PROFILING OF PESTICIDE RESIDUES IN MOBEGO-KABIANGA WETLAND ECOSYSTEM AND ITS RETENTION EFFICIENCY

WELDON KIPKOECH

A Thesis Submitted to the Board of Graduate Studies in Partial Fulfillment of the Requirements for the conferment of Degree of Master of Science in Chemistry of the University of Kabianga

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DECLARATION AND APPROVAL

Declaration

I declare that this thesis is my original work and has not been presented for the conferment of degree or diploma in this or any other university

Signature………………………………. Date………………………….

Weldon Kipkoech

PGC/CHE/006/16

Approval

This thesis has been submitted for examination with our approval as the University supervisors:

Signature……………………………… Date…………………………………

Dr Shadrack Mule

Department of Physical Sciences

University of Kabianga

Signature……………………………… Date…………………………………

Dr Phanice Wangila

Department of Physical Sciences

University of Kabianga

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DEDICATION

I dedicate this work to Joyce Cherono Bett.

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First, I thank God for granting me good health throughout my study. I also thank the University of Kabianga for giving me opportunity to do the study. Moreover, to my supervisors Dr. Shadrack Mule and Dr. Phanice Wangila, am very thankful for their guidance in research and writing of this thesis. I also register my sincere appreciation to staff members, the University of Kabianga, School of Science and Technology, Department of Physical Sciences for their unsolicitated concern over my progress throughout my study. Finally, to Joyce Cherono Bett, my family and friends am very grateful for their financial and moral support.

ABSTRACT

Wetland ecosystems play a critical role in the environment. It provides global significance environmentally, economically, and socially. Wetlands have several important functions which include storage of carbon, storage of nutrients, retention of sediments and pollutants. Wetlands also serve as sinks and transformators in water and nutrient cycle. The unrestricted use of natural wetlands has posed a great concern as these wetlands acts as sinks for point and non-point sources of pollution in surface water runoff from municipal and agricultural sectors. These pollutants can have adverse effects on the working of the wetland in terms of retention and removal of such pollutants. Therefore, this study was undertaken to profile pesticide residues in Mobego-Kabianga wetland ecosystem. In addition, the retention efficiency of pesticide residues was also investigated. Values of physical-chemical parameters including pH, Total Dissolved Solids (TDS), Total Suspended Solids (TSS), temperature, conductivity, dissolved oxygen (DO) and flow rate were measured *in situ* at the inflows, midpoints and at outflows to the wetland ecosystems using Lab Quest vernier caliper instrument. Water, soil/sediments and selected plant materials samples were collected and analyzed for residual pesticides using coupled Gas Chromatography - Mass Spectrometric/Mass Spectrometric (GC-MS/MS) and Liquid Chromatography - Mass Spectrometric/Mass Spectrometric (LC-MS/MS) methods. All results were recorded and analyzed for measure of central tendencies using SAS statistical system version 9.4. From the study, levels of physicochemical parameters ranged from 0.259-1.079 m/s (flow rate), 0.233-10.03 mg/l (dissolved oxygen), 592-764 µs/cm (conductivity), 17-20 ^{o}C (temperature), 6-8 (pH), 384-1646 mg/l (TDS) and 700-910 mg/l (TSS). Variation in the levels of physico-chemical parameters was noted with $p \leq 0.05$. However, TSS was found to have no significant difference with $p=0.06$. In analysis of residual pesticides, 24 prominent residual pesticides were detected and quantified by GC-MS/MS and LC-MS/MS and they include: diazinon, dimethoate, chlorpyriphos, malathion, methidathion, aldrin, BHC, chlordane, DDT, DDD, DDE, metachlor, alachlor, dieldrin, metolachlor, aldicarb, carbaryl, carbofuran, methiocarb, methomyl, deltamethrin, tetramethrin, pyrethrin and cypermethrin. Their levels ranged from 0.001 to 0.861 ppb in water; 0.001 to 0.501 ppb in sediments and 0.001 to 0.466 ppb in plant materials. The calculated retention efficiency was 85 %. However, cypermethrin and dieldrin recorded negative retention efficiency. Significant variation was observed in levels of physicochemical parameters, residual pesticides and retention efficiencies of the wetland ecosystem. It is recommended that a study be carried out to develop environmentally friendly molecules which can be used for pest control and management practices with an aim of protecting wetland ecosystems from effects of chemical pesticides and hence improve retention efficiencies of natural tropical wetland ecosystems.

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LIST OF ABBREVIATIONS ACRONYMS AND

BHC	Benzene Hexachloride
DDD	Dichlorodiphenyldichloroethane
DDE	Dichlorodiphenyldichloroethylene
DDT	Dichlorodiphenyltrichloroethane
FNU	Formarin Nephelometric Units
GC-MS/MS	Gas Chromatography- Mass Spectrometric/Mass Spectrometric method
LC-MS/MS	Liquid Chromatography - Mass Spectrometric/Mass Spectrometric method
IUPAC	International Union of Pure and Applied Chemistry
NTU	Nephelometric Turbidity Units
PCPB	Pests Control Product Board of Kenya
pH	Potential of Hydrogen
POPs	Persistent Organic Pesticides
WHO	World Health Organization
TSS	Total Suspended Solids
TDS	Total Dissolved Solids
SAS	Statistical Analysis System

DEFINITION OF TERMS

Wetland	Land that is saturated by water either permanently or seasonally.
Retention efficiency	Ability of the natural wetland to retain pollutants emanating from agricultural farms and those from domestic uses.
Pesticide	Chemical substance that is used to destroy insects and other organisms which are harmful to plants or animals.
Pesticide residues	Pesticides that remain on or in food after being applied to food crops.
POPs	Persistent Organic Pesticides which resist biodegradation and therefore they accumulate in the environment through food chain.
Organochlorine pesticides	Persistent organic pollutants containing at least one covalently bonded atom of chlorine as the dominant functionality that are extremely hydrophobic and strongly adsorbed by soil as the K_{oc} values indicate. It is used in agriculture to destroy insects.
Organophosphate pesticides	General name for esters of phosphoric acid. Organophosphates are the basis of many insecticides, herbicides and nerve agents. It has phosphate as the dominant functionality.
Carbamate pesticides	Organic compounds which are derived from carbamic acids (NH_2COOH). They are used in agriculture to kill insects.
Pyrethroid pesticides	Class of pesticides in which its active ingredient is derived from plant known as pyrethrum. They are used to kill insects in

	agricultural farms.
Mass transport	Movement of pollutants in an environment.
Advection	Transport of pollutants in the direction of fluid flow.
Diffusion	Movement of pollutants against a concentration gradient.
K_{oc}	Pesticide soil/water partition coefficient which measures the adsorption degree of pesticide to the soil organic matter. High K_{oc} values indicate a strong adsorption to the soil and low K_{oc} values indicates low adsorption of pesticide to the soil.
K_{ow}	Pesticide octanol/water partition coefficient which measures how hydrophilic or hydrophobic a pesticide is. High K_{ow} indicates that the pesticide compound is highly hydrophobic and will partition more on soil than water. Low K_{ow} values indicate that the pesticide is highly hydrophilic and they tend to be more soluble in water.

CHAPTER ONE

INTRODUCTION

1.1 Overview

This chapter gives information on the background of the problem, statement of the problem, justification of the problem, objective of the work and hypotheses. It will also highlight the main aim of the study as well as the scope of the study.

1.2 Background of the study

Wetlands as defined by Ramsar treaty in its article 1.1 is an area of marsh, peat land, whether temporary or permanent, artificial or natural, with static or flowing water, salty or fresh in which it does not exceed six meters at low tide, (Keddy, 2010). In 1990, Kenya joined the Ramsar treaty and has since identified Lake Nakuru and Lake Naivasha as the Ramsar sites of international importance (Akerblom *et al.*, 2008).

Wetlands have been viewed by the society as areas of draining wastes in order to fulfill economic purposes, but recently the idea has changed to holistic view which regards wetlands as important multifunctional ecotones between aquatic ecosystems and terrestrial ecosystems which provides global significance both environmentally, economically, and socially. Wetlands have several important functions which include storage of nutrients, ground water recharge, shoreline stabilization, storm protection, flood mitigation, control of erosion, retention of carbon, sediments, pollutants, and nutrients, (Birch and Taylor, 2000). Wetlands also have economic values which include forestry, peat cutting, mat making and fishery. Furthermore, the wetlands also provide indirect ecosystem services as pollutant and nutrient abatement for global climate regulation, (Birch and Taylor, 2000). Some wetlands also provide recreational activities to tourism as an important socio-economic factor.

National Wetland Conservation and Management policy (2013) has been cited in Kenya which aims at: conserving the remaining wetlands against present and future threats and implementation and restoration of degraded wetlands. The Ramsar convention on wetlands is accepted internationally for world-wide wetland planning and conservation basing on nature of biodiversity and conservation, (Kivaisi, 2001). Wetlands serves as sinks and transformators in water and nutrient cycle at landscape level as expressed by water authorities in many official documents for instance, the United States Clean Water Act or the Agenda 21, the proposed European Water Framework, Directive European Nitrate Directive, (Said *et al.*, 2012).

The Ramsar international wetland conservation treaty was developed and adopted by participating nations in 1971 and 1975 respectively as quoted by Henry and Kishimba (2006) and addressed the global concern regarding wetland degradation and loss. The purpose of Ramsar convention treaty was to promote wise use of the wetlands and to list the wetlands of international importance with objective of wetland conservation. The protection and conservation methods include restricting access to wetland ecosystems, educating the public to combat the myths and misconception that wetlands are wastelands, (Haarstad and Braskerud, 2005).

According to Kenya National Environment Action Plan (2016-2022), the substantial proportion of Kenya’s water resources are found in wetlands and cover about 2 % to 3 % of the country’s surface water, (Ogwok *et al*., 2009). The following are list of wetlands found in Kenya: Lake Baringo, Lake Bogoria, Lake Elmentaita, Lake Naivasha, Lake Nakuru and Tana River Delta

Ramsar Site as reported in the Ramsar list established in response to Article 2.1 on the convention on wetlands. The Ramsar list also include seasonal and temporary wetlands which are found all over the country including springs in the southern parts of Nairobi, west of Ngong hills, Limuru and rock pools. Man-made wetlands include wetlands created for purposes of wastewater treatment, dams, primarily meant for hydropower and water supply, (Sakané *et al.*, 2011).

Wetlands play critical ecological role and as resource for economic, cultural and scientific value. Among the critical values is provision of habitats for a wide range of fauna and flora, provision of water for human, livestock and wild animals' consumption as well as provision of water for agricultural activities respectively (World Wetland Day, 2015). They recharge springs and wells, for livestock and wildlife support systems. Recharging of springs and wells raises the water table and makes the ground water easily accessible. Among other benefits of wetlands include generation of products like fire wood, building materials, honey, medicine natural foods and fisheries activities. They are also the source of pasture during the drought seasons, (Roggeri, 2013). However, poor government policies, population pressure due to increase in human population and immigration, uncontrolled urbanization and industrialization, intensification of agriculture and destruction of forest following an increase in human population, expansion and an urge for growth of economy, over-exploitation of resources, conversion of these wetlands into farms and excessive extraction of water especially during the dry season are the factors that are threatening the survival of the wetlands.

Several pesticides of varied chemical nature are used currently for health, agricultural activities and municipal purposes all over the world and because of their widespread use, these pesticides have been detected in the environment in various matrices including water, soil, plant material and air respectively. Pesticides especially hydrocarbon pesticides are divided into two categories. The two classes are the organochlorine and organophosphorus compounds. Organochlorine pesticides are the class of hydrocarbon pesticides which resist biodegradation and therefore they accumulate in the environment through food chain, (Nollet and De Gelder, 2013).

Recently banned/restricted pesticide residues were detected in water samples from three wetlands in Kenya which include River Nzoia, Kigwal/Kimondi, and Nyando wetland ecosystems within Lake Victoria Basin (Mule *et al*., 2015). The prominent pesticide detected were, Dieldrin, Benzene Hexachloride (BHC), DDT and its metabolites. The levels of these detected pesticides was an indication that these pesticides are currently in use and could result in adverse effects to the environment and human health due to their accumulation in the environment, (Mule *et al*., 2015). Therefore, the presence of these POPs (dieldrin, BHC, DDT and its metabolite) in these three wetlands within Lake Victoria Basin is a cause for greater concern considering that most of these detected pesticides are toxic and has been restricted from reaching the environment for instance, Dieldrin which was banned completely by PCPB in 2011, (Mule *et al*., 2015). These pesticides reach the aquatic environment in several ways which include direct run-off, careless disposal of empty containers, leaching, washing with aerial precipitation which contributes minimum amounts of these pollutants, (Shaw and Haddad, 2004). Residual pesticides were also reported in sediments with organochlorines having a concentration ranging from 9.68 ng/kg to 10.98 µg/kg. Endosulfan and were the main insecticides found in water bodies in Ghana with concentrations ranging from 0.036 µg/L to 62.3 µg/L, (Mohammed *et al*., 2019)

The Persistent Organic Pollutants (POPs) found currently in the environment as reported by the Stockholm Convention treaty can harm the wetland ecosystems because of their toxic nature.

They resist biodegradation, bioaccumulate and are transported through water, air and migrating species, across international boundaries and are deposited far from their sources and hence accumulate in terrestrial aquatic ecosystems, (Vanden, 2002).

Several Persistent Organic Pollutants chemicals have been established by Stockholm Convention treaty and that the members of this treaty are required to minimize the risk of exposure of these pollutants to human health and environment arising from their release, (Mansour, 2009). The members of the treaty also are required to take legal measures in order to restrict these persistent organic pollutants and PCBs or to totally eliminate them from the environment. The 11 Persistent Organic Pollutants chemicals that were banned by the Stockholm convention include hexachlorobenzene, furans, endrin, aldrin, heptachlor, dioxins, polychlorinated biphenyls (PCBs), dieldrin, chlordane mirex, toxaphene, (Fu *et al.*, 2003) . Furthermore, Stockholm convention treaty has also further classified nine other organic pollutants as members of POPs. These POPs are categorized into pesticides (lindane, beta hexachlorocyclohexane, Chlordecone, alpha hexachlorocyclohexane, pentachlorobenzene), industrial chemicals (hexabromobiphenyl, hexabromodiphenyl ether and heptabromodiphenyl ether, tetrabromodiphenyl ether and pentabromodiphenyl ether and perfluorooctane sulfonic acid) and by-products (Sah and Joshi, 2011).

Kenya joined and signed the Stockholm Convention treaty in 2001 and the Kenyan government agreed, to restrict and eliminate the banned pesticides products but it was announced by World Health Organization (WHO, 2011) the lifting of the ban on DDT (Bouwman *et al.*, 2011). However, DDT was restricted for the control of malaria in malaria prone areas in Africa. In 2006, the World Health Organization issued a position statement promoting the use of indoor residual spraying with DDT for malaria vector control in epidemic and endemic areas. Other international organizations concurred because of the great burden of malaria and the relative ineffectiveness of current treatment and control strategies. Although the Stockholm Convention of 2001 targeted DDT as 1 of 11 persistent organic pollutants for phase-out and eventual elimination, it allowed a provision for its continued indoor use for disease vector control (Sadasivaiah, 2007). The Kenyan Ministry of Public Health has adopted the indoor pesticides control method especially in Northern Rift valley where there are high deaths due to malaria infestation of up to 19 % of all deaths in the region (Curtis and Mnzava, 2000). The coastal areas near the Indian Ocean and the Lake Victoria region, for example, are high-burden, and malaria prevalence hovers around 8 % and 27 % respectively. Here insecticide-treated bed-nets are the primary preventive tool whereas indoor spraying with insecticides is targeted towards selected areas with high transmission around Lake Victoria. In the capital city of Nairobi, less than 1% of people harbor the parasite that causes malaria. The presence of the parasite is also low in the country’s arid regions, where it can peak at around 3 % following heavy rains. Kenya’s malaria response in these areas focuses primarily on surveillance, effective diagnosis and treatment, (WHO, 2017)

Pesticides use should be properly controlled especially pesticides for agricultural purposes within the tropical regions as they may result in adverse environmental impact and human health in general. The unrestricted use of natural wetlands has also posed a great concern as these wetlands acts as sinks for point and non-point sources of pollution in surface water runoff from municipal and agricultural sectors. These pollutants can have adverse effects on the working of the wetland in terms of retention and removal of such pollutants (Quin *et al*., 2015)

The levels of pesticide residues in wetland ecosystems vary from one point to another. There levels are attributed to the ability of the wetland to retain them. There is variation in the levels of residual pesticides right from inlet, mid-point and outlet. However, their levels also vary from different environmental matrices i.e soil, water and pant materials, (Mason, 2003)

While retention and fate of heavy metals, nutrients and sediments have been well studied and understood in constructed wetlands, the same cannot be claimed for tropical natural wetlands. Tropical natural wetlands have greater ability to retain and remove the pollutants and thus lowering the level of residual pesticides. Therefore, it is reasonable that profiling of these residual pesticides be studied for purposes of quantification (Haarstad *et al*., 2012). Furthermore, the ability of the natural wetlands to retain the pollutants also be studied as they could be releasing polluted water to bigger rivers, (Mansour, 2009; Wang *et al*., 2009). The study of retention abilities and profiling of residual pesticides of wetland ecosystems provides information that helps in formulation of policies for conservation of these wetland ecosystems.

1.3 Statement of the Problem

The use of various pesticides based products in Kenya is on the rise majorly due to the increase in industrialization and commercialization of agricultural. Agriculture (subsistence and commercial) is the backbone of economy in Kericho County and more so in Mobego-Kabianga region and due to the challenges in controlling pests; pesticides are the most effective method of managing pests and increasing food production. The use of pesticides on farms can be detrimental to the environment if good pesticide management practices are not employed by farmers and all stakeholders in the agricultural industry. Studies have shown presence of residual pesticide pollutants in water resources such as rivers, dams and wetlands from farms where pesticides have been in use. Though the levels and the retention efficiencies of heavy metals in constructed wetlands have been well studied, the same cannot be stated for natural wetlands and thus this project aimed at profiling and retention efficiency of residual pesticides in Mobego-Kabianga wetland ecosystem.

1.4 General Objective

The main objective of the study was to profile pesticide residues, to determine physicochemical parameters and retention efficiency of Mobego-Kabianga wetland ecosystem in Kericho County, Kenya.

1.5 Specific Objectives

The specific objectives of the study were:

i. To determine the selected physical parameters (pH, flow rate, temperature, conductivity, dissolved oxygen, TSS and TDS) of Mobego-Kabianga wetland ecosystem.

ii. To profile and compare the levels of pesticide residues present in Mobego-Kabianga wetland ecosystem in Kericho County.
iii. To determine the retention efficiencies of pesticide residues by Mobego-Kabianga wetland ecosystem in Kericho County.

1.6 Hypotheses of the study

The hypotheses of this study were:

i. No variation in the level of physico-chemical parameters will be observed in Mobego-Kabianga wetland ecosystem in Kericho County.
ii. No variation will be observed in the levels of pesticide residues in Mobego-Kabianga wetland ecosystem in Kericho County.
iii. No variation will be observed in the retention efficiencies of pesticide residues by Mobego-Kabianga wetland ecosystem in Kericho County.

1.7 Justification of the Study

An understanding of the retention efficiencies and profile leveling of pesticide residues by tropical wetlands will serve as baseline information for understanding factors which contribute to the degradation of hydrological functions of such wetlands. The results of this study on the retention efficiencies and profile leveling of pesticide residues provides key information that may assist in developing a solid scientific base on which more precise quality criteria may be formulated and policies in protection and management of tropical wetland ecosystems can be based on. Monitoring programs could then follow to detect any significant change in the levels of pesticide residues and retention efficiency of the wetland ecosystem which would signal a need to control the use of pesticides in wetland ecosystem respectively.

1.8 Significance of the Study

The findings of this study will provide information to policy makers on environmental protection and preservation for purposes of developing policies governing the use of natural wetlands.

1.9 Scope of the Study

The study investigated the retention efficiencies and profile leveling of pesticide residues at Mobego-Kabianga wetland ecosystem (at the upstream of Kabianga River) in Kericho County, Kenya.

1.10 Limitation of the Study

The major limitation that affected the study was limited accessibility of the wetland due to flooding.

1.11 Assumption of the study

Mobego-Kabianga wetland has higher retention efficiency of residual pesticides

CHAPTER TWO

LITERATURE REVIEW

2.1 Introduction

This chapter provides an account of literature review on wetland ecosystems, mass transport processes, profile leveling, retention efficiency, physical and chemical properties of wetland ecosystems, literature review of some prominent types of pesticides detected in the selected wetland ecosystem and conceptual framework. The purpose of literature review will be to outline an understanding of wetland ecosystems and their functional ability in terms of retaining pollutants emanating from the many anthropogenic activities in Mobego-Kabianga wetland.

2.2 Wetland ecosystem

Wetlands are defined as lands which are saturated by surface water and support vegetation growth that are adapted to live in soil that are saturated, (Foster, 2007). They form unique landscape features and acts as mediator between terrestrial and aquatic ecosystems. Wetlands are flooded by water from streams, rivers, lakes, rainfall during rainy season and ground water seepage, (Mitsch and Gosselink, 2000).

Soil saturation and anaerobic conditions are common features of the wetlands and the universal features of wetlands delimit their soil chemistry and biology. The anaerobic conditions of wetlands soil give it a unique biochemical processes to soil and biota. There are four different kinds of wetland ecosystems which include swamps, marshes, bogs and fens. Swamps are fully flooded wetlands and are dominated by woody vegetation for instance, cypress papyrus reeds growing in hydric soils. Marshes are also fully flooded wetlands dominated by herbaceous plants growing in hydric soils. Fens and bogs are regarded as peat lands, wetlands that accumulate decayed and dry vegetation. Riparian wetlands are the wetlands which are connected to adjacent lakes rivers and streams. They are the type of wetlands which undergo wetting and drying as the adjacent water bodies' levels fall and rise, (Turner *et al.,* 2000; USEPA, 2015).

Wetlands are subject to increased attention relative to receiving storm water runoff because of their inherent water storage and water quality improvement capabilities. The role of wetlands as storage areas for storm water discharges was investigated by Shaw and Haddad (2004). The value of natural wetlands, however, extends beyond their water storage and water quality functions to include food chain support, erosion control, groundwater recharge/discharge, and habitat functions (Mitsch and Gosselink, 2000). An understanding of these functions is necessary when contemplating the use of natural wetlands to store and treat urban and agricultural storm water discharges in order to predict and measure potential impacts on wetland functions.

The physical features of wetlands are categorized into three; soil, vegetation and hydrology, (Mansour, 2009). The main determinant of wetland is hydrology as it gives the physical and bio-chemical features of the wetland, (Mitsch and Gosselink, 2000). Hydrology is affected by topography, geology and climate. These factors give rise to various types of wetlands, (Roggeri, 2013). Flat landscape is ideal for wetland formation because they are not drained easily, (Akerblom *et al*., 2008).

Wetland receives water from three sources which include surface runoff, precipitation and ground water (Gauge, 2013). The wetland systems which are flooded only by precipitation are regarded as closed systems and they only support biota that cannot survive in nutrient poor conditions, (Blankenberg *et al*., 2007). Open systems are those wetlands that are supplied with water from adjacent streams or lakes and an inflow affects their chemical and physical properties (De Assis Matos de Abreu *et al*., 2005)

The regime of hydrology is unpredictable in climatic conditions with irregular pattern. Sometimes the hydro periods are affected by the rising and falling of local rainfall, (Battle and Golladay, 2002). The hydro periods in an open system is directly related to frequency of inflows in the adjacent connected stream. These open systems therefore exhibit frequent changes in levels of water, (Hidalgo, 2013). The direction and flow rate in open system is very important as they affect amount of the transported materials between aquatic and terrestrial ecosystems, (El-Kabbany *et al.,* (2000). Inputs to open wetland system contains a lot of materials which include; sediments, organic materials, toxicants and nutrients and all this affects the functioning of the wetland. The out flows from the wetland also have effects on the receiving water, (Kasozi *et al.*, 2006). The outflows from various natural wetlands possess the following characteristics; varied pH, and low organic matter, (Kohler *et al.,* 2004).

Several studies have referred to the potential of wetlands for removal of herbicides and some other organic chemicals (Kadlec, 2008; Budd, 2009; Main *et al*., 2014; Bhatta *et al*., 2016). Since wetlands have the ability to retain and process transported material, it seems reasonable that natural wetlands, acting as buffer strips between agricultural areas and receiving surface waters, could mitigate the effect of pesticides in agricultural runoff, (Kadlec and Wallace, 2008).

2.3 Mass transport processes

In this section the distribution processes of pesticide residues in the environment will be discussed. The purpose of this discussion is to give an understanding of the different processes aiding in the transport of pollutants. Calculation of pollutant fluxes will also be done by application of flux formulae, (Krishnamurthy *et al.*, 2006; Alzraiee and Garcia, 2013).

The transport of pollutants results in movement of pollutants from their place of generation. The major interest by scientist is on the processes that results in transport of pollutants through water or air. However, some pollutants may undergo degradation in the environment if they are dilute, (Tarr, 2003)

Generally, in a typical wetland ecosystem the movement of pollutant can be simulated as in Figure 2.1 (Boivin *et al*., 2005).

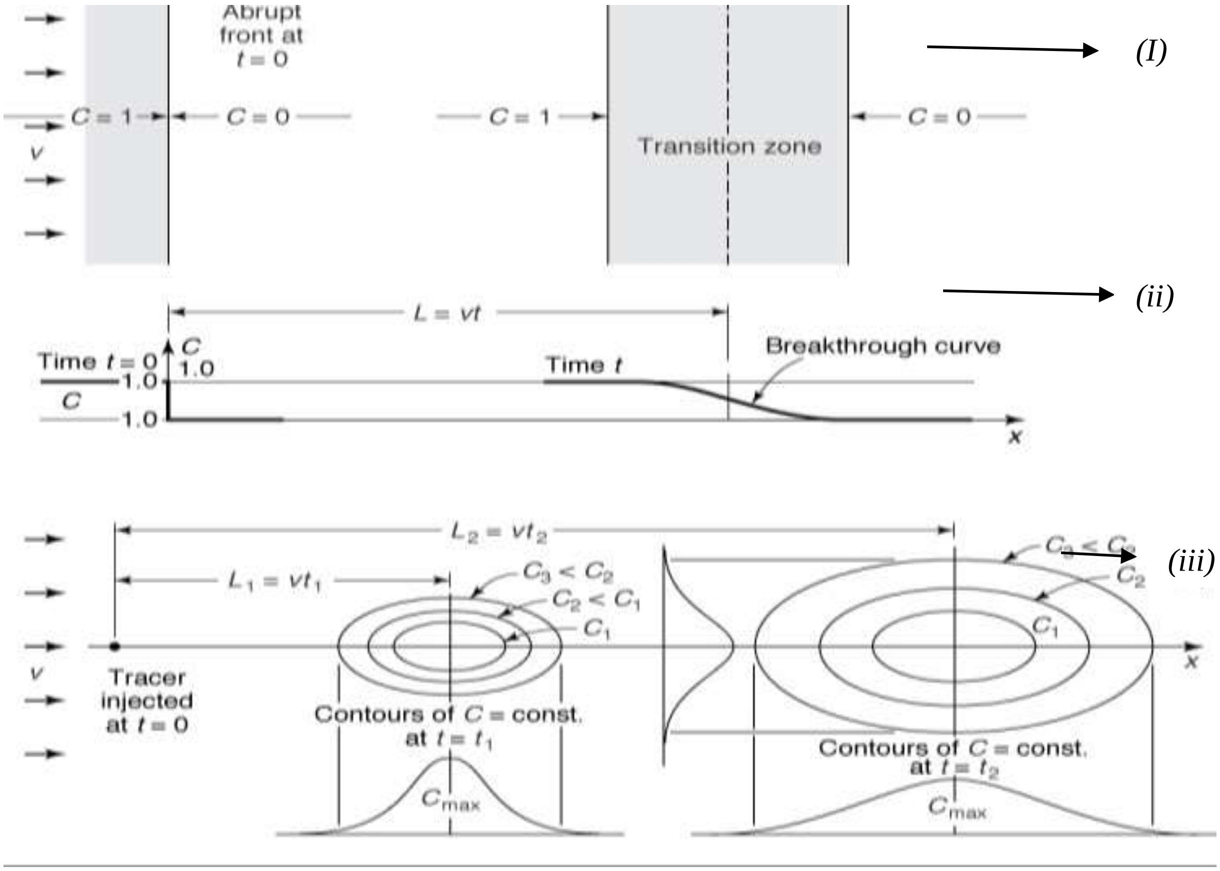


Figure 2.1: Mass flow of chemical species in wetland ecosystem

Figure 2.1 (part *I*) shows the mass flow of a chemical species with respect to time. The input as indicated by C=1 should be greater than C=0 as the species traverses the ecosystem. Part (*ii)* is a plot of concentration with time and indicates the breakthrough curve while part (*iii)* indicates a contour representation of movement of a chemical species within a complex ecosystem. The output in the wetland system is expected to be less than the input concentration ($C_3 < C_1$) for retention of such pollutant to occur. The physical properties controlling such a spread in a system are; Advection, Diffusion and Dispersion (Boivin *et al*., 2005).

2.3.1 Transport/movement of pollutants in wetland

The pollutant transport in an environment is divided into two major classes: Diffusion and advection. Advection refers to the transport of pollutants in the direction of fluid flow. If the river is flowing to west direction, then the advection tends to carry the pollutants to west and if the river is flowing to east then advection will tend to carry the pollutants to east respectively. On the other hand, diffusion involves the transport of pollutants by random motion, (Hamdi, 2007). It is simply the movement of pollutants from a region of high concentration to a region of low concentration aided by concentration gradient. Diffusion provides a uniform concentration profile. Advection is regarded as an independent process for instance, in an example of pollutant spot in river, diffusion spreads out the pollutant spot to less concentrated region while advection carried the pollutant spot downstream, (Boivin *et al.*, 2005).

2.3.1.1 Mass flux density

The value of mass balance calculations (with units of mass/time) is referred to the rate at which the mass is transported across the boundary of the control volume. The mass balance calculations are made with reference to specific control volume, (Shipp *et al.*, 2011). The calculation of diffusive flux and advective flux in this study however will not be restricted to volume that is well defined but instead the flux density will be calculated across an imaginary plane that is oriented perpendicularly to the direction of mass transfer. Therefore, the resulting mass flux density is the rate at which the mass is transferred across the plane per unit time per unit area with the units of *mass time* $^{-2}$/*length*$^{-2}$. The flux density will be represented by the symbol *J*, (Kohler *et al*., 2004).

The total mass flux across a boundary (*m*) can be calculated from the flux density simply by multiplying J by the area of the boundary (A), (Kohler *et al*., 2004).

$$m = J * A \ldots\ldots\ldots\ldots\ldots\ldots \text{(2.1)}$$

2.3.1.2 Calculation of the advective flux

The advective flux density is dependent on the concentration (C) and the rate of flow (V).

$$N = C * v \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(2.2)}$$

The advective flux is defined as the movement of compounds along with the flowing water or air. The flux N is defined as the movement of mass of pollutants in the same direction as the flowing fluid. The symbol V is the velocity of the fluid and is a vector quantity (which has both the direction and the magnitude), (MTP, 2018).

2.3.2 Diffusion

There are two random motions which results in diffusion: The random motion of eddies arising from turbulent flow of fluids and the random motion arising from the molecules in the fluids, (Foster, 2007). Molecular diffusion refers to the random motion of the molecules while turbulent diffusion/eddy diffusion is as a result of turbulent eddies. These forms of diffusion are guided by

Fick's First Law. This law gives the relationship between the concentration and a diffusing substance under a steady state. It states that a given substance (flux) move from a region of higher concentration to a region of low concentration against a concentration gradient. The law can be given in spatial derivative as proposed by (Floury *et al*., 2010).

$$\beta = -D\frac{\partial \phi}{\partial x} \quad \text{..} \quad (2.3)$$

Where

β - It denotes the amount of substance moving across a small area per unit area at a given time (in m^{-2}/s^{-1})

D - It denotes the coefficient of diffusion (in m^2/s) i.e. 0.6 x 10^{-9} m^2/s.

ϕ - It denotes the amount of substance per unit volume (in mol/m^3)

x - It is the position of substance from a give point of reference (in m)

In dilute aqueous solutions the diffusion coefficients of most ions are similar and have values that at room temperature are in the range of 0.6 x 10^{-9} to 2 x 10^{-9} m^2/s. For pesticides molecules the diffusion coefficients normally range from 10^{-11} to 10^{-10} m^2/s. If the flow is laminar, i.e. if there is no turbulence, the diffusion is on the molecular scale, with a thermal diffusibility of the order 1.4 x $10^{-7} m^2 s^{-1}$ in pure water. In river water systems, the water is always turbulent (flow rate is indicative of turbulence) and thus the effective diffusibility is several orders of magnitude greater, but in a wetland, where the river water disperses horizontally and flow rate is minimum, turbulence is also at its minimum and we can assume the given thermal diffusibility (Damalas and Eleftherohorinos, 2011).

2.3.1.3 Dispersion

Many factors influence the way pollutants are dispersed in water system, including water flow rate, vegetative cover, aquatic microorganisms, type of terrain and temperature. To better understand how the processes can affect pollution, the conditions can be described simply as either stable or unstable, where the stability is determined by water flow rate (which stirs the wetland) and temperature (which cause water convection currents). In unstable conditions, pollution is readily dispersed thereby reducing water level concentrations. Temperature greatly affects the dispersion and decomposition of pollutants in water, (Paraíba *et al*., 2003)

2.4 Retention efficiency of wetland ecosystem

There have been reports that wetlands possess the ability of removing pollutants from water transiting through it and constructed wetlands have been made purposely for this function. Pollutants like fertilizers, pesticides and animal waste settle and adsorb to soil sediments, (Zeng *et al.,* 2012). Aerobic and anaerobic processes aid in chemical removal from the wetland. Wetland removes pollutants with decomposers aiding in the decomposition of the pollutants through several processes including denitrification and chemical precipitation, (Main *et al* (2014). Natural wetlands have been reported to control surface water pollution, (Schulz and Peall, 2001; Reichenberger *et al.,* 2007). Limited studies on effectiveness of natural wetland ecosystems in retention of agricultural pesticides have been done, (Birch and Taylor, 2000; Van *et al*., 2013). Variation in values of retention efficiencies of pesticide residues were reported by Venne *et al.,* (2008) and Prüss-Ustün *et al*., 2011).

Kotze (2010) studied the retention efficiency of BHC, dieldrin, DDT by wetland in USA, Playa and reported that these pesticide residues range between 65-79%. Braskerud and Haarstad

(2003b) also studied the retention efficiencies agricultural run-off and reported that dieldrin 75-80 %, BHC rate of 11-58 %, diazinon at a rate of 55-62 % and deltamethrin 89-97%.

All these pesticides were found in wetland with peak concentrations shortly after spraying in summer and winter seasons. The statistical analysis found that the results were statistically different from zero in six of the wetlands to 0.05. This was attributed to the fact that wetlands are complex ecosystems and understanding their functions requires much work. Damalas and Eleftherohorinos (2011) in an earlier work found that pesticides chemical properties do affect their retention in a watershed with several pesticides recording retention efficiencies in watershed between 22 %-75 % and in constructed wetland between 56 %-88 % and any negative retention efficiency may imply that the wetland does not retain such a pollutant (Brock *et al.*, 2000; Bassi *et al.,* 2014).

Other studies done on retention efficiencies of pesticides by constructed wetland were also reported by Davis *et al.,* (2001) and Qu *et al.,* 2011) to be ranging between 73-98 %, organochlorine pesticides at > 75 % (Schulz and Peall, 2001), > 86 % (Braskerud and Haarstad, 2003a), and > 90 % (Kwong, 2002; Bassi *et al.,* 2014). Blankenberg *et al* (2007) recorded the mass balance of pesticides and the fungicides in wetland ecosystems and found that 96 % retention efficiency of applied pesticides on a constructed wetland.

A few studies have been undertaken on the effectiveness of natural wetlands for retention of sediments, nutrients, metals, and organic contaminants in a single investigation (Carleton *et al.*, 2001). Bhatta *et al* (2016) and Budd (2009) reported removal efficiency of constructed wetland for bifenthrin, λ-cypermethrin, esfenvalerate, permethrin, chlorpyrifos and diazinon to be from 68 to 100 % at San Joaquin river basin, California.

Seasonal variation of wetland removal efficiency of pollutants is reported to differ during rainy and dry seasons. For example, wetlands have lower removal efficiency of pollutants during dry season than during rainy seasons due to the fact that river water spreads greatly to cover larger wetland area promoting retention of sediments and pollutants by vegetative cover (Blankenberg *et al*., 2007). Reichenberger *et al* (2007) reported retention efficiency in a wetland along a tributary of Lourens River in South Africa to vary from 77 and 98 % for chlorpyrifos and endosulfan during dry season and between 83 to 99 % during rainy season.

Physical and chemical characteristics of wetland ecosystems play a great role in determination of pollutant retention efficiency in a wetland ecosystem. Some of the wetland characteristics include:

I. Average rainfall of the basin: this will affect the volume (V) of water in the wetland section. This parameter will determine the extent of dilution of the pollutant of interest. The volume of water will also affect other physical parameters such as pH, turbidity, and temperature.
II. Presence of aquatic habitat that supports flood water in the wetland which included microorganisms and plant materials. The vegetation density will determine the extent of water flow rate, dispersion of the pollutant within the wetland section absorption or desorption of pollutants by vegetation roots, temperature of surface water.
III. Size of the watershed which affects the volume of the river water
IV. Proximity of the wetland to the sources of pollutants which influences the level of pesticides in wetland.
V. Potential of tributaries to carry pollutants and flood waters to the wetland which will also determines the level of pollutants in the wetland
VI. pH which affects hydrolysis of pesticides

VII. Soil types which determines adsorption abilities of pesticides.

VIII. Redox reactions which affects the acidity of the wetland (Desta *et al*., 2012).

These characteristics do affect the retention, degradation, dispersion, advention and diffusion, volatilization, and hydrolysis which are the key processes which affect the presence of a pollutant in the wetland.

Coordinate measures of particular stream as well as wetland capacities are both exorbitant and tedious and for the most part past the extent of routine field examinations. For instance, estimations of floodwater confinement and weakening capacities include convoluted instrumentation equipped for estimating day by day streams over a drawn out stretch of time, making an everyday hydrograph, deciding water surface height, top release, surge recurrence and length and stage/release connections. Likewise, one should likewise decide floodplain rise, region, and slant and floodplain harshness. Such examinations are not handy inside an administrative structure.

As an option, roundabout measures in view of the nearness of certain physical or potentially organic attributes can demonstrate that particular capacities are happening not withstanding when the capacity itself isn't specifically discernible. Such markers are known as surrogates and are significant when it is effectively seen in the field and there is a known relationship between the surrogate and its capacity. The retention capacity of the wetland and the centralization of the contamination will go ahead until the point when a state of saturation is arrived. Past the saturation level the wetland is rendered uneffective regarding toxin evacuation and the pollutants leaves the wetland, (Tremolada *et al*., 2006).

The percentage retention efficiency of the wetland is calculated using the formula provided by Johannesson *et al*., (2011)

$$\%R = \frac{[C_{in} - C_{out}]}{C_{in}} \times 100\% \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 2.4$$

Where

C_{in} is the concentration of the pollutant (pesticide residues) entering the wetland system in ng/mL.

C_{out} is the concentration of the pollutant (pesticide residues) leaving the wetland system in ng/mL.

Equation 2.4 above can be used effectively if the system is well controlled so as to know the levels of pollutant input and output hence the wetland retention ability and efficiency can be calculated. In a natural wetland ecosystem, a complex system where the chemical and physical properties of the wetland vary, formula will give an erroneous value and thus an adjustment to the formula to take care of all pathways leading to pesticide inputs and outputs is necessary. The pathways which may lead to increase of pesticide residues in the wetlands may include: flushing from agricultural farms, livestock spraying, runoffs from industrial and municipal areas, seeping of rain water from wetland surrounding fields, aerial deposition, desorption from sediments, plant root systems and aquatic organisms, (Rignot *et al.*, 2008). Output pathways may include: photo degradation, hydrolysis, sorption onto sediments, plant materials and aquatic organisms, and volatilization as shown in the conceptual framework in Figure 2.2. All these pathways should be considered in calculating the retention abilities and efficiencies of any natural wetland ecosystem. It is also worth noting that wetland physico-chemical characteristic, floodwater detention, vegetative density; soil types among others will affect retention ability and efficiency of the wetland.

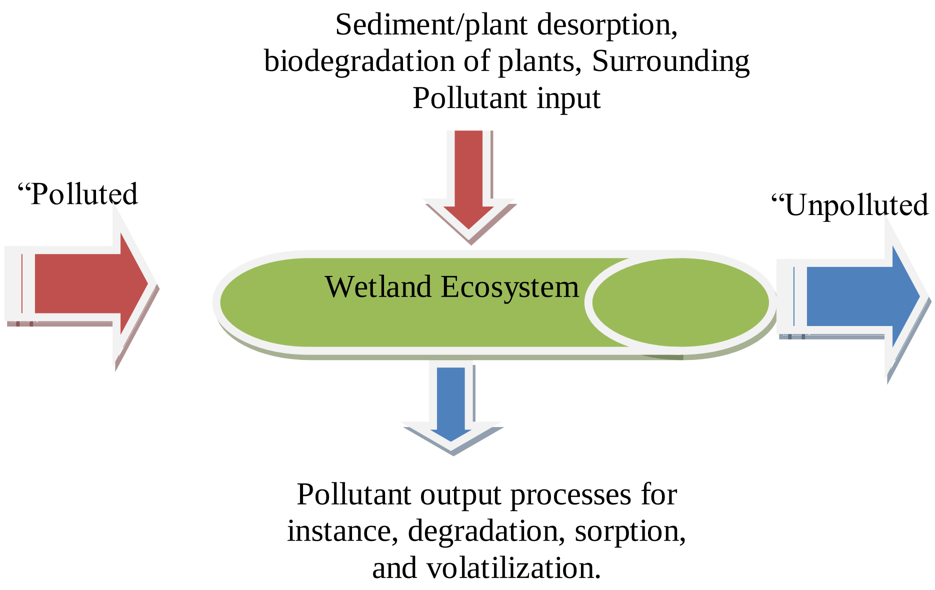


Figure 2.2: Pollutant transport mechanism in a wetland ecosystem

Coordinate measures of particular stream and additionally a wetland capacity, estimations of soil compose (which changes frequently inside the wetland), vegetative thickness estimations are expensive and tedious and large past the extent of routine field examinations, (Said *et al*., 2012). For instance, estimations of floodwater detainment and removal capacities will include complicated instrumentation fit for estimating day by day streams, making an everyday hydrograph, deciding water surface rise, peak release, flood frequency and span and stage/release connections. What's more, one should likewise determine floodplain rise, zone, and slant and floodplain roughness. Such examinations are not handy inside a regulatory framework system.

By measuring the level of pesticide residues in sediments, plant materials, organisms and in water matrix, the values detected will give an average of the performance of the wetland although the low retention time of the water will only allow pesticide residues to majorly partition in sediments, plant materials and in water matrixes. Thus adjusting the above formula and make necessary assumptions to take into considerations the contributions made by chemical, physical and biological processes within and without the wetland, the formula can play a big role in the study (Ogwok *et al.*, 2009).

2.5 Profiling of pesticide residues

Vegetation cover, land use, land management, atmospheric deposition, geology and soil type, climate, topography, and wetland hydrology are the key features of the wetland that affect: (1) the amount of residual pesticides concentrations (2) the mobilization of these pollutants, and (3) the delivery of these pollutants to receiving waters (Lintern *et al*., 2018).

Investigation of the levels of residual pesticides along the wetlands is used to assess the level of contamination. Contamination of rivers has been an issue of global concern and continual challenge in developing countries. The modern phenomena of urbanization, population density, and increasing anthropogenic activities within and around the wetland are contributing contamination factors. Continual monitoring of residual pesticides pollutants in wetlands has been a basis for policy formulation and control of pollution, thereby ensuring safe water bodies from persistent organic pollutants, (Unyimadu *et al*., 2018)

Pesticide residues in wetland are distributed in different environmental matrices. The distribution of these pesticides is affected by redox conditions and transmission media. An organochlorinated pesticide shows low comparable values of the global range and its distribution pattern is affected by river currents (Zhou *et al.*, 2014). The level of pesticides in river varies from one point another. Several factors affect the distribution of such pollutants which may include vegetation cover, river flow rate among other factors. Sediments play an important role in the distribution of contaminants in wetland ecosystems. While pesticide molecules can dissolve in water, a large proportion binds to suspended particles, plant materials and others settles at the bottom of the water body, resulting in the contamination of the wetland (Lalah *et al*., 2003).

Some pesticides, particularly those with hydrophobic nature and low water solubility can be retained on the organic phase of sediments through sorption (Zhou *et al*., 2006). The analysis of pesticide residues along the wetland has therefore proved to be an important approach in assessing the fate of these contaminants in wetlands and contamination history of an area. While the analysis of water samples gives important information on the water quality and the detection of any potential risks, plant materials and sediment analysis enables the detection of pollutant (Zhou *et al*., 2006).

2.6 Physico - chemical properties of wetland ecosystem

Several properties which determine wetland retention abilities and efficiencies of pesticide residues are classified as climatic conditions of the region, physical and chemical properties of pesticide residues. These properties include the amount of rainfall, water flow rate, temperature, pH, octanol/water partition coefficient (K_{ow}), soil/water partition coefficient (K_{oc}), the air/water partition coefficient (K_H the Henry's constant), amount of organic matter in the wetland, concentration of the pesticide residues , its propensity for binding to soil, its vapor pressure, its water solubility, and its resistance to being broken down over time are the most important parameters affecting the pesticide behavior in environment (Zhu *et al.*, 2016). Other factors include soil texture, soil water retention, and the amount of soil organic matter.

2.6.1 Rainfall and wetland river flow rate

Mobility of pesticide residues in an environment under normal environmental conditions is much affected by rainfall. Mobility of pesticide residues in soil is greater in moist climates than in dry ones (Damalas and Eleftherohorinos, 2011; Dunnivant and Anders, 2006). The hydraulic and hydrologic feature of a particular wetland ecosystem widely influences its functions and therefore foster for evaluation of the wetland. Water budget is the process by which water is introduced, stored temporarily and finally removed from the wetland. Direct precipitation, surface runoff, over-bank flow ground water discharge, channel and tidal flow are some of the ways in which water is introduced into the wetland, (Carleton *et al.*, 2001; Gomi *et al.*, 2002).

The process of surface water is tied to regional and local patterns of precipitation. Precipitation influences the water budget. The direct influence is through rainfall and the associated surface runoff and indirectly by inflows from watersheds at the upstream. The river flow rate is increased due to increase in rainfall and hence subsequent increase in surface runoff and soil erosion. The increase in river flow rate also will subsequently be followed by increase in transport of Pesticide residues from their source of release. Portion of pesticide residues will reach the natural systems through surface runoff and during strong rainy seasons (Kohler *et al.,* 2004).

Increase in flow rate of the river is correlated with an increase in precipitation. An increase in rainfall increases surface runoff and outflows of the drainage respectively. Kasozi *et al*., (2006) reported that the velocity of river shouldn’t exceed 0.457 m/s. Very high velocities may sour sediments which are deposited and remove rooted vegetation. High vegetation in a wetland will reduce the flow rate of river and this will result in an increase in retention efficiency and removal of pesticide residues. About 60 - 90 % pesticide reduction factor at low river flow rate was recorded by Braskerud and Haarstad (2003b) in constructed wetland. This was due to the roughness of flow contact which reduced the rate of flow. Vegetation cover increases the Manning coefficient (*n*) of between 10 – 20 factors through provision of dominant dragging force, (Bouwman, 2004).

2.6.2 Wetland temperature

Temperature is an important factor affecting the retention and attenuation of pollutants in natural ecosystems. It controls microbial metabolism of pesticides with regard to bio-remediation especially in situ. Solubility and degradation of hydrophobic substances which are less soluble are dependent on temperature for instance, aliphatic pesticides, (Moor *et al.,* 2015). High temperature in wetland decreases the viscosity of pesticide residues and consequently affecting the distribution of such pesticides in the wetland. At high temperatures, higher rate of reactions is expected because of smaller boundary layers. Under sub-tropical wetland (15 – 22 ^{o}C), pesticide residues are expected to be lost through volatilization, microbial degradation and photo-decomposition as compared to less temperate conditions, (Kadlec and Reddy, 2001).

Adsorption of pesticide residues is decreased at high temperature while desorption is increased and this may result in high concentration of pesticides in water. Variation is also observed in photosynthetic activity of wetland vegetation especially in floodwater due to light intensity and temperature difference, (Main *et al.*, 2014).

2.6.3 Wetland pH

Degradation of pesticide residues is also influenced by the level of pH. Pesticide removal is affected by the pesticide/water contact time, properties of the pesticide and the pH of wetland water. Rapid hydrolysis of pesticides is observed at water with pH of 8-9 during dry season.

Most wetlands have pH of between 7.8-9 during dry season and 6.8-7.5 on wet season, (Akiner and Çağlar, 2006).

Many pesticides, particularly commonly used organophosphate and carbamate insecticides, undergo a chemical reaction in the presence of alkaline water that reduces their effectiveness. This reaction is called alkaline hydrolysis. The pesticide is hydrolyzed and rendered ineffective when it is mixed with water with a pH greater than 7. The more alkaline the water, the more rapidly the pesticide breaks down (McKie, 2018). The hydrolysis can be very fast when the pH of the water is greater than 8 or 9. For every unit increase in pH, the rate of hydrolysis increases 10 times. Some pesticides begin to break down as soon as they are combined with alkaline water in the tank, especially when the pH of the water is very high. As a consequence, the active ingredients start to change to inactive ingredients before the pesticide ever leaves the wetland (McKie, 2018).

Dimethoate has a half-life of 1 hour at a pH of 9. This means that if the pH of wetland water is 9, and one hour elapses between the times dimethoate enters the wetland, 50% of the active ingredient is already lost. However, if the wetland water has a pH of 6, it is not likely that any significant loss of active ingredient will have occurred in one hour (McKie, 2018).

Carbon dioxide from the atmosphere and organic acids formed by decaying organic matter are the two sources of acidity in most near-surface environments, resulting in acidic pH in the range of 5 – 6 (Foster, 2007). A pH of 4 has been selected as the usual lower limit of pH values in natural environments. The pH at the upper end is due to CO_2-water that is in contact with rock carbonates and the pH of 10 due to contact with silicates, (Naiman *et al.*, 2010). Alkaline conditions are not observed in most surface waters because surface waters emit CO_2 to the atmosphere. The pH of 9 is found in near-surface water, (Gingerich and Anderson, 2011). The level of pH rises due to increase in growth of plants and algae. The growth of algae and plants is due to excess pollutants or temperature increase.

2.6.4 Pesticide soil/water partition coefficient (K_{oc})

There is evidence that chemicals applied to the soil surface may be transported rapidly to water resources (Naiman *et al.*, 2010). The hypotheses proposed to explain this rapid transport include preferential flow co-transport with soil particles and colloidal matter and a combination of both these processes. The rate and magnitude of rapid transport seem to be influenced by multiple factors, including not only pesticide properties, but also soil properties (structure, organic matter, clay content and iron oxides), soil hydrological processes and management (for instance, time of application). Especially for the hydrophobic pesticides, their mobility, and therefore the risk of their transport into water resources has been correlated with weak sorption on the soil matrix, as quantified by their $K_{oc.}$ Pesticides with K_{oc} values greater than 1,000 indicate strong adsorption to soil while pesticide with lower K_{oc} values (less than 500) tend to move more with water than adsorbed to sediment, (Yufen *et al.*, 2008). Soil pH can affect the K_{oc} of ionic and partially ionic pesticides. Pesticides with an anion as the active species would have a K_{oc} set low to account for that hydrocarbon's inability to sorb to soil particles. A cationic active species would tend to bind strongly with soil and therefore have a relatively high K_{oc}.

Reports have shown that pesticides have longer persistence in non-flooded soils than in flooded soils due to the high affinity to organic matter, (Osakwe, 2014). Among organochlorine insecticides, DDT, DDD, methoxychlor, and heptachlor degraded faster in flooded soil than in un-flooded soil; DDD was found to accumulate in DDT-treated flooded soil; and endrin was degraded only in flooded soil. Deltamethrin has been reported to have K_{oc} values of 160,000 which is an indication that the pesticide residue will partition itself on the soil (Thatheyus and Selvam, 2013) while diazinon and malathion having K_{oc} values of 2.12 and 291 will tend to dissolve in water as there K_{oc} values indicate (Armour, 2016; Bhateria and Jain, 2016).

2.6.5. Pesticide octanol/water partition coefficient (K_{ow})

The octanol-water partition coefficient (K_{ow}) is a measure of the equilibrium concentration of a compound between octanol and water that indicates the potential for partitioning into soil organic matter (i.e., a high K_{ow} indicates a compound which will preferentially partition into soil organic matter rather than water). K_{ow} is inversely related to the solubility of a compound in water. Cypermethrin was reported to have slightly high water solubility due to its low K_{ow} value of 6.6 (Thatheyus and Selvam, 2013). However, Malathion and diazinon with K_{ow} values of 2.236 and 3.86 have relatively high water solubility which will in turn raises the level of water pollution (Bhateria and Jain, 2016 and Armour, 2016). Pyrethroids are insecticides widely used in urban environments by consumers and professional pesticide applicators. These compounds have been reported to have low water solubility and are hydrophobic, with log K_{ow} values of 7. Pyrethroids have a strong affinity for the organic phase but have been shown to wash off application sites, associated with dissolved organic matter or sediment (Parrry and Yang, 2013)

Values of K_{ow} can be considered to have some meaning in themselves, since they represent the tendency of the chemical to partition itself between an organic phase (for instance, fish, soil) and an aqueous phase. Chemicals with log K_{ow} values (for instance, less than 10) may be considered relatively hydrophilic; they tend to have high water solubility, small soil/sediment adsorption coefficients, and small bio-concentration factors for aquatic life. Conversely, chemicals with high log K_{ow} values (for instance, greater than 10) are very hydrophobic since they have a tendency of accumulating in organisms because they are metabolized only slowly and are effectively stored in tissues (Bouwman, 2004). Arnot and Gobas (2006) reports log K_{ow} of pesticide residues to be from 3.83 to 6.91 and for organophosphorus pesticides to be between 0.78 and 4.96

2.6.6 Wetland total suspended solids and total dissolved solids

Runoff and surface-water commonly contain suspended solids and dissolved solids. Adsorption to suspended particles and the associated dissolved solids may significantly decrease the freely dissolved concentration of a hydrophobic pesticides and, hence, its availability to aquatic ecosystem. The study on phase distribution and bioaccumulation of two synthetic pyrethroids, bifenthrin and permethrin, in water samples containing suspended solids showed that the uptake of bifenthrin and permethrin by wetland plants consistently decreased with increasing levels of suspended solids in the range of 0 to 200 mg/L, (Yang *et al*., 2006). Parry and Young (2013) on his study on effects of solids on concentration of pollutants in water, suggested that pyrethroid toxicity to aquatic systems may be mitigated by the presence of dissolved solids) and suspended solids respectively.

Adsorption of pesticides in wetland is affected by TSS and TDS. Pesticides are classified as hydrophobic and hydrophilic. Hydrophobic pesticides tend to get adsorbed to soil and suspended solid particles in water than to water. Hydrophilic pesticides on the other hand are more adsorbed to water than to soil matter. The sorption of isoproturon (0.74±0.20 µg/g), atrazine (0.56±0.16 µg/g) and 2, 4-D ((2, 4-dichlorophenoxy) acetic acid) (0.12±0.03 µg/g), pesticides was dominated by dissolved solids and suspended solids representing 20-30 % variation in sorption values. The sorption of isoproturon was greatly affected by the presence of dissolved solids. Therefore total dissolved solid and total suspended solids are the major factors governing the sorption of these pesticides, (Spark and Swift, 2002).

2.6.7 Dissolved oxygen

The levels of dissolved oxygen in natural waters are dependent on the physical, chemical and biochemical activities prevailing in the water bodies. The analysis of dissolved oxygen is a key test for measuring the status of pollution of wetlands. A fall in level of oxygen in aquatic ecosystem results in health effects of the system. The system may suffer from hypoxia conditions which may results in depletion of very important aquatic plants and animals. Dissolved oxygen is used by wetland micro-organism during decomposition process (Prasad *et al*., 2014)

Removal of cypermethrin (least water soluble pesticide) from water systems was investigated and the results showed that when amount of dissolved oxygen was in range of 8-9 mg/L, >85 % degradation of Cypermethrin was noted. In contrast, at 5-6 mg/L dissolved oxygen, only 38 % degradation occurred. When the concentration of dissolved oxygen further increased from 9 to 12mg/l, no pronounced effect on degradation of cypermethrin was observed (Jilani, 2008).

2.6.8 Conductivity

Conductivity is a measure of ability of water to pass electric current and is affected by presence of dissolved solids. Higher amount of dissolved solid corresponds to higher conductivity of waters and vice versa (Rusydi, 2018). For health reasons, WHO (2011) established a standard permissible of electrical conductivity of water to be not more than 1,500 µS/cm. Dissolved solids affect the remediation of pesticides in water through adsorption. The established linear correlation between conductivity and TDS therefore implies that the ionic particles in water may adsorb some of the residual pesticide for instance the adsorption of DDT on $Mn^{2+,}$ $Ni^{2+,}$ $Cu^{2+,}$ Co^{2+} and Zn^{2+} as reported by Lalah *et al* (2010).

2.7 Literature of selected pesticides

The following are properties of selected classes of pesticides residues. Four classes of residual pesticides are discussed and they include; carbamates, organochlorines, organophosphorus and synthetic pyrethroids.

2.7.1Organochlorine

Organochlorines are persistent organic pollutants containing at least one covalently bonded atom of chlorine as the dominant functionality that are extremely hydrophobic and strongly adsorbed by soil as the K_{oc} values indicate for instance BHC with K_{oc} value of 1080 respectively (Behfar *et al*., 2013). The persistence of organochlorine pesticides combined with a high octanol/water partition coefficient, $\log K_{ow}$ (Bai *et al*., 2015a), provides the necessary conditions for their bio-concentration in organisms because of its lipophilic properties. The Henry's Law constants, 5.14 x 10^{-6}, of the above organochlorine pesticide indicate that it is expected to volatilize in surface water. However, the volatilization in surface water is expected to be attenuated by adsorption to suspended solids and sediments in rivers. They are also not expected to volatilize from dry soil surfaces based upon their vapor pressures. Residual levels of organochlorine pesticides endosulfan, endosulfan, DDT, DDE, heptachlor, dieldrin, aldrin and endrin were investigated to evaluate the status of pesticide pollution in the surface water (Tongo *et al*., 2014). On the study, pesticide concentrations (µg/l) ranged from 0-0.001 (endosulfan sulfate), 0-0.0005 (endosulfan), 0.0003-0.0007 (DDT), 0.0002-0.001 (DDE), 0.0007-0.0337 (heptaclor), 0.0002-0.002 (dieldrin), 0-0.0003 (endrin) and 0.0003-0.1727 (aldrin). The order of abundance of these pesticide residues in water samples was dieldrin.> DDT > > endrin >endosulfan > DDE > aldrin > endosulfan (Tongo *et al*., 2014). Further, Navarrete *et al* (2018) also revealed the presence of total BHCs (i.e., α-BHC, β-BHC, δ-BHC) on surface and ground water. Their physical chemical properties are as in Table 2.1.

Table 2.1 Physical -chemical properties of organochlorines

Chemical property	BHC	Dieldrin	DDT and its metabolites
Vapor Pressure, mmHg at 25 °C	9.4×10^{-6} (Zhao and Lee, 2001)	9.96×10^{-7} (Whitacre, 2012)	1.51×10^{-7} (Martinez *et al.*, 2012)
Henry's Law Constant (atm.m^3/mol at 25°C	5.14×10^{-6} (Behfar *et al.*,2013)	1.11×10^{-4} (Whitacre, 2012)	8.32×10^{-6} (Yuan *et al.*, 2014)
Octanol-water partition coefficient ($\log K_{ow}$)	3.3 (Behfar *et al.*, 2013)	5.45 (Zhao and Lee, 2001)	4.89 to 6.91 (Yuan *et al.*, 2014)
Organic-carbon normalized partition coefficient (K_{oc})	1,080 (Behfar *et al.*, 2013)	434 (Whitacre, 2012)	518 (Henry and Kishimba, 2006; Whitacre, 2012; Yuan *et al.*, 2014)
Water Solubility mg/L	7.3 mg/L (Whitacre, 2012)	186 μg/L (Whitacre, 2012)	0.001mg/L (Whitacre, 2012)

2.7.1.1 Hexachlorocyclohexane (HCH)

BHC commonly known as Lindane and its IUPAC name γ-Hexachlorocyclohexane, (γ-HCH) is an organochlorine pesticide which has a chemical formula of $C_6H_6Cl_6$ and a molecular weight of 290.83 g/mol Behfar *et al.*, 2013). The structural formula of BHC is as shown in Fig 2.3

α -Hexachlorocyclohexane β-Hexachlorocyclohexane

Figure 2.3: Structural formula of BHC

Hexachlorocyclohexane is a γ-isomer of Lindane ("γ-HCH"). However, there are a lot of concerns on the issues. The International Agency for Research on Cancer (IARC) has classified lindane as carcinogenic to humans (Group 1). There is sufficient evidence in humans for the carcinogenicity of lindane for non-Hodgkin lymphoma (NHL) which is a cancer originating from lymphatic system (IARC, 2016). The current way of formulating the standards of Lindane are conversion and treatment of toxic isomers to less toxic chemicals through cracking process. Different estimated and calculated half-life values for lindane have been reported to be: 11 years at pH 8 and 20°C in seawater; 42 years at pH 7.6 and 5°C in Lake Huron, and 110 years in the Arctic Ocean at pH 8 and 0°C (USEPA, 2011). Lindane is stable to light. Since lindane does not contain chromophores that absorb light, direct photolysis either in air, water or soil is not expected to occur. Hydrolysis is not considered an important degradation process for lindane in aquatic environments under neutral pH conditions (Vega *et al.,* 2018).

Hexachlorocyclohexane (HCH) isomers (α-, β- and γ- (Lindane)) were recently included as new persistent organic pollutants (POPs) in the Stockholm Convention, and therefore, the legacy of HCH and Lindane production became a contemporary topic of global relevance (Vijgen *et al.*, 2011). In a preliminary assessment, the countries and the respective amount of HCH residues stored and deposited from Lindane production are estimated. Between 4 and 7 million tons of wastes of toxic, persistent and bio-accumulative residues (largely consisting of alpha- (approx. 80 %) and beta-HCH) are estimated to have been produced and discarded around the globe during 60 years of Lindane production. For approximately 1.9 million tones, information is available regarding deposition. Countries are: Austria, Brazil, China, Czech Republic, France, Germany, Hungary, India, Italy, Japan, Macedonia, Nigeria, Poland, Romania, Slovakia, South Africa, Spain, Switzerland, Turkey (Vijgen *et al*., 2011).

BHC is used globally in agriculture as an insecticide on fruits, vegetable crops, for seed treatment, in forestry, and for livestock (Vijgen, 2006). BHC has been listed as a pollutant of concern by EPA's due to its persistence in the environment, potential to bioaccumulate, and toxicity to humans and the environment. The use of BCH was banned under the Stockholm Convention by the year 2001 because of its environmental persistence and toxicity as reported by Birch and Taylor (2000). The Kenya Pests Control Products Board also banned its use in the year 2004 as a fungicide (Pesticide Control Products Board of Kenya, 2011). Blankenberg *et al* (2006) reported some of the physical properties of Benzene Hexachloride as log octanol/water partition coefficient (log K_{ow}) of 3.3 and soil/water partition coefficient, K_{oc} of 1,100 implying that it is highly soluble in water and it also adsorb strongly on the soil matter posing a great risk to the environment.

Benzene Hexachloride (BHC) (as Lindane) is restricted for use in seed dressing only by Pesticide Control Products Board of Kenya (2011). Several products with Lindane as the active ingredient and are present in the market and used by farmers for seed dressing are shown in Table 2.2 below with LINDANE / THIRAM WP also used in controlling soil borne diseases and insect pests. BCH has been listed as a pollutant of concern by Birch and Taylor (2000) and Pesticide

Control Products Board of Kenya (2011) also banned its use as a fungicide but restricted its use as an insecticide in seed dressing only.

Table 2.2 Selected pesticide products sold in Kenyan market containing lindane and approved by Pesticide Control Products Board of Kenya (2011)

Pesticide	Active Ingredient	Uses
BELL LINDANE 20EC Manufactured by Sharda International, India and distributed by Bell Industries Ltd.	200L of Lindane	It is an insecticide used to treat seeds. Used to control a pest that affects the maize plantations. It has been restricted only for seed dressing.
LINDANE / THIRAM WP Seed dressing Manufactured by Crompton Uniroyal and distributed by Chemtura Ltd.	27 % w/w Thiram + 20 % w/w of Lindane	It is a fungicide +insecticide that are used to control soil and seed borne pests and diseases respectively.
MISTOMATIC Lindane Liquid Manufactured by Crompton Uniroyal, Nairobi. And distributed by Dascot Ltd., Nairobi.	20 % w/w of pure Lindane	It is an insecticide used for seed dressing. Used for dressing sunflower seeds, maize seeds and rapeseed

2.7.1.2 Dieldrin

Dieldrin, $C_{12}H_8OCl_6$ is a chlorinated pesticide whose IUPAC name is 1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-*endo*-1,4-*exo*-5,8, -dimethanonaphthalene (HEOD) with a molecular weight of 380.9g/mol as reported by Whitacre (2012). The structural formula of dieldrin is as shown in Figure 2.4:

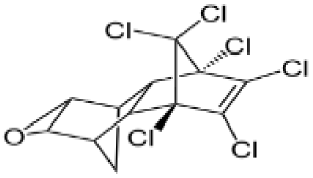


Figure 2.4: Structural formula of dieldrin

The common name of dieldrin is aldrin which is an insecticide containing 95 % (*w/w*) of HEOD. Aldrin quickly breaks down to dieldrin once it enters the atmosphere, Whitacre (2012). Dieldrin is an extremely persistent organic pollutant with octanol/water partition coefficient $\log K_{ow}$ of 5.45 and soil/water partition coefficient, K_{oc} of 4.33 which tends to bio-magnify as it passes along the food chain (Fillinger *et al.,* 2009). Dieldrin was banned by Pest Control Products Board of Kenya in 2004 after being used as a pesticide in controlling locusts and mosquitoes, a wood preserve and for termite control due to its harmful effects on humans, fish and wildlife (Fillinger *et al.,* 2009; Pesticide Control Products Board of Kenya, 2011).

2.7.1.3 DDT and its metabolites

Dichlorodiphenyltrichloroethane (DDT) has a chemical formula of $C_{14}H_9Cl_5$ and its IUPAC name is 1, 1, 1-trichloro-2, 2-*bis*-(*p*-chlorophenyl) ethane. The structural formula of DDT is shown in Figure 2.5 below:

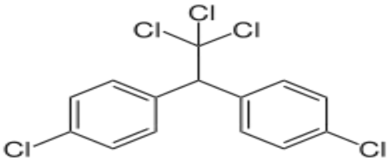


Figure 2.5: Structural formula of DDT

Commercial DDT is a mixture of several closely – related compounds (Bouwman *et al.*, 2011). The major component (65 - 80 %) is the *p, p′*-isomer and the nearly inactive o, p′ isomer is also present in significant amounts (15 %), up to 4 % of *p, p′*-DDD and up to 1.5 % of 1-(*p*-chlorophenyl)-2,2,2-trichloroethanol (Bouwman *et al.*, 2006). o, p′ isomer is inactive with low toxicity. However, in the late 1950's o, p'- isomer was found to cause cell death in the adrenal gland in dog and has since the 1960's been used as a drug for adrenal cancer in humans with the aim to decrease cortisol hypersecretion and inhibit tumour growth though its efficacy and potency is low (Cantillana, 2015). p, p'-isomer is toxic and persistent in the environment than the parent compound, DDT. This persistence, induced by its high lipophilicity and low reactivity, provides the necessary conditions to bioaccumulate in organisms and to biomagnify in food webs (Cantillana, 2015). DDT is a persistent organic pollutant that is extremely hydrophobic and strongly adsorbed by soil ($K_{oc} = 5.18$).

The persistence of DDT combined with a high octanol/water partition coefficient, $\log K_{ow}$ of 4.89 to 6.91 (Qu *et al.,* 2011), provides the necessary conditions for it to bio-concentrate in organisms because of its lipophilic properties. Depending on conditions, its soil half-life can range from 22 days to 30 years (Bai *et al.*, 2015b). Volatilization, and run-off among others are some of the routes that results in degradation and loss of DDT is absorbed by soils and organisms quickly when applied to aquatic systems. Similarly, DDD and DDE also have similar physical and chemical properties and are persistent in the environment (Blankenberg *et al.*, 2006). The structural formula of 1, 1-*bis*-(4-chlorophenyl)-2, 2-dichloroethene (DDE) is as in Fig 2.6.

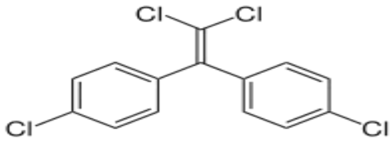


Figure 2.6: Structural formula of DDE

DDT has been used in agriculture as an insecticide and to combat insect vectors of diseases such as malaria and typhus. Because of its effectiveness at killing insects, it has been used as a mainstay to fight malaria in Africa (Curtis *et al.*, 2003). Due to its toxicity, persistence and bio-accumulation in the environment, DDT was banned for use in agricultural practices in the year 1972 by Stockholm Convention but restricted for indoor spray to eradicate mosquitoes. Its soil half-life is 2-15 years and 150 years in aquatic environment (Vanden Bilcke, 2002). In Kenya, DDT has been restricted for indoor control of malaria as recorded by Pests Control Products Board of Kenya (2011). However, its presence in the environment possesses a great threat especially to aquatic organisms and humans as it is highly persistence and bio-accumulates. Some of the products containing DDT as an ingredient are indicated in Table 2.3. DDT is having similar structure to the insecticide methoxychlor and the acaricides dicofol.

Methoxychlor has a chemical formula of $C_{16}H_{15}Cl_{3}O_{2}$, and its molecular weight is 345.65 g/mol (figure 2.6a). It is an organochlorine pesticide used worldwide against several insect pests, resulting in human exposure. This pesticide mimics endocrine hormone functions, interfering with normal endocrine activity in humans and wildlife (Fuentes *et al*., 2014). Most of the information available from human and animal studies suggests that methoxychlor does not cause cancer. The International Agency for Research on Cancer (IARC) and the EPA have determined that methoxychlor is not classifiable as to its carcinogenicity to humans (ATSDR, 2002).

a. Methoxychlor b. dicofol

Figure 2.7: Structural formula of metachlor and dicofol

Dicofol has a chemical formula of $C_{14}H_9C_{l5}O$ with IUPAC names 2, 2, 2-Trichloro-1 (figure 2.6b). Dicofol is used extensively in agriculture and horticulture to control spider, mites and soft-bodied mites in apples, pears, soft fruit, cucumbers, tomatoes, hops, vines, lettuce and ornamentals Dicofol is structurally similar to DDT. DDT is an intermediate for the synthesis of dicofol (Mohammed and Fasnabi, 2016). Dicofol has been listed as a persistent toxic compound in a series of multilateral agreements, for instance, Convention on Long-range Transboundary Air Pollution Protocol on persistent organic pollutants (POPs), and banned in many developed countries (Li *et al.* 2015). Dicofol was proposed in 2013 as a candidate for POPs in the Stockholm Convention (UNEP 2015a). However, the inclusion of dicofol among the legacy POPs is controversial. For example, there is a lack of evidence of dicofol’s environmental stability. Dicofol is not stable under alkaline condition when it decomposes to dichlorobenzophenone (DCBP) (UNEP 2015a).

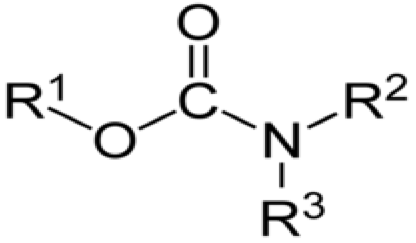
Due to structural similarity of DDT, dicofol and methoxychlor they are therefore possessing the same chemical and physical characteristics and are considered to be of similar concern as DDT and its metabolites DDE and DDD. These concerns relate to persistence, bioaccumulation, environmental long-range transport, and adverse effect in wildlife and humans (UNEP 2015a)

Table 2.3 Pesticide products sold in the market containing DDT and approved by Pesticide Control Products Board of Kenya (2011)

Pesticide	Active Ingredient	Uses
KELTHANE 18.5 EC PURIFIED It is an Emulsifiable Concentrate that is distributed by Lachlan Kenya Ltd but manufactured by Dow Agrosciences S.A. Middle / East Africa Ltd	197 g/L of Dicofol with not more than 0.1 % DDT content.	It is used as Agricultural miticide in deciduous fruits, nuts, berries, ornamentals vegetables, tea, Citrus, in cotton.
MITIGAN 18.5 EC It is an Emulsifiable Concentrate that is distributed by Amiran (K) Ltd and manufactured by Makhteshim Chemical Works Ashdod, Israel	185 g/L of Dicofol with less than 0.1 % DDT containing related compounds.	It is a miticide for controlling different species of mites affecting different varieties of crops (tea, ornamentals, grapes, mangoes, roses, pears, peaches, citrus, apples, cotton).These mites include citrus red mite, red spider mites among others.
VAPCOTHION EC It is an Emulsifiable Concentrate that is distributed by Osho Chemical Industries Ltd and manufactured by Vapco Ltd., Jordan	25 % w/v Dicofol + 8 % w/v Tetradifon with less than 0.1 % DDT containing related compounds	It is a non-systematic acaricide that is used to control red spider mite affecting cotton and rose plants

2.7.2 Carbamates

Carbamates are organic compounds which are derived from carbamic acids (NH_2COOH), (Miller and Chin, 2002). The general chemical formula of carbamates is as shown below in figure 2.8



R^1, R^2 and R^3 are alkyl groups

Figure 2.8: General chemical structure of carbamates

Carbamates are pesticides which are being used in agriculture as herbicides, insecticides, nematodes, sprout inhibitors and fungicides. Furthermore, carbamates pesticides are also used in public health in controlling the vectors, biocides as well as household’s products respectively. Carbamates undergo volatilization due to their low vapor pressure. Additionally, their low Henry’s law constants suggest that they will not volatilize from aqueous solutions. However, bendiocarb and carbaryl could become airborne from binding to particulates or as a spray drift immediately following application. Propoxur has extremely high potential to groundwater infiltration due to its high solubility in water and long half-life. It does not also has low adsorption to the soil organic matter, (Lenné *et al.*, 2005). Carbaryl is highly degraded in water solution by hydrolysis (Gunasekara, 2007).

The soil sorption coefficients (K_{oc} = 50 to 300), octanol/water partition coefficients ($\log K_{ow}$ = 1.40 – 2.36), (Ogwok *et al.,* 2009) and water solubilities of carbamates indicate that they moderately bind to soils and sediments. Thus, suspended particulates or mud in natural water may remove some carbamates from the aqueous phase (Lenné *et al.*, 2005). Generally, carbamates pesticides will be highly distributed in water rather air. Therefore, in very moist environment like where there is water run-off these pesticides compounds will be highly distributed. The water run-off is the major route through which these compounds move. Whether carbamates pesticides are applied directly or indirectly to the plants they will finally get their way into the soil. Bio-degradation of carbamates is affected by several factors which include the following; pH, soil moisture, soil temperature, photo-decomposition, adsorption, type of the soil and volatility.

The solubility of carbamates and the type of soil are two very important factors that dictates the movement of carbamates in the environment, (Plachá *et al.*, 2009). Different type of soil have different binding abilities whereby humic soil and clay soil registering the highest value i.e binding ability, (Damalas and Eleftherohorinos, 2011).

2.7.2.1 Bendiocarb

Bendiocarb is an acutely toxic carbamate insecticide used in public health and agriculture and is effective in a range of nuisance and disease vector insects such as aphids, mites, cockroaches, mosquitoes, and ants (Wijngaarden *et al.*, 2005). Its chemical formula is presented as $C_{11}H_{13}NO_4$ with molar mass of 223.23 g/mol. Its IUPAC name is 2, 2-Dimethyl-1, 3-benzodioxol-4-yl) *N*-methyl carbamate and its structural formula is as shown in Figure 2.9 below:

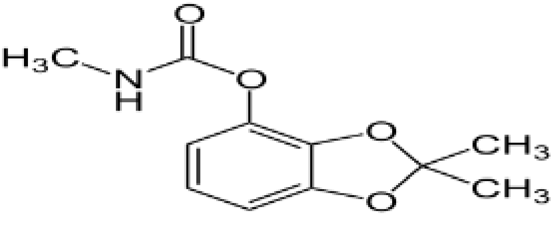


Figure 2.9: Structural formula of bendiocarb

Bendiocarb is one of 12 insecticides recommended by World Health Organization for use in malaria control in Third World countries. There is a possibility that bendiocarb is used for agricultural and health activities within Lake Victoria Basin. Hydrolysis of bendiocarb is pH dependent with maximum hydrolysis at acidic pH. Bendiocarb has been reported also to have K_{ow} of $5.01x10^{1}$ at a pH of 7, Henry law constant of $4.00x10^{-3}$ and a half-life of 13.2 hours PPDB (2018). It is highly toxic to mammals but tends not to bioaccumulate. It has a moderate to high toxicity for most aquatic organisms and birds (PPDB, 2012; PPDB, 2018).

Bendiocarb's production may result in its release to the environment through various waste streams from agricultural firms; its use as an insecticide will result in its direct release to the environment. All pesticide products containing bendiocarb were cancelled and no longer allowed to be used in the USA as of December 31, 2001 due to its health and environmental effects to aquatic animals (Bai *et al.,* 2015b). Bendiocarb exist in both the vapor and particulate phases in the atmosphere as the vapor pressure indicates (3.45×10^{-5} mm Hg at 25^{o}C). Vapor-phase bendiocarb will be degraded in the atmosphere by reaction with photo-chemically produced hydroxyl radicals; the half-life for this reaction in air is estimated to be 16 hours (Michael *et al.,* 2007). Particulate-phase bendiocarb will be removed from the atmosphere by wet or dry deposition. Photolysis half-lives on water and in soil are 0.33 and 37 days, suggesting that bendiocarb may be susceptible to direct photolysis by sunlight. If released to soil, bendiocarb is expected to have very high to moderate mobility based upon a K_{oc} range of 28 to 575 (Horner and VanWijngaarden, 2004).

Volatilization of bendiocarb from moist soil surfaces is not expected to be an important fate process based upon an estimated Henry's Law constant of 3.9×10^{-8} atm.m^{-3}/mole. A mean soil half-life of 12 days has been reported, suggesting that bio-degradation is an important environmental fate process in soil (Wijngaarden *et al.,* 2005). If released into water, bendiocarb is not expected to adsorb to suspended solids and sediment based upon the K_{oc} values

(Wijngaarden *et al.*, 2005). Volatilization from water surfaces is not expected to be an important fate process based upon this compound's estimated Henry's Law constant. An estimated BCF of 4.1 suggests the potential for bio-concentration in aquatic organisms is low. Hydrolysis, particularly under neutral or alkaline conditions, is expected to be a major fate process for this compound (Horner *et al.*, 2004).

2.7.2.2 Carbaryl

Carbaryl, $C_{12}H_{11}NO_2$, whose IUPAC name is 1-naphthylmethylcarbamate, is a carbamate insecticide whose molecular weight is 201.2 g/mol (PubChem, 2018). Carbaryl (1-naphthyl methylcarbamate) is a chemical in the carbamate family used chiefly as an insecticide. The structural formula of carbaryl is shown in Fig 2.10.

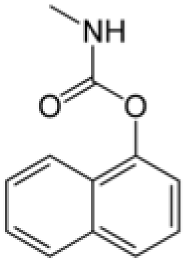


Figure 2.10: Structural formula of carbaryl

It is white and crystalline in nature and is the most used insecticide in the USA for agricultural and range-land protection. It was introduced in 1958 and commonly distributed with a brand name Sevin, (PCPB, 2011). Carbaryl is one of the most frequently used carbamate insecticide and is widely used for the control of a variety of pests in fruit, vegetables, forage, cotton and many other crops, as well as on poultry, livestock and pets (Roudani *et al.*, 2017). Birch and Taylor (2000) has recorded the physical parameters of carbaryl as: log octanol/water partition coefficient ($logK_{ow}$) of 1.85 at 20°C and soil/water partition coefficient, K_{oc} of 205 to 457.1, it has a half-life of 8 days^{-1} month. Albrechtsen *et al* (2001) has reported the half-life of carbaryl ranging from 4 to 72 days in oil with 78 days at anaerobic conditions and 7 days in aerobic soil conditions, an average of 3.2 days on plant leaves and a long time on water (>1500 days at pH of 5, 12.1 days at pH of 7 and 3.2 hours at pH of 9).

Carbaryl, a carbamate, has been widely used as acaricide for agricultural purposes and public health activities as recorded by Albrechtsen *et al* (2001) and Pesticide Control Products Board of Kenya, (2011). Pesticide Control Products Board of Kenya, (2011) has listed some of the approved products which contain carbaryl are in Table 2.4 below. The table indicates various formulations of carbaryl in the SEVIN products and is used as broad-spectrum insecticides for control of pests in crops and as acaricides.

Table 2.4 Selected pesticide products sold in the market containing carbaryl as approved by (Pesticide Products Board of Kenya, 2011)

Pesticide	**Active Ingredient**	**Uses**
SEVIN 85 S WP (for veterinary use): It is distributed by Bayer Animal Health Antipest (K) Ltd and manufactured by Bayer Crop Science, Germany.	85 % m/m Carbaryl	It is an Acaricide used to control ticks on cattle.
SEVIN PET DUDU DUST: It is distributed by Environmental Science East and West Africa, Nairobi. Manufactured by Bayer Crop Science, Germany.	7.5 % Carbaryl	It is an insecticide used to control fleas and ticks in dogs and cats.
SEVIN 85 S (for agricultural use): It is distributed by Bayer East Africa Ltd and manufactured by Bayer Crop Science, Germany.	85 % m/m Carbaryl	It's a broad spectrum insecticide. Used to kill insects on apples, strawberries, bears, citrus and grapes.
SEVIN DUDU DUST: It is distributed by Environmental Science East and West Africa, Nairobi. Manufactured by Bayer Crop Science, Germany.	7.5 % Carbaryl	It is an insecticide used to control crawling insects like ants , cockroaches among others

2.7.2.3 Propoxur

Propoxur, *o*-isopropoxyphenyl N-methylcarbamate ($C_{11}H_{15}NO_3$) has a relative molecular mass of 209.5g/mol. The structural formula of propoxur is as shown in Figure 2.11 below:

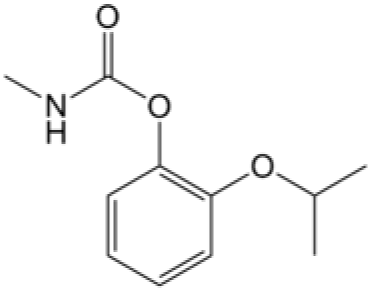


Figure 2.11: Structural formula of propoxur

Propoxur is a non - systematic carbamate insecticide used against household pests and fleas and in control of anopheles' mosquitoes, ants, moths and other agricultural pests. This compound is used to control mosquitoes, fleas, ants among others and is not applied to food crops. It is also used to kill snails, cockroaches and leaf hoppers respectively, (Birch and Taylor, 2000).

Public health and agricultural activities are the main source of propoxur into the wetland ecosystems. This compound does not adsorb onto the soil. Propoxur have been reported to degrade more water than in the soil, (Pohanish, 2002). Furthermore, propoxur also can remain in the environment for long (weeks to months) as compared to other carbamates (U.S. EPA, 2011). Photolysis of propoxur is higher in the surface of water (Mkindi *et al.*, 2015). The degradation of propoxur increases with increase in temperature and pH (Kasozi *et al.*, 2006). Propoxur has an octanol/water partition coefficient, $\log K_{ow}$ of 1.56 at 20 ^{o}C. Sediment Adsorption has K_{oc} values of < 1 to 10^3). The bio-accumulation in plants and fish has no effects, (Pohanish, 2002).

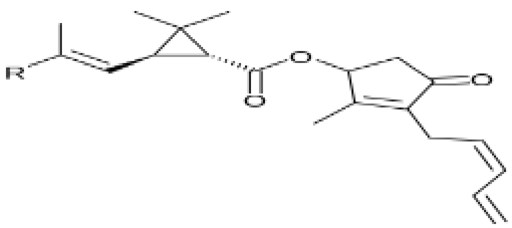
The possible sources of propoxur, is insecticide products used by farmers and approved by Pest Control Products Board of Kenya (2011) had propoxur as its main ingredient (Table 2.5). It is also noted that some of insecticide products used by farmers and contain propoxur may not have been approved by PCPB as the list of pesticide products present in all agrovets within Kigwal/Kimondi wetland did not list propoxur as a major ingredient although PROPOXUR VM, 80 sold by Bayer Environmental Science SA may be used as an ingredient in making other insecticide products.

Table 2.5 Selected pesticide products sold in the market containing propoxur as approved by Pesticide Control Products Board of Kenya, (2011)

Pesticide	**Active Ingredient**	**Uses**
PROPOXUR VM,80: It is manufactured by Bayer Crop Science, Germany.	80 % w/w Propoxur	It is a technical insecticide used to formulate "Baygon Dust" products.
BAYGON DUST: Manufactured by S.C Johnsons.	1 % w/w Propoxur	It is an insecticide used to control fleas, cockroaches and ants.
BLATTANEX: It is manufactured by Bayer Crop Science, Germany.	20 % w/w Propoxur	It is an insecticides used to control pests in processing and commercial firms.

2.7.3 Synthetic pyrethroids

A pyrethroid is an organic compound similar to the natural pyrethrins produced by the flowers of pyrethrums (*Chrysanthemum cinerariaefolium* and *C. coccineum*). Pyrethroids now constitute the majority of commercial household insecticides (Soderlund, 2012). In the concentrations used in such products, they may also have insect repellent properties and are generally harmless to human beings in low doses but can harm sensitive individuals. They are usually broken apart by sunlight and the atmosphere in one or two days, and do not significantly affect groundwater quality (Braskerud and Haarstad, 2003b). The pyrethroid is related to pyrethrin I and II as shown in Figure 2.12 below.



Pyrethrin I, R = CH_3

Pyrethrin II, R = CO_2CH_3

Figure 2.12: General structures of pyrethrin I and II

Synthetic pyrethroids are synthesized derivatives of naturally occurring pyrethrins, which are taken from pyrethrum, the oleoresin extract of dried chrysanthemum flowers. The insecticidal properties of pyrethrins are derived from ketoalcoholic esters of chrysanthemic and pyrethroic acids. Generally, the detected synthetic pyrethroids have low vapor pressure; low Henry's Law constant and large K_{oc} and they are not very soluble in water. If released into the environment, it is expected that the synthetic pyrethroids will be adsorbed onto sediments and have no mobility based on their low K_{oc} values. Based on their Henry's Law Constants, volatilization from moist soil surface and surface water is not expected to be an important fate process in the wetland ecosystems (Laskowski, 2002).

Synthetic pyrethroids are highly hydrophobic, display a higher affinity for soils and sediments as shown by their higher organic normalized soil sorption coefficients and their correspondingly lower water solubility. Because of their higher affinity for soil and sediment than pyrethrins, synthetic pyrethroids demonstrate a higher tendency to be associated with sediments in the environment with half-life times being between 14 to 20 weeks (Laskowski, 2002).

2.7.3.1 Cypermethrin

Cypermethrin, $C_{22}H_{19}O_3NCl_2$ is a synthetic pyrethroid insecticide whose IUPAC name is (±)-β-Cyano-(3-phenoxyphenyl)methyl(±)-*cis/trans*-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropane carboxylate (Laskowski, 2002). Its structural formula of cypermethrin is as shown below in Fig 2.13

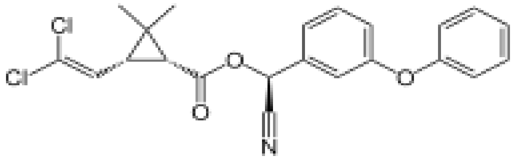


Figure 2.13: Structural formula of cypermethrin

The physical parameters of cypermethrin includes: octonal-water partition coefficient $\log K_{ow}$ of 6.60 and soil/water adsorption coefficient (K_{oc}) of 6.1 x 10^4 mL/g. Cypermethrin has a field dissipation half-life of 4-12 days with aerobic half-life of 6 – 20 days and anaerobic half-life of less than 14 days (Thatheyus and Selvam, 2013). Cypermethrin displays low water solubility, hence is hydrophobic. Cypermethrin is a non-polar pesticide and readily adsorbed onto soil surface and bound there. Cypermethrin also photodegrades rapidly on soil surfaces to many byproducts, with half-lives of 8-16 days (Wijngaarden *et al.*, 2005). Many photo-reactions are involved in photo-degradation and the photo-degradation rates are closely correlated with the organic matter content of the soil (Thatheyus and Selvam, 2013). The photo-products of cypermethrin are PBA and DCVA with >15 % recovery of each after 32 days of irradiation (Arnot and Gobas, 2006). Under aerobic conditions, these metabolites may undergo further breakdown to CO_2 at a much slower rate. The persistence of its metabolites is unknown (Thatheyus and Selvam, 2013). Cypermethrin has high applications in agriculture and public health programs especially as an active compound in acaricides, insecticides for controlling pests in French beans, cabbages, beans and maize alongside controlling mosquitoes, and cockroaches in public health activities as indicated in Table 2.6 below.

Table 2.6 Selected pesticide products sold in the market containing cypermethrin and approved by Pesticide Control Products Board of Kenya, (2011)

Pesticide	**Active Ingredient**	**Uses**
ECTOMIN It is manufactured and distributed by Ultravetis East Africa Ltd	100 g/L Cypermethrin high-cis	Insecticide/Acaricide to control ticks and fleas
ECTOPOR It is manufactured and distributed by Ultravetis East Africa Ltd	20 g/L Cypermethrin high-cis	Insecticide for veterinary use for the control of ticks on Cattle
DOMINEX 100 EC: It is distributed by Juanco SPS Ltd and manufactured by FMC Corporation, USA.	100 g/L Alpha-cypermethrin	It is used to control tsetse flies and ticks
DERAPHON GRANULES: It is distributed by Dera Chemicals Industries (K) Ltd and manufacture by United Phosphorous Ltd, India.	5 % w/w Cypermethrin	Used to control stock borer in maize stock.
ECTOMIN 100 EC: It is distributed by Ultravetis E.A Ltd and manufactured by Norvatis Animal Health Inc. Basel, Switzerland.	100 g/L Cypermethrin high-cis	Used to control mites, ticks on cattle by spraying and dipping.
DOMINATOR EC: It is distributed by Osho Chemicals Ltd and is manufactured by M/S Rallis Ltd, India.	10 % w/w Alpha-cypermethrin	It is used to control ticks in cattle by dipping.
DURANETLLIN: It is distributed by Caroga Pharma Ltd	0.55 % Alpha-cypermethrin	Used to control mosquitoes

2.7.3.2 Deltamethrin/Decis

Deltamethrin has a chemical formula of $C_{22}H_{19}Br_2NO_3$ ([(*S*)-cyano-(3-phenoxyphenyl)-methyl] (1*R*, 3R)-3-(2, 2-dibromoethenyl)-2,2-dimethyl-cyclopropane-1-carboxylate) with a structural formula as in figure 2.14 below.

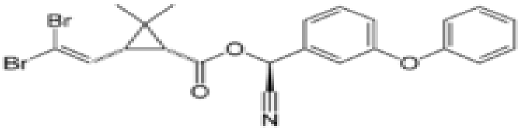


Figure 2.14: Structural formula of deltamethrin

Decis is also known to have the same chemical formula as deltamethrin but different chemical structures. Deltamethrin is the most popular and widely used insecticide in Kenya and within Lake Victoria Basin, used to kills insects in maize, cereals, fruits and stored products (Macharia, 2015). It is a member of the safest classes of pesticides although it is highly toxic to aquatic life, particularly fish and therefore must be used with extreme caution around water. It is neurotoxic to humans and has been found in human breast milk; however, deltamethrin is also applied in animal health and public health capacities (Karingu and Ngugi, 2013).

Deltamethrin is used in controlling mosquitoes. Depending on the nature of physicochemical properties of this compound and the prevailing environmental conditions, deltamethrin therefore partition itself to various environmental matrices (Åkerblom *et al.*, 2008). Deltamethrin has solubility of ≥2 µg/ℓ and vapor pressure of 0.002 mPa. The octanol-water partition coefficient (log k_{ow}) of deltamethrin is 5.4 implying that it is lipophilic (Thatheyus and Selvam, 2013).

Studies done on degradation of deltamethrin showed that sediments acts as the main sink of deltamethrin (Alamdar *et al.*, 2014). However, deltamethrin are reported to have short have life in water and therefore it decomposes into an acid (decamethrinic acid) and its isomers. The additional accumulation of deltamethrin in animals does not affect the fate of deltamethrin in the environment (Bai *et al*., 2015b). Table 2.7 below shows some of the products found in the market and approved by PCPB.

Table 2.7 Selected pesticide products sold in the market containing deltamethrin as approved by Pesticide Control Products Board of Kenya, (2011)

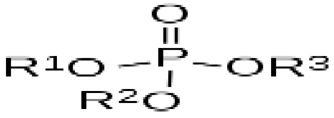
Pesticide	Active Ingredient	Uses
KATRIN It is distributed by Twiga Chemicals Ltd	Deltamethrin 25 g/L	Used to control aphids, thrips and white flies in French beans and roses.
DELETE It is distributed by Mogadishu Road Industrial Area, Kenya	Deltamethrin 50gm/l	Used to control ticks
DECIS TAB: Manufactured by Plaasken (pty) Ltd, South Africa.	25 % Deltamethrin	It is used to control thrips, aphids on barley and French beans
DELTAGUARD POUR ON: It is distributed by Twiga Chemicals Ltd and manufactured by Gharda Chemicals Ltd, India.	1 % w/w Deltamethrin	Used to control lice and tsetse flies on cattle.
DECIS 2.5 EC: Distributed by Bayer E.A Ltd and manufactured by Bayer Crop Science, Germany	25 g/L Deltamethrin	Use to control stock borer in cereals, vegetables among others
DECIS FORTE EC: Distributed by Bayer E.A Ltd and manufactured by Bayer Crop Science, Germany	100 g/L Deltamethrin	It is used to control thrips, aphids on barley and French beans
DELETE EC: Distributed by Intervet South Africa Ltd and manufactured by Bayer Crop Science, Germany	Deltamethrin 50 g/L	Used to control fleas, ticks and mites in cattle.

2.7.3.3: 5-phenyl rhodanine

5-phenyl rhodanine, $C_9H_7NOS_2$, whose IUPAC name 5-phenyl-2-thioxo-1,3-thiazolidin-4-one, is a sulfur based synthetic pyrethroid chemical used as a major ingredient in pyrethroid products used in agricultural activities as reported (Laskowski, 2002). There is unlimited data on the chemical and physical properties of 5-phenylrhodanine in the environment.

2.7.4 Organophosphates

An organophosphate (sometimes abbreviated OP) or phosphate ester is the general name for esters of phosphoric acid. Organophosphates are the basis of many insecticides, herbicides and nerve agents. The United States Environmental Protection Agency lists organophosphates as very highly acutely toxic to bees, wildlife, and humans (Leong *et al.,* 2007). Recent studies suggest a possible link to adverse effects in the neuro-behavioral development of foetus and children, even at very low levels of exposure. Organophosphates are widely used as solvents, plasticizers and EP additives. Figure 2.15 below shows the general chemical formula of an organophosphate.



$$R^1O-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle R^2O}{|}}{P}}-OR^3$$

Where: R^1, R^2 and R^3 are alkyl groups

Figure 2.15: General chemical formula of organophosphates

Organophosphate pesticides (OPs) are generally regarded as safe for use on crops and animals due to their relatively fast degradation rates. Based on the Henry’s Law Constants of organophosphates which is 1.4×10^{-6} atm. m^3/mol at 25 ºC (Armour, 2016), they are expected to be essentially nonvolatile from water surfaces and from moist soil surfaces as indicated by their vapor pressure. Based on their water solubility figures, the organophosphates are slightly soluble in water but miscible with most organic solvents.

2.7.4.1 Diazinon

Diazinon, $C_{12}H_{21}N_2O_3PS$; IUPAC name is *O*, *O*-Diethyl *O*-[4-methyl-6-(propan-2-yl) pyrimidin-2-yl] phosphorothioate) has a molecular weight of 304.3 g/mol. Its structural formula is as in Figure 2.16 below. Diazinon sold as Diazon is majorly used to control sucking and chewing insects and mites on a range of crops including bananas, citrus fruits, vegetables, potatoes, and sugar cane (Armour, 2016). Diazinon is an organophosphate used in control ants, cockroaches and indoor pest control. It is also used as an acaricide (a chemical which kills mites and ticks) applied in cattle dips (Alamdar *et al.*, 2014). It has been outlawed in the United States because it is toxic to aquatic organisms. Diazinon has a water solubility of 40 mg/L at room temperature, soil/water partition coefficient K_{oc} of 2.12 and octanol/water partition coefficient, $\log K_{ow}$ of 3.86 as indicated by Alamdar *et al* (2014). Diazinon has hydrolysis half-life of 138 days, aerobic soil half-life of 40 days and anaerobic soil half-life of 16 days.

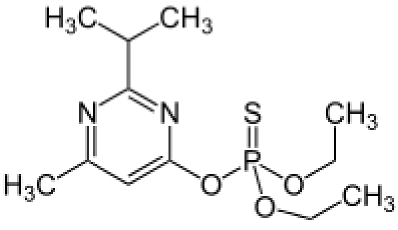


Figure 2.16: Structural formula of diazinon

Pesticide Control Products Board of Kenya (2011) has recorded several products which contains diazinon as the main ingredient (Table 2.8).

Table 2.8 Selected pesticide products sold in the market containing diazinon and approved by Pesticide Control Products Board of Kenya (2011)

Pesticide	Active Ingredient	Uses
AGROZINON 60 EC: Distributed by Bell Industries Ltd and manufactured by Asiatic Agricultural Industries Ltd, Singapore	600 g/L Diazinon	It is used in horticultural farming.
BASUDIN 600 EW" It is distributed by Ultravetis E.A Ltd and manufactured by Sagro Singapore Ltd	600 g/L Diazinon	Used to control pests like leaf miners, scale insects, leaf hoppers among others.
DIASINA 60 EC: Distributed by Biomedical Lab Ltd and manufactured by Wenzhou Pesticide Factory, China.	600 g/L Diazinon	Used in controlling whiteflies and aphids in tomatoes
DIAZOL 60 EC: It is manufactured by Makhteshim Chemicals Ltd	600 g/L Diazinon	Used in controlling a wide range of pest attacking vegetables, coffee among others.

2.7.4.2 Malathion

Malathion, $C_{10}H_{19}O_6PS_2$, whose IUPAC name is Diethyl - 2-[(dimethoxyphosphorothioyl) sulfanyl]butanedioate has molar mass of 330.4g/mol with a density of 1.23g/mL (Qu *et al.*, 2011). Its structural formula is indicated in Figure 2.17 below:

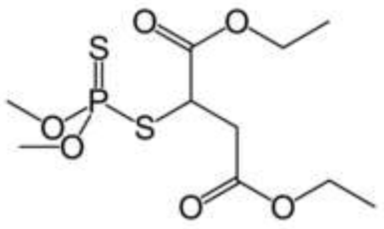


Figure 2.17: Structural formula of malathion

Malathion is an organophosphate pesticide used in residential landscaping, agriculture and public recreation areas and in public health pest control programs (Qu *et al* (2011). Malathion has an octanol/water partition coefficient $\log K_{ow}$ of 2.36 with soil/water partition coefficient, K_{oc} of 291.0. Its hydrolysis half-life is 6 days with aerobic soil half-life of 3 days and anaerobic soil half-life of 30 days thus it is a low persistent hydrocarbon in soil. It is moderately bound to soil, and is soluble in water, so it may pose a risk of groundwater or surface water contamination in situations which may be less conducive to breakdown (Nollet and De Gelder, 2013). Osakwe (2014) has recorded the presence of Malathion in wells of California, U.S.A with a high concentration of 6.17µg/L. Table 2.9 below indicates some of the products sold in the market as containing Malathion which have been approved by Pesticide Control Products Board of Kenya (2011).

Table 2.9 Selected pesticide products sold in the market containing malathion and approved by Pesticide Control Products Board of Kenya (2011)

Pesticide	**Active Ingredient**	**Uses**
DERA MALATHION 50 EC: It is manufactured by Cheminova, Denmark	500 g/L Malathion	It is used in a wide range of agricultural crops.
DERA BLUE CROSS DUST: It is manufactured by Cheminova, Denmark	2 % w/w Malathion	Use to control pests that attack beans and grains in store.
FEDOTHION 50 EC: It is distributed by Dera Chemicals Ltd and manufactured by Cheminova.	50 % w/w Malathion	It is used to control aphids and Diamond-black moth that attacks cabbages.
FYFANON: It is manufactured by manufactured by Cheminova Lemvig, Denmark	95 % w/w Malathion	It is used as an AI in Malathion formulation.
FYFANON 50 EC: It is by manufactured by Cheminova Lemvig, Denmark	500 g/L Malathion	It is used to control chewing and sucking insects in crop field.
MAGIC 50 EC: It is manufactured by Bharat Ltd, India.	500 g/L Malathion	Used in controlling Diamond-back moth, aphids, thrips among others in cabbages.

2.7.4.3 Sumithion

Sumithion also known as fenitrothion, $C_9H_{12}NO_5PS$ with IUPAC name *O*, *O*-dimethyl *O*-4-nitro-*m*-tolyl phosphorothioate with a molecular weight of 277.2 g/mol (Said *et al.*, 2012). The chemical structure of sumithion is as indicated in Figure 2.18 below.

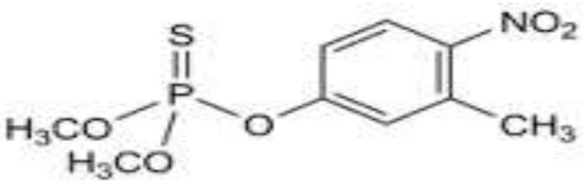


Figure 2.18: Structural formula of sumithion

Sumithion is an organophosphorus insecticide highly effective against aphids, merely bugs, scale insects and borers. It is used against pests in mango, citrus, beans, pineapple, tomato, cabbages and ornamentals. Sumithion is noted to be very stable under acidic conditions at 37 ^{0}C, while under alkaline conditions it is hydrolyzed rapidly with half-life of 3 days and less than 24 hours at pH 11 and pH 13, respectively as recorded by Amoros *et al* (2000). Another study indicated the half-life for the disappearance of sumithion at 23 ^{o}C and pH 7.5 in buffered water and natural water to be 21.6 and 49.5 days, respectively (Oo, 2001). In a field experiment (pH 7.0-7.5, 19-23 ^{o}C), the half-life of sumithion is 1.5-2 days upon spraying of a 10 % sumithion EC-formulation and half-life of less than 1 week in soils (Amoros *et al.*, 2000). Sumithion has octanol/water partition coefficient log K_{ow} of 3.38 with soil/water partition coefficient, K_{oc} of 2.53 at pH of 5.5 to 7.4 (Oo, 2001).

Sumithion is best known as fenitrothion which is an organophosphorus insecticide highly effective against pests in tomatoes, cabbages and ornamentals among others (Albrechtsen *et al.*, 2001). Its use within Kigwal/Kimondi river catchment area is a major source of its presence in the wetland. Pesticide Control Products Board of Kenya (2011) has indicated several compounds which have sumithion as the main ingredient and available to farmers in the market as indicated in Table 2.10 below.

Table 2.10 Selected pesticide products sold in the market containing sumithion and approved by Pesticide Control Products Board of Kenya (2011)

Pesticide	Active Ingredient	Uses
SUMIALPHA: Distributed by Twiga Chemicals Ltd and manufactured by Sumitomo Chemicals Ltd, Japan.	83 % w/w Esfenvalerate	It is used in the formulation of locally Sumithion Super.
SUMITHION: Distributed by Twiga Chemicals Ltd and manufactured by Sumitomo Chemicals Ltd, Japan.	95 % w/w Fenitrothion	Used for formulation purposes
SUMITHION 50 EC: Distributed by Sumitomo Ltd, Nairobi and manufactured by Sumitomo Chemicals Ltd, Japan.	500 g/L Fenitrothion	Used to control insects like army worm that attacks beans , coffee
SUMITHION SUPER: Distributed by Twiga Chemicals Ltd and manufactured by Sumitomo Chemicals Ltd, Japan.	12.5 g/L Esfenvalerate + 350 g/L Fenitrothion	Used to control insects that attacks coffee plantation.

2.7.4.4 Glyphosate

Glyphosate, $C_3H_8NO_5P$ whose IUPAC name is *N*-(phosphonomethyl) glycine is an Organophosphorus with molecular mass of 169.07 g/mol. Glyphosate is soluble in water at room temperature but is insoluble in organic solvents such as ethanol, acetone and xylene. It has a vapor pressure of 1.31×10^{-2} mPa at 25 °C. Glyphosate also hydrolyses at pH range of 3 to 9 and relatively stable to photo degradation, (Tomlin, 2006).

Glyphosate is a non-selective, post-emergent, broad-spectrum, systematic herbicide which is used to suppress all plant types including vines, trees, shrubs, grasses and perennials. It is effective against more than 100 annual broadleaf weed and grass species and more than 60 perennial weed species. Below is figure 2.19 showing the molecular structure of glyphosate

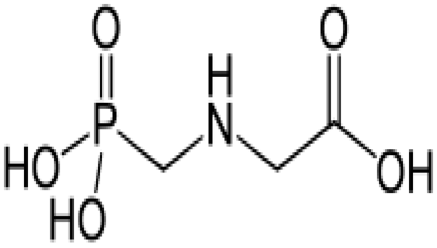


Figure 2.19: Structural formula of glyphosate

Table 2.11Selected pesticide products sold in the market containing glyphosate and approved by Pesticide Control Products Board of Kenya (2010)

Pesticide	Active Ingredient	Uses
ROUND-DUP It is manufactured by Monsato Europe and distributed by Monsato Kenya Ltd	Glyphosate 480g/L	It is used in minimum tillage in controlling annual and perennial weeds in tea and coffee plantations.
GLYWEED It is manufactured by Sabero Organics Ltd, China and distributed by Orbit Chemicals Industries Ltd	Glyphosate 480g/L	It is a non-selective herbicide used to control annual, biennial and perennial weeds in baby corn
TWIGA SATE It is manufactured by Agrochem Egypt and distributed by Twiga Chemicals Ltd	Glyphosate 480g/L	It is post emergence herbicide used to control annual and perennial grasses and broad-leaved weeds.
WOUND OUT It is manufactured by Vapco, Jordan and distributed by Osho Chemicals Ltd	Glyphosate 480g/L	It is an herbicide used to control annual, biennial and perennial weeds in tea.
GLYCEL It is manufactured by Excel Crop Care ltd, India and distributed by Elgon Kenya Ltd	Glyphosate 480g/L	It is a non-selective herbicide and post-emergence herbicide used to control grasses and broad-leaved weeds.

2.7.4.5 Ammonium lauryl sulphate

Ammonium lauryl sulphate**,** $C_{12}H_{29}NO_4S$ whose IUPAC name is Ammonium dodecyl sulfate and it has molecular mass of 283.427 g/mol. It is an active ingredient of Duo-dip. The molecular structure is as shown in figure 2.20. It is an Organophosphorus acaricide and is mainly used in veterinary in controlling lice, mites and ticks in livestock. It is also used as pesticide to control pests in agricultural farms, (PCPB, 2010).

Ammonium lauryl sulphate has been reported to have low acute toxicity. However, data on skin sensitization, genotoxicity, chronic exposure, carcinogenicity and reproductive toxicity have not been established (NICNAS, 2019)

Figure 2.20: Structural formula of ammonium lauryl sulphate

2.7.4.6 Chlorfenvinphos

Chlorfenvinphos, $C_{12}H_{14}Cl_3O_4P$ whose IUPAC name is [(*EZ*)-2-Chloro-1-(2, 4-dichlorophenyl) ethenyl] diethyl phosphate has molar mass of 359.564 g/mol. Chlorfenvinphos is the active ingredient and is a common name for Organophosphorus compound (branded as Steladone). It is used as a pesticide and as an acaricide. It is used in controlling ticks, flies, lice, mites on cattle and for blowfly. They are also applied on organic waste and breeding places of insect’s larvae. It is very toxic, (PubChem, 2019)

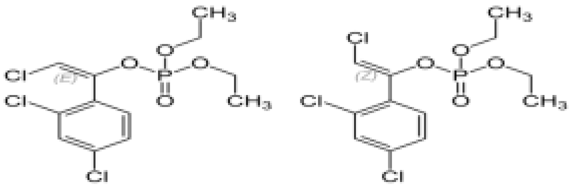


Figure 2.21: Structural formula of chlorfenvinphos

2.8. Conceptual framework

The following conceptual framework was adopted to guide in the study. The conceptual framework represents both independent and dependent variables. The independent variables are grouped into two: sources of pesticide residues and transport mechanism of pesticides to wetland ecosystem. These variables contribute high levels of pesticide residues to the inlet section of the wetland. The dependent variables are the wetland sections which have various physical and chemical properties aimed at retaining the pollutants present in water traversing the ecosystem as shown in Figure 2.22 below.

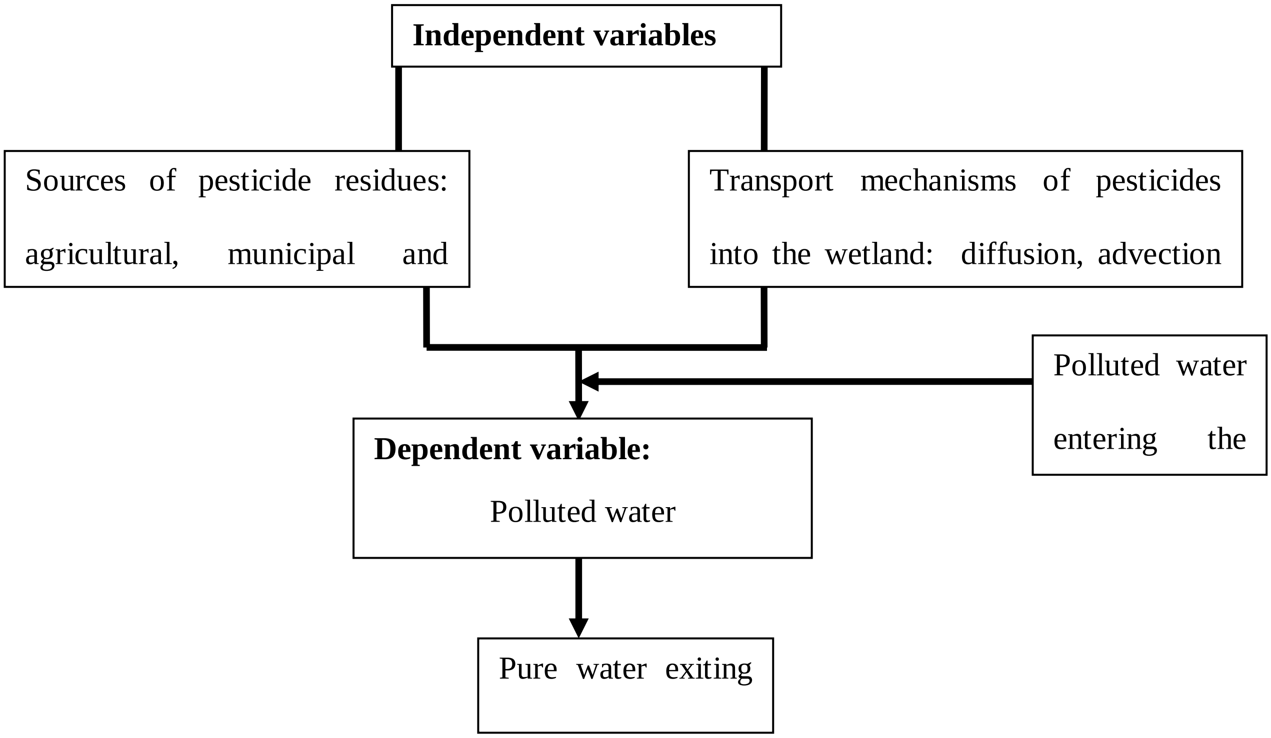


Figure 2.22: Retention efficiency of wetland

CHAPTER THREE

MATERIALS AND METHODS

3.1 Introduction

This chapter describes the selected site descriptions, materials and methods, sampling and field work, laboratory preparation and analysis of collected samples.

3.2 Study Area

3.2.1 Mobego-Kabianga wetland ecosystem description

Mobego-Kabianga wetland ecosystem is situated in Kericho West Sub-County in South Western end of Rift-Valley Province of Kenya and within the proximity of famous multinational tea growing companies, Unilever and James Finlay. It is located approximately 26 km from Kericho town.

Plate 3. 1 A satellite map of Mobego-Kabianga wetland ecosystem, (Google map, 2018)

3.3 Materials and Methods

3.3.1 Chemicals and Reagents

Selected pesticide standards of 98.9 % to 99.8% purity were used. These included DDT, methoxychlor, dieldrin, chlordane, toxaphene, mirex, kepone, Lindane, and Benzene Hexachloride. Tridecane (Internal standard,) was also used. Solvents and chemicals: anhydrous sodium sulphate, methanol, and phosphate buffer (pH 6.8) were used.

3.3.2 Sampling procedures

This study used the experimental design method where samples were collected using purposeful randomized sampling method. Plant samples of papyrus reeds, water and sediment) were collected from the wetland at three sampling points (inlet, midpoint and exit) as shown in figure 3.2 below. Samples were collected during dry season.

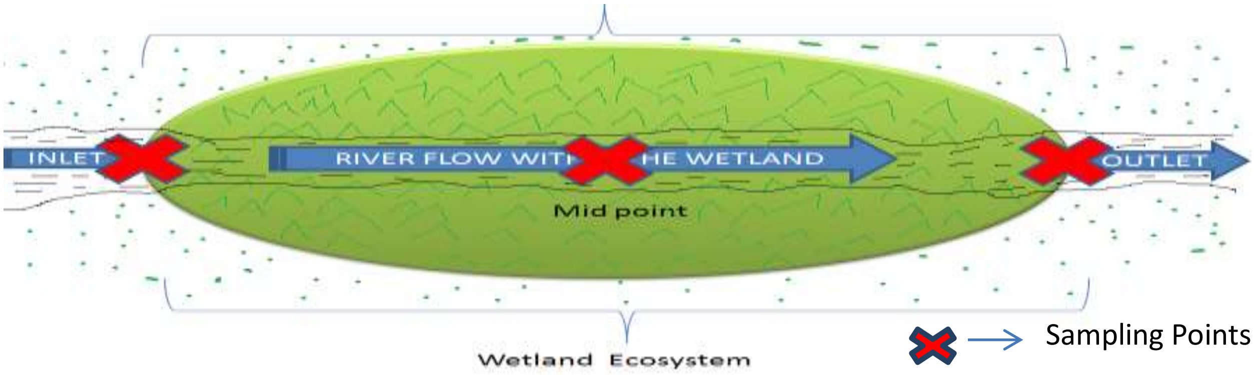


Figure 3.1: Wetland sampling points

Surface water was collected randomly as in figure 3.2 at depth of 10 – 20 cm at the wetland ecosystem using grab method, and stored into a well labeled dark clean amber glass bottle. Sediment samples were collected at the base of the wetland using a stainless steel shallow water bottom dredge into a clean well labeled polythene bag. Papyrus reed plant materials were also collected and packed into a well labeled polythene bag. All samples were stored in an icebox at 4^{o}C and transported to Department of Physical Sciences, University of Kabianga, where preparation of the samples for residual pesticides analysis was done as in Section 3.3.4.

Plate 3. 2 Pictures showing papyrus reeds growing along Mobego-Kabianga wetland

3.3.3 Measurement of physicochemical parameters

3.3.3.1: pH

pH meter (HI 98128 (pHep®5) was used to measure the pH of water and soil samples. The pH electrode was rinsed properly with the distilled water in order to prevent contamination of the samples. Calibration of pH meter was also done by the use of buffer solution (pH=7). The pH electrode was then dipped into the test sample solutions and stirred with magnetic bar for 30 seconds. The pH values were recorded when the pH reading was stable, (vlab.amrita.edu, 2012).)

3.3.3.2 Flow Rate

The river flow rate was measured in situ by use of LabQuest vernier caliper flow rate probe. The flow rate probe was lowered into the stream about 60 cm. It was then left for 30 seconds and the readings were taken and recorded (LabQuest®, 2019)

3.3.3.3 Temperature

Temperature was measured in situ by use of LabQuest vernier caliper, temperature probe. The temperature probe was lowered into the stream about 60 cm. It was then left for 30 seconds and the readings were taken and recorded (LabQuest®, 2019)

3.3.3.4 Total dissolved solids

Water samples were stirred for five minutes and 50 mL of the aliquot was taken and filtered by use of filter paper (Whatman, No. 3 mm) three times. The filtrate was transferred into an evaporating dish where it was dried, cooled and weighed. TDS concentration was calculated using the formula 3.1 below in mg/L, (Fatihah, 2018).

$$\frac{(A-B)X1000}{mL.of.Sample} \text{ ……………………………. 3.1}$$

Where;

A = weight of dried residues + evaporating dish in mg

B = weight of dish in mg

3.3.3.5 Total suspended solids

Water sample was stirred for five minutes. 50 mL of the aliquot was taken into a filter paper (Whatman, No. 3) and filtered three times while stirring. The residue was dried, cooled and weighed. TSS concentration was calculated by the use of the formula 3.2 below, (Fatihah, 2018)

$$\frac{(A-B)X1000}{mL.of.sample} \text{ …………………………3.2}$$

Where;

A = weight of filter paper + dried residues in mg

B = weight of filter paper in mg

3.3.3.6 Dissolved oxygen

Dissolved oxygen was measured in situ by use of LabQuest vernier caliper, dissolved oxygen probe. The dissolved oxygen probe was lowered into the stream about 60 cm. It was then left for 30 seconds and the reading was taken and recorded (LabQuest®, 2019)

3.3.3.7 Conductivity

Conductivity of water was also measured in situ. LabQuest vernier caliper, conductivity probe was used. Conductivity probe was lowered into water and readings were taken after 30 seconds (LabQuest®, 2019)

3.3.4 Sample preparation for analysis

The following are sample preparation procedures for water, sediment and plant samples.

3.3.4.1 Extraction of water samples

5 mL of water sample from the inlet of Mobego-Kabianga wetland was mixed with phosphate buffer (pH 6.8) to stop any micro-organic process. The sample was passed through glass wool to remove sediments and then mixed with 35mL of methanol and vortexed using vortex mixer (Scientific SA8 Vortex Mixer AC/DC Input) for 10 minutes. The mixture was then centrifuged at a rate of 13,000 rotations per minute for 5 minutes at a temperature of 25ºC. The supernatant solution was sucked from the sampling bottle and passed through anhydrous $Na_2SO_{4\,(s)}$ to remove any traces of moisture and concentrated by passing them through $N_{2\,(g)}$. One (1) µL of tridecane was added to 40 µL of extracted water sample and 1µl of the mixture injected to LC-MS/MS (Agilent-6420) and GC-MS/MS (Agilent-7870A) for residual pesticide analysis (Bhateria *et al.*, 2016)

3.3.4.2 Extraction of sediment samples

Collected sediment samples were air dried and finely ground using mortar and pestle and packed in polythene bags. 5 g of the finely ground sediment sample from the inlet of Mobego-Kabianga wetland ecosystem were mixed with 70% methanol: water solution in a 250 mL volumetric flask to make a 100 mL light slurry and left for 12 hrs to extract. The supernatant solution was collected and phosphate buffer (pH 6.8) added to it to stop any micro organic processes. The procedure as in *Section 3.3.4.1* was followed until a chromatogram was obtained. (Blankenberg, 2007)

3.3.4.3 Extraction of plant material samples

To analyze for residual pesticide levels in plant samples, air dried finely ground (using micro-miller) homogeneous mixture of roots, stem, and leaves of papyrus reeds was crushed and 10g of the mixture of each sample was mixed with 70 % methanol and left for 2 hours to extract while shaking it using Bionics Bench Top Shaker. The mixture was passed through glass wool to remove the solid materials (Armbruster, 2008). The procedure as in *Section 3.3.4.1*was followed until a chromatogram was obtained.

3.3.5 Statistical analysis and data presentation

All data obtained was analyzed using SAS version 9.4 for central tendencies with confidence limit of 95 %. Analyzed data was presented in form of tables, charts and graphs using Microsoft Excel program.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Introduction

This chapter provides information on pesticide and land use survey, data analysis and presentation, interpretation, conclusions and recommendations.

4.2 Geographical description of the wetland

Mobego-Kabianga wetland ecosystem is situated 0^{o}26`29” S 35$^{o}$08`58” E of Belgut constituency which is located in Kericho County in the highland west of the Rift-Valley, Kenya. The wetland has an elevation of 1732m above the sea level and it stretches averagely 3792m long and 202m wide. It is one of the largest wetland in the region and it serves as the water catchment area for the entire residence of Kabianga. About 90% of the water is used by the locals for watering the livestock, irrigation and for general domestic purposes. The wetland also serves as an important source of water to University of Kabianga and its environs. The upper part of the wetland comprises of Kipsolu, Nyabangi and Mobego while the lower part of the wetland comprises of Cheptakum and Kabianga respectively.

The wetland is fed by several tributaries. The wetland also is surrounded by exotic vegetation (Eucalyptus trees) with little or no indigenous trees and about 87% of the wetland is covered by the papyrus reed plants. Due to the presence of these vegetation in the wetland, water tends to flow at a slow rate and hence depositing most of the pollutants in the wetland.

4.3 Land and pesticides use survey in Mobego-Kabianga wetland ecosystem

This section entails the pesticide use survey, land use survey, analysis of questionnnaires, farmers' knowledge on pesticides and encroachment of the wetland.

4.3.1 Analysis of questionnaire

A survey on land use and pesticides used within Mobego-Kabianga wetland ecosystem was carried out by the help of structured questionnaire and observations among small scale and large scale farmers in Mobego-Kabianga wetland ecosystem. Sixty households (age between 40 to 60 years) living along the wetland about 50 to 500 m from the wetland was interviewed. Therefore, after administration of questionnaires, content analysis was done and presented below (table 4.1 and table 4.2).

4.3.1.1 Land use

Mobego-Kabianga wetland ecosystem is situated in Belgut Sub-County in Kericho County where agriculture is the backbone of economy. From the interviews and observations, it was noted that the residents rely majorly on agriculture for production of food and wealth. Table 4.1 below gives a summary of the land use along Mobego-Kabianga wetland.

Table 4.1 Summary of crops planted/livestock reared along Mobego-Kabianga wetland

Region	Type of crop planted/livestock reared	No. of respondents (%)
Cheptakum	Tea	66
	Maize	7
	Beans	7
	Sukuma wiki	7
	Livestock	13
Mobego	Tea	80
	Maize	Nil
	Beans	Nil
	Sukuma wiki	7
	Livestock	13
Nyabangi	Tea	73
	Maize	7
	Beans	Nil
	Sukuma wiki	Nil
	Livestock	20
Kipsolu	Tea	86
	Maize	Nil
	Beans	7
	Sukuma wiki	Nil
	Livestock	7

From table 4.1 above, it was noted that of all the regions tea farming was leading (i.e Cheptakum (66 %), Mobego (80 %), Nyabangi (73 %) and Kipsolu (87 %)). The rest of the crops i.e maize, beans and sukuma wiki were noted to be the least planted crops along the wetland with the rate below 10 %. Furthermore, the rearing of livestock was also notably low with Nyabangi registering 20 % higher and Cheptakum, Mobego and Kipsolu registering lower percentages of 13 %, 13% and 7 % respectively.

The following are some of the pictures of land uses along the wetland.

Plate 4. 1 Crops (kales, tea, maize and beans) and livestock reared within the wetland

4.3.1.2 Pesticide Use

With the infestation of pests in agricultural crops, pesticides have been the only viable option to eliminate pests. Table 4.2 gives a summary of the pesticide use along Mobego-Kabianga wetland region.

Table 4.2 Pesticides used along Mobego-Kabianga wetland ecosystem

Region	***In crops***	***Frequency***	***In livestock***	***Frequency***
Cheptakum	Roundup Ridomil	Monthly	Triatix Duo-dip Delete Steladone	Weekly
Mobego	Roundup Ridomil	Monthly	Triatix Duo-dip Agrozinon	Weekly
Nyabangi	Roundup	Monthly	Triatix Delete Duo-dip Steladone	Weekly
Kipsolu	Roundup	Monthly	Duo-dip Delete	Weekly

The table above summarizes the types of pesticides used and the frequency of application which varies from plant to plant and from animal to animal. On this study, about 99 % of the farmers across the wetland from were found to be using pesticides and about 1 % employed organic farming. Triatix was used in Mobego, Cheptakum and Nyabangi but its use in Kipsolu was not registered. Amitraz is an active ingredient of triatix belongs to chemical family called formammidine. It is used in controlling external parasites by dipping and spraying. Amitraz is a poisonous chemical which may cause central nervous system depression and also respiratory/cardiovascular symptoms as reported by Eizadi-Mood *et al* (2011).

Ridomil was used only in Cheptakum and Mobego. Metalaxyl is an active ingredient of ridomil belonging to benzenoid fungicide family and is used as a foliar spray in agricultural farms. This chemical is harmful to human and it is also relatively non-toxic to most non target arthropod and vertebrate species (Sukul and Spiteller, 2000)

Delete was found to be used in Cheptakum, Nyabangi and Kipsolu. Deltamethrin is the active ingredient of delete belonging to chemical family of Pyrethroid which is a man-made pesticide and is found in many products used to control pest. Delete is used to control external parasites through dipping and spraying. However, aquatic toxicity by delete was been reported by Benld *et al* (2008).

Round-up and duo-dip were being used across the wetland i.e Cheptakum, Mobego, Nyabangi and Kipsolu. On the other hand, steladone was also used only in Cheptaku and Nyabangi. However, agrozinon was only used in Mobego. Glyphosate, ammonium lauryl sulphate, chlorfenvinphos and diazinon are also other active ingredients of round-up, duo-dip, steladone and agrozinon respectively belonging to a chemical family called organophosphorus. Roundup is used to control annual and perennial weeds in agricultural farms. Ridomil is used as fungicide to control early and late blight in potatoes and tomatoes. Duo-dip and steladone are used to control external parasites through dipping and spraying while agrozinon is an insecticide for use in horticultural crops. Human exposure to these chemicals causes circulatory or respiratory problems (Robb and Baker, 2019)

4.3.1.3 Farmers’ Knowledge on Pesticides

Table 4.3 Summary of knowledge of farmers on handling, storage, application, toxicity and disposal of pesticides in Mobego-Kabianga wetland ecosystem

Item description	Knowledgeable (%)	Unknowledgeable (%)
Pesticide safety procedures	67	33
Pesticide storage procedures	83	17
pesticide application procedures	48	52
Pesticide disposal procedures	75	25
Pesticide toxicity	92	8

From table 4.3 above, it was noted that many farmers had knowledge on the application procedures (48 %), toxicity (92 %), storage (83 %), safety (67 %) and disposal (75 %) procedures of the pesticides. It was also noted that public awareness and training by agricultural extension officers greatly improved their knowledge on pesticide management. However, some farmers had no idea about application (52 %), toxicity (8 %), storage (17 %), safety (33%) and disposal (25 %) procedures. Lack of knowledge on application, storage, safety and disposal to these farmers possess a great risk to the environment as their poor pesticides disposal and application skills may drain residual pesticides into environment. Therefore, it is of great concern that these unknowledgeable numbers of farmers be trained on various aspects with regard to pesticides usage and their safety to avoid human health problems.

4.4 Encroachment of the wetland

The Kenya National Wetland Conservation and Management Policy (2013) which give emphasis on protection of wetlands with regard to ecological and socio-economic importance are critical in conservation and management of Mobego-Kabianga wetland ecosystem by National Environmental and Management Authority. Mobego-Kabianga wetland ecosystem being one of the many wetlands in Kenya has faced varied challenges including communities draining away the wetland water rendering it dry and subsequent land subdivision. Furthermore, some sections of the wetland have been converted into farms. Grazing of livestock on the wetland is also another major threat to the wetland. Most of the farmers have converted the wetland into grazing lands threatening the survival of the wetland as shown in plate 4.2.

Plate 4. 2 Photos of livestock grazing and subdivision of the wetland ecosystem

The residence of Kabianga majorly relies on the water transiting through the wetland for different usage which includes bathing, drinking, washing clothes and some for crop irrigation as shown in plate 4.3.

Plate 4. 3 Photos showing individuals fetching water and washing clothes

4.5 Physico-chemical parameters of the wetland

This section entails the description of physic-chemical parameters affecting the retention efficiency of Mobego-Kabianga wetland ecosystem.

4.5.1 Rainfall

Figure 4.1 below shows mean rainfall of Mobego-Kabianga wetland ecosystem for the years 2008 to 2017. The values were obtained from Meteorological Department data collection center in Kericho (Kericho Climate-Data, 2018). The data was analyzed and presented as shown in figure 4.1:

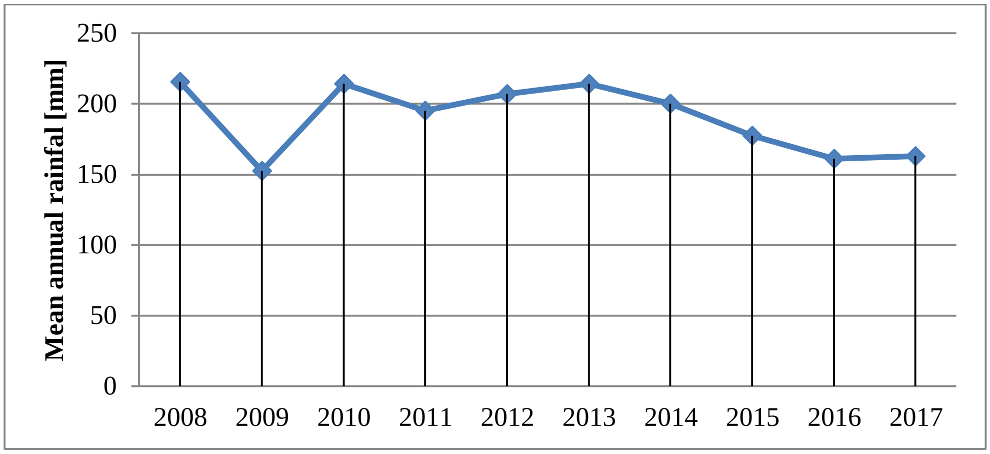


Figure 4.1: Annual rainfall of Mobego-Kabianga wetland ecosystem

The mean annual rainfall pattern of Mobego-Kabianga wetland ecosystem for the last ten years shows drastic change. The amount of rainfall received by the wetland showed a sharp decrease from the year 2008 to the year 2009. This was due to the severe drought that was experienced in Kenya between the year 2008 and 2009 that affected all parts of Kenya (Zwaagstra *et al*., 2010). There was an increment of rainfall amount from the year 2011 to 2013 with year 2013 registering the highest amount of rainfall. However, a gradual decrease in the amount of rainfall received by the wetland was also observed from the year 2013 to the year 2017 respectively. The gradual decrease in the amount of the rainfall received from the year 2013 to the year 2017 is likely to have been affected by intense deforestation and uncontrolled cropping and grazing in the region. The change in rainfall amount may be attributed to increase in human activities which lead to increase in temperature causing climate change (Trenberth, 2018). According to Pereira *et al* (2009), wetlands with high precipitation, high run-off of sediments, nutrients, organic matter and high river input tend to support higher and more diversified wetland plant species. Apart from providing optimal conditions for development of these plants it also creates conducive conditions which favors the development of freshwater species associated with this ecosystem and thus making it diverse. However, the decrease in rainfall amount in wetlands reduces the diversification and production of wetland plant species. It also reduces plant coverage area and thus in a very short period of time these plants will fail to survive and reproduce due to new hydrological conditions, (Ellison, 2000; Gilman, 2008).

4.5.2 pH

Figure 4.2 below shows the mean water pH of Mobego-Kabianga wetland ecosystem.

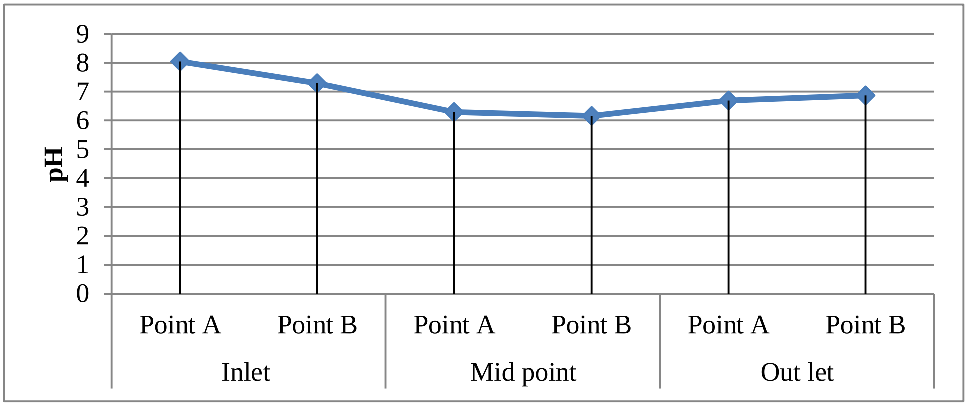


Figure 4.2: Mean water pH of Mobego-Kabianga wetland ecosystem

The mean pH values obtained showed that there were higher pH values at the inlet of the wetland and subsequent decrease at the midpoint and outlet respectively. The inlet of the wetland is undisturbed and therefore the vegetation (Cyperus papyrus reeds) is dense. The higher values recorded at the inlet and outlet of the wetland may be due to decomposition of vegetation and microorganisms. The dying off and decomposition of these plants results in the presence of decomposers which will in turn modifies the pH of the wetland through production of carbon (IV) oxide (Moiseenko, 2005).

Reid and Mosley (2015) studied the causes of high pH in a constructed wetland and proposed that high pH in wetlands is due to the microbial activities predominantly ammonification or sulfate production or due to evaporative concentration of waters associated with high concentration of magnesium and sodium carbonate. Basing on previous studies, three possible causes of high pH have been studied (Reid and Mosley, 2015): A: diffusion of carbon dioxide by photosynthesizing plants, B: microbial sulfate reduction, C: evaporative concentration of saline, carbonate rich surface water. Therefore, the higher pH may be attributed to microbial sulfate reduction, evaporative concentration of saline, carbonate rich surface water and high carbon dioxide demand from the growing plants coupled with the slow diffusion of carbon dioxide from the atmosphere (Reid and Mosley, 2015).

The gradual decrease in the wetland pH at the midpoint may be due to degradation of the wetland and hence less vegetation and thus low amount of decomposers. Furthermore, the low level of growing plants suggests the low carbon dioxide demand and hence low pH. The recorded pH values were in accordance with those noted by Reid and Mosley (2015) which ranged between 6 to 11

Wetland pH affects the hydrolysis of pesticide residues. Akiner and Caglar (2006) reported a rapid hydrolysis of residual pesticides at a pH of 8 to 9 during the dry season. Deer and Beard (2017) also noted that pesticides hydrolyze rapidly and hydrolysis rate is high at pH range of 8 to 9. For every pH point increase, the rate of hydrolysis will increase by approximately 10 times.

4.5.3 Temperature

The mean values of temperature were recorded in the figure 4.3 below.

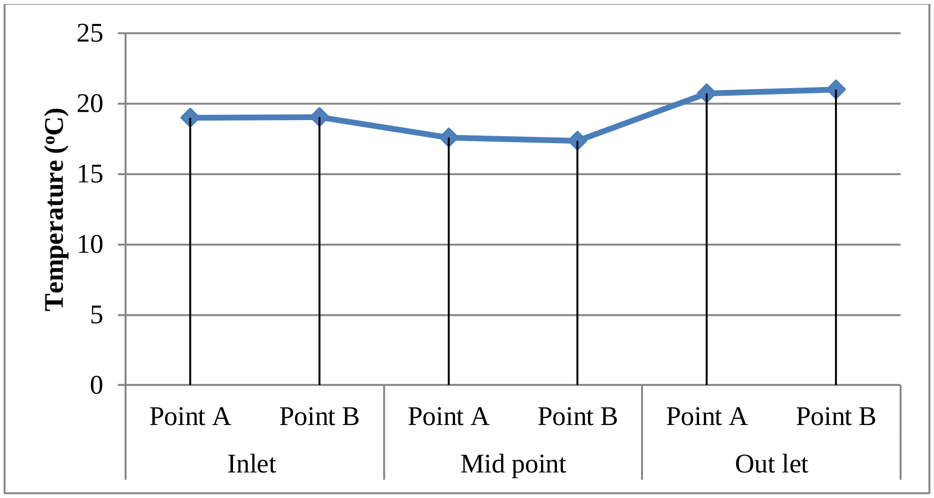


Figure 4.3: Mean values of temperature of Mobego-Kabianga wetland ecosystem

It showed that the temperature at the inlet was low but there was slight increase as water traverses the wetland. The temperature at the outlet was moderately high. The lower temperatures at the inlet and midpoint may be attributed to the dense vegetation cover as opposed to the outlet where the vegetation cover is less. As the vegetation increases, the level of humidity also tends to increase and consequently the temperature will decrease (Tong *et al.*, 2014). Due to low vegetation cover at the outlet of the wetland, the temperatures therefore tend to rise. In addition, a high level of total suspended solids (following high water flow rate and stirring) increases water temperatures. This is because suspended particles absorb more heat from solar radiation than water molecules will. This heat is then transferred to the surrounding water by conduction and thus the rise in temperature.

Wetland water temperature increases the solubility of pesticides but it can also influence organism tolerance limit, (Bhadja, and Vaghela, 2013). The mean temperature values recorded was slightly higher than those noted by Udom *et al* (2017) on experiment on wetland water temperature which ranged between 20 to 30 °C. However, the obtained mean temperature values was in agreement with values recorded by Eisavi *et al* (2016) on measurements of surface water temperatures which ranged between 16°C to 20°C. Wetland temperature affects the adsorption of pesticide residues. At low temperatures, high adsorption of pesticide residues and variation of photosynthetic activities is expected, (Main *et al*., 2014)

4.5.4 Dissolved oxygen

The levels of dissolved oxygen in Mobego-Kabianga wetland ecosystem are represented in figure 4.4.

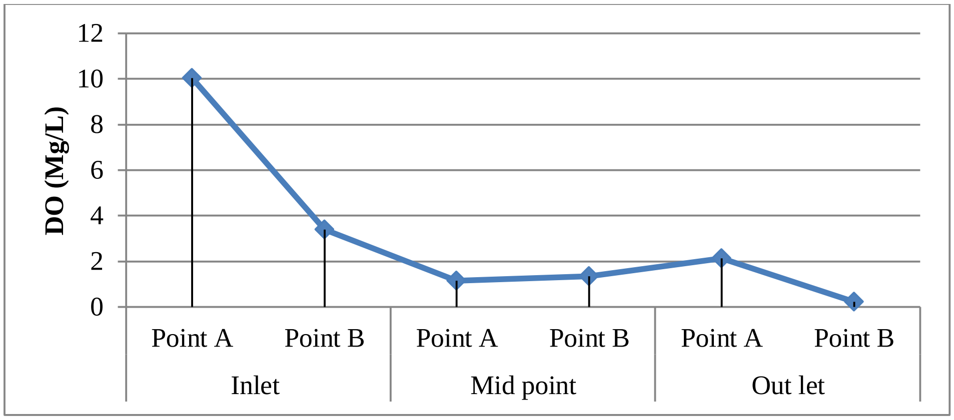


Figure 4.4: Mean values of dissolved oxygen in Mobego-Kabianga wetland ecosystem

Higher DO values were recorded at the inlet and gradual decrease was observed at the midpoint and the outlet respectively (figure 4.4). The higher amount of dissolved oxygen at the inlet of the wetland may be due to replenishment of oxygen from atmosphere or as a by-product of photosynthesis from aquatic plants (Wetzel and Likens, 2000). The level and solubility of oxygen is affected by temperature, the solubility decreases as the temperature increases meaning that colder wetlands will hold maximum dissolved oxygen than warmer wetlands (Perlman, 2013). The higher level of dissolved oxygen at the inlet may be attributed to low temperatures due to high vegetation coverage within the wetland. The low level of algae growth and decomposition at the inlet of the wetland also accounts for the higher level of dissolved oxygen.

The gradual decreases in the level of dissolved oxygen at the midpoint and at the outlet may have been due the excessive growth of algae. As the algae die and decompose, the process consumes dissolved oxygen and results in low level of dissolved oxygen in wetland. Furthermore, the decrease in level of DO may also have been due to the increase in wetland temperature (Peterson and Risberg, 2009). Pesticides have been reported to reduce the level of DO due to inhibition of photosynthesis and hence affecting the zooplanktons, (Usui and Kasubuchi, 2011)

The recorded DO values at the inlet of the wetland was in agreement with the values recorded by Pal *et ,.al* (2015) on the natural wetland which was approximately 9 to 10 mg/L.

4.5.5 Flow rate

The mean water flow rate of Mobego-Kabianga wetland ecosystem was recorded in figure 4.5.

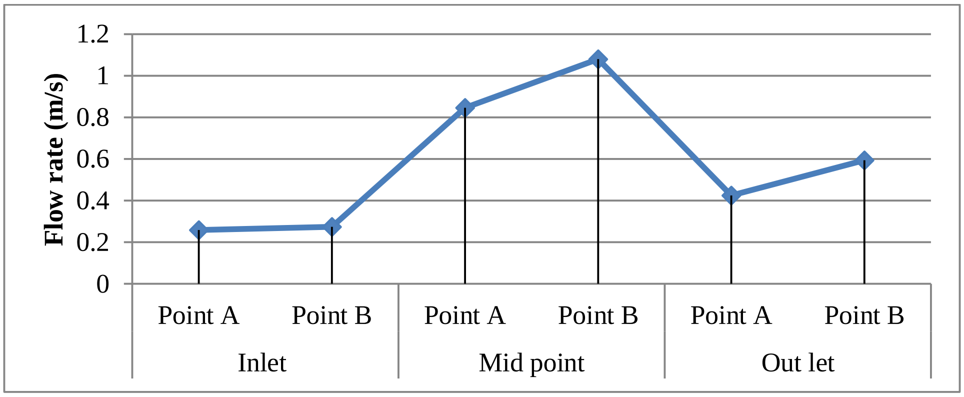


Figure 4.5: Mean flow rate values of Mobego-Kabianga wetland ecosystem

The rate of water flow was very low at the inlet of the wetland and there was a sharp increase at the mid of the wetland and subsequent outlet. This may be attributed to the low topography of the wetland as the wetland moved down the stream. At the midpoint of the wetland, the flow rate of water tends to increase. This is attributed to the increase in the topography of the land i.e from point A to point B of the midpoint. Close to the outlet of the wetland the topography of the land tends to rise slightly increasing the flow rate of water at the outlet.

The recorded flow rate values was not in agreement with the flow rate values recorded by Stern *et a*l., (2001) which recorded a slightly higher flow rate values of between 1.24 to 23.08 m/s. This variation may be attributed to high vegetation cover along the wetland. The flow rate of river affects the retention and removal of pesticide residues. Increase in flow rate is correlated to increase in precipitation. High flow rate is followed by increase in transport of pesticide residues from their source of release, (Kohler *et al*., 2004).

4.5.6 Total suspended solids

The mean values of total suspended solid are shown in figure 4.6 below.

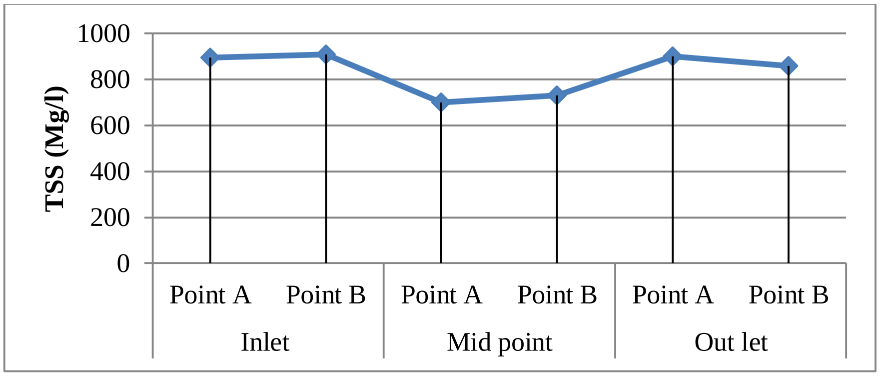


Figure 4.6: Mean values of total suspended solids of Mobego-Kabianga wetland ecosystem

Higher values of TSS were noted at the inlet of the wetland. However, the midpoint recorded slightly lower TSS value and finally the outlet showed an increment in the amount of TSS respectively. The higher values of total suspended solids at the inlet may be due to presence of higher level of inorganic materials, algae and bacteria. Organic particles from decomposing materials can also contribute to the TSS concentration. As algae, plants and animals decay, the decomposition process allows small organic particles to break away and enter the water column as suspended solids. Chemical precipitation is also considered as a form of suspended solid, (Murphy, 2007; EPA, 2012). In addition, the slight decrease in the amount of TSS at the midpoint may be due to low algae growth and animals decay. It may also be due to low or no chemical precipitation. However, TSS value rose at the outlet which is attributed to high flow rate of water due to removal of vegetation cover (papyrus reeds). Spark and Swift (2002) reported the ability of TSS to adsorb residual pesticides in water. The mean values of TSS recorded were in agreement with the values recorded by Wang and Tian (2015).

4.5.7 Total dissolved solids

Figure 4.7 shows the mean values of total dissolved solids.

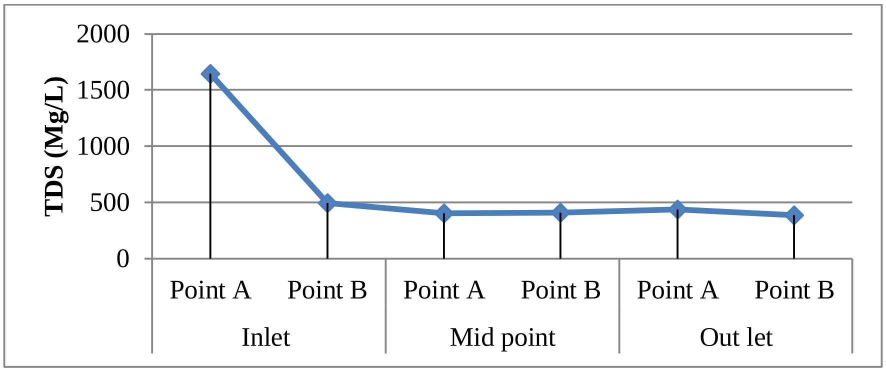


Figure 4.7: Mean values of total dissolved solids of Mobego-Kabianga wetland ecosystem

Higher mean values of TDS were noted at the inlet of the wetland and reduction of TDS values was observed at the midpoint and the outlet of the wetland. The higher values of TDS may be due to pre-deposition of solids from non-point sources. Furthermore, agricultural activities may be perceived to be the major source of these dissolved solids because this wetland is located in an agricultural set up especially at the inlet of the wetland (Bhateria and Jain, 2016). TDS influences the conductivity and adsorption of residual pesticides. The rise in level of dissolved solids means the rise in electrical conductivity. The dissolved solids have been reported to have little or no effects on sorption and transport characteristics of the pesticides (Spark and Swift, 2002). However, the sorption of 2, 4-dichlorophenoxyacetic acid was slightly affected by TDS. These effects however may have been due to competition for the adsorption sites between pesticides and dissolved solids, (Spark and Swift, 2002).

The mean values of TDS at the inlet of the wetland was not in agreement with the values recorded by Muigai *et al* (2010). However, the values recorded at the midpoint and the outlet of the wetland was in accordance with those noted by Muigai *et al* (2010) which ranged between 200 to 600 mg/L.

4.5.8 Conductivity

Figure 4.8 below shows the mean values of electrical conductivity of Mobego-Kabianga wetland ecosystem.

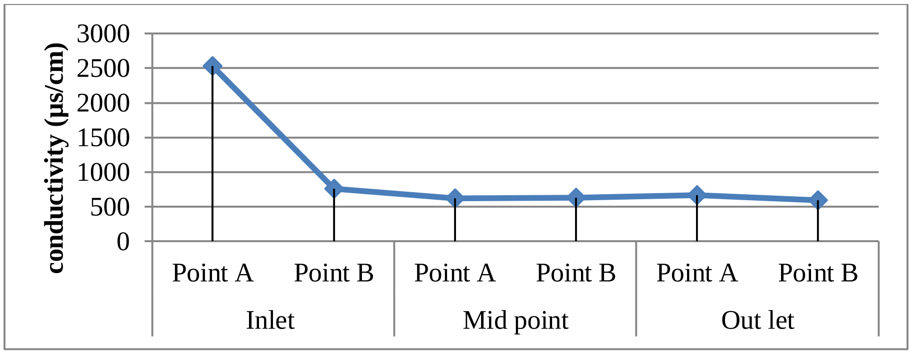


Figure 4.8: Mean values of electrical conductivity of Mobego-Kabianga wetland ecosystem

Conductivity is a measure of ability of water to pass electric current and is affected by presence of dissolved solids. The conductivity values were higher at the inlet of the wetland. The conductivity became constant at the midpoint and at the outlet of the wetland respectively. Higher level of dissolved solids means higher conductivity of the system (US EPA, 2019). The high conductivity at the inlet may have been due to high level of dissolved solid from pre-deposition from non-point sources. The constant rate of conductivity down the wetland may have been due to absence of pre-deposition and non-point sources of dissolved solids.

The conductivity of Wetland Rivers in the United States ranged from 50 to 1500 µs/cm, (US EPA, 2019). This range of conductivity values is lower than the conductivity values recorded in Mobego-Kabianga wetland which range from 500 to 2500 µs/cm. However, the recorded conductivity values was in agreement with the data that was established by Starrett (2002) ranging from 500 to 3000 µs/cm

Conductivity of the wetland water is affected by temperature because temperature affects the concentration of ions in water. At higher temperature most of the salts are soluble. Therefore, as the temperature increases the level of ions also increases and thus increases in conductivity, (USEPA, 2019).

4.6 Statistical Analysis of Physicochemical Parameters of Mobego-Kabianga Wetland

Table 4.4 Statistical analysis of physicochemical parameters of Mobego-Kabianga wetland ecosystem

Point	FR	DO	Cond	Temp	pH	TDS	TSS
Inlet	0.2750±0.006	3.4000±0.100	764.30±5.500	19.000±0.100	7.3000±0.100	1646.0±41.00	895.00±7.000
midpoint	0.8353±0.006	1.2000±0.265	616.70±31.90	17.600±0.100	6.3000±0.100	401.00±15.00	700.00±141.0
Outlet	0.4103±0.036	2.4670±0.451	671.30±5.100	20.700±0.100	6.7000±0.100	435.00±4.000	900.00±141.0
mean	0.5080	2.3556	684.10	19.100	6.7660	827.00	831.70
Sig.	0.0001	0.0140	0.0050	0.0001	0.0033	0.0001	0.0622

Key;

FR: Flow rate

TDS: Total dissolved solids

DO: Dissolved oxygen

Temp: Temperature

pH: Potential of hydrogen ions

TSS: Total suspended solids

Cond: Conductivity

Sig: Significant difference

From the study, it was observed that there was a significant difference in flow rate (p=0.0001), dissolved oxygen (p=0.0140), conductivity (p=0.0050), temperature (p=0.0001), pH (p=0.0033) and total dissolved solids (p=0.0001) across the wetland i.e the inlet, midpoint and the outlet. However, no significant difference was observed in the levels of total suspended solids in along the wetland (p=0.0622). Furthermore, there was significant difference in the level of flow rate, dissolved oxygen, conductivity, temperature and pH across the wetland (table 4.4). However, there was no significant difference in the level of total dissolved solids at the midpoint and outlet of the wetland. Total suspended solids also showed no variation in levels at the inlet and outlet of the wetland (table 4.4). The recorded physicochemical properties were in agreement with values noted by Tripathi *et al* (2014) which showed significant difference at $p \leq 0.05$.

4.7 Screening of pesticides in Mobego-Kabianga wetland ecosystem

Screening of these pollutants (pesticides) was done by the use of gas-chromatography–mass-spectrometry- mass spectrometry (GC–MS/MS) and liquid chromatography–mass spectrometry-mass spectrometry (LC–MS/MS) based screening analyses in order to identify and classify the various organic pollutants into the respective classes of pesticides. The screened pesticides were further quantified and their retention efficiency determined. Table 4.5 below shows different classes of pesticides that were screened by the use of liquid chromatography–mass spectrometry-mass spectrometry (LC–MS/MS) technique.

Table 4.5 Screening of pesticide residues by use of LC–MS/MS technique

Organophosphates	Carbamates	Pyrethroids
Acephate	Aldicarb	Etofenprox
Azinphos-ethyl	Carbaryl	Fenpropathrin
Azinphos-methyl	Carbofuran	Flucythrinate
Chlorfenvinphos	Carbosulfan	Piperonyl butoxide
Chlorpyriphos	Improvalicarb	Pyrethrin
Diazinon	Methiocarb	Tetramethrin
Dimethoate	Methomyl	
Ethephon	Oxamyl	
Fenamiphos	Thiodicarb	
Fenitrothion		
Fenthion sulfoxide		
Fenthion		
Fenthion-sulfone		
Fosthiazate		
Malathion		
Mecarbam		
Methamidophos		
Methidathion		
Monocrotophos		
Omethoate		
Phorate		
Phosalone		
Phosphamidon		
Pirimifos-methyl		
Profenofos		
Temephos		
Triazophos		
Trichlorfon		

Through the use liquid chromatography–mass spectrometry- mass spectrometry (LC–MS/MS) technique, three classes of pesticide residues were detected i.e Organophosphorus, Carbamates and pyrethroids. Organophosphates recorded the highest percentage of up to 65 % of residual molecules followed by Carbamates with 21 % and pyrethroid with 13 %.

Table 4.6 Screened pesticide residues by use of GC–MS/MS technique

Organophosphates	Organochlorines	Carbamates	Pyrethroids
Bromophos	Aldrin	Chlorpropham	Acrinathrin
Bromophos-ethyl	Alpha-BHC		Allethrin
Cadusafos	Alpha-Endosulfan		Bifenthrin
Carbophenothion	Beta-BHC		Cyfluthrin
Coumaphos	Beta-Endosulfan		Cypermethrin
Dichlorvos	Chlordane		Deltamethrin
Disulfoton	Chlorobenzilate		Etofenprox
Edifenphos	Chlorothalonil		Fenvalerate
EPN	Chloroneb		Lambda-Cyhalothrin
Ethion	Chlordane		Permethrin
Ethoprophos	DDD		Phenothrin
Fenchlorphos	DDE		Resmethrin
Fonofos	DDT		Tau-Fluvalinate
Isazofos	Delta-BHC		Tefluthrin
Leptophos	Dieldrin		Tetramethrin
Methacrifos	Endosulfan sulfate		
Mevinphos	Endrin		
Parathion	Lindane		
Parathion-methyl	Heptachlor		
Phosmet	Heptachlor-exo-epoxide		
Prothiofos	Hexachlorobenzene		
Pyraclofos	Methoxychlor		
Pyrazophos	Mirex		
Pyridaphenthion	Nonachlor		
Quinalphos	Nonachlor-cis		
Sulprofos	p,p-DDT		
Terbufos			
Tetrachlorvinphos			
Tolclofos-methyl			

Gas chromatography–mass spectrometry- mass spectrometry (GC–MS/MS) technique detected four classes of pesticide residues which include organophosphate, Organochlorines, Carbamates and pyrethroids. Jayaraj *et al*., (2016) recorded the same classes of pesticide residues. Higher percentage of Organophosphorus was detected (40 %). Several organophosphates were detected by LC-MS/MS and GC-MS/MS techniques. However, no organochlorines were detected by LC-

MS/MS but most of organochlorines were detected by GC-MS/M. Only one carbamate pesticide residue was detected by LC-MS/MS.

4.8 Levels of residual pesticides in Mobego-Kabianga wetland ecosystem

The levels four residual classes of pesticides were recorded at the inlet, midpoint and outlet of the wetland and are discussed below.

4.8.1 Residual organophosphates

Residual organophosphates were at inlet, midpoint and outlet were discussed.

4.8.1.1 Inlet water samples

Figure 4.9 shows levels of detected residual pesticides in composite water samples collected at the inlet of Mobego-Kabianga wetland ecosystem.

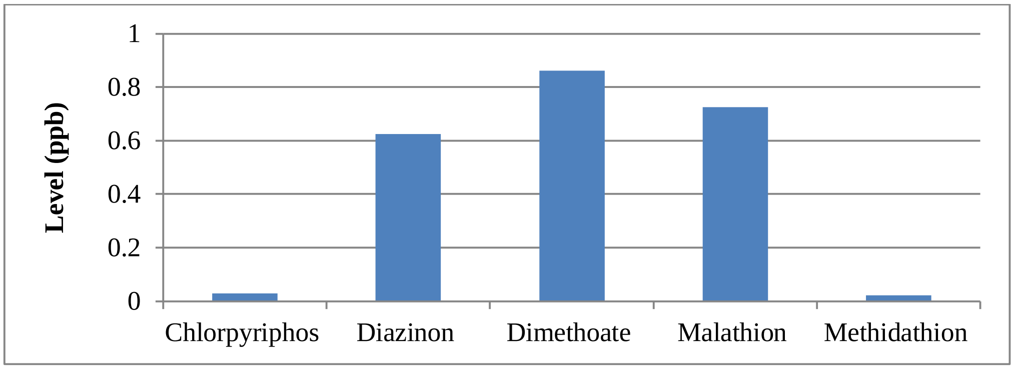


Figure 4.9: Levels of residual organophosphates in water at the inlet of Mobego-Kabianga wetland ecosystem

Chlorpyriphos, Diazinon, Dimethoate, Malathion and Methidathion were detected. The levels of detected residual pesticides were in the order Dimethoate > Malathion >Diazinon >Chlorpyriphos and Methidathion. Dimethoate, Diazinon and Malathion recorded the highest levels of 0.861 ppb, 0.624 ppb and 0.724 ppb respectively. However, continued use of these organophosphates in the environment may results in accumulation in the aquatic system. Therefore, proper measures must be taken in order to curb this vice.

The low level of residual Chlorpyriphos and Methidathion in water may be due to their low octanol/water partition coefficient (logK_{ow}) (i.e Chlorpyriphos logK_{ow}, 4.00 and Methidathion logK_{ow}, 2.57) which implies that these residual molecules is getting adsorbed more on soil than on water (Zou and Zhao, 2011). Malathion is an organophosphate pesticide used in residential landscaping, agriculture and public recreation areas and in public health pest control programs (Qu *et al* (2011). Malathion on the other hand has an octanol/water partition coefficient logK_{ow} of 2.36 with soil/water partition coefficient, K_{oc} of 291.0, (Bhateria and Jain, 2016). This therefore explains why Malathion binds moderately to soil. Due to low K_{ow}, Malathion also tends to moderately dissolve in water.

Organophosphate pesticides (OPs) are generally regarded as safe for use on crops and animals due to their relatively fast degradation rates. Based on the Henry's Law Constants of organophosphates which is 1.4×10^{-6} atm. m^3/mol at 25 degrees Celsius, therefore they are expected to be essentially nonvolatile from water surfaces and from moist soil surfaces as indicated by their vapor pressure, (Armour, 2016).

4.8.1.2 Midpoint water samples

Figure 4.10 shows the presence and levels of residual pesticides detected in composite water samples collected at the midpoint of the wetland. Chlorpyriphos, Diazinon, Dimethoate, Fenthion and Malathion were detected.

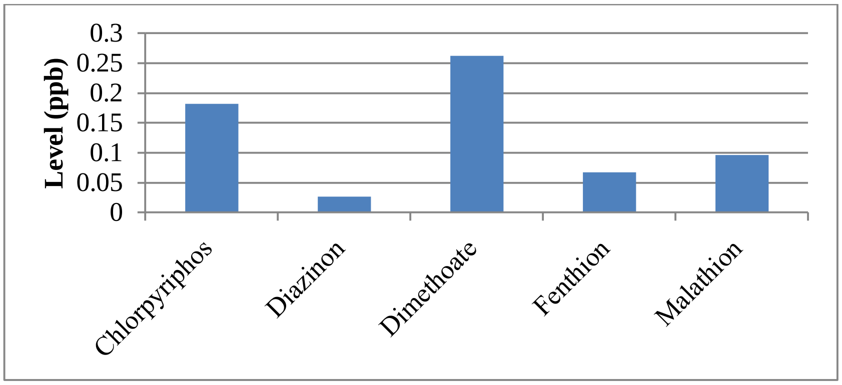


Figure 4.10: Levels of residual organophosphates in water at the midpoint of Mobego-Kabianga wetland ecosystem

Dimethoate recorded the highest value of 0.262 ppb respectively. The higher levels of dimethoate in water may be attributed to its low soil sorption ability (K_{oc}, 20) and higher water solubility (39, 800 mg/L) as reported by Van Scoy *et al* (2016).

4.8.1.3 Outlet water samples

Figure 4.11 shows the levels of detected residual pesticides in composite water samples at the outlet of the wetland ecosystem.

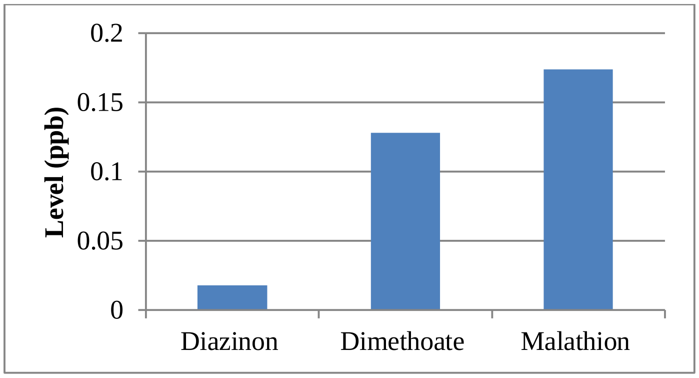


Figure 4.11: Levels of residual organophosphates in water at the outlet of Mobego-Kabianga wetland ecosystem

Diazinon, dimethoate and Malathion were only detected. The levels of Malathion and dimethoate were higher with 0.174 ppb and 0.128 ppb respectively (figure 4.11). Most of the residual organophosphates were not detected in water samples at the outlet. Chlorpyriphos and Fenthion were detected at water samples at midpoint but they were not detected at the outlet. The absence of these residual compounds at the exit of the wetland is an indication that it had been converted to its metabolites, absorbed or adsorbed onto plant and sediments respectively. This may also suggest that they have not been used lately in the area of study. Methidathion was only detected at the inlet of the wetland and it was not detected at the midpoint and at the outlet of the wetland. Its absence also may be attributed to its sorption and desorption into plants and water matrices.

Malathion was detected at the inlet, midpoint and the outlet of the wetland. It recorded the highest value at the inlet, 0.724 ppb (figure 4.9) and lower value of 0.096 ppb at the midpoint (figure 4.10). However, the concentration at the outlet increased to 0.174 ppb (figure 4.11). This may be due to deposition from non-point sources as water traverse the wetland.

4.8.1.4 Inlet soil samples

Figure 4.12 shows the levels of detected residual pesticides in composite soil samples collected at the inlet of the wetland.

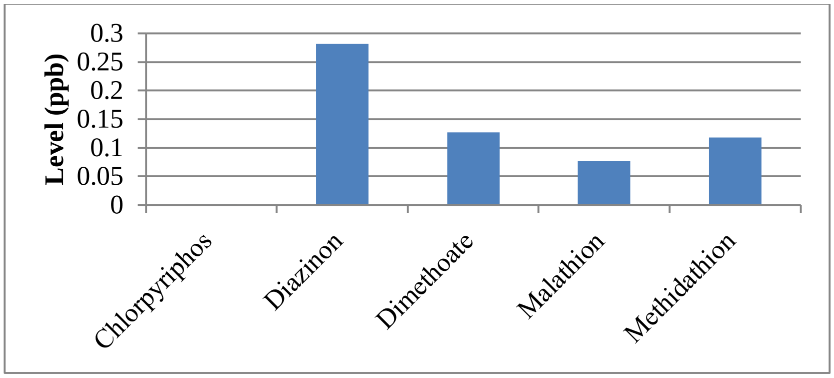


Figure 4.12: Levels of residual organophosphates in soil at the inlet of Mobego-Kabianga wetland ecosystem

Analyzed composite soil samples showed the presence of Chlorpyriphos, diazinon, Dimethoate, Malathion and Methidathion. Analysis showed that diazinon (0.281 ppb) level was high followed by dimethoate (0.127 ppb) > Methidathion (0.118 ppb) > Malathion (0.077 ppb) and finally Chlorpyriphos (0.001 ppb) as shown in figure 4.12. The higher level of diazinon may have been due to its adsorption and accumulation in the soil matrix. Diazinon has a water solubility of 40 mg/L at room temperature, soil/water partition coefficient K_{oc} of 2.12 and octanol/water partition coefficient, $\log K_{ow}$ of 3.86 as indicated by Alamdar *et al* (2014). The sources of these molecules are from organophosphate-containing agricultural inputs (pesticides).

Malathion has an octanol/water partition coefficient $\log K_{ow}$ of 2.36 with soil/water partition coefficient, K_{oc} of 291.0. It is moderately bound to soil, and is soluble in water, so it may pose a risk of groundwater or surface water contamination in situations which may be less conducive to breakdown (Nollet and De Gelder, 2013).

4.8.1.5 Midpoint soil samples

Figure 4.13 shows the level of detected residual pesticides in composite soil samples at the midpoint of the wetland.

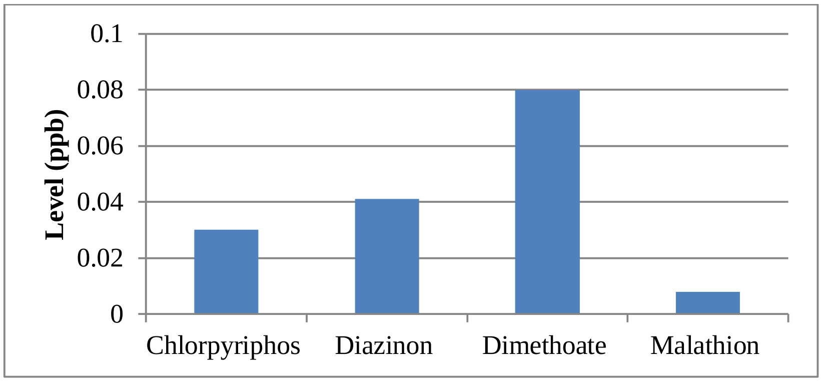


Figure 4.13: Levels of residual organophosphates in soil at the midpoint of Mobego-Kabianga wetland ecosystem

Analyzed composite soil samples showed the presence of the following residual pesticides: Chlorpyriphos, diazinon, dimethoate and Malathion. Dimethoate recorded the highest value of 0.08 ppb with Malathion recording the lowest value of 0.008 ppb respectively (figure 4.13). The recorded high level may be due to high soil adsorption. Malathion recorded the lowest value and this may be due to its low soil adsorption but high water adsorption coefficient (logK $_{ow}$) (Nollet and De Gelder, 2013).

4.8.1.6 Outlet soil samples

Figure 4.14 shows the levels of detected residual pesticides in composite soil samples collected soil samples at the outlet of wetland.

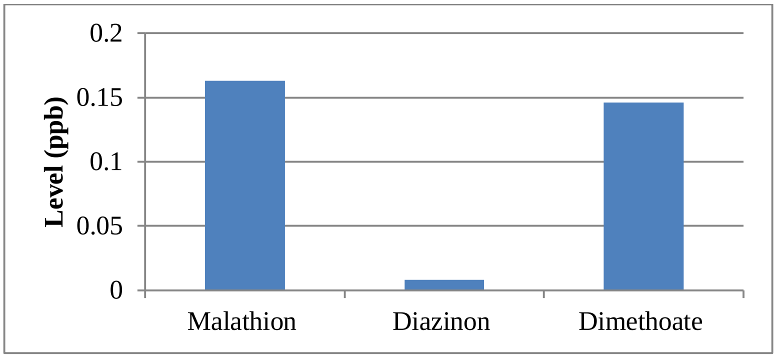


Figure 4.14: Levels of residual organophosphates in soil at the outlet of Mobego-Kabianga wetland ecosystem

Analysis revealed the presence of Malathion, diazinon and dimethoate residual organophosphates. The levels of Malathion and dimethoate were higher, (I.e 0.163 and 0.146 ppb) compared to the levels at the midpoint and the inlet respectively.

Dimethoate and Malathion recorded higher values of 0.127 ppb and 0.077 ppb (figure 4.15) in soil at the inlet as compared to the midpoint levels with 0.08 ppb and 0.008 ppb (figure 4.14). However, there was an increase in dimethoate and Malathion levels at the outlet from 0.127 ppb and 0.077 ppb to 0.146 ppb and 0.163 ppb respectively.

Chlorpyriphos was detected in soil samples at the inlet and at the midpoint of the wetland but not detected at the outlet of the wetland due to absorption and adsorption by papyrus reeds and water. The level of Chlorpyriphos was higher in soil at the midpoint with 0.030 ppb (figure 4.14) compared to the inlet soil samples which recorded lower value of 0.001 ppb (figure 4.13). The increase in the level of Chlorpyriphos at the midpoint may have been due to deposition from non-point sources or from agricultural sectors which is the major activity in the region. Fenthion was not detected in soil samples at the inlet, midpoint and outlet of the wetland (0.00 ppb). This may have been due to decomposition of Fenthion into other compounds.

4.8.2 Residual Organochlorines in Mobego-Kabianga Wetland Ecosystem

4.8.2.1 Inlet water samples

Figure 4.15 shows the levels of detected pesticide residues in composite water samples collected at the inlet of the wetland.

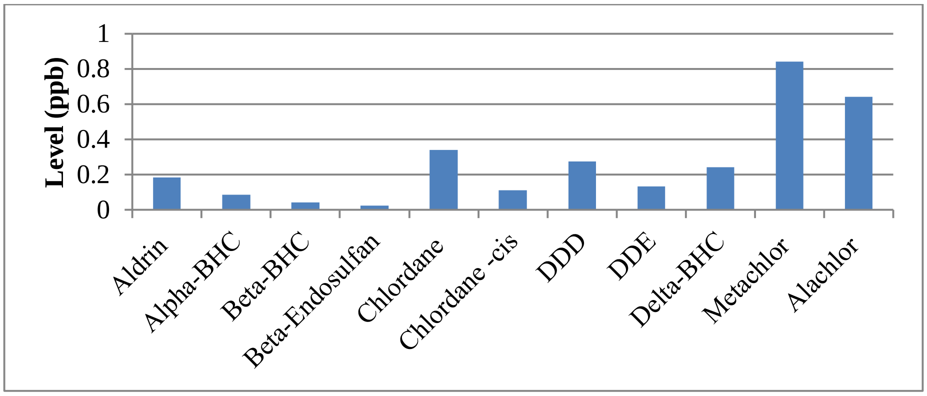


Figure 4.15: Levels of residual organochlorines in water at the inlet of Mobego-Kabianga wetland ecosystem

Aldrin, Alpha-BHC, Beta-BHC, Delta-BHC, DDD and DDE were the major molecules among eleven (11) detected organochlorine in the composite water sample. Metachlor recorded the highest value of 0.841 ppb followed by alachlor (0.641 ppb) > chlordane (0.341 ppb) and DDD (0.275 ppb) as indicated in figure 4.15. DDT was not detected in composite water samples at the inlet but its metabolites DDD and DDE were detected. This may have been due to decomposition of DDT into these respective metabolites. The presence of Aldrin and BHC is a matter of concern as BHC was banned for use due to its environmental impact by Stockholm Convention in the year 2001 however Kenya Pesticide Control Products Board (2011) banned its use as a fungicide in the year 2004. They are persistent organic pollutants that are extremely hydrophobic and strongly adsorbed with K_{oc} of 1,080 (Behfar *et al*., 2013).

The persistence of Organochlorines combined with a high octanol/water partition coefficient, logK_{ow}, provides the necessary conditions for their bioconcentration in organisms because of its lipophilic properties. The Henry's Law constants of the above Organochlorines indicate that they are expected to volatilize in surface water. However, the volatilization in surface water is expected to be attenuated by adsorption to suspended solids and sediments in rivers. They are also not expected to volatilize from dry soil surfaces based upon their vapor pressures. BHC is soluble and has ability to pollute underground water (Bouwman *et al*., 2011).

4.8.2.2 Midpoint water samples

Figure 4.16 shows the level of detected residual organochlorinated pesticides in composite water collected at the midpoint of the wetland.

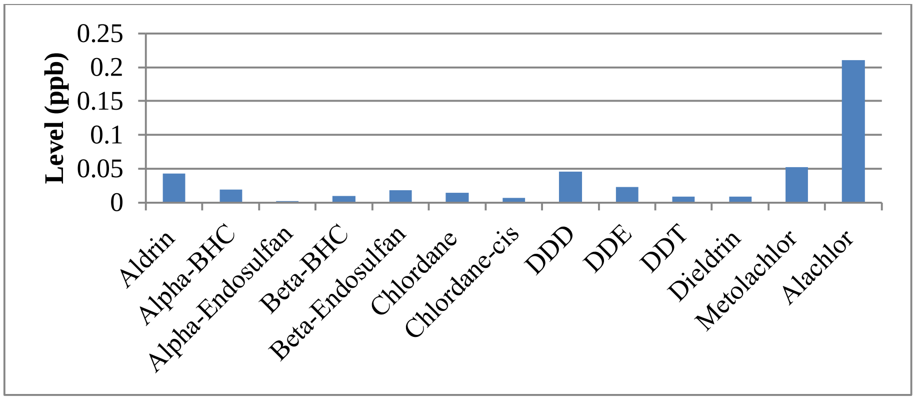


Figure 4.16: Levels of residual organochlorines in water at the midpoint of Mobego-Kabianga wetland ecosystem

Thirteen residual organochlorines were detected in the composite water samples. About 90 % of the detected molecules were of low concentration ranging from 0.002 ppb to 0.046 ppb respectively. Aldrin, DDD, Metolachlor and alachlor recorded the highest values of 0.043 ppb, 0.046 ppb, 0.052 ppb and 0.211 ppb.

DDT and its metabolites DDD and DDE were detected in water samples at the midpoint. DDT was not detected in water samples at the inlet and at the outlet but it was detected in water sample at the midpoint. The presence of DDT at the midpoint may be due to high usage of DDT containing compounds at the midpoint of the wetland following agricultural activities along the wetland.

However, aldrin, DDT and its metabolites are among the persistent organic pollutants that were banned by Stockholm convention treaty because of their toxicity in the environment and therefore their presence in the environment is of great concern, (Fu *et al.*, 2003)

Alachlor is most commonly used on annual grasses and the broadleaf weeds that grow around peanuts, corns, and soybeans, (PCPB, 2010). Alachlor is highly carcinogenic. Studies done showed strong positive association with use of alachlor and laryngeal cancer and a weaker association with myeloid leukemia. The strength and robustness of the association with laryngeal cancer suggests that long-term occupational exposure to alachlor may be a risk factor for laryngeal cancer, (Lerro *et al*., 2018).

4.8.2.3 Outlet water samples

Figure 4.17 shows the levels of detected residual organochlorinated pesticides in composite water samples collected at the outlet of the wetland.

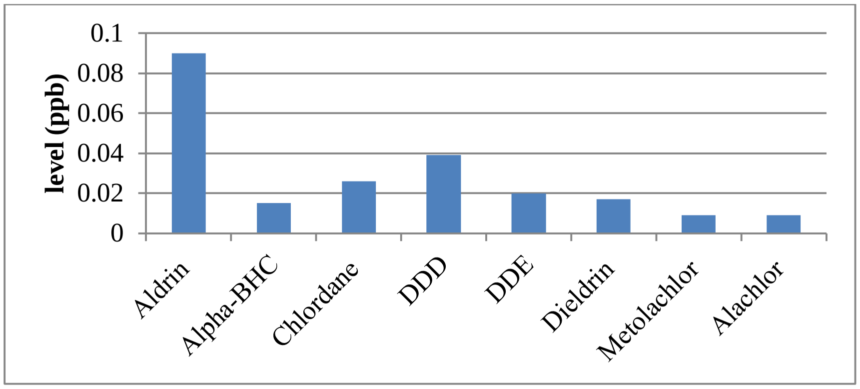


Figure 4.17: Levels of organochlorines in water at the outlet of Mobego-Kabianga wetland

Analyzed water samples showed the presence of the following residual organochlorines: aldrin, BHC, DDD, DDE, chlordane, dieldrin, Metolachlor and alachlor as shown in figure 4.17. Aldrin recorded the highest value of 0.09 ppb (figure 4.17). The level of aldrin was also higher in collected water samples at the inlet of the wetland. However, its level decreased at the midpoint of the wetland indicating that some were adsorbed to papyrus reeds or they were adsorbed to soil sediments. At the outlet of the wetland, there was a corresponding increase of aldrin level at the outlet of the wetland which is also an indication of further deposition from non-point sources along the wetland ecosystem.

DDT was not detected in water collected at the inlet and the outlet of the wetland but it was detected in water samples collected at the midpoint of the wetland. This implies that DDT containing pesticides are highly used at the midpoint of the wetland. However, there was no DDT detected at the exit of the wetland implying that all the DDT were absorbed or adsorbed into soil sediments or plant materials or they decomposed into other compounds respectively.

Dieldrin was not detected in water collected at the inlet of the wetland but it was detected in water collected at the midpoint and at the outlet of the wetland. The level of aldrin was higher at the outlet (0.017 ppb) than the midpoint (0.009 ppb). This may be due to several agricultural activities down the wetland which may be draining these compounds to the wetland.

DDD was detected in composite water samples at the inlet, midpoint and at the outlet. However, their levels ware varied. At the inlet the recorded level was 0.275 ppb (figure 4.18), midpoint was 0.046 ppb (figure 4.16) and at the outlet 0.039 ppb (figure 4.17). The level of DDD was noted to follow a decreasing pattern from inlet to outlet. DDE also showed the same trend as DDD as their levels also was decreasing from inlet to outlet i.e inlet 0.134 ppb (figure 4.15), midpoint 0.023 ppb (figure 4.16) and outlet 0.020 ppb (figure 4.17). These decrease in levels of DDD and DDE may be attributed to sorption and desorption from soil and plant materials along the wetland.

4.8.2.4 Inlet soil samples

Figure 4.18 shows the levels of detected residual organochlorine pesticides in soil samples collected at the inlet of the wetland.

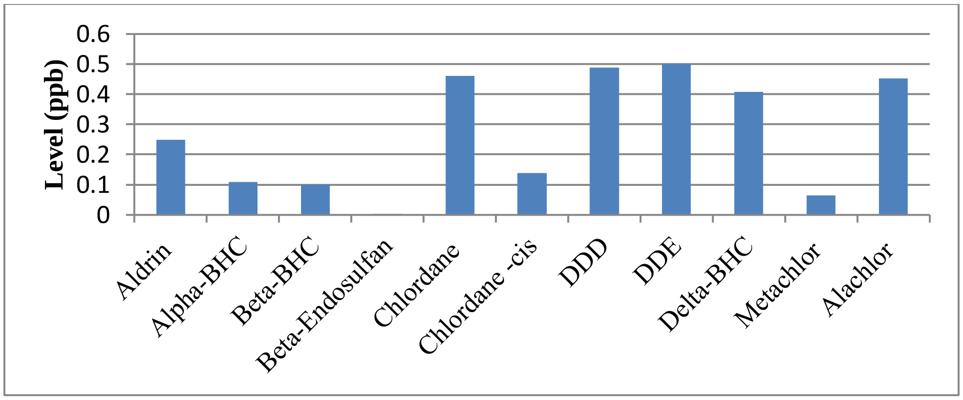


Figure 4.18: Levels of organochlorines in soil at the inlet of Mobego-Kabianga wetland

From the collected soil samples, analysis showed a detection of 11 residual molecules as shown in figure 4.18 with chlordane, DDD, DDE, BHC and Alachlor being prominent. Agricultural inputs are the main sources of these molecules. Most are used to control pest that affects the maize plantations. BHC has been restricted only for seed dressing. There are a lot of concerns on the issues relating to the pollution of BHC and the subsequent isomers of Hexachlorocyclohexane (i.e. alpha-HCH and beta-HCH) which are reported to be more toxic than BHC, (Zhao and Lee, 2001).

The use of BCH was banned under the Stockholm Convention by the year 2001 because of its environmental persistence and toxicity as reported by Birch and Taylor (2000). Blankenberg *et al.*, (2006) reported some of the physical properties of benzene Hexachloride as log octanol/water partition coefficient (log K_{ow}) of 3.3 and soil/water partition coefficient, K_{oc} of 1,100.

DDE and DDD are the metabolites of DDT and are equally highly persistent and have similar chemical and physical properties (Blankenberg *et al.*, 2006). Due to its toxicity, persistence and bio-accumulation in the environment, DDT was banned for use in agricultural practices in the year 1972 by Stockholm Convention but restricted for indoor spray to eradicate mosquitoes. Its soil half-life is 2-15 years and 150 years in aquatic environment (Vanden Bilcke, 2002). DDE and DDD recorded the highest values of 0.501 ppb and 0.488 ppb as indicated in figure 4.21. However, the level of DDD and DDE in soil sample was noted to be decreasing from inlet, midpoint and outlet which imply the decrease in their usage along the wetland. The decrease in levels of these compounds also may be attributed to absorption by plants and partitioning to water.

4.8.2.5 Midpoint soil samples

Figure 4.19 shows the levels of detected residual pesticides in composite soil samples collected at the midpoint of the wetland.

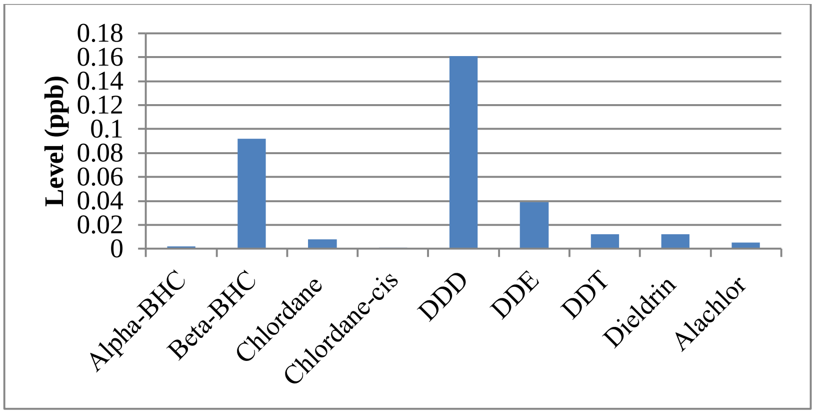


Figure 4.19: Levels of residual organochlorines in soil at the midpoint of Mobego-Kabianga wetland ecosystem

The following are the detected residual molecules in composite soil samples: BHC, DDD, DDE, DDT, chlordane-cis, dieldrin and alachlor (figure 4.19). DDD recorded the highest value of 0.161 ppb. DDD and DDE are metabolites of DDT and their chemical and physical properties are similar. They have similar human toxicities and therefore these molecules may cause health problems to human and animals if their concentration in environmental matrices is not controlled. Turusov *et al* (2002) on his study reported that they are possibility that these molecules are carcinogenic and long human exposure causes liver problems.

4.8.2.6 Outlet soil samples

Figure 4.20 shows the level of detected residual pesticides in composite soil samples collected at the outlet of the wetland.

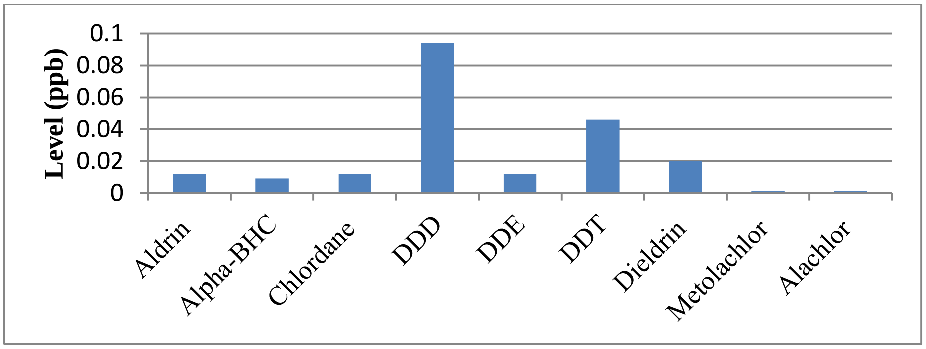


Figure 4.20: Levels of residual organochlorines in soil at the outlet of Mobego-Kabianga wetland ecosystem

The following are the residual organochlorines detected at soil samples: aldrin, BHC, DDD, DDE, DDT, dieldrin, Metolachlor and alachlor. DDD and DDT recorded the highest values (0.094 ppb, 0.046 ppb). The levels of DDD were observed to be decreasing from inlet, midpoint to outlet i.e 0.488 ppb, 0.161 ppb and 0.094 ppb. This decrease is an indication of low deposition of these pollutants down the wetland ecosystem. DDE also showed the same trend as DDD as its levels were decreasing down the wetland. DDT and dieldrin was detected in soil only at the midpoint and at the outlet of the wetland and their levels in soils were noted to be increasing from midpoint to outlet of the wetland. Ideally, DDT was expected to partition more on water than soil as indicated high K_{ow} as reported by Qu *et al* (2011). However, the results showed an increase in level of DDT in water than in soil. This behavior may be attributed to deposition of DDT from agriculture and other non-point sources.

4.8.2.7 Inlet plant samples

Figure 4.21 shows the levels of detected residual pesticides in composite plant samples collected at the inlet of the wetland.

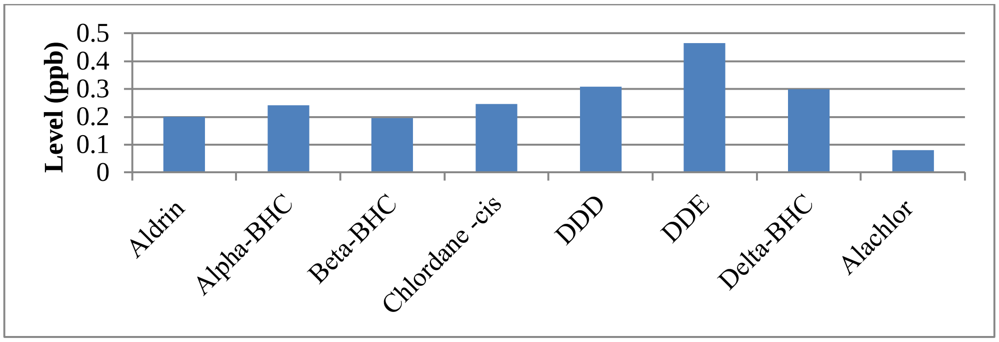


Figure 4.21: Levels of residual organochlorines in plant at the inlet of Mobego-Kabianga wetland ecosystem

Analysis of composite plant sample showed a detection of residual Aldrin, Alpha-BHC, Beta-BHC, Chlordane-cis, DDD, DDE, Delta-BHC and Alachlor. DDD (0.308 ppb), DDE (0.466 ppb) and Delta-BHC (0.300 ppb) recorded higher levels (figure 4.21). DDE and DDD levels were noted to be decreasing from inlet to outlet. DDD and DDE have soil half-life of 2-15 years and 150 years in aquatic environment (Vanden Bilcke, 2002). In Kenya, DDT has been restricted for indoor control of malaria as recorded by Pests Control Products Board of Kenya (2011).

4.8.2.8 Midpoint plant samples

Figure 4.22 shows the levels of detected residual pesticides in composite plant samples collected at the midpoint of the wetland.

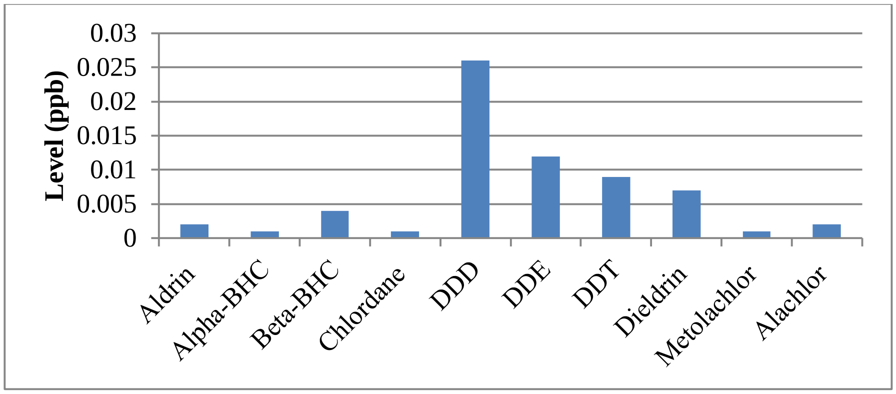


Figure 4.22: Levels of residual organochlorines in plants at the midpoint of Mobego-Kabianga wetland ecosystem

During analysis of plant samples, the following were the residual organochlorine pesticides that were detected: Aldrin, BHC, DDD, DDE, DDT, dieldrin, Metolachlor and alachlor (figure 4.22). DDD recorded the highest level of 0.026 ppb. The identity and levels of detected residual pesticides in papyrus reed plant materials collected at the midpoint of the wetland showed that DDD recorded quite high levels of 0.026 ppb in such samples. The presence of DDD and DDE are a confirmation that DDT is present in the wetland ecosystem.

4.8.3 Residual carbamates in Mobego-Kabianga wetland ecosystem

4.8.3.1 Inlet water samples

Figure 4.23 shows the levels detected residual pesticides in composite water samples collected at the inlet of the wetland.

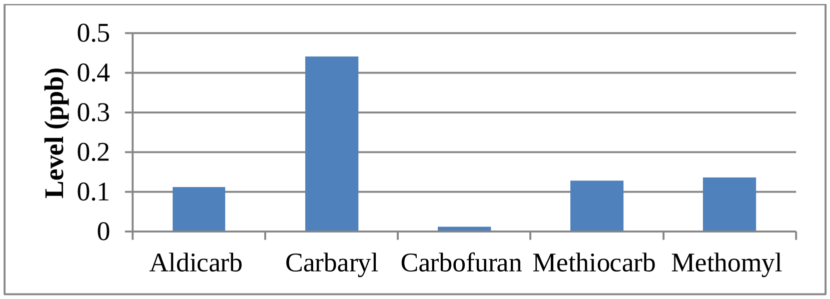


Figure 4.23: Levels of residual carbamates in water at the inlet of Mobego-Kabianga wetland ecosystem

The carbamates detected in composite water sample were carbaryl, Aldicarb, Carbofuran, Methiocarb and Methomyl (figure 4.23). Carbaryl recorded the highest level (0.442 ppb) and Carbofuran recorded the least amount of 0.012 ppb. This implies that the use of carbaryl should be controlled to avoid pollution to the environment. Carbaryl has been found to be in several commercial pesticides as broad-spectrum insecticide used in controlling ticks and fleas and on horticultural crops. It is also sold as acaricide for the control of ticks in livestock. Birch and Taylor (2000) has recorded the physical parameters of carbaryl as: log octanol/water partition coefficient ($\log K_{ow}$) of 1.85 at 20 ^{o}C and soil/water partition coefficient, K_{oc} of 205 to 457.1, it has a half-life of 8 days-1 month.

The low vapor pressure measured for the carbamates makes the possibility of volatilization of carbamates unlikely. Additionally, their low Henry's law constants suggest that they will not volatilize from aqueous solutions. However, carbaryl could become airborne from binding to particulates or as a spray drift immediately following application (Wijngaarden *et al*., 2005).

4.8.3.2 Midpoint water samples

Figure 4.24 shows levels of detected residual carbamate pesticides in composite water samples at the midpoint of the wetland.

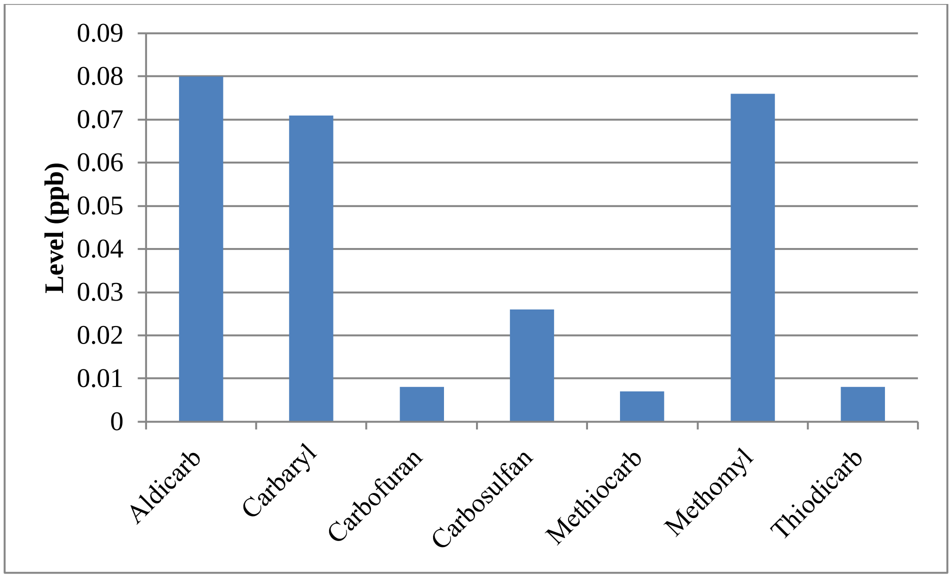


Figure 4.24: Levels of residual carbamates in water at the midpoint of Mobego-Kabianga wetland ecosystem

Residual carbamate detected include: Aldicarb, carbaryl, Carbofuran, Carbosulfan, Methiocarb, methomyl and Thiodicarb (figure 4.24). Aldicarb, carbaryl and methomyl recorded higher values of 0.08 ppb, 0.071 ppb and 0.076 ppb with their sources not known.

4.8.3.3 Outlet water samples

Figure 4.25 shows the levels of detected residual pesticides in composite water samples collected at the outlet of the wetland.

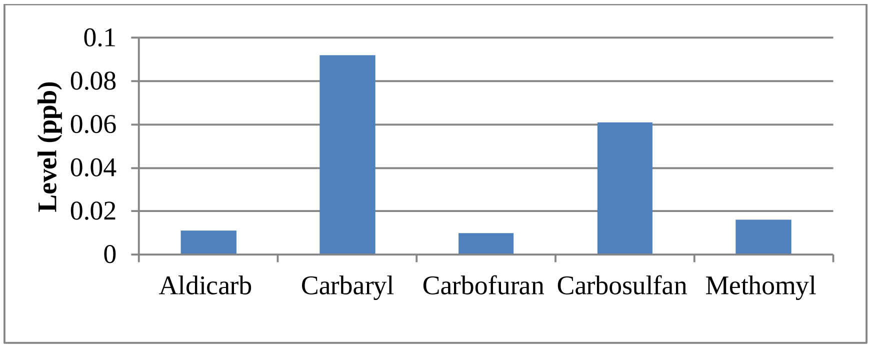


Figure 4.25: Levels of residual carbamates in water at the outlet of Mobego-Kabianga wetland ecosystem

Analysis of collected water samples showed the presence of the following residual carbamates: Aldicarb, carbaryl, Carbofuran, Carbosulfan and methomyl as noted in figure 4.25. Carbaryl and Carbosulfan recorded higher levels (0.092 ppb, 0.061 ppb). The level of carbaryl was higher (0.442 ppb) in water samples collected at the inlet and gradually decreased at the midpoint of the wetland to 0.071 ppb respectively. This may be attributed to sorption to soil and plant materials. There was a slight increase in the level of carbaryl at the exit of the wetland (0.092 ppb) and this may be due deposition from non-point sources of these residual compounds. Carbosulfan was detected only in water samples at the midpoint and at the outlet of the wetland. Their levels were noted to be increasing from 0.026 ppb at the midpoint to 0.061 ppb at the outlet of the wetland which is an indication of its high usage along the wetland.

4.8.3.4 Inlet soil samples

Figure 4.26 shows the levels of detected residual pesticides in composite soil samples collected at the inlet of the wetland.

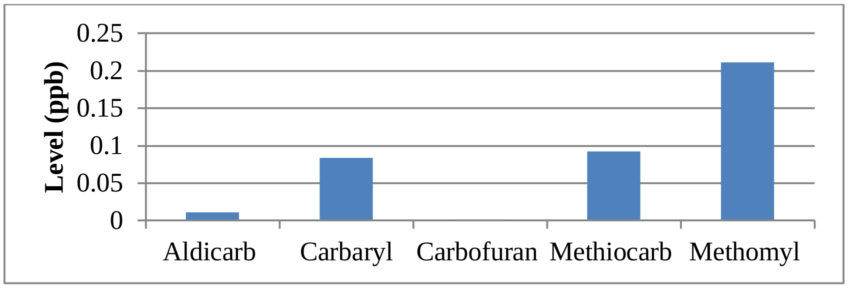


Figure 4.26: Levels of residual carbamates in soil at the inlet of Mobego-Kabianga wetland ecosystem

The detected carbamates in soil included Aldicarb, Carbaryl, Carbofuran, Methiocarb and Methomyl. Methiocarb and Methomyl recorded the highest values of 0.092 ppb and 0.211 ppb but their sources are not known. Carbamates are the forms of pesticides which are being used in agriculture as herbicides, insecticides, nematodes, sprout inhibitors and fungicides, (PCPB, 2011). The soil sorption coefficients (K_{oc} = 50 to 300), octanol/water partition coefficients ($\log K_{ow}$ = 1.40 – 2.36), (Ogwok *et al.*, 2009) and water solubilities of carbamates indicate that they moderately bind to soils and sediments. Therefore, the high level of methomyl may be due to adsorption to the soil sediments over a long time.

4.8.3.5 Midpoint soil samples

Figure 4.27 shows the levels of detected residual pesticides in composite soil samples at the midpoint of the wetland.

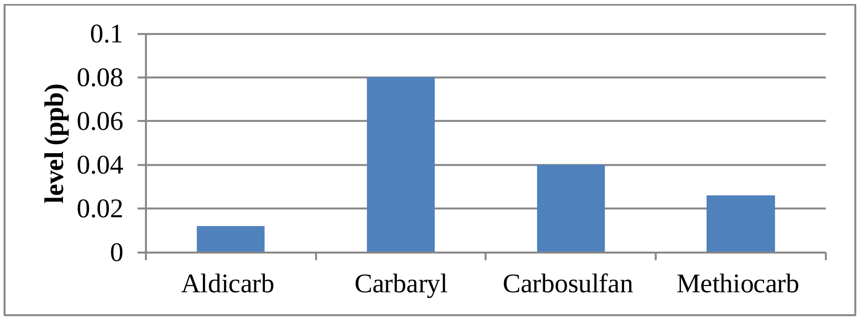


Figure 4.27: Levels of residual carbamates in soil at the midpoint of Mobego-Kabianga wetland ecosystem

Carbaryl, Aldicarb, Carbosulfan and Methiocarb are the residual carbamates that were detected in soil samples at the midpoint of the wetland as indicated in figure 4.27. Carbaryl recorded the highest value of 0.08 ppb. Carbaryl is reported to have low vapor pressure, 1.17 x 10^{-6} mmHg and is not readily volatilized into the air and therefore it remains in soil. The increase in carbaryl level in soil therefore may be attributed to its low volatility (Yuan *et al.*, 2014).

4.8.3.6 Outlet soil samples

Figure 4.28 shows the levels of detected residual pesticides in composite soil samples collected at the outlet of the wetland.

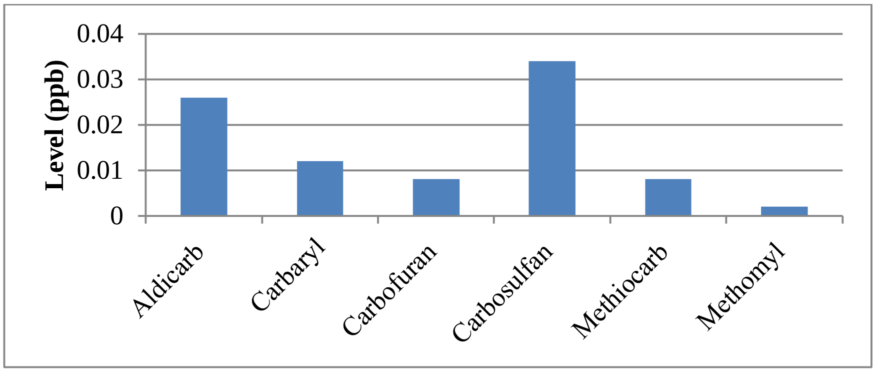


Figure 4.28: Levels of residual carbamates in soil at the outlet of Mobego-Kabianga wetland ecosystem

Soil samples collected showed the presence of the following residual carbamates: Aldicarb, carbaryl, Carbofuran, Carbosulfan, Methiocarb and methomyl (figure 4.28). Aldicarb and Carbosulfan recorded the highest values of 0.026 ppb and 0.034 ppb. The level of Aldicarb in soil was noted to be increasing from inlet, midpoint and outlet (0.011 ppb, 0.012 ppb and 0.026

ppb) respectively. Carbosulfan was not detected in soil sample at the inlet of the wetland but it was detected in soil samples at the midpoint and at the outlet with its levels increasing from midpoint to outlet (0.04 ppb, 0.034 ppb). This increase in levels implies that these compounds are highly used at the midpoint and at the outlet of the wetland. However, Methiocarb was found to show different trend as its levels were decreasing in soil from the inlet to outlet of the wetland (0.092 ppb, 0.026 ppb and 0.008 ppb).

4.8.4 Residual pyrethroids in Mobego-Kabianga wetland ecosystem

This section entails the description of levels of residual pyrethroids in plants, soil and water samples in Mobego-Kabianga wetland ecosystem

4.8.4.1 Midpoint water samples

Figure 4.29 shows the levels of detected residual pesticides in composite water samples collected at the midpoint of the wetland.

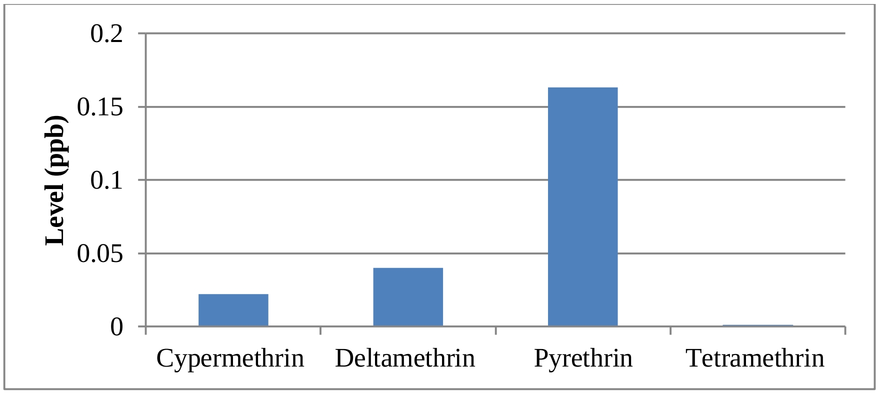


Figure 4.29: Levels of residual pyrethroid in water at the midpoint of Mobego-Kabianga wetland ecosystem

In the analysis of composite water samples, residual cypermethrin, deltamethrin, pyrethrin and tetramethrin were detected with 0.022 ppb, 0.040 ppb, 0.163 ppb and 0.001 ppb levels as indicated in figure 4.29. Pyrethrin was noted to record higher level of 0.163 ppb. Pyrethrins are expected to volatilize from water and moist soils. However, in aqueous systems, volatilization will be mitigated by sorption to soils and sediments. Photolysis also is noted to aid in decomposition of pyrethroids. Therefore, the presence of high level of pyrethrin in water sample indicates that their levels is may be due to desorption from soil matrices.

4.8.4.2 Outlet water samples

Figure 4.30 shows the levels detected residual pesticides in composite water samples collected at the outlet of the wetland.

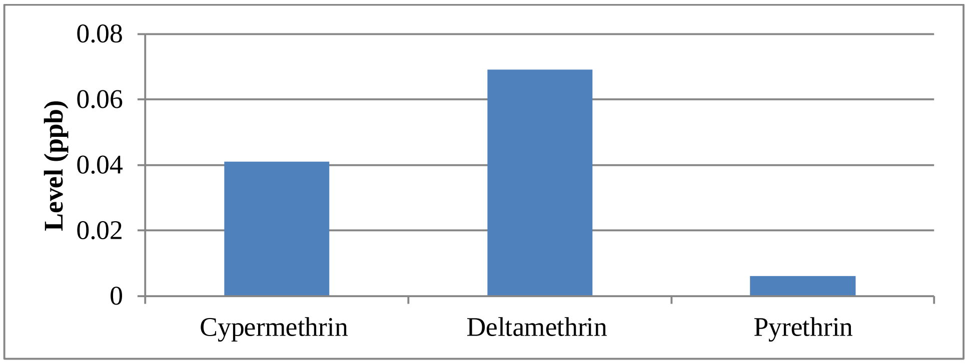


Figure 4.30: Levels of residual pyrethroid in water at the outlet of Mobego-Kabianga wetland ecosystem

Analysis of water samples showed the presence of residual cypermethrin, deltamethrin and pyrethrin. Cypermethrin and deltamethrin recorded higher values of 0.041 ppb and 0.069 ppb (figure 4.30). Pyrethrin recorded the lowest level of 0.006 ppb which is an indication that most of pyrethrins had decomposed along the wetland. Only two residual carbamates were detected in water samples at the inlet of the wetland i.e deltamethrin and Tetramethrin. Pyrethrin was detected only in water at the midpoint and at the outlet of the wetland which signals their usage in the midpoint and outlet of the wetland. Furthermore, Tetramethrin was also detected at the inlet and at the midpoint only and was not detected at the water exiting the wetland. This therefore implies that they have been adsorbed or absorbed by plants and soil sediments.

4.8.4.3 Outlet soil samples

Figure 4.31 shows the levels of detected residual pesticides in composite soil samples collected at the outlet of the wetland.

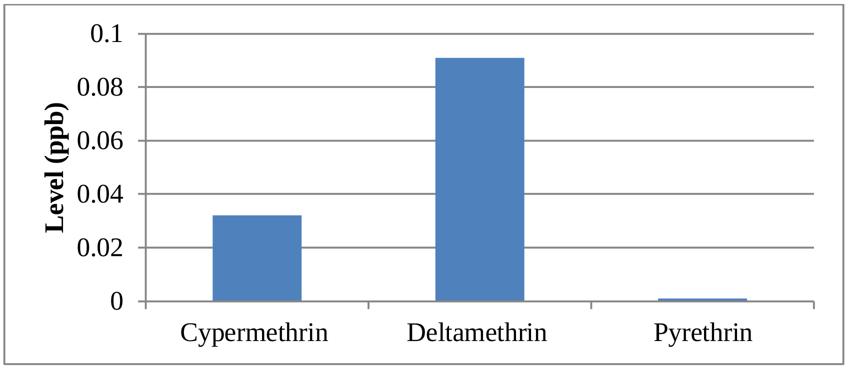


Figure 4.31: Levels of residual pyrethroid in soil at the outlet of Mobego-Kabianga wetland ecosystem

In analysis of soil samples, the following residual pyrethroids were detected: Cypermethrin, deltamethrin and pyrethrin (figure 4.31). Deltamethrin was noted to have the highest value of 0.091 ppb. The levels of deltamethrin in soil samples showed a decreasing pattern from inlet to outlet of the wetland i.e 0.822 ppb, 0.110 ppb and 0.091 ppb. Tetramethrin was detected only in soil at the inlet but it was not detected at the midpoint and at the outlet of the wetland. This may be due to absorption and adsorption into water and plant materials. Cypermethrin was detected only in soil samples at the midpoint and at the outlet of wetland with its levels showing upward trends from midpoint to outlet (0.009 ppb, 0.032 ppb) due to deposition from corresponding point and non-point sources.

4.8.5Comparison of levels of different classes of residual pesticides in wetland

Comparison of levels of different classes of residual pesticides in water, soil and plants at the inlet of the wetland are are entailed in this section.

4.8.5.1 Inlet

4.8.5.1.1 Water samples

Figure 4.32 shows level-comparison of different classes of residual pesticides detected in composite water samples collected at the inlet of the wetland.

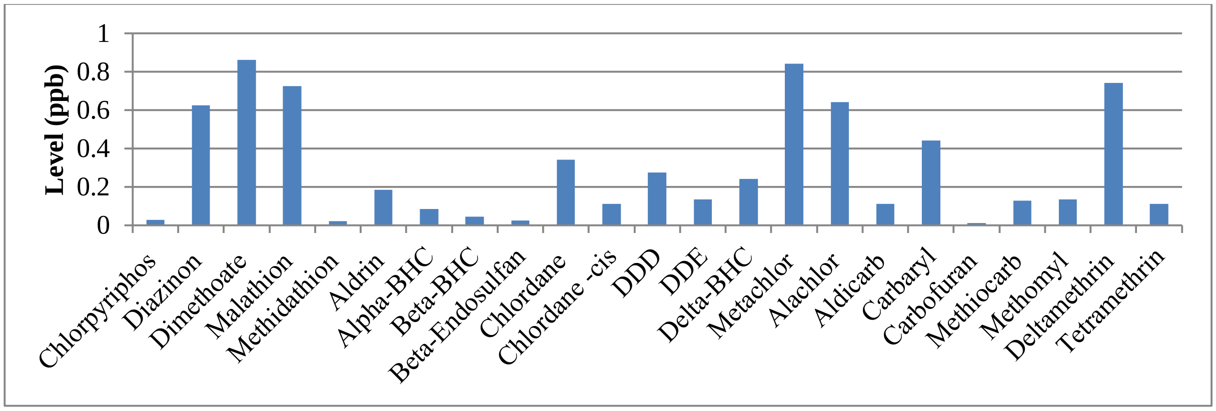


Figure 4.32: Comparison of levels of different classes of residual pesticides in water at the inlet of Mobego-Kabianga wetland

The water samples showed the presence of four classes of pesticides i.e organophosphates, organochlorine, carbamates and pyrethroids as shown in figure 4.35. The detected organophosphate molecules in this study included Chlorpyriphos (0.028 ppb), Diazinon (0.624 ppb), Dimethoate (0.861 ppb), Malathion (0.724 ppb) and Methidathion (0.022 ppb). Their levels showed a rising trend except Chlorpyriphos and Methidathion which recorded lower levels.

The detected organochlorine detected in this study included Aldrin (0.184 ppb), Alpha-BHC (0.086 ppb), Beta-BHC (0.044 ppb), Beta-Endosulfan (0.026 ppb), Chlordane (0.341 ppb), Chlordane –cis (0.110 ppb), DDD (0.275 ppb), DDE (0.134 ppb), Delta-BHC (0.241 ppb), Metachlor (0.841 ppb) and Alachlor (0.641 ppb). Of all the Organochlorines detected, only Metachlor and Alachlor recorded the highest values. The higher level of Metachlor and Alachlor may be attributed to its higher octanol water partition coefficient while the low concentration of these residual molecules may be due to their high soil partition coefficient.

The detected carbamates included Aldicarb (0.112 ppb), Carbaryl (0.442 ppb), Carbofuran (0.012 ppb), Methiocarb (0.128 ppb) and Methomyl (0.136 ppb). Carbaryl showed a rising trend of all the detected carbamates. However, only two pyrethroid pesticide molecules were detected with deltamethrin (0.741 ppb) recording the highest value respectively.

Therefore, the analyzed water samples showed a comparative increase in the levels of Dimethoate (0.861 ppb), Malathion (0.724 ppb), Metachlor (0.841 ppb) and deltamethrin (0.741 ppb). The rising in levels of these molecules is a cause for concern as this might pose a great danger to the environment and human health. The high levels of these molecules are an indication of its high use.

Deltamethrin is also known to be toxic to humans. As a neurotoxin, it attacks the nervous system and causes a variety of negative side effects and fatality. In 2011, a Japanese woman ingested large doses of pesticides that contained deltamethrin, which resulted in motor neuron death, (PubChem, 2019)

Diazinon is known to be toxic at higher concentration. In a study carried out on its health effects on humans, it was found that diazinon caused headache, nausea, skin irritation and runny nose.

However, in acute symptoms, it caused impaired balance, reaction time, color vision, slotted pegboards, organic brain dysfunction and delayed menarche, (Dahlgren *et al*., 2004).

4.8.5.1.2 Soil samples

Figure 4.33 shows level-comparison of different classes of residual pesticides detected in composite soil samples collected at the inlet of the wetland.

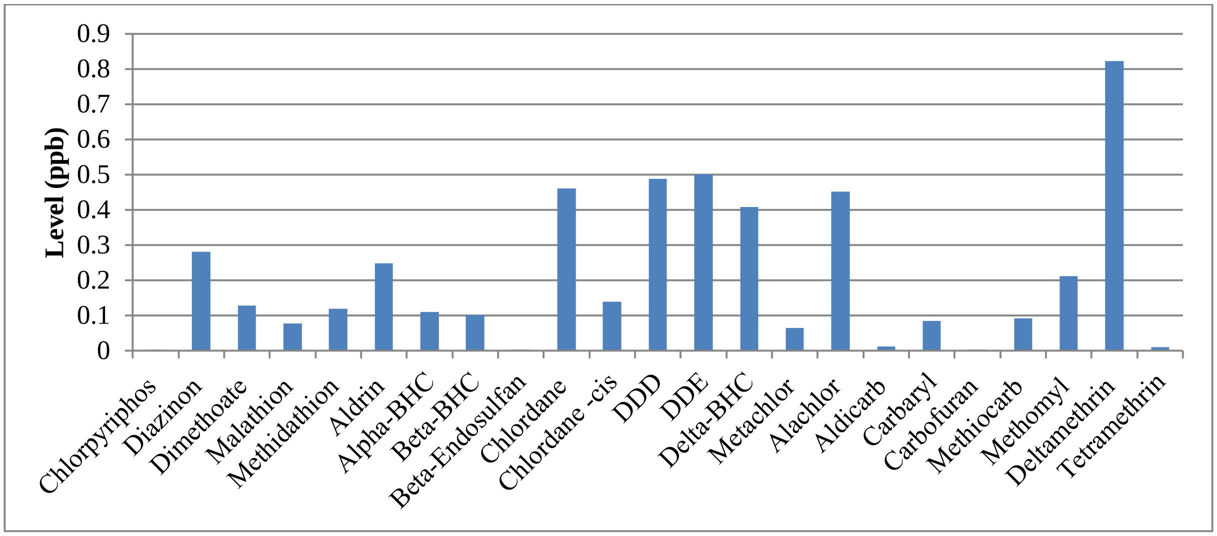


Figure 4.33: Comparison of levels of different classes of residual pesticides in soil at the inlet of Mobego-Kabianga wetland

Analyzed soil sample indicated that organochlorine residual pesticides are on the rise. There was more residual organochlorine detected as compared to the rest of classes of pesticides as noted in the figure 4.36. Their levels also were high with chlordane (0.461 ppb), DDD (0.488 ppb), DDE (0.501 ppb), Delta-BHC (0.408 ppb) and Alachlor (0.451 ppb) recording slightly high values. Pyrethroid residual pesticides recorded the lowest percentage with only two molecules detected with deltamethrin (0.822 ppb) having the highest values of all the classes. Chlorpyriphos (0.001

ppb), Beta-endosulfan (0.001 ppb), Aldicarb (0.011 ppb), Carbofuran (0.002 ppb) and Tetramethrin (0.009 ppb) showed almost negligible values.

However, about 98 % of detected organophosphates and carbamates in soil showed a decreasing trend. Their levels in soil were lower than their levels in water. This may be due their high ability to partition themselves to water rather than to soil as dictated by their $\log K_{ow}$ values which may be higher, (Armour, 2016).

The level of residual organochlorines: Beta-Endosulfan, DDE, Metachlor, and Alachlor also recorded lower values in soil than in water. This may be due their higher water partition coefficient and therefore they tend to dissolved in water than adsorbing to the soil. Residual aldrin, BHC, chlordane, chlordane-cis and DDD recorded higher values in soil than in water. This may be attributed to their high soil partition coefficient. The level of deltamethrin increased in soil as compared to that in water while Tetramethrin decreased and this also may be due to adsorption and desorption processes.

4.8.5.1.3 Plant samples

Figure 4.34 shows level-comparison of different classes of residual pesticides detected in composite plant samples collected at the inlet of the wetland.

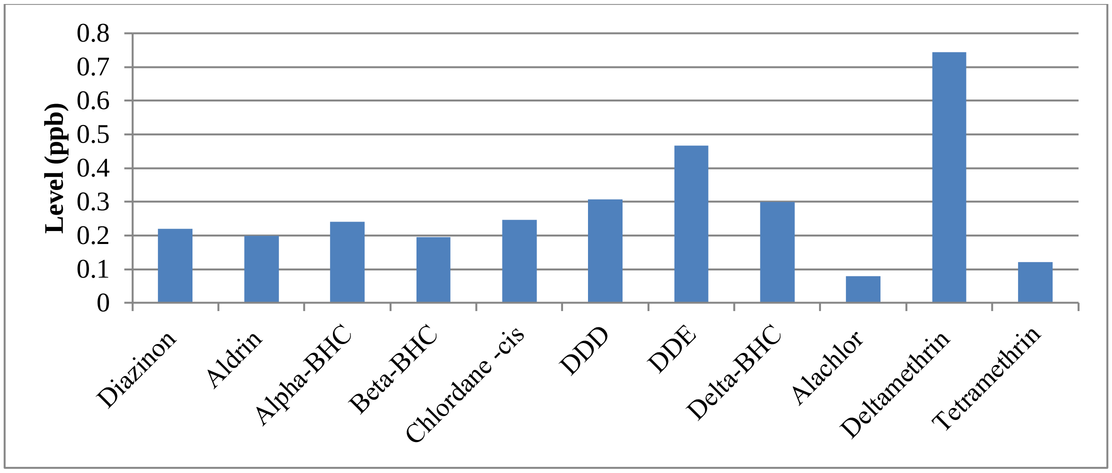


Figure 4.34: Comparison of levels of different classes of residual pesticides in plants at the inlet of Mobego-Kabianga wetland.

From the analyzed plant sample, higher percentage of Organochlorines (73 %) was detected. Residual Aldrin, Alpha-BHC, Beta-BHC, Chlordane –cis, DDD, DDE, Delta-BHC and Alachlor was detected (figure 4.34). Residual carbamates were not detected in plants which imply that all the residual carbamates were all adsorbed to soil matrixes or were all dissolved in water. The absence of these molecules in plants may have also been due to decomposition into other molecules and subsequent evaporation by the plants.

4.8.5.2 Midpoint

Comparison of levels of different classes of residual pesticides in water, soil and plants at the midpoint of the wetland are are entailed in this section.

4.8.5.2.1 Water samples

Figure 4.35 shows level-comparison of different classes of residual pesticides detected in composite water samples collected at the midpoint of the wetland.

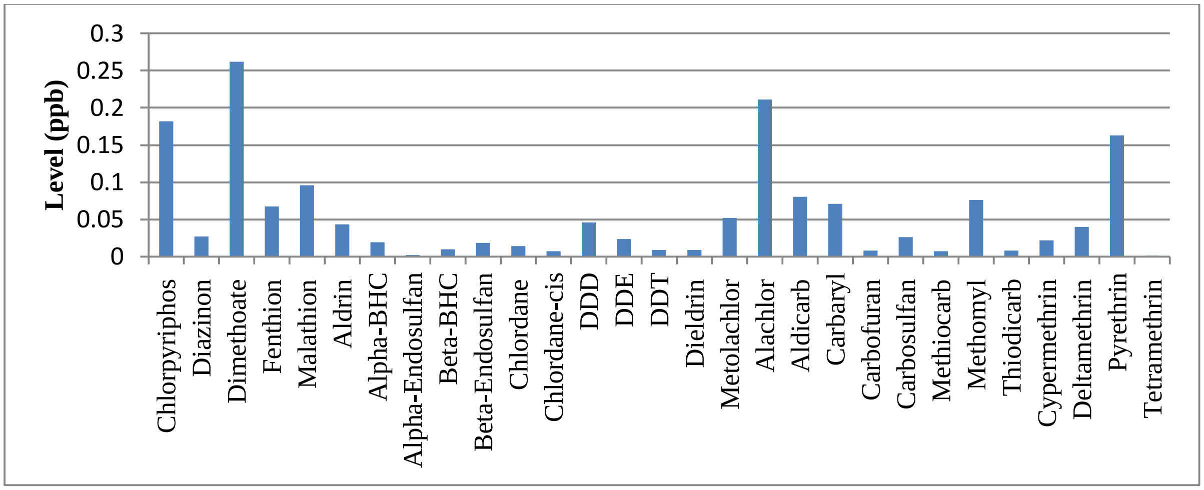


Figure 4.35: Comparison of levels of different classes of residual pesticides in water at the midpoint of Mobego-Kabianga wetland

High levels of Chlorpyriphos, dimethoate, alachlor and pyrethrin residual pesticides were observed as recorded in the figure 4.38. Aldrin and dieldrin are among the residual molecules. These molecules however were banned by Stockholm convention treaty. And therefore they are not allowed to get into the environment because of their toxicity to human and animals, (Fu *et al.*, 2003). Their presence therefore in the environment is a cause for alarm and proper measures must be put in place to protect them from getting access to market.

4.8.5.2.2 Soil samples

Figure 4.36 shows level-comparison of different classes of residual pesticides detected in composite soil samples collected at the midpoint of the wetland.

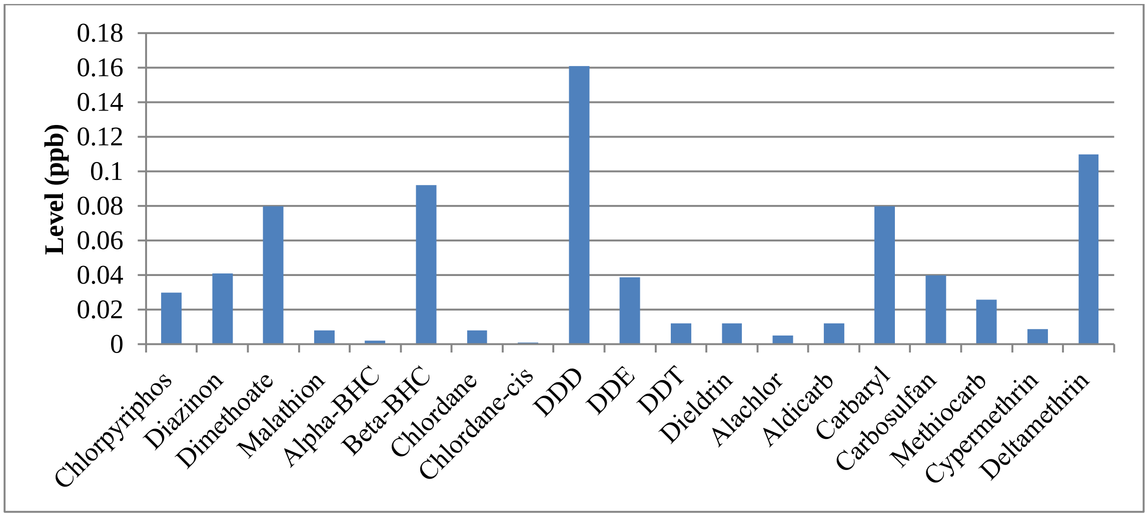


Figure 4.36: Comparison of levels of different classes of residual pesticides in soil at the midpoint of Mobego-Kabianga wetland

Analysis of residual classes of pesticides revealed the presence of organophosphates, organochlorines, carbamates and pyrethroids as shown in figure 4.36. DDD and deltamethrin recorded the highest levels of 0.161 ppb and 0.11 ppb compared to other residual classes of pesticides. DDD production and use as an insecticide has resulted in its widespread direct release to the environment. DDD is a metabolite of DDT and the former use of DDT has resulted in the direct release of DDD to the environment as indicated by its presence in soil samples collected in the wetland. DDD If released to the soil, is expected to have no mobility based upon a $\log K_{oc}$ range between 130,600 and 131,800, (Martinez *et al.*, 2012). Volatilization from moist soil is expected to be an important fate process based on its Henry's Law constant of 6.60×10^{-6} atm. m^3/mole. However, adsorption to soil particles is expected to attenuate volatilization. This may be a major process of retaining DDT in the wetland matrix; Biodegradation is not also an important environmental fate process in water as studies have indicated no degradation in aqueous inoculum. DDE is a metabolite of DDT and was also detected in soil samples collected in the wetland just like DDD. Its persistence to the environment is also a major concern and its toxicity is as much as for its parent compound DDT, (Yuan *et al*., 2014)

4.8.5.2.3 Plant samples

Figure 4.37 shows level-comparison of different classes of residual pesticides detected in composite plant samples collected at the midpoint of the wetland.

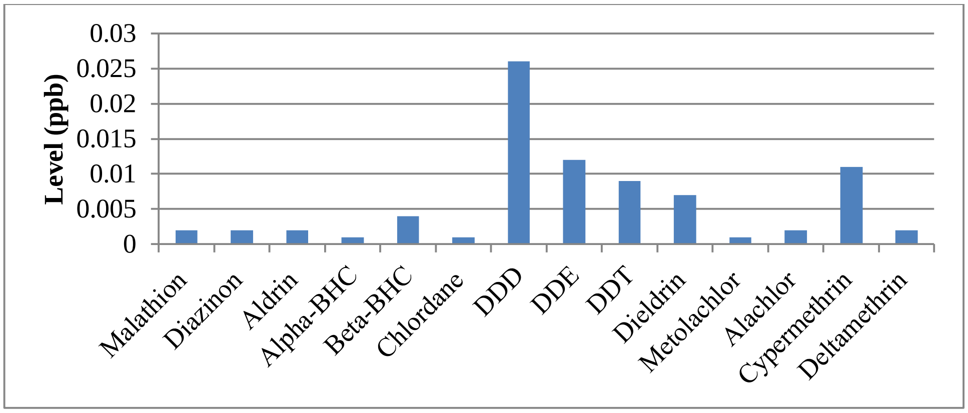


Figure 4.37: Comparison of levels of different classes of residual pesticides in plants at the midpoint of Mobego-Kabianga wetland

In comparison of the residual classes of pesticides in papyrus reed plant, DDD, DDE, DDT, dieldrin and cypermethrin recorded the highest values of 0.026 ppb, 0.012 ppb, 0.009 ppb, 0.007 ppb and 0.011 ppb respectively (figure 4.36). About 80 % of residual Organochlorinated pesticides were detected in papyrus reed while residual organophosphates and pyrethroids were in lower levels. The detection of more residual organochlorines in plants may be due to its poor sorption to soil and water matrices. Only two organophosphates (Malathion, diazinon) and pyrethroid (cypermethrin, deltamethrin) were detected in papyrus plant samples. The analysis showed no presence of residual carbamates in papyrus plant samples. The absence of residual carbamates in papyrus red may be due to its phyto-remediation by the plant which decomposes the compounds into other by-products other than carbamates. However, the absence of carbamates in papyrus reed may also be due to its strong adsorption to soil with sorption coefficients of (k_{oc}=50 to 300) as indicated by Ogwok *et al,* (2009).

4.8.5.3 Outlet

Comparison of levels of different classes of residual pesticides in water, soil and plants at the outlet of the wetland are are entailed in this section.

4.8.5.3.1 Water samples

Figure 4.38 shows level-comparison of different classes of residual pesticides detected in composite water samples collected at the outlet of the wetland.

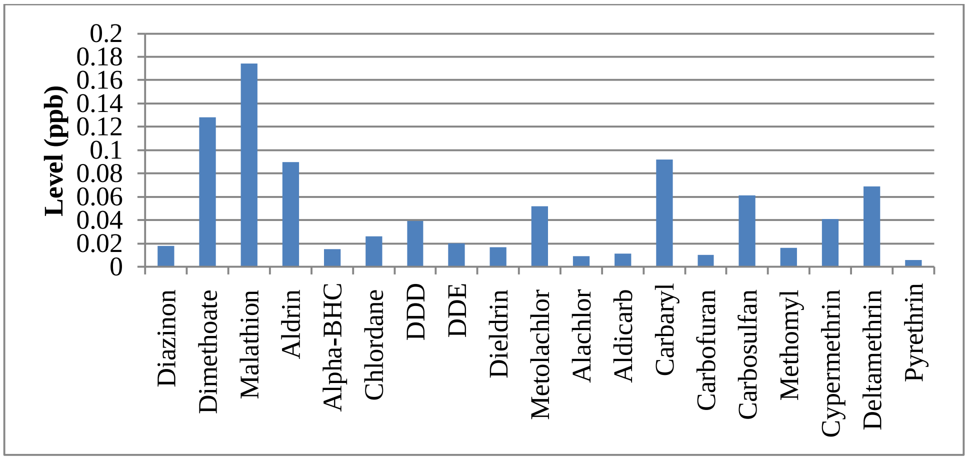


Figure 4.38: Comparison of levels of different classes of residual pesticides in water at the outlet of Mobego-Kabianga wetland

High levels of dimethoate (0.128 ppb), Malathion (0.174 ppb) aldrin (0.090 ppb), carbaryl (0.092 ppb) and deltamethrin (0.069 ppb) in water samples was recorded which is an indication of its high uses in the region. The level of dimethoate was noted to be decreasing from inlet, midpoint to outlet i.e 0.861 ppb, 0.262 ppb to 0.128 ppb. This may be due to reduction in the usage of deltamethrin containing pesticides. Malathion, aldrin, carbaryl and deltamethrin showed almost the same pattern as their levels were noted to be decreasing in water samples from inlet to midpoint of the wetland and this may be attributed to their decrease in usage in farms or due to absorption and adsorption to soil and papyrus reeds. However, all of them also showed a rise in levels in water at the outlet of wetland and this also may be due to increase in their increase in their usage or due to desorption from soil and papyrus reed plants.

4.8.5.3.2 Soil samples

Figure 4.39 shows level-comparison of different classes of residual pesticides detected in composite soil samples collected at the outlet of the wetland.

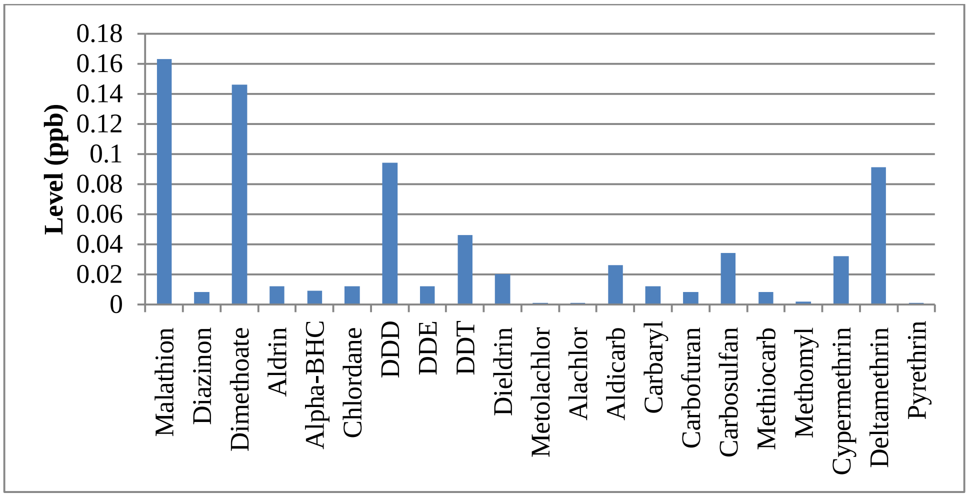


Figure 4.39: Comparison of levels of different classes of residual pesticides in soils at the outlet of Mobego-Kabianga wetland

In comparison of analyzed soil samples, several classes of residual pesticides were detected (figure 4.39). However, only small percentage of these detected residual pesticides had elevated levels. The following are the residual pesticides which recorded slightly higher levels in soil sediments: Malathion, dimethoate, DDD and deltamethrin (0.163 ppb, 146 ppb, 0.094 ppb and

0.091 ppb). The level of DDD in soil was noted to be decreasing from inlet to outlet i.e from 0.488 ppb, 0.161 ppb to 0.094 ppb. The corresponding deltamethrin was also observed to follow the same decreasing trend. This may be due to reduction of usage of these compounds in agricultural farms or due to absorption by papyrus reed plants. Dimethoate and Malathion showed higher values in soils at the inlet but a decrease in these levels were noted in soils at the midpoint. However, an increase in levels of Malathion and dimethoate was observed at the soil sediments at the outlet of the wetland and this could be due to deposition from non-point sources of these molecules.

4.8.5.3.3 Plant samples

Figure 4.40 shows level-comparison of different classes of residual pesticides detected in composite plant samples collected at outlet of the wetland.

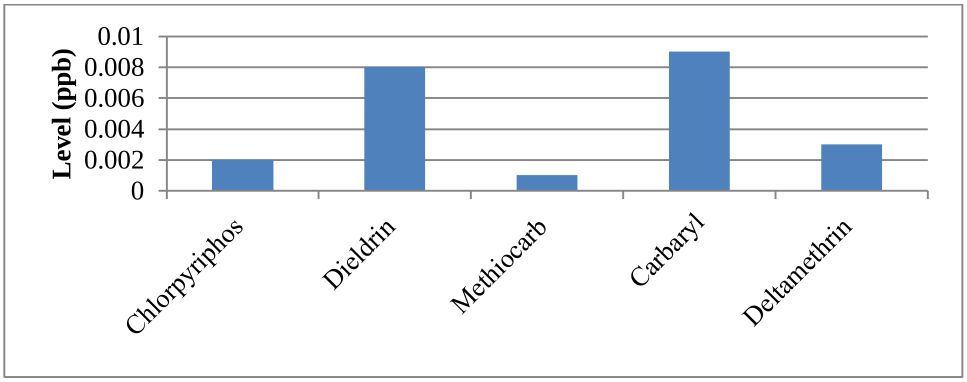


Figure 4.40: Comparison of levels of different classes of residual pesticides in plants at the outlet of Mobego-Kabianga wetland

In analysis of plant samples, the following were the detected: Chlorpyriphos, dieldrin, Methiocarb, carbaryl and deltamethrin (figure 4.43). Dieldrin and carbaryl recorded higher values of 0.008 ppb and 0.0.009 ppb. Most of the residual pesticides were detected in plant samples (papyrus reed) in the midpoint and inlet of the wetland. About 37 % of the residual pesticides were detected in plat sample at the inlet and about 46 % were detected in plant sample at the midpoint of the wetland. Only 17 % of the residual pesticides were detected in plant sample at the outlet of the wetland. This decrease in levels of these residual pesticides in plant samples from inlet to outlet implies that they have been adsorbed to soil sediments or reduction in their usage along the wetland. However, no residual carbamates were detected in papyrus reeds either at the inlet or at the midpoint except Methiocarb and carbaryl which was detected in plant samples at the outlet. The presence of these carbamates at the outlet is an indication of deposition from agricultural farms downstream.

4.9 Statistical analysis of levels of residual pesticides in Mobego-Kabianga wetland

The Table 4.7 below shows statistical analysis of residual pesticides detected in water samples collected at Mobego-Kabianga wetland ecosystem. SAS version 9.4 was used for determination of central tendencies with 95 % confidence limit.

Table 4.7 Statistical analysis of levels of residual pesticides in Mobego-Kabianga wetland

Note: Means with the same letters in the same row are not significantly different at $P \leq 0.05$

	W_{in}	W_{mid}	W_{out}	Sig.	S_{in}	S_{mid}	S_{out}	Sig.	P_{in}	P_{mid}	P_{out}	Sig.
Alachlor	$0.5137^{A}\pm0.186$	$0.2087^{B}\pm0.007$	$0.0060^{B}\pm0.003$	0.0295	$0.4340^{A}\pm0.015$	$0.0047^{B}\pm0.003$	$0.0030^{B}\pm0.002$	0.0010	$0.0793^{A}\pm0.007$	$0.0050^{B}\pm0.003$	Nd	0.0.0001
Aldicarb	$0.1123^{A}\pm0.003$	$0.0633^{B}\pm0.015$	$0.0107^{C}\pm0.003$	0.0009	$0.0110^{B}\pm0.002$	$0.0117^{B}\pm0.003$	$0.0253^{A}\pm0.005$	0.0016	Nd	Nd	Nd	Nd
Alpha-BHC	$0.0850^{A}\pm0.005$	$0.0180^{B}\pm0.003$	$0.0147^{C}\pm0.003$	0.0001	$0.1047^{A}\pm0.005$	$0.0023^{C}\pm0.002$	$0.0083^{B}\pm0.002$	0.0001	$0.2367^{A}\pm0.006$	$0.0030^{B}\pm0.002$	Nd	0.0001
Beta-BHC	$0.0410^{A}\pm0.003$	$0.0127^{B}\pm0.003$	Nd	0.0003	$0.1023^{A}\pm0.003$	$0.0823^{B}\pm0.009$	Nd	0.0002	$0.1953^{A}\pm0.005$	$0.0050^{B}\pm0.004$	Nd	0.0001
Carbofuran	$0.0120^{A}\pm0.003$	$0.0083^{A}\pm0.004$	$0.0107^{A}\pm0.005$	0.7009	$0.0020^{B}\pm0.001$	Nd	$0.0087^{A}\pm0.004$	0.0350	Nd	Nd	Nd	Nd
Chlordane	$0.3267^{A}\pm0.012$	$0.0110^{B}\pm0.003$	$0.0250^{B}\pm0.006$	0.0001	$0.4503^{A}\pm0.011$	$0.0077^{B}\pm0.003$	$0.0137^{B}\pm0.004$	0.0001	Nd	$0.0053^{A}\pm0.004$	Nd	0.1486
Chlorpyriphos	$0.0260^{B}\pm0.005$	$0.1820^{A}\pm0.003$	Nd	0.0001	$0.0040^{B}\pm0.003$	$0.0277^{A}\pm0.003$	Nd	0.0011	Nd	Nd	$0.0033^{A}\pm0.002$	0.0371
Carbaryl	$0.4310^{A}\pm0.011$	$0.0717^{C}\pm0.003$	$0.0923^{B}\pm0.003$	0.0001	$0.0840^{A}\pm0.004$	$0.0533^{A}\pm0.025$	$0.0120^{B}\pm0.003$	0.0260	Nd	Nd	$0.0067^{A}\pm0.005$	0.1407
Cypermethrin	Nd	$0.0220^{B}\pm0.003$	$0.0417^{A}\pm0.004$	0.0010	Nd	$0.0097^{B}\pm0.004$	$0.0310^{A}\pm0.006$	0.0097	Nd	$0.0113^{A}\pm0.004$	Nd	0.0098
DDD	$0.2750^{A}\pm0.005$	$0.0383^{B}\pm0.008$	$0.0390^{B}\pm0.004$	0.0001	$0.4663^{A}\pm0.020$	$0.1650^{B}\pm0.004$	$0.0923^{C}\pm0.006$	0.0001	$0.3067^{A}\pm0.006$	$0.0253^{B}\pm0.004$	Nd	0.0001
DDE	$0.1340^{A}\pm0.005$	$0.0220^{B}\pm0.004$	$0.0177^{B}\pm0.003$	0.0001	$0.5033^{A}\pm0.007$	$0.0347^{B}\pm0.005$	$0.0127^{C}\pm0.003$	0.0001	$0.4453^{A}\pm0.039$	$0.0130^{B}\pm0.004$	Nd	0.0001
Deltamethrin	$0.7237^{A}\pm0.021$	$0.0410^{C}\pm0.004$	$0.0683^{B}\pm0.008$	0.0001	$0.8107^{A}\pm0.011$	$0.1083^{B}\pm0.008$	$0.0900^{B}\pm0.008$	0.0001	$0.7423^{A}\pm0.008$	$0.0033^{B}\pm0.003$	$0.0033^{B}\pm0.003$	0.0001
Diazinon	$0.6193^{A}\pm0.018$	$0.0273^{B}\pm0.003$	$0.0177^{B}\pm0.003$	0.0001	$0.2807^{A}\pm0.005$	$0.0413^{B}\pm0.010$	$0.0083^{C}\pm0.004$	0.0001	$0.2200^{A}\pm0.010$	$0.0027^{B}\pm0.002$	Nd	0.0001
Dieldrin	Nd	0.0083 ± 0.003	0.0170 ± 0.004	0.0039	Nd	0.0120 ± 0.003	0.0200 ± 0.005	0.0262	Nd	0.0073 ± 0.005	0.0080 ± 0.005	0.0575
Dimethoate	$0.8637^{A}\pm0.00$	$0.2620^{B}\pm0.003$	$0.1277^{C}\pm0.003$	0.0001	$0.1240^{A}\pm0.004$	$0.0500^{B}\pm0.030$	$0.1450^{A}\pm0.005$	0.0157	Nd	Nd	Nd	Nd
Malathion	$0.7130^{A}\pm0.012$	$0.0907^{C}\pm0.005$	$0.1740^{B}\pm0.004$	0.0001	$0.0740^{B}\pm0.004$	$0.0077^{C}\pm0.003$	$0.1630^{A}\pm0.003$	0.0001	Nd	$0.0027^{A}\pm0.002$	Nd	0.1590
Methiocarb	$0.1270^{A}\pm0.004$	$0.0070^{B}\pm0.002$	Nd	0.0001	$0.0917^{A}\pm0.004$	$0.0250^{B}\pm0.005$	$0.0077^{C}\pm0.003$	0.0001	Nd	Nd	$0.0027^{A}\pm0.002$	0.0724
Methomyl	$0.1350^{A}\pm0.005$	$0.0750^{B}\pm0.005$	$0.0150^{C}\pm0.004$	0.0001	$0.2063^{A}\pm0.006$	Nd	$0.0030^{B}\pm0.003$	0.0001	Nd	Nd	Nd	Nd
Tetramethrin	$0.1133^{A}\pm0.035$	$0.0020^{B}\pm0.001$	Nd	0.0098	$0.0093^{A}\pm0.004$	Nd	Nd	0.0194	$0.1210^{A}\pm0.004$	Nd	Nd	0.0001

Key: W_{in}: inlet water
W_{mid}: Midpoint water
W_{out}: Outlet water
S_{in}: Inlet soil
S_{out}: Outlet soil
P_{in}: Inlet plant
P_{mid}: Midpoint plant
P_{out}: Outlet plant
Nd: Not detected
S_{mid}: Midpoint soil
Sig: Significant difference

Table 4.7 shows statistical analysis of levels of residual pesticides in soil, water and plant materials in Mobego-Kabianga wetland ecosystem. It indicates the partition of residual pesticides in the wetland. The concentration of alachlor in water samples collected across the wetland (inlet, midpoint and outlet) was significantly different (p=0.0295). However, the concentration of alachlor in water collected at the midpoint and at the outlet was not significantly different (table 4.7). It was also noted that the concentration of alachlor in soil and plant samples (Cyperus papyrus reed) across the wetland was significantly different with p-value of 0.001 and 0.0001 respectively. It was also noted that the concentration of alachlor in soil samples at the midpoint and outlet of the wetland was not significantly different while the concentration of alachlor in plant samples collected at the inlet and midpoint was significantly different (table 4.7). No significant difference was also observed in the concentration of alachlor in water, soil and plant material at the inlet of the wetland (table 4.7). Furthermore, no variation in concentration of alachlor was noted in water at the inlet and outlet, soil at midpoint and outlet and plant material at the midpoint (table 4.7). Mahugija *et al* (2017) also observed no significant variation at $p \leq 0.05$

The concentration of aldicarb in water samples collected across the wetland was significantly different (p=0.0009). There was also significant difference in concentration of aldicarb in soil samples collected across the wetland with p-value of 0.0016. However, there was significant difference in concentration of aldicarb in water samples collected at the inlet, midpoint and outlet of the wetland (table 4.7). No significant difference was observed in concentration of aldicarb in soil collected at the inlet and midpoint of the wetland. No variation in levels of aldicarb was noted in midpoint water and outlet soil samples. There was also no significant difference in concentration of aldicarb in midpoint water, inlet soil and midpoint soil samples (table 4.7).

The concentration of alpha-BHC collected in water, soil and plant materials across the wetland was significantly different with p-value of 0.0001 respectively. The concentration of alpha-BHC in water, soil and plant samples was also significantly different (table 4.7). No variation in level of alpha-BHC was observed in inlet water samples. There was also no significant difference in levels of alpha-BHC in midpoint soil, outlet soil and midpoint plant samples (table 4.7). The concentration of beta-BHC was significantly different in water, soil and plant materials collected from the wetland with p-value of 0.0003, 0.002 and 0.001 respectively. The recorded values of alpha-BHC were not in agreement with values noted by Lari *et al* (2014) with 0.39 ppb.

The concentration of carbofuran in water collected across the wetland was not significantly different (0.7009). However, the concentration of carbofuran in soil collected across the wetland was significantly different (p=0.0350). It was also noted that there was no significant difference in concentration of carbofuran in water samples collected at the inlet, midpoint and outlet of the wetland (table 4.7). No variation in concentration of chlordane in water and soil samples collected across the wetland (p=0.0001). However, variation in levels of chlordane was noted in plant samples collected across the wetland (0.1486). There was no significant difference in concentration of chlordane in soil and water samples collected at the midpoint and outlet of the wetland (table 4.7). The recorded level of carbofuran was much lower than the level noted by Chowdhury *et al* (2012) with 198.7 ppb.

Chlorpyriphos was noted to have variation in concentration in water, soil and plant materials with p-value of 0.0001, 0.0011 and 0.0371. No variation in levels of chlorpyriphos was observed in midpoint water samples, midpoint soil samples and outlet plant samples. It was also noted that there was no variation in concentration of chlorpyriphos in midpoint water, midpoint soil and outlet plant samples (table 4.7). Variation was noted in concentration of carbaryl in water and soil samples collected across the wetland with p-value of 0.0001 and 0.0260. However, no variation in levels of carbaryl was observed in plant samples collected across the wetland (p=0.1407). Furthermore, no significant difference was also noted in concentration of carbaryl in inlet water samples, inlet soil samples, midpoint soil samples and outlet plant samples (table 4.7) the recorded values of chlorpyriphos were below the values recorded by Hasanuzzaman *et al* (2018) in water samples, 37.3 ppb.

Cypermethrin was also noted to have variation in concentration in water, soil and plant samples collected across the wetland with p-value of 0.001, 0.0097 and 0.0098. No significant difference was observed in the concentration of cypermethrin in outlet water, outlet soil and midpoint water samples (table 4.7). Deltamethrin recorded a variation in concentration in water, soil and plant materials across the wetland with p-value of 0.0001. Furthermore; tetramethrin was noted also to have variation in concentration in water, soil and plant samples across the wetland with p-values of 0.0098, 0.0194 and 0.0001. The recorded level of deltamethrin and cypermethrin were higher than those recorded by Harnandes *et al* (2014), cypermethrin (0.0007 ppb) and deltamethrin (0.002ppb)

The concentration of DDD across the wetland was noted to vary significantly in water, soil and plant materials (p=0.0001). DDE also registered variation in concentration in water, soil and plant materials across the wetland with p-value of 0.0001. No variation in concentration of DDD and DDE was observed in water, soil and plant samples at the inlet of the wetland (table 4.7). Diazinon also showed similar trend whereby significant variation in concentration of diazinon in water, soil and plant material across the wetland was registered with p-value of 0.0001. Fosu-Mensah *et al* (2016) also observed that there was no significant difference in levels of diazinon with $p \leq 0.05$. Hasanuzzaman *et al* (2018) recorded slightly higher values of diazinon ranging from 4.11 to 257 ppb.

Concentration of dieldrin in water and soil samples was noted to vary significantly across the wetland (p=0.0039, 0.0262). However, no variation in level of dieldrin was observed in plant samples across the wetland (p=0.0575). Malathion also was noted to have similar trend in which variation in the level of Malathion was observed in water and soil samples across the wetland (p=0.0001) with variation in concentration in plant samples across the wetland (p=0.1590). The recorded values of dieldrin were in agreement with the values recorded by Fosu-Mensah *et al* (2016) ranging from 0.01-0.03 ppb respectively. The recorded levels of Malathion were lower than the levels noted by Hasanuzzaman *et al* (2018) with 84.64 ppb.

Dimethoate showed significant variation in concentration in water and soil across the wetland (p=0.0094, 0.040). Methomyl also was noted to have significant difference in concentration in water and soil samples across the wetland (p=0.0001). However, methiocarb showed significant variation in concentration in water and soil (p=0.0001) but no variation in concentration in plant samples across the wetland was noted, p=0.0724. The recorded values dimethoate in water samples was not in agreement with the values noted by Qayoom *et al* (2018) with 0.04567 ppm

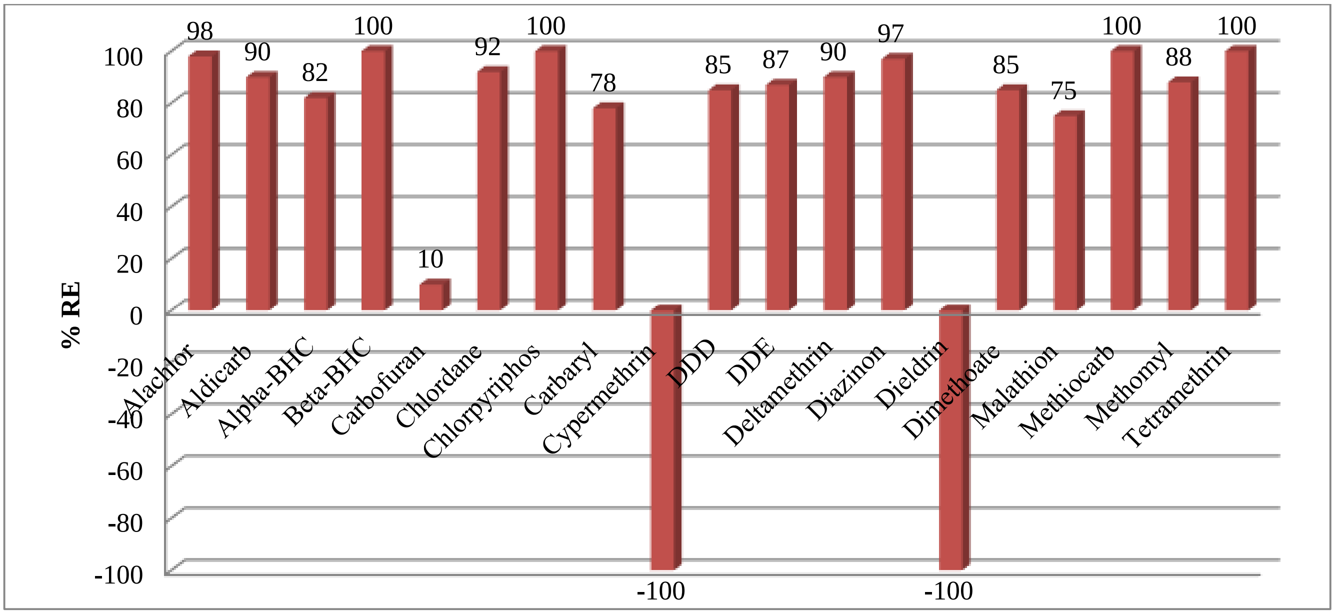
4.10 Retention efficiency of Mobego-Kabianga wetland ecosystem

The pollutant retention efficiencies in Mobego-Kabianga wetland ecosystem were calculated using equation 4.1 below as adopted from Johannesson *et al.*, (2011):

$$\%R = \frac{[C_{in} - C_{out}]}{C_{in}} \times 100\% \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 4.1$$

If the calculated retention efficiency is positive, it implies total or partial retention of the pollutant in question whereas negative retention efficiency indicates a non-retention of the pollutant.

Figure 4.41 shows calculated retention efficiency of selected residual pesticides in Mobego-Kabianga wetland ecosystem. Various values of retention efficiency was recorded with alachlor, aldicarb, alpha-BHC, beta-BHC, chlordane, chlorpyriphos, carbaryl, DDD, DDE, deltamethrin, diazinon, dimethoate, malathion, methiocarb, methomyl and tetramethrin being highly retained in Mobego-Kabianga wetland ecosystem with carbofuran being less retained in the wetland. Cypermethrin and dieldrin indicated their ability to move in the aqueous layer (water) as their levels at the outlet was greater than their levels at the inlet. This may be due to the increase of their concentrations from sediment perturbations, inputs from surface water flow from surrounding streams and re-suspension of sorbed residual pesticides from sediments.



Key: Negative (-) = non retention %; Positive = retention %

% RE; percent retention efficiency

Figure 4.41: Retention efficiency of selected residual pesticides in Mobego-Kabianga wetland ecosystem

The positive retention efficiency (% RE > 0%) of such wetland is attributed to partitioning of the residual pesticides in different wetland matrixes such as plants materials, sediments, organisms' among others. degradation of residual pesticides into other compounds also amounts to positive retention efficiency of the wetland. Some of the processes which played a major role in contributing to the positive retention ability of the wetland included the adsorption onto sediment particles, absorption to plant materials and aquatic organisms, volatilization of residual pesticides into the air (negligible) and degradation residual pesticides. The recorded values of the soil/water partitioning coefficients (K_{oc}) of these residual pesticides were between 2.12 to 160,000 (Birch & Taylor, 2000) and octanol/water partitioning coefficients ($\log K_{ow}$) ranging between 1.7 to 6.91

indicating that the residual pesticides had greater potential of partitioning in sediments than in water.

CHAPTER FIVE

CONCLUSIONS AND RECOMMENDATIONS

5.1 Introduction

This chapter provides information on summary of the study, conclusions and recommendations respectively.

5.2 Summary

From the study, seven physicochemical parameters were recorded; flow rate, dissolved oxygen, conductivity, temperature, pH, TDS and TSS respectively. The levels of these parameters ranged from 0.259-1.079 m/s (flow rate), 0.233-10.03 mg/l (dissolved oxygen), 592-764 µs/cm (conductivity), 17-20 ^oC (temperature), 6-8 (pH), 384-1646 mg/l (TDS) and 700-910 mg/l (TSS). Variation in the levels of physico-chemical parameters was noted with $p \leq 0.05$. However, TSS was found to have no significant different ($p=0.06$). The measured physico-chemical parameters were within WHO recommended limits. However, TSS and conductivity were above the WHO permissible limits as reported by Kosoko *et al* (2015); Dimowo (2011) and Ewa *et al* (2011).

From the study to profile various classes of residual pesticides in water, soil and plant materials from Mobego-Kabianga wetland ecosystem at the upstream of Kabianga river, several residual pesticides were detected which include: diazinon, dimethoate, chlorpyriphos, malathion, methidathion, aldrin, BHC, chlordane, DDT, DDD, DDE, metachlor, alachlor, dieldrin, metolachlor, aldicarb, carbaryl, carbofuran, methiocarb, methomyl, deltamethrin, tetramethrin, pyrethrin and cypermethrin. Residual organophosphate recorded higher levels in water samples at the inlet, midpoint and outlet with 0.861 ppb, 0.262 ppb and 0.174 ppb. However, low levels of residual pesticides were noted in plant samples with 0.744 ppb pyrethroid at inlet, 0.026 ppb organochlorine at midpoint and 0.009 ppb carbamate at the outlet. The values of detected residual pesticides ranged from 0.001 ppb to 0.861 ppb in water, 0.001 ppb to 0.501 ppb in soil and 0.001 ppb to 0.466 ppb in plant materials. The detected residual pesticides were below the Maximum Residue Limit (MRL) recommended by USEPA as reported by Li and Jennings (2017).

The average retention efficiency of Mobego-Kabianga wetland ecosystem was 85 % with cypermethrin and dieldrin recording negative retention efficiency of 100 % respectively. From the survey on land and pesticide use within the wetland it was found that farmers do use several pesticides in control of pesticides. It was also noted that Mobego-Kabianga wetland has been seriously encroached following livestock grazing and land subdivision. Therefore, the destruction of this wetland will affect its ability to retain the pollutants and thereby posing health risk to inhabitants.

5.3 Conclusion

From the study, several residual pesticides were detected in soil, water and plant samples. Their levels were lower than the permissible limits. Furthermore the average retention efficiency of the detected residual pesticides was 85 % with negative retention efficiency noted in cypermethrin and dieldrin.

Using SAS instrument, it was noted that there was an overall variation in levels of physicochemical parameters, residual pesticides and retention efficiencies in water, soil and plant materials in Mobego-Kabianga wetland ecosystem. Therefore, null hypothesis was rejected and alternative accepted.5.4 Recommendations

The following are the recommendations:

i. To develop wetland conservation and management policies which controls presence of banned POPs into the wetland ecosystems
ii. To investigate the sources of banned POPs
iii. Develop environmentally friendly pesticide molecules

5.5 Suggestion for futher research

Further research to be carried out with the aim of comparing the toxicity levels of residual pesticides and their degradation products to ascertain whether the degradation products are more/less toxic than the parent molecule.

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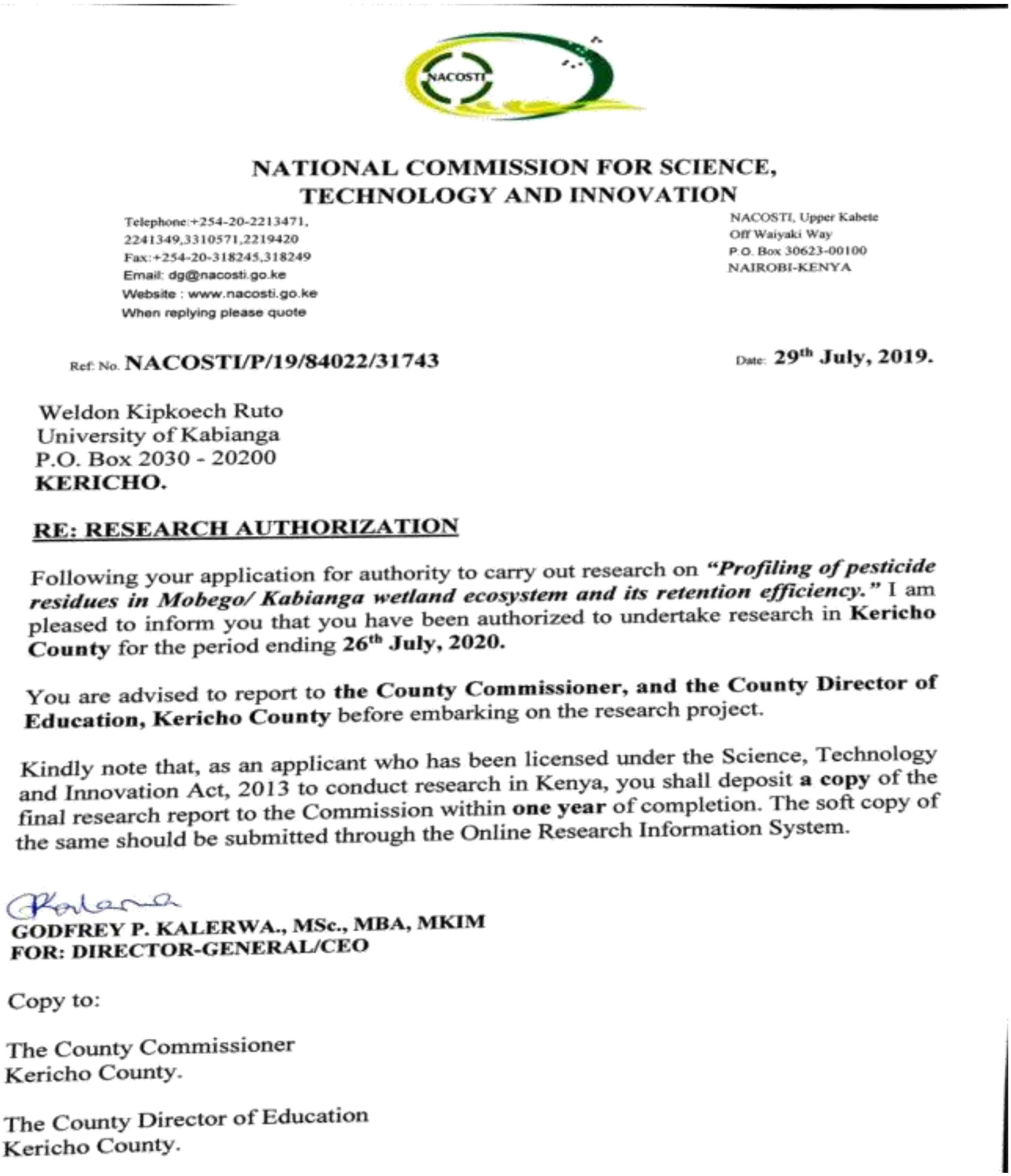
APPENDICES

APPENDIX I

Research Authorization Permit



NATIONAL COMMISSION FOR SCIENCE,
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2241349,3310571,2219420
Fax:+254-20-318245,318249
Email: dg@nacosti.go.ke
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P.O. Box 30623-00100
NAIROBI-KENYA

Ref: No. **NACOSTI/P/19/84022/31743**

Date: **29th July, 2019.**

Weldon Kipkoech Ruto
University of Kabianga
P.O. Box 2030 - 20200
KERICHO.

RE: RESEARCH AUTHORIZATION

Following your application for authority to carry out research on ***"Profiling of pesticide residues in Mobego/ Kabianga wetland ecosystem and its retention efficiency."*** I am pleased to inform you that you have been authorized to undertake research in **Kericho County** for the period ending **26th July, 2020.**

You are advised to report to **the County Commissioner, and the County Director of Education, Kericho County** before embarking on the research project.

Kindly note that, as an applicant who has been licensed under the Science, Technology and Innovation Act, 2013 to conduct research in Kenya, you shall deposit **a copy** of the final research report to the Commission within **one year** of completion. The soft copy of the same should be submitted through the Online Research Information System.

GODFREY P. KALERWA., MSc., MBA, MKIM
FOR: DIRECTOR-GENERAL/CEO

Copy to:

The County Commissioner
Kericho County.

The County Director of Education
Kericho County.

APPENDIX II

Mean values of physicochemical parameters of Mobego-Kabianga wetland ecosystem

Parameters	Inlet		Midpoint		Outlet	
	Point A	Point B	Point A	Point B	Point A	Point B
Flow rate	0.259±0.361	0.275±0.006	0.846±0.021	1.079±0.020	0.424±0.029	0.594±0.195
DO	10.03±0.324	3.4±0.1	1.15±0.238	1.333±0.153	2.12±0.964	0.233±0.058
conductivity	2530±60.50	764.3±5.508	618.4±22.72	631.7±21.13	669.3±5.909	592.2±3.834
temperature	19.00±0.100	19.05±0.071	17.60±0.100	17.37±0.058	20.70±0.100	20.98±0.171
pH	8.050±0.129	7.300±0.100	6.300±0.100	6.167±0.058	6.700±0.100	6.875±0.096
TDS	1646±40.93	496.8±3.580	401.9±14.77	410.6±13.73	435.0±3.841	384.9±2.492
TSS	895±7.071	910±14.14	700±141.4	730±127.2	900±141.4	860±113.1

APPENDIX III

Rainfall measurement [mm] in Kericho for the last 10 years (adopted from meteorological department, Kericho County)

	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
2008	24.1	105.3	337.9	166.3	172.8	211.5	236.6	244.8	291.5	371.5	212.2	23.7
2009	114.9	47.2	34	298.8	230	114.6	96.6	147.5	190.6	236.1	81.1	239.5
2010	74.8	177.1	283.5	297.6	248.5	205	239.3	263.6	210	373.7	93	103
2011	53.1	12.1	292.7	148.5	194.7	231.1	165.5	169.8	261.1	204.8	503.7	103.3
2012	0	26.8	27.7	398.4	391.1	226.9	160..9	298.9	239.1	269.4	227.6	172.3
2013	114.9	12.4	217	449.9	349	237.2	119.2	217.1	308.1	290.9	124	132.7
2014	23.4	36.1	211	107.2	280	228.3	100.5	207	180.8	340.8	550.7	137
2015	1.3	23.6	23.1	357.1	348	231.3	145.7	173.6	159.2	203.3	245.5	215.8
2016	180.6	23.6	92.2	327.1	353.5	157.2	151.7	184.9	118.4	225.9	78.5	39.4
2017	28.7	115.6	127.4	234.8	324.1	132.4	156.1	274.8	271.6	148.3	93.5	47.1

APPENDIX IV

Questionnaire

Date: …………………………….

Place…………………………….

Project: Profiling of pesticide residues in Mobego-Kabianga wetland ecosystem and its retention efficiency.

Please fill out all the questions of this questionnaire. Thank you

1. Are you a farmer? Yes……… No…….
2. What is the size of your farm in terms of acreage? ………………….
3. What is the size of your farm under farming? ……………………….
4. What type of crops do you grow in your farm?
   i. ……………………………………………….
   ii. ………………………………………………
5. Do you keep livestock? Yes…………… No……………
6. How many livestock do you keep? ....
7. What do you normally use to weed your farm?
   i. ……………………………………………..
   ii. …………………………………………….
8. Do you use pesticides in your farm? Yes………………. No………………….
9. If yes in question 8 above, what was the purpose for its use?
   i. ……………………………………………………………..
   ii. ……………………………………………………………..
10. If you do not use pesticides, then how do you control pests or weeds?

i. ……………………………………………………….

ii. ………………………………………………………..

11. Which type of chemical (pesticide) do you use for plant and animal protection

	Crop	Animal
Type of Pesticide	1	1
	2	2
	3	3
	4	4
	5	5
	6	6
Frequency of application (weekly/monthly/yearly among others)		
Dosage applied		

12. If there is pesticide left over, where do you dispose

i. Outside the house: …………………….

ii. In the bushes: …………………………

iii. In the latrine: ………………………….

iv. In the river: …………………….........

v. Any other (specify)………………………

13. Where do you wash the equipment used?

i. At home: ……………………………………

ii. At the nearby river: …………………………

iii. At the nearby pond: …………………………

iv. Others, specify: ……………………………

14. Where does the residue from the washed equipment go?

i. To the nearby river/stream: ………………

ii. To the bush: ………………………………

iii. Others, specify: ……………………………

15. Do you wear protective clothing when applying pesticides? Yes: … No: ……

16. If No, why?

    i. It's too expensive:

    ii. ii. It not available:

    iii. I feel uncomfortable

    iv. I don't know how to use them

17. What type of protective cloth do you use? Tick the following list

    i. Gloves

    ii. Overalls

    iii. Eye glasses

    iv. Face mask

    v. Boots/shoes

    vi. Long-sleeve shirt

    vii. Long pants

    viii. Others (specify)………………

18. How often do you change the above protective gears? ....

19. Have you ever been trained on how to apply pesticides to your farm? Yes: ……………
    No: …………...

20. If yes, by who?

    i. By agricultural officer: ………………

    ii. By neighbor: ………………………….

    iii. By friend: ……………………………..

iv. During agricultural show: ……………...

v. Others, specify: ………………………….

21. Where do you store the remaining pesticide?

i. In the house..

ii. Outside the house………………………………

iii. Other, specify…………………………………………………….

22. In your opinion, do you think pesticides are harmful to your health/environment?

....

23. Are pesticide containers used for any other purpose after use? If yes indicate:

……………………………………………………………………………………………

……………………………………………………………………………………………

24. How are the containers/packages disposed off?

....