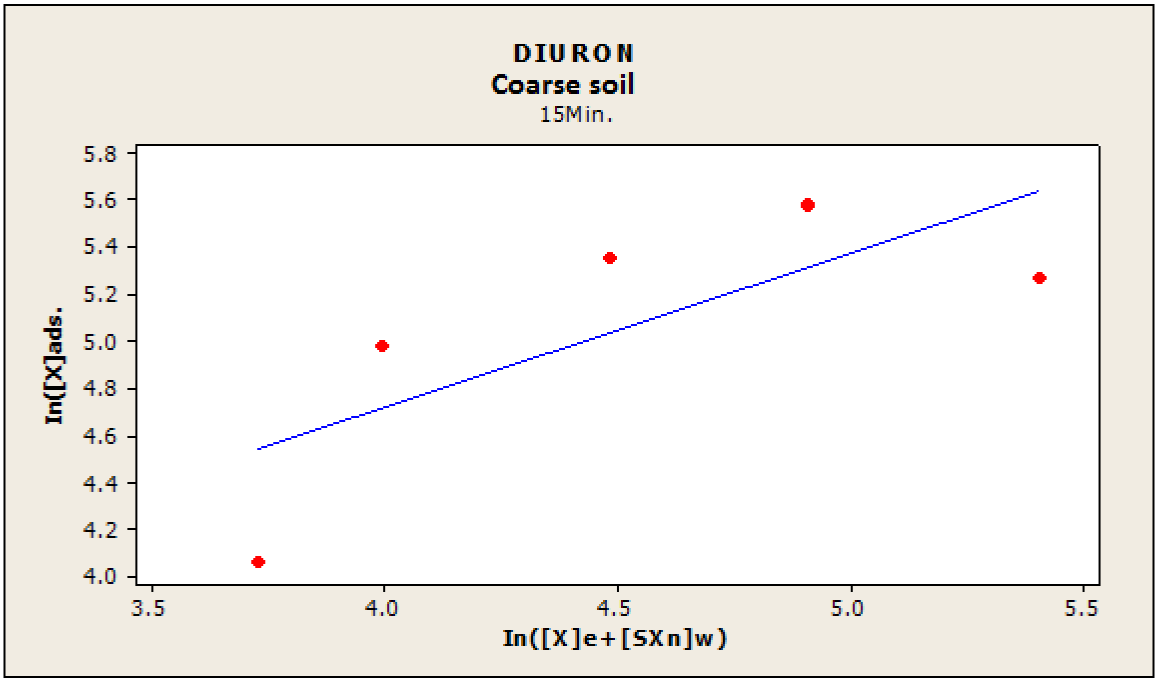


Figure 4.10 (a)i: Adsorption of Diuron by Lake Naivasha soil; 15 Minutes, coarse soil {In($[X]_{ads.}$)=2.105+0.654 In($[X]_e+[SX_n]_w$)}.

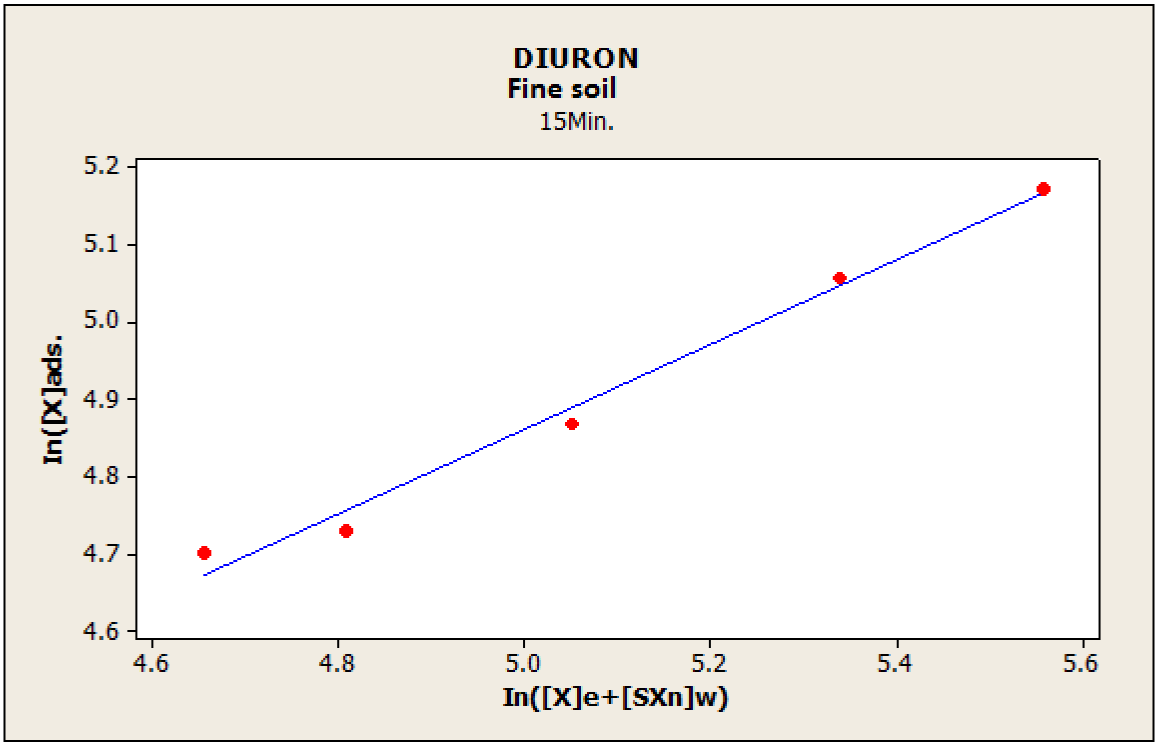


Figure 4.10 (a)ii: Adsorption of Diuron by Lake Naivasha soil; 15 Minutes, fine soil {In($[X]_{ads.}$)=1.954+0.5617 In($[X]_e+[SX_n]_w$)}.

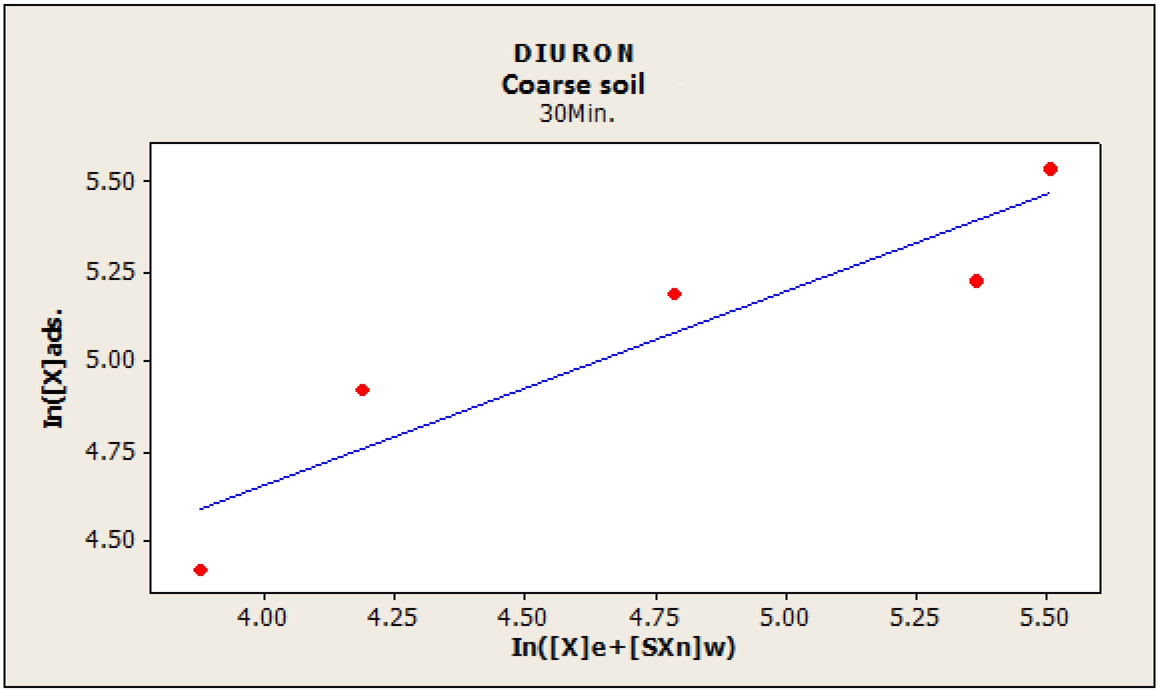


Figure 4.10 (b)i: Adsorption of Diuron by Lake Naivasha soil; 30 Minutes, coarse soil {In($[X]_{ads.}$)=2.469+0.546 In($[X]_e$+$[SX_n]_w$)}.

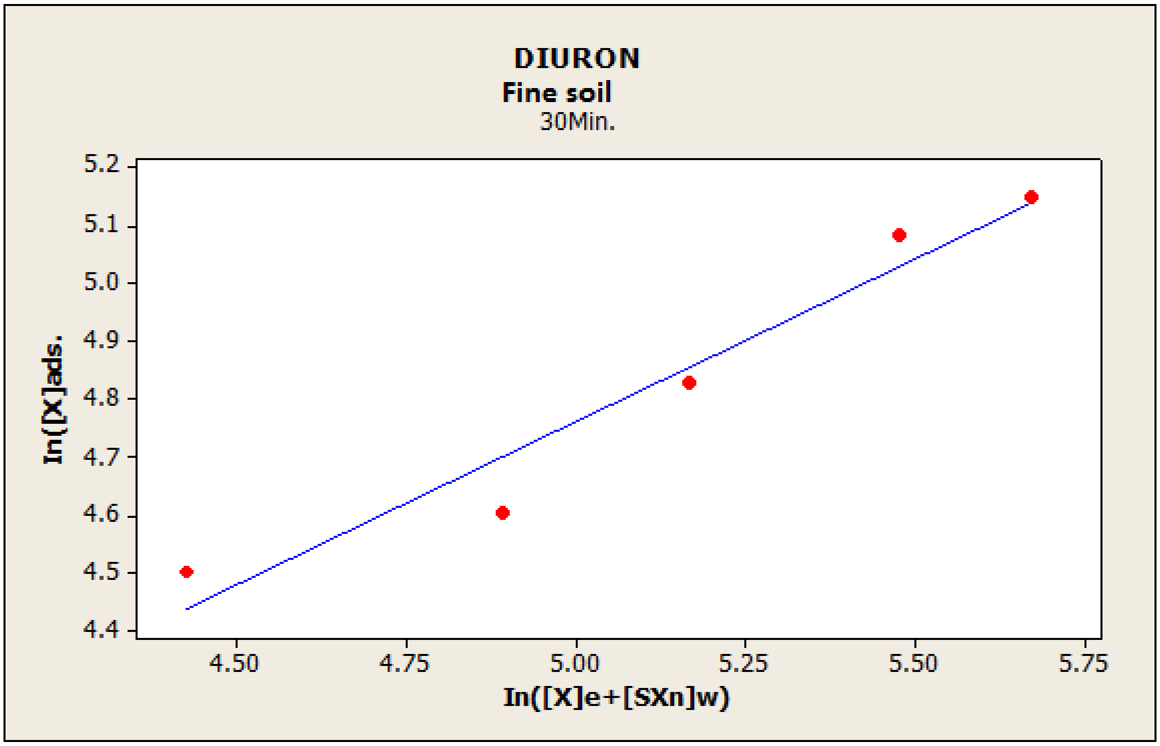


Figure 4.10 (b)ii: Adsorption of Diuron by Lake Naivasha soil; 30 Minutes, fine soil {In($[X]_{ads.}$)=2.722+0.548 In($[X]_e$+$[SX_n]_w$)}.

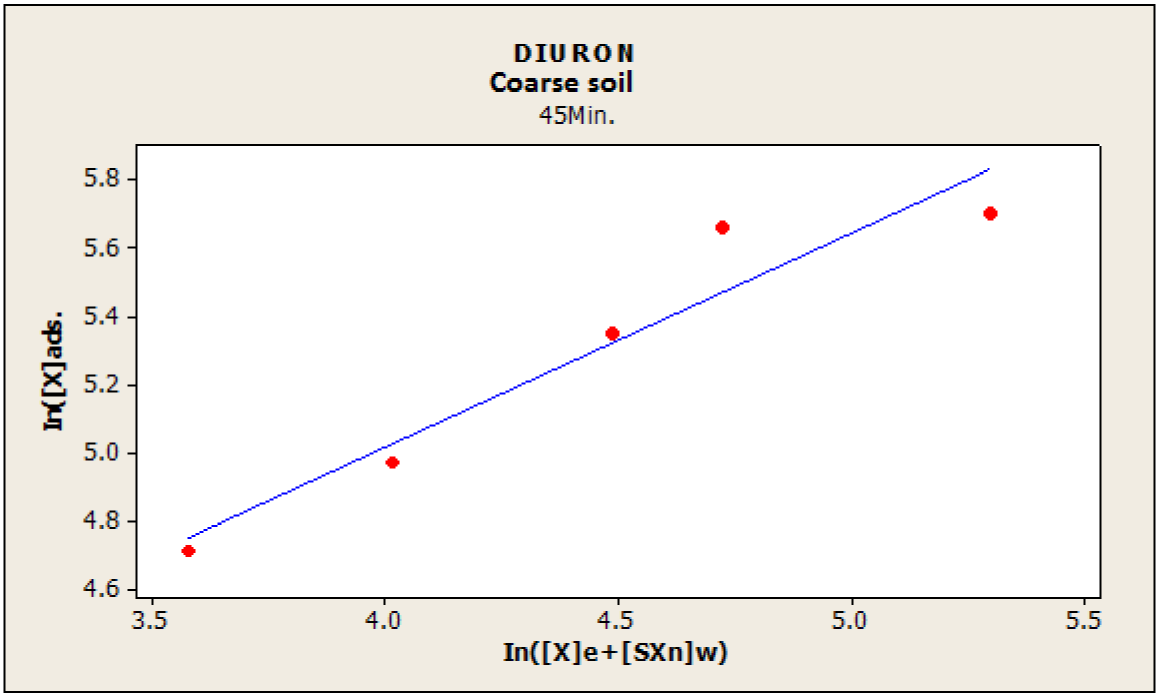


Figure 4.10 (c)i: Adsorption of Diuron by Lake Naivasha soil; 45 Minutes, coarse soil {In([X]$_{ads}$.)=2.508+0.6273 In([X]$_e$+[SX$_n$]$_w$)}.

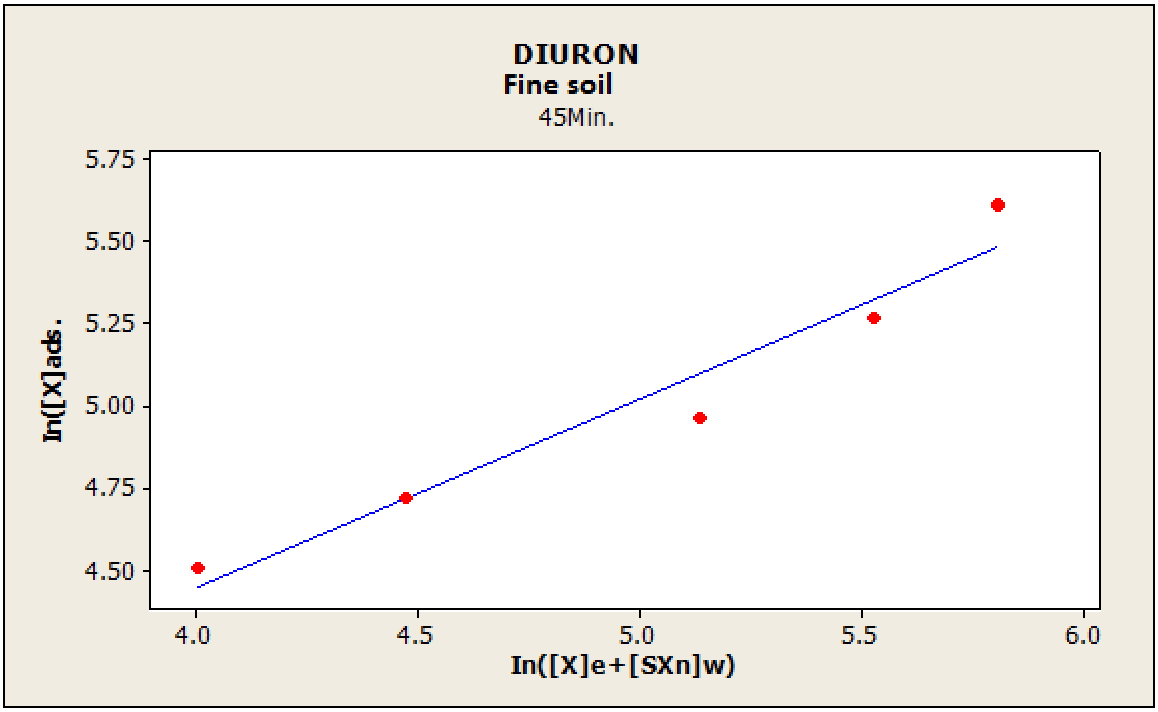


Figure 4.10 (c)ii: Adsorption of Diuron by Lake Naivasha soil; 45 Minutes, fine soil {In([X]$_{ads}$.)=2.142+0.5756 In([X]$_e$+[SX$_n$]$_w$)}.

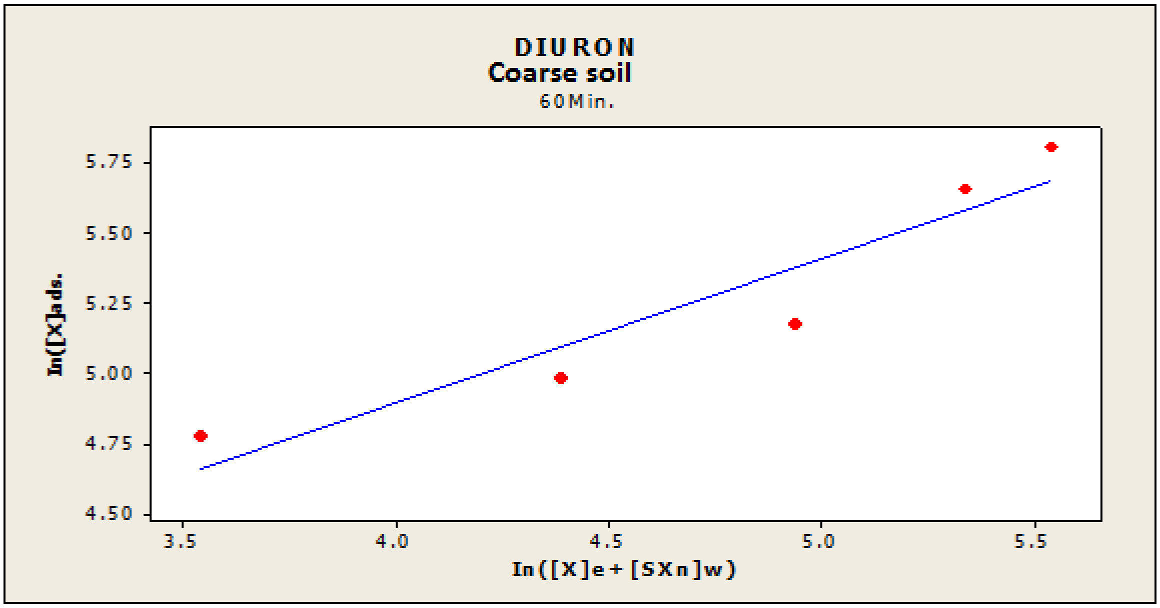


Figure 4.10 (d)i: Adsorption of Diuron by Lake Naivasha soil; 60 Minutes, coarse soil {In($[X]_{ads.}$)=2.842+0.5134 In($[X]_e$+$[SX_n]_w$)}.

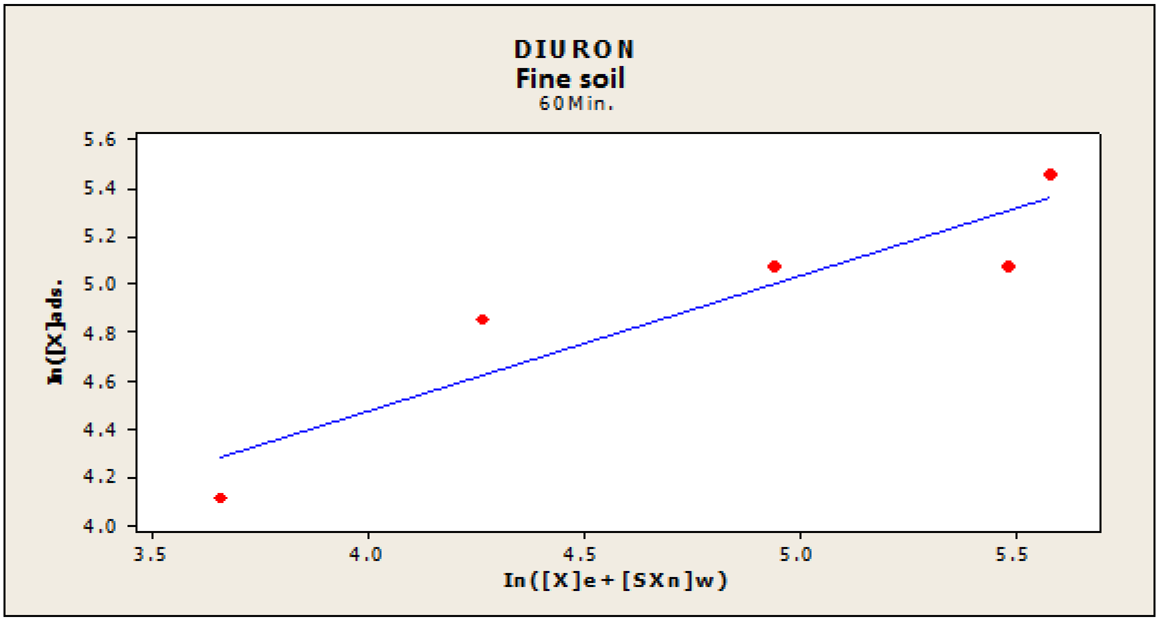


Figure 4.10 (d)ii: Adsorption of Diuron by Lake Naivasha soil; 60 Minutes, fine soil

{In($[X]_{ads.}$)=2.244+0.5585 In($[X]_e$+$[SX_n]_w$)}.

The results for the plots obtained after shaking for 15, 30, 45, and 60 minutes for Diuron largely agrees with the expected results, keeping all factors constant. Increased shaking time serves to increase the solute substrate contact time, which in turn increases equilibration. Still the fine sediments plots had a better regression linear plot than the coarse sediment as expected.

In addition, Diuron plots indicated better sorption outcomes generally compared to Carbaryl, because Diuron has low water solubility and higher molecular mass which increases its retention in the soil-water medium.

4.5: Determination of thermodynamic parameters

From the linear regression lines (Figures 4.7 and 4.8), the values of n, the number of adsorbed molecules and the apparent equilibrium constants were estimated and presented in Table 4.8 for Cabaryl and Table 4.9 for Diuron.

Table 4.8: Values for n, K' and ΔG' for the adsorption/desorption of carbaryl by different soil samples.

	n		ln(nK')		K'		ΔG' (J/Mol)	
Equilibration time(minutes)	Fine soil	Coarse soil	Fine soil	Coarse soil	Fine soil	Coarse soil	Fine soil	Coarse soil
15	0.7728	0.6529	2.4557	2.6503	11.6549	14.1585	-6.0842	-6.5664
30	0.7566	0.5854	2.5539	2.8145	12.8571	16.6848	-6.3275	-6.9731
45	0.7134	0.4732	2.9097	3.5312	18.3513	34.1660	-7.2090	-8.7488
60	0.6862	0.4367	3.0565	3.4755	24.2530	32.3143	-7.5727	-8.6108
Average	0.7323	0.5371	2.7440	3.1179	16.7791	24.3309	-6.7984	-7.7248
Average of Fine and Coarse	n	0.6347	ln(nK')	2.9310	K'	20.5550	ΔG' (J/Mol)	-7.2616

Table 4.9: Values for n, K' and ΔG' for the adsorption/desorption of Diuron by the different soil samples.

	n		ln(nK')		K'		ΔG' (J/Mol)	
Equilibration time(Minutes)	Fine soil	Coarse soil	Fine soil	Coarse soil	Fine soil	Coarse soil	Fine soil	Coarse soil
15	0.5617	0.6540	2.5308	2.5297	12.5634	12.5491	-6.2702	-6.2674
30	0.5480	0.5460	2.7235	3.0741	15.2332	21.6312	-6.7476	-7.6164
45	0.5756	0.6273	2.6943	2.9743	14.7954	19.5765	-6.6753	-7.3691
60	0.5585	0.5134	2.8265	3.5087	16.8863	33.4042	-7.0029	-8.6930
Average	0.5610	0.5852	2.6938	3.0217	14.8696	21.7903	-6.6740	-7.4865
Average of Fine and Coarse	n	0.5731	ln(nK')	2.8578	K'	18.3300	ΔG' (J/Mol)	-7.0803

In the linear plots of Figures 4.7 and 4.8, the y-intercept and the slope gave the values of ln(n $K^{'}$) and n respectively. These were obtained from their respective linear equations given under each plot. Other thermodynamic data is also represented in these respective tables. Average values of the apparent equilibrium constant $K^{'}$ of 20.56 and 18.33 were obtained for Carbaryl and Diuron, respectively. These were determined from equation 3.14 which was represented as:

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

This corresponds to the linear equations of the plots represented in Figures 4.7 and 4.8 whereby In$[X]_{ads}$ is the natural logarithm of the adsorbed pesticide concentration on the soil sediments, In($[X]_e$ + $[SX_n]_w$ is the natural logarithm of the concentration of pesticide not adsorbed on the soil sediments (found in the aqueous medium) as determined before under section 4.4 on variation of spiking levels and shaking time, while n is taken to be the number of adsorbed pesticide molecules per single adsorption site and K' is the apparent equilibrium constant . The value of n was taken to be equivalent to the gradient of the respective plots, while In(nK’) was taken to be the y-intercept for each plot.

Since:

$$\text{In}(nK') = \text{In } n + \text{In } K \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(4.4)$$

Then:

$$\text{In } K = \frac{\text{In}(nK')}{\text{In } n} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(4.5)$$

Which were used to generate the values of K that was taken to be the apparent equilibrium constant , K’.

The values of n and $\Delta G^{'}$ calculated for Carbaryl were 0.63 and -7.26 kJ/mol respectively, while those of Diuron were 0.57 and -7.08 kJ/mol, respectively.

Sample calculation of n and K’ for carbaryl based on figure 4.9(a)i was shown as:

The equation of the linear regression plot is given as $\text{In}([X]_{ads.})=2.224+0.6529\ \text{In}([X]_e+[SX_n]_w)$, which is comparable to equation 3.15. Hence In(nK’) = 2.24 as obtained from the y-intercept, while the gradient gave the value of n as 0.6529, thus In0.6529+InK’=2.224 , meaning InK’=2.65033, which in turn gave the value of K’ as 14.1587

ΔG’, the apparent Gibbs free energy, was determined from:

$$-\Delta G = RT\ \text{In } K' \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(4.6)$$

Where R is the universal gas constant (8.314 JK/mol), T is the temperature in kelvin (298K), and K’ is the apparent equilibrium constant.

Sample calculation of $\Delta G^{'}$ for carbaryl based on figure 4.9(a)i was shown as:

From the equation of the linear regression plot, K' calculated was 14.1587, hence

-ΔG = RT In K was expressed as -ΔG =8.314x298xIn14.1587 which gave the value of

ΔG to be -6.5664 JK/mol.

The negative apparent Gibb's free energy values depict a spontaneous adsorption process. Since the values are below 20.00 kJ/mol expected for cases where strong interaction forces are involved one may conclude that the adsorption of these pesticides in the sediments involves a physisorption process. These negative Gibbs free energy values are in line with other similar researches done. Hulscher and Cornelissen, 1996, found that sorption of organic pollutants occurs when the free energy of the sorption exchange (ΔG) is negative. This can be due to the affinity of chemical species for the absorbing surface relative to its affinity for the solvent or the change in randomness or disorder of the system upon sorption which attributes to the physisorption process.

The values of n and $K^{'}$ obtained for these pesticides differ slightly from those reported for Amitraz (0.26±0.03 for n and 111±19 for K') [Zaranyika et. al.…1998]. Such variations may be attributed to among other factors the different chemical structures of the pesticides involved, differences in the nature of soil particle and morphology.

As explained earlier, the exponent n is the number of pesticide molecules associated with a single adsorption site, S, to give the pesticide-site complex $SX_{n.}$ The value of n of 0.63 for Carbaryl and n of 0.57 for Diuron suggests that each molecule of the pesticide is associated with a single adsorption sites. The major adsorption interactions which bind small organic molecules in the soil particles of colloidal dimensions range from 1nm to 1mm [Burchill et al., 1981]. Further on combining equation 3.11 and 3.14 we obtain equation 4.7 which gives the relationship between the apparent equilibrium constant, K', and the true equilibrium constant, K:

$$K' = K[X]^n{}_e / \left([X]_e + [SX_n]_w \right)^n \text{...}(4.7)$$

It is apparent that the extent to which K' deviates from K depends on the value of $[SX_n]_w$ and the value of n.

Desorption is a special case of thermal dissociation, hence we can use transition state theory to obtain the apparent desorption rate constant, $K_d{}^{'}$, in terms of the apparent adsorption/desorption equilibrium constant, K', thus [Benson, 1960]:

$$k'_d = \frac{kT}{h} K' \quad \text{……………………………..}(4.8)$$

$$K_d{}^{'} = (kT/h)K'. \ . \ \text{….……………………..} \ (4.9)$$

Where; k is the Boltzmann constant, T is the absolute temperature and h is the planks constant.

But the apparent desorption rate constant K'_d is given by:

$$K'_d = [X]^n [S] / [SX_n] \text{.................................}(4.10)$$

The mean apparent lifetime of a molecule of Carbaryl in adsorbed state under aerobic soil condition is 15.5 days and that of Diuron is 337 days as obtained from Table 2.2 by taking the average for aerobic soil half-lives. Such short apparent life time of the adsorbed state points to physisorption, rather than chemisorption, as suggested by the ΔG results, obtained in this work.

Also, the K'_d value is a measure of how tightly the pesticide binds/sticks to sediment particles. The greater the K'_d value, the less likely a chemical will leach or contribute to runoff. A very high value means it is strongly adsorbed onto soil and organic matter and does not move with the surface or river running water. In this case, the soil acts as a sink for the pesticide residues and thus reduces the extent of pesticide contaminant down- stream. Pesticides are less likely to leach out or occur as surface runoff when the K'_d is greater than 5 [Burchill., et al., 1981].

As noted earlier, this research work is presented based on the adsorption model of a binary dilute solution, linked to the Freundlich empirical isotherm. This is mainly due to its empirical simplicity since just a single parameter can be used to predict sorption of a given compound to any soil and the soil adsorption coefficient values for different compounds closely correlate with the physicochemical properties of the organic solute. However, this model is unable to account for complex sorption aspects like contribution of minerals to sorption, variability of the soil adsorption coefficient values between soils, and non-linear sorption isotherms.

Thus, it is recommended that other models like the Langmuir adsorption model, Redlich-Peterson model and the Polanyi-Manes adsorption models could be used for confirmation purpose.

CHAPTER FIVE

CONCLUSION AND RECOMMENDATIONS

5.1: Conclusion

From the above studies, there is existence of adsorption/desorption processes of Carbaryl and Diuron by the Lake Naivasha sediments. The adsorption of these pesticides onto suspended/dissolved particles increases with increase in mass of the substrate (soil). For Carbaryl, Table 4.4 and Figure 4.5 indicates this, with a relatively lower adsorption having averagely 8% percentage deviation between the highest and the lowest concentrations adsorbed by the sediments. On the other hand, for Diuron, Table 4.5 and Figure 4.6 indicates a relatively higher average percentage deviation of 61.68% between the highest and lowest concentrations adsorbed by the soil, values obtained by taking the average difference between highest and lowest adsorbed pesticide expressed as a percentage of the lowest values respectively. This indicates that Diuron is more adsorbed on the Lake Naivasha sediments as compared to Carbaryl under the same experimental conditions.

In this study, it was found out that several factors like spiking levels and contact time affect the Carbaryl and Diuron adsorption/desorption processes. From Table 4.6 and Figure 4.7 for Carbaryl and Table 4.7 and Figure 4.8 for Diuron, it was observed that greater equilibration occurred under longer shaking times. This was largely due to increased duration for solute-substrate interaction which in turn increased the rate of adsorption. Higher concentrations translated to increased number of pesticide molecules available to be sorbed per single adsorption site according to the Linear adsorption model of a binary solution.

Negative ΔG' obtained in these studies is an indication of spontaneous adsorption process but at the same time the low free energy values are indications that the pesticide molecules were simply physisorbed onto the sediment adsorption sites. The high clay content coupled with the small amount of organic carbon in the sediment may be among the factors that account for the observed adsorbed pesticides aspects. Adsorption of Diuron was higher than that of carbaryl and is highly co-related with soil organic matter. However, relative to Carbaryl, Diuron is generally considered more persistent in the environment. The data of the present work supports this. They have frequently been detected in both ground and surface water, and are regulated as known ground water contaminants in most places. Since Diuron has a low Henry's law constant and a low vapor pressure, its volatilization is considered insignificant. This indicates that the increased use of these pesticides can significantly cause environmental pollution either from their parent compounds or either from their respective metabolites. Comparatively, Diuron and its related formulated products such as bromacil, hexazinone and paraquat are considered more persistent than Carbaryl, hence causing more environmental contamination and pollution.

5.2: Recommendations

As a result of this work done on adsorption of carbaryl and diuron on lake Naivasha region soil where their active ingredients are mostly used in combination with other pesticides or chemical subatances, it is recommended that:

i)These pesticides, if they have to be used, should be highly regulated since they are relatively effectively adsorbed. Their aerobic degradation in the soil is much faster than in water medium hence are likely to have minimum contamination in soil as compared to aquatic environment. From this study, Diuron is more persistent to the environment as compared to Carbaryl, hence it should be applied after heavy rains to minimise the risk of crop damage.

ii)The national or county government should enact legistation to minimise or prevent effluent from the flower farms and processing units neighbouring the lake from being directly disposed into the lake or its water channels.

iii)Effective waste water treatment process should be put in place to treat the water and other discharg originating from the flower farms and their processing units to minimise or eliminate the pesticide components and other organic wastes before mixing with the main water lake.

iv)The environmental authorities sould either regulate or ban the direct use of diuron and its related chemicals near lake Naivasha.

v)Education/awareness to the concerned parties (farmers, horticulturists etc.) on different properties of the pesticides and their potential effects on the environment would likely minimise their contamination and pollution effects.

vi)These results obtained could be used as a precedent in further studies of the pesticides, in determining further apparent thermodynamic properties or otherwise. In addition, these results could be used in determining the best conditions and soil types under which these pesticides adsorbs effectively, and hence applied in better usage with minimum environmental harm.

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APPENDIX:

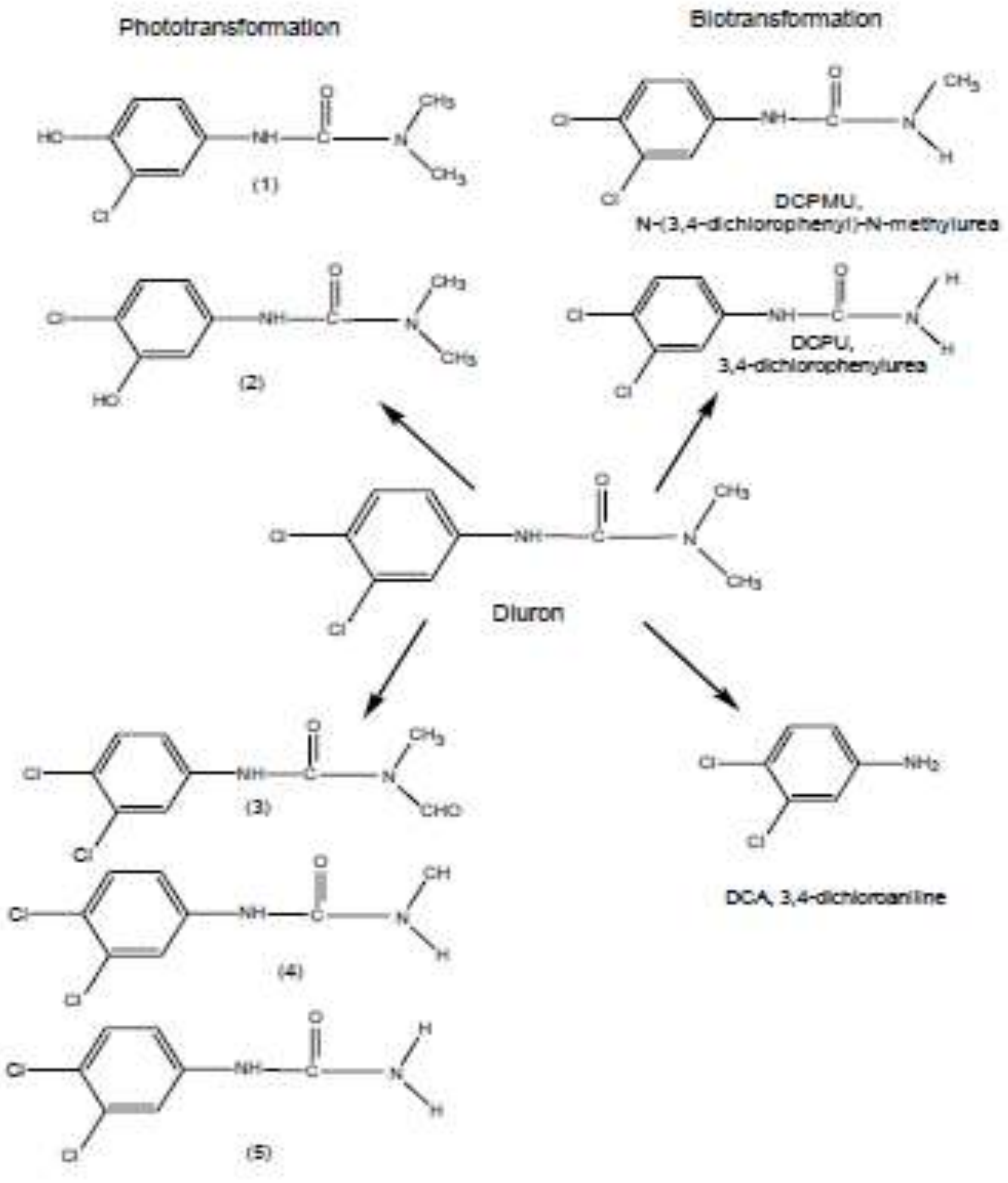

Fig 2.4 (a): General scheme of the photo degradation and biotransformation of Diuron (Bonnemoy et al., 2001).

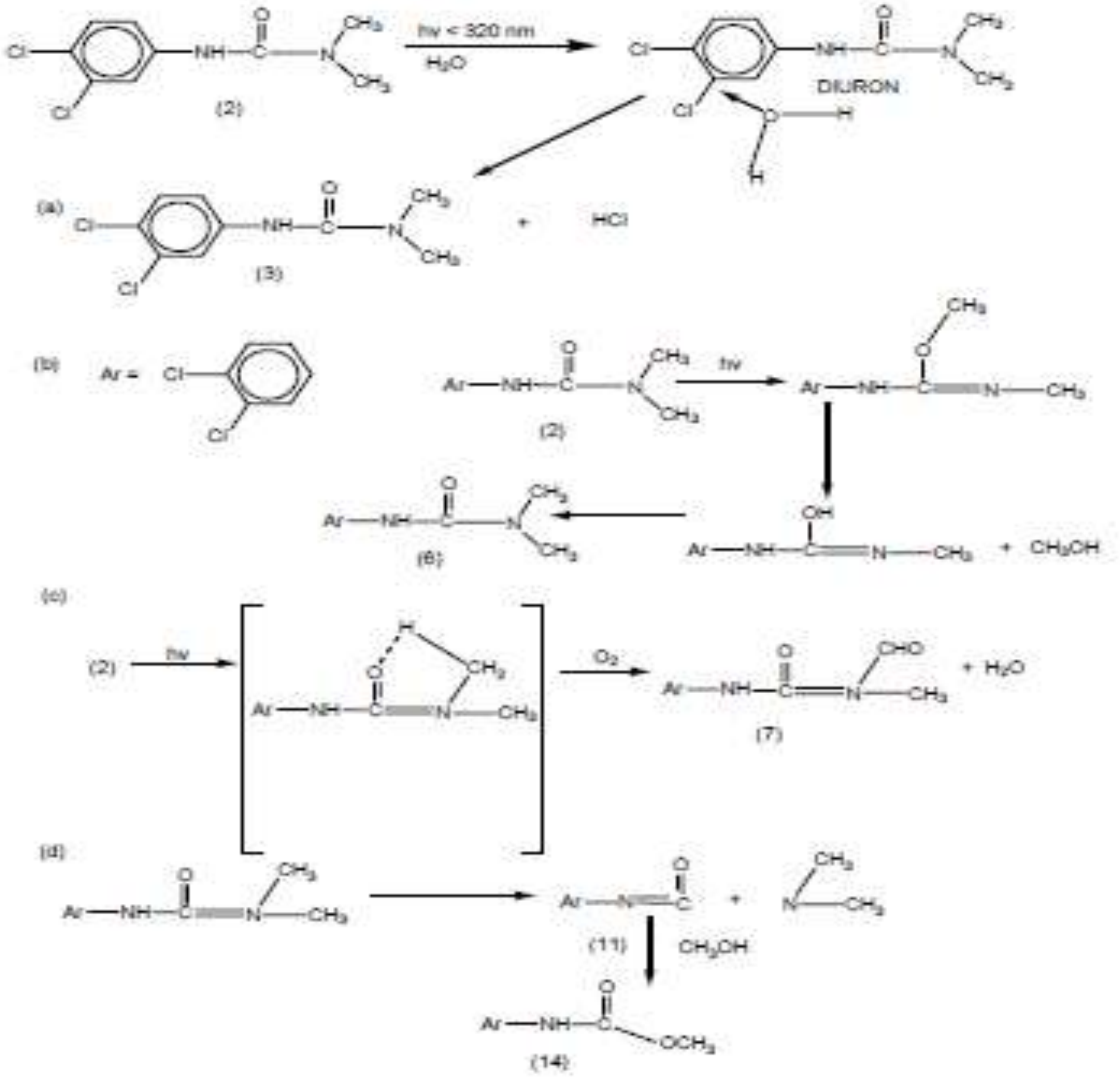

Fig. 2.4(b) Routes of formation of photoproducts of Diuron (Boule et al., 1997).