UNIVERSITY OF NAIROBI

IMPROVING AQUACULTURE AND FISHERIES PRODUCTIVITY BY REDUCING IMPACTS OF PESTICIDES CONTAMINATION IN AHERO FISHPONDS, KISUMU COUNTY

BY
ARTHUR OUMA WERE (B.ED SCIENCE)
I56/88144/2016

A Research thesis submitted in partial fulfillment of the requirements for the a ward of the
Master of Science Degree in Environmental Chemistry of the University of Nairobi
November, 2021

DECLARATION

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

Sign: Date: …….29th November, 2021

ARTHUR OUMA WERE (I56/88144/2016)

This thesis has been submitted for research with our approval as the University Supervisors.

Sign: … Date: …………29th November, 2021

DR.VINCENT O. MADADI

Department of Chemistry, University of Nairobi

Sign: … Date: …..29th November, 2021

PROF. JACOB P. KITHINJI

Department of Chemistry, University of Nairobi

DEDICATION

I would wish to dedicate this research work to my wife Milkah, my daughters Mercy and Susan, my son Andrew and my parents Mr. and Mrs. Joel Were. They were a great source of inspiration to me during this study.

ACKNOWLEDGEMENT

I would wish to thank my supervisors Dr. Vincent Madadi and Professor Jacob Kithinji for their guidance and positive criticism while I was undertaking this study. I would also wish to extend my appreciation to Dr. Madadi and Professor Midiwo for support in the provision of most of the chemicals I used during my laboratory work.

I would also appreciate the support given to me by Kenya Marine Fisheries and Research Institute (KMFRI) staff, chemistry department during the first season sampling. They ensured that every procedure was followed according to the required standards of sampling and using the right apparatus for samples collection.

May I wish to acknowledge the student colleagues working in the Pesticide laboratory of Chemistry department, Chiromo Campus. They included Osoro, Florence and Celestine. I thank them for their invaluable support and guidance on laboratory procedures.

I wish also to thank the government of Kenya through the Teachers Service Commission for the study opportunity through paid study leave.

May I thank the Almighty God for the gift of life, financial provision and the knowledge to go through this study successfully.

ABSTRACT

Pesticides contamination in water, sediments, soil and *Tilapia zili* from fishponds in Ahero were investigated to assess the extent of pollution and likely health hazards from fishpond environment. The use of pesticides in agriculture for improving farm productivity has resulted in increased residues in sediments, soil and water. Sediments and water have become a major concern as they are the feeding and breeding points for aquatic organisms. Some of the pesticide residues are toxic to the environment and as a result threaten fish productivity and have great potential risk to human health. Various studies have been carried out previously around River Nyando basin and Winum Gulf of Lake Victoria on physico-chemical parameters, heavy metals and organochlorine pesticides. However, the focus of these studies has been based on OCPs and other inorganic pollutants in lake and river waters around the Lake Victoria basin. Little attention has been given to farmed fish in Ahero irrigation scheme despite the fact that it is located along the Nyando basin and has the potential of being exposed to residues of various pollutants deposited from the highlands which come as a result of flood during rainy season. The main objective of this study was to improve aquaculture productivity in the country and contribute to sustainable food security by reducing the impact of pesticides contamination in fisheries production. Fish, water, sediments and soil samples were obtained from the localities of fishponds, extracted and analysed for physical-chemical parameters, heavy metals, nutrients and Organochlorine pesticides (OCPs). Both short rain (dry) and long rain (wet) seasons were covered during sampling stage. The 17 OCPs were analysed using gas chromatograph, while atomic absorption spectrophotometer was used to analyse the heavy metals. Some of the Physical-chemical parameters analysed included electrical conductivity, TDS, TSS, pH and temperature. Nitrites, nitrates and phosphates levels were analysed with the use of UV-vis spectrophotometer. The concentrations during rainy season were found to be higher than that during the short rains. Nitrites concentration in water samples ranged between 0.01 to 0.02 mg/L and from 0.02 to 0.25 mg/L during short rains and long rains seasons respectively. Phosphates concentrations in water samples ranged from 0.63 to 2.1 mg/L and from 2.7 mg/L to 8.78 mg/L during short rains and long rains seasons respectively. The concentrations of nitrates in the samples of water ranged from 0.01 to 0.06 mg/L and from 0.36 to 1.44 mg/L during dry and wet seasons respectively. OCPs residue concentrations ranged from below limits of detection (LOD) to 8.05 µg/kg for β-HCH in Kasuku pond, below LOD to 2.71 µg/kg for heptachlor epoxide in Lawi pond, below LOD to 13.16 µg/L for endrin in Lawi pond and from below LOD to 5.81 µg/kg for heptachlor epoxide in Kasuku pond in soil, sediment, water and fish samples, respectively during the dry season. For the long rainy season, the residue levels ranged from below LOD to 6.66 µg/kg for α-HCH in Lawi pond, below LOD to 11.95 ±2.5 µg/kg for dieldrin in Ebenezer pond, below LOD to 25.40 ±2.31 µg/L for dieldrin in Lawi pond and from below LOD to 10.10 ±0.03 µg/kg for β-HCH in Alan pond in soil, sediment, water and fish samples consecutively. Dieldrin recorded the highest concentration in sediment during the dry season while endrin was recorded as the highest level in water during the wet season. Heavy metals notably recorded higher levels during both dry and wet seasons. Chromium concentration was from 2.79± 0.00 mg/kg to 6.01±0.8 mg/kg, 5.65 mg/kg to 8.53 mg/kg and 4.05± 0.00 mg/L to 7.24± 0.00 mg/L in soil, sediment and water samples respectively during the dry season. Cadmium levels were from 0.02 to 0.17 mg/kg, below LOD to 0.02 mg/kg and below LOD to 0.09 ±0.00 mg/L in soil, sediment and water samples, respectively during the dry season. Lead concentrations varied from below LOD to 6.38± 0.00 mg/kg, below LOD to 13.73± 0.00 mg/kg and below LOD for soil, sediment and water samples consecutively. Zinc concentrations ranged from 2.00± 0.00 mg/kg to 6.06± 0.00 mg/kg, 1.79± 0.01 mg/kg to 4.79± 0.00 mg/kg and below LOD to 0.22±0.00 mg/L in soil, sediment and water samples successfully. Copper levels varied from values below LOD to 1.36± 0.00 mg/kg, below LOD to 1.01± 0.00 mg/kg and below LOD to 0.02 ± 0.00 mg/L in soil, sediment and water samples consecutively. Even though the levels of heavy metals, OCPs and nutrients were found to be below the WHO allowable limits, there was a growing concern that with their bioaccumulation in fatty tissues over time, their levels may rise to become toxic to the aquatic environment and human health. The study found the presence of OCPs and other inorganic pollutants in sediments, water, soil and fish samples whose levels changed with seasonal variation due to anthropogenic activities. The study recommended monitoring and regulation of anthropogenic activities to reduce the impact of pesticides contamination in fish and their aquatic environment.

TABLE OF CONTENTS

CHAPTER ONE

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

AAS- Atomic Absorption Spectrophotometer
BDL- Below detection limit
DDT- Dichlorodiphenyl Trichloroethane
EAP- Environment Action Programme
ESP-Economic Stimulus Programme
GC/MS- Gas Chromatography/Mass Spectrometer
HPLC- High Performance Liquid Chromatography
KALRO- Kenya Agriculture and Livestock Research Organization
KMFRI- Kenya Marines and Fisheries Research Institute
LRET- Long-range environmental transport
LOD – Limits of detection

OCPs- Organochlorine pesticides OP- persistent organophosphates pH- Potential hydrogen, i.e a logarithmic scale used to specify the acidity or alkalinity of an aqueous solution

POPs- persistent organic pollutants
SDGs-Sustainable development goals
SPSS- Statistical Programme for Social Scientists
TDS- Total dissolved solids
TSS- Total suspended solids
WHO- World Health Organization

UNITS OF MEASUREMENT

g	Grams
Kg	Kilograms
L	Litre
Mm	Millimeter
mg/L	Milligram per litre
Ppb	Part per billion
Ppm	Parts per million
µg	Microgram
MT/y	Metric tons per year

CHAPTER ONE

1. INTRODUCTION

1.1 Background information

The world demand for food production will continue to rise due to continuous increase in population in both developed and developing countries (Ahmed *et al*., 2014). Consequently, d aquaculture has great potential to increase food security and eliminate hunger (Ahmed *et al*., 2014). According to FAO (2014), the world per capita fish supply is projected at 20 kg and besides, fish production from marine and inland waters is expected to contribute a lot to food security and nutrition for a global population approximated at 9.7 billion by 2050. Fish remains one of the most traded food commodities worldwide and more so, by nutrition, fish contributes about 30% of animal protein, making it one of the most sort source of protein globally (FAO, 2014). According to FAO (2020), aquaculture has been the main source of fish available for human consumption since 2016, contributing to 52 percent of total production internationally. Fish production is projected to increase due to growing consciousness on the health benefits of consuming fish, increased technology and increased incomes across the globe (FAO, 2020). This however has recently been interfered with as a result of the outbreak of corona virus disease (COVID-19) which according to FAO (2020), the estimates for 2020 registered a decline in the quantity for both fish exports and imports compared to 2019 and 2020. Moving into the future, FAO (2020) projects that total global fish production is expected to grow from 179 million tons in 2018 to 204 million tons in 2030. Aquaculture production is projected to rise to 109 million tons in 2030 with a growth of 32 percent based on 2018 production (FAO, 2020).

There is a likelihood that Asia might continue to lead the world's fish production accounting for well above 89 percent for the increase in production by 2030 (FAO, 2020). In the global scene, Africa contributes 1.8% of aquaculture production, confirming that its productivity is quiet insignificant compared to other continents (Munguti *et al.,* 2014). Consequently, aquaculture sector is expected to grow tremendously in Africa by up to 48 percent occasioned by additional culturing capacity put in place in the recent years (FAO, 2020). Numerous research studies and donor support to the tune of hundreds of million dollars notwithstanding, aquaculture is yet to realize its full potential in Africa (Randall *et al*., 2008). Africa harbours a mix of rich biological diversity of native fish resources and the recognition to exploit this potential has existed for quite a while (Curtis *et al*., 2012). Notably, Egypt, Nigeria, Ghana and

Uganda have registered substantive quantities in aquaculture production by realizing an increase in production from 110,200 to 2,196,000 tons from 1995 to 2018, an equivalent of 15.55% annual growth (FAO, 2016; Halwart, 2020). This development has been attributed to good private sector partnership with governments thus getting increased funding, a lot of sensitization on the importance of aquaculture as a tool for eliminating poverty by ensuring food security and there has been more interests in aquaculture across various African countries (Satia, 2016). Aquaculture has employed well above 6 million people in Africa who are mainly women in charge of trading and marketing of fish as a means of earning income (Satia, 2016). Some of the main challenges that have made aquaculture industry not to realize its full potential as expected is over relying on donor funded projects, lack of technical skills and management of aquaculture sector by the national governments as opposed to private sector (Randall *et al.*, 2008). A number of African countries, through a collaboration of aquaculture producers are playing significant roles in enhancing success of aquaculture productivity. These include among other strategies; information transfer, knowledge sharing and supporting aquaculture related undertakings (Satia, 2016).

In Kenya, aquaculture has registered considerable progress since 1900s when it was commenced by the colonialists. The main reason for this initiative was majorly for the purposes of recreation (Munguti *et al.*, 2014). This developed into static pond culture with fish species such as tilapia, common carp and catfish in the 1920s (Munguti *et al.*, 2014). There was further advancement in fish farming with more interests in consuming fish which came with the establishment of Kiganjo and Sagana fish farms in Kenya in 1948 (Munguti *et al.*, 2014). On the realization of the potential of aquaculture in enhancing food security and creating employment among the unemployed youth, the government of Kenya has put efforts that have ensured aquaculture productivity increasing significantly from 1,000 MT/y (metric tons per year) in the year 2000 to 12000 MT/y in 2010, representing 7% of the national harvest (Munguti *et al.*, 2014). Further, the national government has come strongly to support fish farmers with a clear mandate of boosting their productivity which has eventually led to the introduction of economic stimulus program (ESP) in 2010 (Munguti *et al.*, 2014).

Fisheries and aquaculture development has been earmarked by the national government as one of the flagship projects to contribute towards the achievement of the vision 2030 (Munguti *et al.*, 2014). Consequently, the sector has seen increase in ESP to boost food security and nutrition, economic development, creation of employment to the youth and women and poverty alleviation. On the contrary, the sector is facing several challenges which might be considered as basic. For instance, lack of adequate knowledge on aquaculture investment among the famers has been mentioned by various studies to be a hindrance to the success of aquaculture productivity (Munguti *et al.*, 2014). This has been coupled by lack of information sharing on the economic value of aquaculture industry and how it can be harnessed optimally by the local communities and the country at large (Kaliba *et al*., 2007). In addition, lack of quality feeds and fish seeds has been an impediment to the success and growth of the aquaculture sector. This has made life so unbearable to the farmers as the operation costs to have a fishpond, introduce fingerlings and feed them on quality and certified feeds have been very high (Gitonga *et al*., 2004). The issue of environmental pollutants getting access into the fishponds and other aquatic environments and how they affect aquaculture productivity has not been given the attention it deserves (Munguti *et al*., 2014). Pesticides used by farmers in the nearby farms end up affecting non-target organisms such as fish in fishponds, rivers, lakes and marine environments. Pesticides contaminate surface waters and this causes adverse effects on human well-being, wildlife, including the growth, survival and reproduction of aquatic animals (Adeboyejo *et al.,* 2011). In addition, food contamination through pesticide residues has compromised food safety in Kenya, being blamed for rising cases of birth defects and cancers (Wamanji, 2018).

Fish in the lakes, streams and other water bodies have not been sufficient enough to feed the ever growing population. As a result, there have been increase in the construction of fishponds to boost fisheries and aquaculture production, a way to enhance food security in the country (Munguti *et al.,* 2016). Pesticides are meant to improve the crop yield by keeping pests away from crops. However, when pesticides are sprayed, their effects also reach non-target plants and living organisms in different ecosystems through dispersion processes, pesticide residues being washed off by run-offs and leaching processes into groundwater (Abong'o *et al*., 2014). Due to increase in population in the country and changes in weather patterns as a result of climate change and global warming effects, there is a continuous pressure to produce more food to meet the rising demand. Farmers especially in developing countries, whose major economic survival is through agriculture, have scaled up their efforts of production by eliminating pests, which hamper their production by engaging in spraying of their crops against pests. Target organisms by sprayed pesticides are only able to receive about 5% of it (Aly *et al*., 2017). It implies that majority of these chemicals reach non-target organisms including soil-microorganisms, bacteria, insects, birds, animals, fish and human population (Agarry, 2013).

Ahero is agriculturally rice intensive through irrigation. Maize and other horticultural crops like vegetables, watermelons, onions, and tomatoes among others are also grown through irrigation. Various pests mostly infest these crops (Abong'o *et al.,* 2014). These pesticide residues are often transferred to other aquatic environments such as streams, rivers, lakes and fishponds, where they reach non-target organisms (Abong'o *et al.*, 2014). In addition, deposits suspected of carrying pesticide residues transported by River Nyando from the highlands (where tea and coffee are grown) of Nandi and Kericho, agrochemical and sugar industries may find their way into nearby fishponds and other aquatic ecosystems through run-off and eroded soil. Such deposits have negative effects on human health and the different ecological niches, and especially if they carry residues of pesticide pollutants (Abong'o *et al.*, 2014).

Ahero being in Kano Plains along the Nyando River basin receives a lot of sediment deposits from the highlands of Kericho and Nandi hills where it derives its source. Ahero is largely characterized by rice farming and small-scale horticultural farming of vegetables and fruits (Abong'o *et al.,* 2014). Fishponds in Ahero ward and its environs are highly impacted by pesticide residues being washed from rice fields of Ahero through run-offs from the flooding water from the highlands of Nandi and Kericho. During irrigation of rice fields by the Irrigation Board, water floods the rice fields and if not controlled might wash away residues of pesticides through run-offs into the nearby fishponds. Moreover, River Nyando passes through different factories including agrochemicals, Muhoroni and Chemelil Sugar factories among others, which empty their effluents into it. Nandi and Kericho regions have big tea and coffee plantations. These crops are sprayed against pests and there is also intensive use of different types of fertilizers whose residues are washed into River Nyando (Abong'o *et al.*, 2014).

According to Abong'o, (2009) and Abong'o *et al.* (2014), pesticide use is likely to increase across the globe owing to the fact that farmers are facing economic pressure to increase agricultural production for both local consumptions and to meet the international market demands. Due to rapid expansion of agriculture, which has been necessitated by increase in population, there has been increase in demand for agrochemicals in Kenya and pesticides have become an integral part of plant, livestock and public health protection (NES, 2006). If this trend continues, it follows that effects of toxic pesticides will continue to be felt in the environment and both human health and aquatic productivity will continue to be at risk.

The government of Kenya (2010-2012) established various fishponds (farmed fish) in different regions in the country with Ahero irrigation scheme inclusive through the economic stimulus program (ESP) to boost food security, create employment to the youth and women (Munguti *et al.*, 2014). As a result of pesticide use by farmers in the nearby farms to kill various pests, residues of such pesticides reach the non-target organisms including fish in fishponds nearby (Abong'o *et al.*, 2014). This is possible through wind, precipitation, run-offs and leaching to the surface water and groundwater (Abong'o, 2009). This phenomenon puts aquaculture and fisheries productivity at risk, and may derail the government's effort of attaining food security by 2030. Despite awareness that has been created by various studies and a call to ban some of the pesticides which are toxic to human health and the environment, they have continued to be used by farmers and their impacts have continued to be felt across the globe (Abong'o *et al.*, 2014).

Aquaculture productivity has not been given the much attention as far as environmental contamination from industrial pollutants are concerned. Studies have devoted much of their efforts on other strategies that enhance improved aquaculture productivity. These include: aquaculture policy design, fingerlings and feeds improvement and private-governments' partnerships. Pesticide contamination to the aquatic environment has emerged to be a great threat to food security not only to the country, Kenya but also to the global family. Serious and prompt interventions on how to mitigate the effects of pesticides contamination will not only ensure aquaculture productivity for sustainable food security, but more importantly take into account the production of quality and safe fish for human consumption.

1.2 Statement of the problem

The aquatic environment has continued to be interfered with as a result of environmental pollution caused majorly by the use of organochlorine pesticides by farmers. Studies have shown that organochlorine pesticides are toxic and persistent in the environment and this affects aquaculture productivity and human health. Aquaculture productivity is affected when the toxic pesticide residues get into the aquatic environment through surface run-off and percolation from the nearby farms which have been sprayed. Fishponds have continued to supplement the fish productivity in Kenya in addition to fish caught from natural waters like rivers, streams, lakes and Indian Ocean. Fishponds have become the most affected environments by residues of pesticides. On the contrary, no much efforts have been put to safeguard such fish from pesticides contamination. This affects their productivity because when they get exposed to toxic pesticides, their growth rate is retarded, some of the fish die and there is delayed laying and hatching of eggs. Consequently, this decline in productivity affects food security in the country. Moreover, the contaminated fish becomes a health hazard to human who consumes them (Aly *et al.*, 2017). There is ban on use of organochlorine pesticides in developed and some developing countries. However, in Kenya the use of organochlorine pesticides has been restricted to controlling of malaria causing vectors in malaria infested regions including the Nyando basin (Abong'o, 2009). This however does not restrict the toxic pesticide residues from reaching non-target organisms in the aquatic environments. It becomes apparent that there has been use of organochlorine pesticides without due regard to its effects in the aquatic environment and human health.

1.3 Objectives of the study

1.3.1 General Objective

The goal of this study was to improve aquaculture production in the country and contribute to sustainable food security by reducing the impact of pesticides contamination in fisheries productivity.

1.3.2 Specific objectives

1) To determine the extent of pesticide concentrations in fish, sediments, water and soil from fishponds and the surrounding localities.
2) To determine the physico-chemical parameters of water, sediments and soil and their impact on pesticide persistence.
3) To determine the nutrient levels in water from fishponds and potential impact on sustainable fish productivity in the region.
4) To determine the effects of seasonal changes in terms of human activities on pesticide concentrations in fish.

1.3.3 Significance and Justification of the study

The study anticipated to improve aquaculture and fisheries by reducing pesticides contamination in Ahero fishponds, Kisumu County. Aquaculture is significant to food security through farmed fish production. Understanding safe use and handling of pesticides can help to minimize impacts of pesticides contamination on fisheries productivity by calling upon the County government through county fisheries department to sensitize farmers. Pesticide used in irrigation schemes may get into fishponds through percolation, seeping and run-offs. There are anticipated levels of physical-chemical parameters and nutrients to rise above the normal. Consequently, physiological disorders in fish from fishponds may occur. Hence the study sought to contribute towards boosting fish productivity and ensuring food security and safety for the people and the nation at large. Recent studies in both River Nyando and Lake Victoria basin have based their research on the presence of OCPs, heavy metals and other inorganic pollutants on water both in the rivers and the lakes. They have also focused on soil and sediments within the basins. However, there has been little attention on how these potential pollutants affect the farmed fish in fishponds within Ahero creating a research gap. The stakeholders including research institutions, county and national governments to design policies on training farmers and other chemical handlers on safe use of pesticides, seeking alternative pesticide management methods such as practicing organic farming, crop rotation, weeding out weeds instead of using herbicides and planting pest resistant crops.

CHAPTER TWO

2. LITERATURE REVIEW

2.1 Pesticides

These are toxic chemical agents used for the purpose of suppressing any pests or vectors causing human or animal disease, during production, processing or storage of food, agricultural commodities or animal foodstuff (Tano, 2011).

2.2 Types of Pesticides

Classification of pesticides takes different approaches depending on their uses. For instance, those pesticides used for killing insects are called insecticides; rodenticides used to kill rats, mice and other rodents; those used to kill and destroy weeds are called herbicides; those used to kill fungus are called fungicides and those used to kill bacteria and other harmful organisms by either chemical or biological means are called biocides (Aly *et al*., 2017).

2.2.1 Types of pesticides according to their Formula

There are various types of pesticide formulas used to spray against pests. Fine white in colour suspension of oil droplets in water mixed with active ingredients in what is referred to as emulsifiable concentrate, while wettable powders are fine suspended particles in water. In addition, granules can be got from a combination of the active ingredient with soil for outdoor application while baits are obtained by mixing food base especially used for control of rodents (Tano, 2011).

2.2.2 Types of pesticides according to their major routes

Pesticides may be absorbed into the body via three routes: the skin (dermal absorption); the lungs (inhalation) and the mouth through the stomach and intestine (ingestion). In addition, systematic pesticides are applied to either plants or soil to move throughout the plants or soil by the foliage or the roots and move throughout the target plant. When the target insect chews or sucks the plant, it is killed or rendered unconscious (Ellsworth and Jones, 2001).

2.2.3 Types of pesticides according to their origins

2.2.3.1 Biopesticides

According to Rosell *et al*. (2008) biopesticides are naturally occurring substances, materials, or organisms, plants and animals which can be used as pesticides. For example, use of beetles in Lake Victoria to get rid of water hyacinth by feeding on them. One thing that has made biopesticides to gain popularity among research scientists is its inaction on non-target organisms and its biodegradable ability, making it non-persistent thereby avoiding environmental pollution as opposed to conventional pesticides and this makes them be used as alternative pest management method (Rosell *et al*., 2008).

2.2.3.2 Chemical Pesticides

This category comprises of the most commonly used pesticides in agriculture and control of other vector causing infections. They include organophosphates (Chlorpyrifos, Diazinon and Malathion), carbamates and organochlorines. Most of these pesticides have the property of being persistent in soil for longer periods making them accumulate thereby raising the toxic levels of soil (Aly *et al*., 2017).

Consequently, the chemicals may be assimilated by the plants and are accumulated in edible plant products, especially in the root parts. Besides, there are residues that seep into groundwater and deposited as sediments which later fish derive their food and are accumulated through the food chain (Aly *et al*., 2017). Such contaminated fish put human health at risk when they feed on them. For instance, highly toxic phosphates (Diazinon, Chloropyrifos and Malathion) may persist for a few months, while organochlorines like DDT, aldrin and chlordane are known to persist for at least for 4-5 years or even more. Intensive use of DDT to control plant pests and diseases is very dangerous to human health due to their accumulation in the food chain, which is responsible for carcinogenic, mutagenic and teratogenic effects in human beings (Biego *et al*., 2014).

2.3 Biodegradation of Pesticides

Biodegradation refers to disintegration or breakdown of a chemical compound by fungi, bacteria or other biological means (Aly *et al*., 2017). This is a major breakthrough towards detoxifying the environment of the ever-downloading toxic pesticide residues that according to studies have contributed to health hazards to both aquatic organisms and human beings.

Biochemical reactions catalyzed by enzymes become very instrumental in the biodegradation of pesticides which have always remained very complex. This follows the principle of microbial infallibility, that for every naturally occurring organic compound, there is a corresponding microbe enzyme system responsible for its disintegration, thus being able to remove its pollutant nature from the environment (Gale, 1952). It becomes apparent that with the continuous use of pesticides, the perceived microorganisms in the soil which are responsible for pesticides degradation and reducing their toxicity levels from the environment are consequently being eliminated, thereby exacerbating environmental contamination and human health is continuously under threat (Aly *et al.*, 2017). This phenomenon also interferes with soil nutrients which are necessary for crop yield, thus putting the country's effort to boost agricultural productivity at risk. This eventually threatens food security which is one of the global SDGS and which has been prioritised by the national government as one of the four flagship projects (2018-2022).

2.3.1 Fungal degradation of pesticides

Extensive application of persistent organophosphate (OP) like endosulfan on cotton, fruits and vegetables has led to the contamination of soil and water environment at several sites in the world and microbial degradation using various strains of bacteria and fungi offers an effective approach to remove such toxicants from the environment (Reddy *et al.*, 2012).

2.3.2 Bacterial degradation of pesticides

OP compounds do not seriously affect bacteria because bacteria do not possess acetylcholine esterase, and some microorganisms, animals and plants can use OPs as source of energy (Singh *et al.*, 2006).

2.4 Importance of pesticides in Crop production

The modern farmer has become more conversant and informed about what he needs to improve the productivity of his/her crops. This comes along with the desire to keep up with the rising demand for quality farm produce (Smith, 2011; Agarry, 2013). Increased crop yield, animal production and reduced post-harvest losses are associated with the use of pesticides (Muller, 2000). This has ensured increased food production. In addition, use of pesticides has ensured food sufficiency in agriculture sector especially in developing countries. Poor families can afford to take their children to school and meet other family basic needs with this kind of sustained food production as a result of use of pesticides (Wang'ombe, 2014).

2.5 Impacts of use of pesticides to the Environment

Pesticides can be good as has been described above. However, pesticides can also be bad, especially on how it is handled, used, stored and when it is finally released into the environment (Abong'o, 2009). Studies by UNEP (2012) reveal that out of the persistent organic pollutants (POPs), 16 out of 22 most hazardous and toxic chemicals are pesticides. There have been reported cases of contamination and instant death of fish and other aquatic animals when they are exposed to toxic pesticides. Fish get most of its food from sediment particles which are mostly deposited by materials from different sources, hence there is a likelihood of exposure to pesticides (Biego *et al.*, 2014). Water overflows and through percolation from rivers and underground water to nearby fishponds are responsible for this phenomenon. In addition, effects of agricultural activities from farms nearby fishponds may seep, percolate or drift through air into the fishpond and affect the fish. There has been evidence of pesticides residue levels in fish, water, soil and sediment (Abong'o, 2009; Abong'o *et al.*, 2014). However, there has been little attention on farmed fish in fishponds around Nyando basin, particularly in Ahero Irrigation Scheme. In addition, during rainy seasons, water floods the area making it a good site for mosquito breeding. Most of these organochlorine pesticides, especially DDT whose use has been restricted to malaria vector control by EPA has been used by public health before and due to its potential for long-range environmental transport (LRET) and its persistent to the environment, its effects may be felt among the fish in the aquatic environment. This raises a critical environmental concern that needs attention for possible environmental solutions through research.

2.6. Depletion of organisms diverseness in an Ecosystem

Organisms in ecosystems exist in an intricate co-dependence relationship in such a way that the disappearance of one key species as a result of pesticides, can have far reaching and erratic consequences on the environment (Sacramento, 2008). This phenomenon results in array of negative effects that change trophic dynamics and can cause the disappearance of other organisms in the ecosystem (Kegley, 1999). For instance, zooplanktons are famous for being keystone species in marine and inland waters environments that limit the population density of fish species especially Tilapia (Sacramento, 2008).

2.6.1 Pesticides may cause pest resistance

Constant spraying of pesticides in a particular environment may cause a situation where pests become resistant to pesticides (Henry, 2003). However, from the onset, quiet a number of them become vulnerable to pesticides while others adapt and become very resistant to the pesticides. It is important that such pests be managed through use of various pesticides alternately one after the other so as to lessen the existing resistance (Sacramento, 2008).

2.6.2 Pesticides disrupt the natural balance between pests and predator insects

The presence of beneficial organisms is very invaluable in creating ecological balance. For instance, they help in pollinations across flowers among other vegetations. In the event that pesticides are sprayed haphazardly, both pests and beneficial organisms are killed (Abon'go, 2009). Consequently, pests' population recovers immediately as a result of their significant number and their adaptability, but beneficial organisms fail to recover, causing a revival of the number of target pests as well as secondary pests that reproduce quickly in the absence of natural predators to control their numbers. Consequently, more pesticide residues are loaded into the environment thus affecting both the environment and human health.

2.7 Heavy Metals

Heavy metals are known to have great potential for toxicity to both the environment and human health (Samir, 2008). Examples of toxic heavy metals according to WHO (2019) include: cadmium, chromium, lead, mercury, arsenic. Other heavy metals are essential elements in human body. However, at high levels they become toxic and affect human health (Samir, 2008). Examples of essential heavy metals are copper and zinc among others. Among the heavy metals investigated in the study included: lead, copper, zinc, chromium and cadmium.

2.7.1 Lead

The knowledge of lead and its impact on the environment has significantly improved in the recent years according to recent research studies. However, there is continued lead poisoning in the environment and more particularly on human health. According to recent studies, the presence of lead and its compounds in aquatic environment in sufficient amounts may cause acute or chronic toxicity to organisms like fish (Tenai, 2014). When human beings eat such fish, lead accumulate in the body through fatty tissues and as a result the human body gets exposed to lead poisoning. A case in point is from residents of *Owino Uhuru*, near Mombasa, Kenya who protested against a lead smelter that opened next to the settlement that killed workers, poisoning residents, and polluted the community in November, 2013 (Ericson *et al.*, 2014). This is a demonstration that the Kenyan government has not taken the necessary measures to protect the environment and human lives against lead exposure and poisoning. If this trend continues without proper legislation and enforcement of environmental laws, then a bigger population in the country and the aquatic organisms will increasingly suffer out of lead exposure, its toxicity and even death (Tenai, 2014).

2.7.2 Copper

Copper is one of the most toxic metals to aquatic organisms and ecosystems and is moderately soluble in water and binds easily to sediments and organic matter (Baldwin *et al.*, 2003). Cu $^{2+}$ is the most toxic form of copper. Fish and other crustaceans are 10 to 1000 times more sensitive to the toxic effects of copper than are mammals, (Wright *et al.*, 2002). This implies that copper is more toxic to aquatic organisms than animals and human beings. According to Solomon, (2007), copper is an essential trace nutrient required in small amounts of between 520 ug/g by humans, other mammals and aquatic animals including fish for carbohydrate metabolism and the functioning of over 30 enzymes. Solomon (2007), explains further that essential copper is instrumental for pigments in the blood of vertebrates and shellfish, respectively. On the other hand, oxygen concentration levels above 20 ug/g may be toxic (Wright *et al.*, 2002). The fact that copper is used to kill algae and molluscs, is a clear demonstration that it is highly toxic to aquatic organisms. Long exposure to copper with considerable concentration levels may be directly or indirectly lethal to aquatic organisms and human health when they feed on such organisms like fish (Wright *et al.*, 2002). This phenomenon may kill fish receptors thus paralyzing their neurons leading to reduced appetite, reduced food uptake, growth and reduced sensitivity rendering them vulnerable to predation (Mclutyre *et al.*, 2008). In addition, according to Taub, (2004) long exposure to significant levels of copper of between 10-20 µg/L, sperm and egg production are reduced. There is premature hatching of eggs leading to high incidences of abnormalities and reduced survival rates. This impacts negatively on their productivity and thus acts as impediment to national government’s effort to ensuring food security in our country.

2.7.3 Cadmium

Cadmium is one of the heavy metals in group 12 (IIB) of the periodic table. Cadmium metal is of considerable environmental and occupational concern (Wambua, 2015). The most common source of cadmium compounds in the environment is sedimentary rocks and marine phosphates with approximately 15 mg/kg of cadmium (Tchounou *et al.*, 2012). Cadmium is used in industrial activities that include alloys, pigment and batteries. In developed countries, there has been serious environmental concern on the use of cadmium and the allowable limits into the environment. Cadmium exposure to human has been majorly through inhalation or cigarette smoke and ingestion of food. Other routes include employment in primary metal industries, working in cadmium contaminated workplaces. Moreover, eating of foodstuff rich in cadmium may to a greater extent increase the concentration of cadmium in human body (Wambua, 2015). Levels of cadmium in human body can be detected by examining blood and urine samples and it has been established that people who smoke cigarettes have high levels of cadmium in their blood and urine (Tchounou *et al.*, 2012). Symptoms of one suffering from cadmium exposure and its consequence effects include irritation of the pulmonary and gastrointestinal walls, abdominal pain, sensation, nausea, vomiting, muscle cramp, loss of consciousness and convulsions (Tchounou *et al.*, 2012). Moreover, recent studies reveal that at lower concentration of cadmium, at 1 to 100μg/, cadmium binds to proteins, decreased DNA repair, activates protein degradation and up regulate cytokines and proto-oncogenes (genes codes for proteins that help regulate cell growth) (Tchounou *et al.*, 2012). Cadmium exposure has been concluded to be a human carcinogen and causes lung cancer, cancers of the prostate, kidney, liver, hematopoietic system and stomach (Tchounou *et al.*, 2012). These are major and current diseases killing the Kenyan population and has been a major concern for individuals from different research institutions to come up with solutions that will control or eliminate cadmium and other heavy metal exposure from the environment (Wambua, 2015). There has been attention on river Nyando as far as the presence of cadmium is concerned by previous studies but no focus on the farmed fish in the local fishponds. It is out of this concern that the study sites were investigated for the presence of cadmium with a view to come up with precautionary measures that will prevent contamination of fishponds.

2.7.4 Zinc

Zinc is an essential heavy metal with low melting point and it is one of the heavy metals essential to life and it has a wide range of uses (Sauer *et al.*, 2017). It is a naturally occurring element whose main source is the rocks in the earth's surface. As zinc is a reactive element, it is not found freely in nature but it is found mixed with other elements or compounds. For instance, the most common zinc compounds include sphalerite (ZnS), smithsonite ($ZnCO_3$) and hemimorphite ($Zn_4SiO_7OH_2$) H2O) (Sauer, 2017).

Zinc is a trace element in human which is not stored in the body thus requires continuous dietary intake (Sauer, 2017). Zinc is responsible for quality sperm and fertilization in men and it also plays the role of antioxidant. On the other hand, dietary zinc deficiency of less than 5 ppm paralyses reproduction in males and females (Sauer, 2017). Zinc is reportedly non-toxic at low concentrations, however on higher concentration levels, it has toxic effects which impairs copper absorption, resulting to copper deficiency (Sauer, 2017). According to The Kenya Micro-Nutrient Survey (2016), there are incidences of zinc deficiency among the preschool children aged below 59 months in Kenya which stood at 86 per cent in the rural areas and in the urban areas 76.4 per cent (Njanja, 2017). Previous studies have no documented data on the presence of zinc in the aquatic ecosystems around the River Nyando basin, particularly in fishponds in Ahero irrigation scheme It is critical to investigate the levels of zinc at the sites of study so that precautionary measures may be taken before aquatic and human health are put at risk as a result of zinc toxicity.

2.7.5 Chromium

Chromic (Cr) is a transition metal. Chromium enters the environment through air, water and soil from a wide range of natural and anthropogenic sources. The major effluent to the environment is through industrial processes that include, metal processing, tannery facilities, chromate production and stainless steel welding. Increased concentration levels of chromium in the environment has been associated with waste water release from metallurgical and chemical industries (Ondiere, 2016).

Chromium in its hexavalent form (Cr VI), which is majorly released to the environment from anthropogenic activities is a toxic industrial pollutant in high concentrations and various agencies have found it to be a human carcinogen and specifically responsible for the cancer of the respiratory tract in humans (Ondiere, 2016). Since it is a widely used metal in various industrial processes, it follows that it is a constant pollutant in many environmental systems

(Wambua, 2015). No recorded data on any earlier investigation on levels of chromium at the sites of study, thus making this investigative study very invaluable for future precautions and safety on both aquatic and human health.

2.8.0: AAS, GC-MS and UV/Vis

These are the machines to be used in carrying out the analytical procedures in determining the concentrations of various OCPs, nutrients in water and thus determining water quality and for determining the concentration of heavy metals in the samples.

2.8.1: AAS (Atomic Absorption Spectrometer-Single Beam DW-AAA4530F

This analytical machine is used to determine the concentration of numerous elements and particularly in heavy metals. It operates by determining the selective absorption of light by gaseous atoms produced by spraying a solution into a flame (FAAS) or by evaporation in a carbon tube (CFAAS) (elgalabwater.com)

2.8.2: GC-MS (Gas Chromatography/Mass Spectrometer-Agilet 6890 series USA) The GC-MS has two main components the GC where the chemical mixture is separated and the MS components where identification of the chemical is done. GC-MS is mostly used for analyzing environmental samples because of it is accuracy. The main working principle of GC is that a mixture will separate into different elements on higher temperatures (Maštovká and Lehotay, 2004). Volatiles are carried by the carrier gas through the stationary phase. The instrument purity gas is introduced to GC machine at first. The carrier gas comes in through the injection pot just at the liner and moves in to the stationary phase with the sample and finally into the detector. The injector is maintained at high temperatures (150-250 °C) this is to change the liquid sample to gaseous form. The volatile sample is carried to the stationary phase by the carrier gas (Karasek and Clement, 2008).

In the column the sample interacts with the stationary phase. The sample is carried through the stationary phase of the column whose particles don’t move; hence there is collision between the stationary and mobile phases (Steve *et al.,* 2005). All molecules that are associated to a particular chemical are carried through the stationary phase almost at the same speed and they are seen like a band of particles. The velocity at which the particles move on the stationary phase is determined by factor like; the chemical component of the stationary phase, structure of sample and the oven temperature (Steve *et al.,* 2005). The operating temperatures of the oven and dimension of the stationary phase influence the breadth of the particle group. Retention time is the duration a particle takes from the time of injection until it comes to the detector. The retention time usually is given to specific particle peak (McCready *et al.,* 2000). Depending on the interaction of the sample with the column it leaves the column and enters the detector. Software is usually used to run the GC. The identification of a sample in GC-MS is usually by the use of retention time and pure sample (standard). The pure standard is analysed using the GC-MS and its retention time is compared with the sample. If the retention time of the sample and standard match then the sample has the analyte of the standard (Clescer *et al.*, 2007).

The GC-MS has two detached main components; the Gas Chromatograph (GC) where disconection occurs and a detector (mass spectrometer or Mass Selective Detector) where identification of the solutes occurs. The other components of the GC include injection port, carrier gas, oven and column. Most of the GC has automated injection.

The carrier gas which sometimes is called mobile phase in GC is a crucial, but limiting, aspect in separation. The mobile phase is the means to transport components of a sample through the stationary phase. Selection of carrier gas is determined by aspects like the kind of solutes to be analysed and the cost (Clescerl *et al.,* 2007). The commonly used carrier gas is helium because it’s inert to most compounds. When the sample is injected, mostly 1µL of sample is injected into the GC through the injection port with the temperature maintained at 300 °C so that all the samples injected are vaporized. The Common injection mode systems are split, pulsed split, splitless and pulsed splitless (Clescerl *et al.,* 2007). Components of the GC-MS are illustrated in Appendix VII.

2.8.3: UV-Vis 1700, SHIMADZU-JAPAN

This analytical machine is mainly used for the purposes of detecting, identifying and quantifying data from sample materials like gases, liquids and solids. It can thus be used both for determining chemical composition and determining physical properties of a substance. The basic components include: a sample holder, the part which separates light into corresponding wavelengths and a detector (Clescerl *et al.*, 2007).

.

CHAPTER THREE

3. MATERIALS AND METHODS

3.1 Study design and study area

Research design was a cross-sectional study within Ahero Ward covering rice fields with specific target on the location of fishponds. Sampling sites were purposively selected with due regard to water discharge points into the fishponds with some fishpond sites receiving water flowing from the rice fields emanating from river Nyando during irrigation. Some sites were located within the shore of river Nyando, thus receiving their water direct from the river, while other sites were about 100 m from river Nyando and therefore did not receive direct source of water from either rice irrigated fields or river Nyando. The study was conducted with a previous study conducted in the area on the presence of organochlorine pesticide residues in River Nyando basin being the baseline. A pre-visit was conducted a head of sample collection for introduction and outlining the purpose of the study to the fishpond owners who were basically the local farmers. Samples collected included water from the fishponds, *zili fish* which is the commonly reared fish in the region, sediments from the bottom of the fishponds and soil dug about 30 centimeter deep from the surrounding of the fishpond. A total of five sites were identified for sample collection. The samples were analysed for the presence of heavy metals with the help of atomic absorption spectrophotometer (AAS), the presence of organochlorine pesticides (OCPs) was analysed with the help of GC/MS and water quality was analysed for the presence of nutrients such as nitrites, nitrates and phosphates with the help UV-Vis spectrophotometer (UV-Vis 1700, SHIMADZU-JAPAN)

Ahero is in Nyando Sub-county of Kisumu County situated along the busy Nairobi –Kisumu highway, 25km from Kisumu town, located south east of Kisumu town, the capital of Kisumu

County. From one of the previous studies by Abong'o *et al.*, (2015), it receives annual rainfall of between1000 mm near Lake Victoria and 1360 mm towards the highlands of Kericho and Nandi Hills. It is usually a hot and humid area of temperatures between 23 ^{0}C and 27.5^{0}C

(Abong'o *et al.*, 2015).Ahero region receives a lot of sediment deposits from the highlands of Kericho and Nandi hills where it derives its source. Ahero is largely characterized by rice farming and small scale horticultural farming of vegetables and fruits. Ahero Irrigation Scheme covers about 2,586.5 acres of land and approximately 570 farmers are involved in active farming (Abong'o *et al.*, 2014). Local farmers also practice aquaculture production through farmed fish in fishponds. The region is prone to floods during long rains (March-May) and around this time there is increased farming activities. As expected, there is a lot of overflows which discharge into the nearby agricultural fields and fishponds as it finds its final destination into the Gulf of Lake Victoria. Figure 3.1 illustrates the Map of the study area. More pictures of the study sites are in appendix VII.

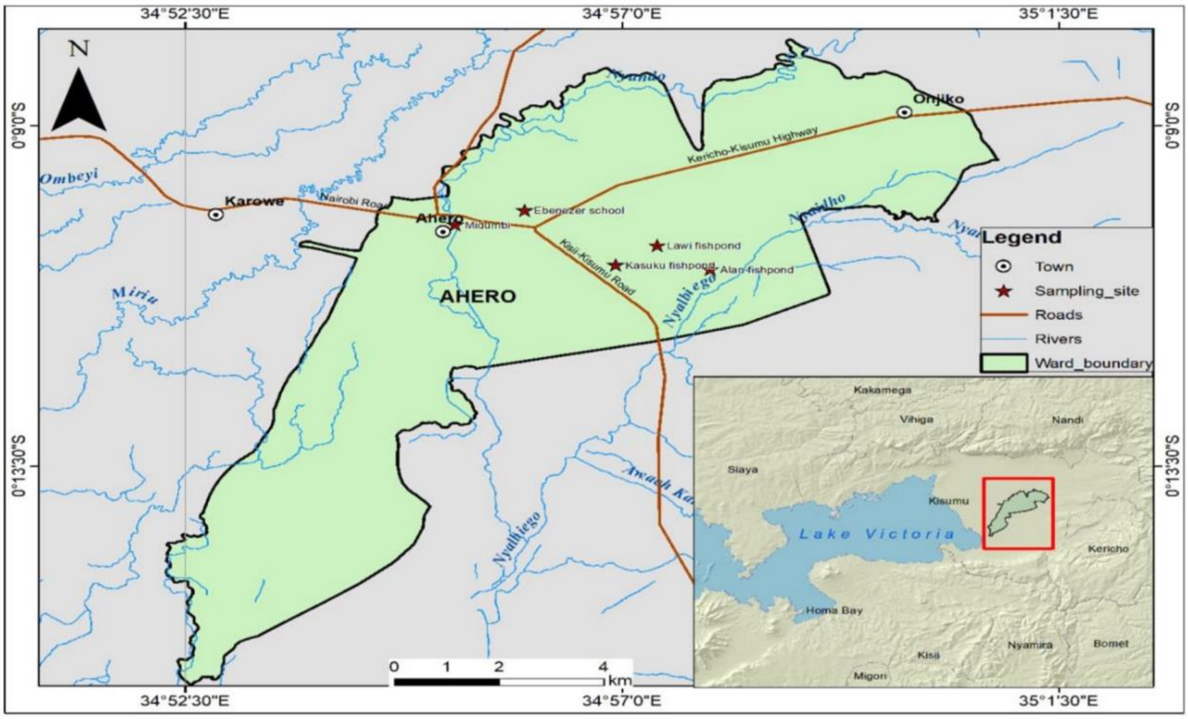


Figure 3.1 The map of study area

3.1.1 Plan for collection of Samples

Sampling was done during wet and dry seasons. The first sampling was covered between December (2017) and February (2018) while the second one was undertaken between March and April (2018). This was due to different seasons that affect pesticide levels and agricultural activities in the study area. December, 2017 -February, 2018 captured the scenario due to pesticides applied to the fields before and during the dry spell or rather short rains while samples collected between March-April 2018 reflected the rainy period when most food crops, vegetables, rice and fruits were in the field, being sprayed against pesticides.

3.1.2 Collection of Water samples

Water was sampled by drawing using clean four 500 ml amber glass bottles and another 500 ml plastic bottle sealed with aluminium foil and covered with a cork then put in ice-box packed with ice inside.

3.1.3 Collection of Sediment samples

Sediment samples were collected from the same sites of fishponds using a clean stainless shovel. The three composite samples were then mixed, a 500 g representative samples picked, wrapped in a clean piece of aluminum foil, put in a black polythene bag and labeled. Everything was packed in a cooling box and transported to the laboratory, stored in a deep freezer at -20 ^{o}C before the extraction process.

3.1.4 Collection of fish samples

Fish samples were collected from the same sites of fishponds using clean fishing nets. Three fish samples were caught per pond of the five sampled ponds, wrapped in a clean piece of aluminum foil and labeled then packed in a cooling box and transported to the laboratory, stored in a deep freezer at -20 ^{o}C before the extraction process. This was carried out during both dry and wet seasons.

3.1.5 Collection of Soil samples

Soil samples were collected from farms surrounding fishponds. They were dug using a precleaned hoe and scooped using stainless steel shovel down to the depth of 15-30 cm from three different locations within the site. 500 g representative sample was scooped from the mixture of the three composite samples and wrapped using a clean piece of aluminium foil and labeled. This was then transferred into a cooling box, transported to the laboratory, and stored in a deep freezer at -20 ^{o}C awaiting extraction process.

3.2 Chemicals and Reagents used

Triple distilled n-hexane, dichloromethane, acetone and HPLC grade iso-octane were used for extraction. Aluminium oxide, anhydrous sodium sulphate, sodium chloride, dipotassium hydrogen phosphate, hydrochloric acid and sodium hydroxide were also used. Nitrogen of High purity (99.999 %) was used for concentrating samples. Helium of high purity (99.999 % N6) was used for chromatography. High purity pesticide standard mixture was also provided. Distilled water for preparing solutions and rinsing glassware was available from the department of Chemistry, University of Nairobi.

3.3 Apparatus used and other Instruments

Sediment, soil, and fish samples were extracted with the help of Soxhlet set up comprising of Soxhlet extractors, condensers and heating mantles. This component of apparatus is commonly preferred because the required compound has a limited solubility in the solvent being used and in addition, the impurities obtained remain insoluble in the analyte. As may be known, the soxhlet extractors do not need much attention although there is high efficiency due to its design of being easy to operate. Extraction of water samples was done using 2.0 L glass separating funnel, whereas LABCONCO rotary evaporator was used for concentrating sample extracts and glass alumina chromatographic column 25 cm x 1.5 cm diameter was used in clean-up process. Solvents were distilled using Fractional distiller, pH of samples was measured using Scientific pH meter model IQ 150, while scientific Martin instruments model Mi 306 was used to measure TDS, electrical conductivity and temperature. Analytical Fisher scientific A-160 weighing balance was used to take all the weights measurements. Soil, sediments and fish samples were stored in a deep freezer before extraction process. HPLC grade was used for GC/MS (AGILET 6890 SERIES; USA) analysis of pesticides. Glassware used in this study included; Beakers, glass vials, auto sampler vial, conical flasks, Pasteur pipettes, desiccators, measuring cylinders and syringes for sample injection.

3.4 Preparation of Reagents

Aluminium oxide (Al_2O_3) was put in the oven for activation at a temperature of 200°C. Deactivation then followed with HPLC water (8 % w/w). Activated Al_2O_3 was then added in 250 mL Erlenmeyer flask and shaken to remove lump. A deactivated Al_2O_3 was left overnight to condition. Oven-baking at 200 °C was applied on anhydrous sodium sulphate for 16 hours. 29.2 mL, 0.2 M HCl and 50 mL, 0.2 M dipotassium hydrogen phosphate was mixed to prepare buffer solution. Triple distillation was applied on all the general-purpose grade solvents before use.

3.5 Extraction

3.5.1 Pesticides Extraction from Water Samples

Water samples extraction was done by solvent–solvent extraction procedure. Water of 2.0 L was measured, transferred into 2.0 L beaker and the pH noted. This was then followed by drawing 50 mL of 0.2 M dipotasium hydrogen phosphate buffer, added to the sample and pH recorded and then adjusted by drop by drop adding of 0.1 M hydrochloric acid or 0.1 M sodium hydroxide solutions while carefully stirring to adjust the pH to 7.0. The neutral solution was then transferred to 2.0 L separating funnel and treated with 100 g of sodium chloride to help salting out of OCPs from the aqueous phase. This was then followed by the addition of 60 mL of triple distilled DCM. The mixture was then shaken while releasing pressure and allowed to settle to enhance separation into two phases. The lower organic layer was then collected into a pre-cleaned dry flask and process repeated twice. Anhydrous Na_2SO_4 was added to the extracts for drying followed by addition of 2 mL of iso-octane as a keeper then concentrated to about 3 mL using rotary evaporator. The extracts were then put into vials for cleaning-up process.

3.5.2 Pesticides Extraction from Sediments Samples

For the extraction of sediments, Soxhlet extraction was used. Sediment samples were first removed from the freezer then allowed to thaw for about 4 hours before being divided in triplicate of 20 g each, and then dried with anhydrous sodium sulphate (Na_2SO_4). The extraction was done with 200 mL of hexane: acetone (3:1v) in a 250 mL round bottomed flask for 16 hours. After which, 2 mL of iso-octane was added as a keeper then concentrated to about 3 mL. The extract was then transferred into vials for clean-up process.

3.5.3 Extraction of Pesticides from Soil Samples

Soil samples underwent the same procedure as sediments using the same solvents and equipment. After 16 hours extraction, 2 mL of iso-octane was added to the extract and concentrated to about 3 mL using rotary evaporator. The concentrated samples were then transferred into the vials for clean-up process.

3.5.4 Extraction of Pesticides from Fish Samples

Fish samples were removed from the freezer then allowed to thaw for four hours. The three fish samples from each fishpond were then cut using a clean dry knife on both sides, removing the fat tissues into a dry mortar. The composite mixture was then homogenized using a pestle, divided in triplicate of 10 g each and finally dried with anhydrous sodium sulphate overnight. The extraction was done with 200 mL of hexane: acetone (3:1 v/v) in a 250 mL round bottomed flask for 16 hours inside the Soxhlet unit. After which, 2 mL of iso-octane was added as a keeper then concentrated to 3 mL. The extracts were then transferred into vials for clean-up process.

3.6 Cleaning up of Samples

Cleaning up of samples was carried out using anhydrous sodium sulphate packed in alumina chromatographic column 25 cm x 1.5 cm diameter then 15 g of aluminium oxide and 1 g anhydrous sodium sulphate were added. The extracts were each introduced into the column, eluting with 165 mL of HPLC grade-hexane into round bottomed flask. 2 mL of iso-octane was then added to each extract then concentrated to 1 mL. The extracts were then transferred into clean pre-weighed auto vials and concentrated to 0.5 mL under a gentle stream of white spot nitrogen then taken to the GC/MS (AGILET 6890 SERIES; USA) for analysis.

3.7 Analysis of nutrients

In the nutrients analysis, nitrites, nitrates and phosphates in the water samples were considered.

3.7.1 Preparation of chemicals and reagents for nitrates and nitrites analysis

To 250 mL of distilled water, 105 mL of conc. hydrochloric acid, 5.0 g sulfanilamide and 0.5 g N-(1-naphthyl) ethylenediamine dihydrochloride was added. The mixture was stirred to dissolution, after which 136 g of sodium acetate ($C_2H_3NaO_2$) was added and the mixture stirred to dissolve before diluting to 500 mL with distilled water.

Nitrate stock

To 100 mL volumetric flask, 0.163 g KNO_3 was added and dissolved and made up to the mark with distilled water to make a concentration of 100 ppm.

Nitrate Standard solution

To 100 mL volumetric flask, 10 mL of the nitrate stock solution was diluted with distilled water and topped up to the mark to make a concentration of 10 ppm of a working standard solution. From this, different calibration standards of 0.0, 1.0, 2.0, 4.0 and 6.0 and 8.0 mg/L were prepared by serially diluting appropriate amount of 10 ppm of the working standard. The absorbance of each sample measured at 275 nm with the UV-Vis spectrophotometer using the reagent blank as reference solution was read. **Nitrite stock**

To 100 mL volumetric flask, 0.15 g $NaNO_2$ was dissolved and topped up with distilled water to the mark to make a concentration of 100 ppm of the stock solution.

Nitrite standard solution

To 100 mL volumetric flask, 10 mL of nitrite stock solution was diluted with distilled water and topped up to the mark to make 10 ppm concentration solution. Calibration standards of 0.0, 1.0, 2.0, 4.0 and 6.0 and 8.0 mg/L were prepared by serially diluting appropriate amount of the 10 ppm of the stock solution. 90 mL of each of the standards including the blank and the sample were transferred into corresponding empty 100 mL volumetric flask. In each of the contents in the flask, 5 ml of 0.2% sulphanamide solution and 2 mL of 6 M HCl to form a diazonium compound with nitrite ions present. After 3 minutes, 1 mL volumetric ammonium sulphamate solution was added to each of the flask. They were then left for 3 minutes before addition of 1 mL naphthylene diamine dihydrochloride. Each of the flask contents was then topped to 100 mL mark. Absorbance of each sample measured at 534 nm with the UV-Vis spectrophotometer using the reagent blank as reference solution was read.

3.7.2 Preparation of chemicals and reagents for phosphorous analysis

Reagents used included: pH indicator, concentrated HCl of 1d H_2O, vanadate- molybdate reagent. For solution A, 25 g of ammonium molybdate $(NH_4)_6 Mo_7O_{24}.4H_2O$in 300 mL dH_2O, was dissolve while solution B, dissolve 1.25 gm ammonium metavanadate, NH_4VO_3 by heating to boiling in 300 mL of distilled water and cooled, then 330 mL of con. HCl was added and cooled to room temperature. Thereafter solution A was poured into solution B, and the mixture diluted to 1 litre.

The pH was adjusted to >10, and 1 drop indicator was added to 50 ml sample, and the coulour discharged (removed) with 1M HCl before diluting to 100 mL with distilled H_2O. 50 mL of the sample and blank sample were separately transferred to 100 mL volumetric flask and 10 mL vanadium molybdate reagent added to the standards and diluted to the mark (100 mL) by distilled H_2O and allowed to stay for 10 minutes. The colour of the absorbance of each sample was measured at $\lambda = 420$ nm using UV-Vis spectrophotometer against the reagent blank as reference solution.

3.8 Analysis of heavy metals

3.8.1 Analysis of heavy metals from Sediments and soil samples

5.0 g of each of the samples (sediments and soil) were weighed in triplicate using analytical weighing balance and put in the oven for an overnight drying. The samples were then reweighed to determine the dry mass and hence the moisture content was determined. The samples were then digested using 10.0 mL of analytical grade concentrated 11.36 M HCl and 14M HNO_3 in the ratio of 1:3 v/v (aqua-reagent mixture) at a temperature of 90 ^oC for about 45min to leach out the heavy metals. 1.0 mL of concentrated per chloric acid was added to aid in breaking down the organic compounds. The samples were then allowed to cool and then filtered using Whatman filter paper no.42. The solutions were transferred quantitatively to their corresponding flasks and distilled water added to the required mark. Atomic Absorption Spectrophotometer (AAS; Model AA-6300 SHIMADZU- JAPAN 2014) was calibrated using standard solutions for analysis.

3.8.2 Analysis of heavy metals from water samples

100 mL of the water samples were taken in duplicate and digested using 10.0 mL of analytical grade concentrated 11.36 M HCl and 14 M HNO_3 in the ratio of 1:3 v/v at a temperature of 90 ^oC for 45 min to leach out the heavy metals. 1.0 mL of concentrated per chloric acid was added to aid in breaking down the organic compounds. The samples were then cooled and the contents transferred quantitatively to their corresponding 50 mL volumetric flasks after filtering using Whatman paper no. 42 and distilled water was used to fill up to the mark. This was then ready for analysis in the Atomic Absorption Spectrophotometer (AAS; Model AA-6300 SHIMADZU- JAPAN 2014).

3.9 Sulphur Removal from Soil and Sediment Samples

In order to eliminate sulphur from the sediment and soil extracts, the extracts were transferred into a 250 mL separate beaker each followed by the addition of 1 g of copper powder. Each of the extract was then shaken thoroughly before being filtered, eluted with 20 mL of HPLC hexane and 2 mL of iso-octane added to the sample before concentrating it. The analytes were then transferred to clean auto vials and concentrated to 0.5 mL under a gentle stream of nitrogen.

3.10 Determination of pH of Sediment, Soil and Water Samples

YSI Multi Parameter instrument as illustrated in the appendix VII of the pictorial representation was used to determine the pH of water samples. The meter was calibrated using buffers of pH 7.0 for water samples before use. The pH for soil and sediment samples was done by Kenya Agriculture, Livestock and Research Organization (KALRO), Nairobi and other Physicalchemical parameters were also analysed at the same place.

3.11 Moisture content determination of Sediments and Soil Samples

Moisture content of each sediment and soil samples were determined by heating 5 g of the sample in pre-cleaned and pre-weighed glass vials in an oven 105 ^{o}C for 24 hours. The difference in weight between wet and dry sample was used to calculate the moisture content of their corresponding samples.

3.12 Total Suspended Solids

Water samples were shaken thoroughly to homogenize and 100 mL filtered through dried pre-weighed Whatman filter paper No.1. The residue retained on the filter paper was dried overnight in an oven at 105 ^{o}C to a constant weight. Total Suspended Solids (TSS) was then calculated as the weight of the residue per volume of the sample filtered and the result expressed in mg/L.

$$\text{TSS (mg/L)} = \frac{(A\text{-}B)\ \text{X}\ 1000}{\text{Sample volume (mL)}}$$

Where:

A = weight of filter paper + dried residue (mg) and
B = weight of filter paper (mg)

3.13 Measurement of water temperature, total dissolved solids and electrical conductivity

The temperature of water samples was measured in degree Celsius, using a digital thermometer by directly dipping the thermometer in water and recording it to one decimal place. The instrument was calibrated before use and the variables mentioned above were determined electronically by dipping YSI Multi Parameter instrument in the collected water samples in the field as illustrated in appendix 4.

3.14 Pesticides Analysis

Tables 3.1 shows the limits of detection values and average percentage recovery tests respectively for various OCPs that were investigated in the study. Figure 3.2 shows a sample calibration curve for *a-HCH* as the rest are illustrated in Appendix I.

Table 3.1: Limits of detection values for various OCPs

Pesticides	LOD (ng/L)	LOQ (ng/L)	Accuracy (%)	Linearity
a-HCH	1.1	3.3	94.82±8.31	0.9967
β-HCH	1.60	4.8	87.52±4.09	0.9962
γ-HCH	1.60	4.8	92.06±9.58	0.9991
∂-HCH	-	-	82.54±6.95	-
p,p'-DDT	1.70	5.1	99.89±3.41	0.9909
p,p'-DDE	1.80	5.4	78.35± 5.12	-
p,p'-DDD	1.60	4.8	99.31±2.84	0.9778
a-endosulfan	1.10	2.2	102.58±4.95	0.993
b-endosulfan	1.5	4.5	93.23±7.13	0.9861
Endosulfan sulphate	2.10	6.3	78.25± 6.00	0.9951
Aldrin	3.60	10.8	94.26±5.23	0.9935
Dieldrin	3.10	9.3	114.83±3.33	0.9818
Endrin	2.20	6.6	70.01±4.21	0.9902
Endrin aldehyde	2.20	6.6	77.81±8.63	0.9949
Heptachlor	1.10	3.3	92.08±4.56	0.9991
Heptachlor epoxide	1.10	3.3	98.35±2.45	0.9959
Methoxychlor	1.60	4.8	88.23±6.86	0.9951

Mean ± S.D

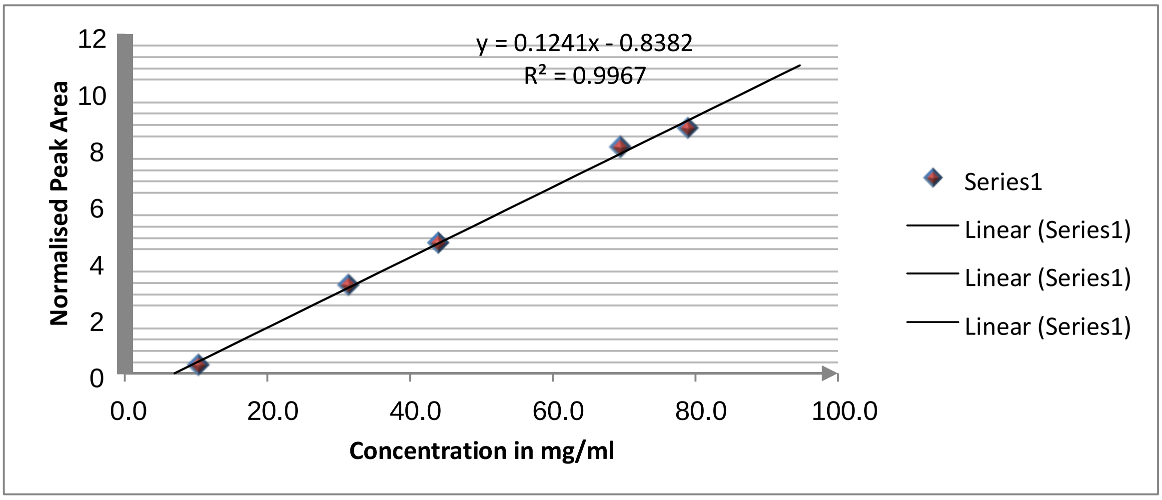


Figure 3.2: Sample calibration curve for a-HCH

3.15 Quality Assurance and Quality Control

Quality control and quality assurance was achieved by spiking each matrix with internal standard (isodrin) just before extraction to check extraction efficiency and recoveries. Extraction and analysis of samples were done in triplicates. Field blanks with anhydrous Na_2SO_4 and distilled water were carried along side during every field trip to track field contamination and then subjected to the entire analytical procedure as the samples.

3.16 GC Analysis and Quantification of the Extract Samples.

Analysis of pesticides in sediment, soil, water and fish extracts was carried out using a gas chromatograph. The extract samples were taken through clean up, derivatization, transfer to vapor phase and concentration stages. The analytes were then sealed into 2 ml, thin-walled vials before being injected onto the head of a chromatographic column and punctured from the outside. The column's temperature was at least 50 ^{o}C above the boiling point of the least volatile component of the sample. This enhanced high level of accuracy and precision of the GC. Data processing was done using Chemstation software.

3.17 Statistical Data Analysis

Data obtained was analysed using Microsoft excel. Correlations between the seasonal variation and the level of pesticide residues detected was done using Statistical Programme for Social Scientists tools (SPSS; VERSION 2.0). Results obtained were then represented by use of text, graphs and statistical tables to show the interrelationships of various variables and parameters and sample type on levels of pesticide residues in the fishponds.

3.18 Correlation analysis

Pearson's correlation coefficient which have numerical values (r) ranging between + 1.00 to – 1.00 was determined by use of SPSS. They represent a linear relationship two sets of data (Situma, 2010). A direct relationship in variables is signified by positive values while negative values denote indirect variation relationship. Linear correlation strength is determined by the value of r, that is, zero values indicate no correlation between sets of data, below 0.5 are considered weak, while those with values of 0.5 and above are considered strong. The significance of the correlations is indicated by the value of p. correlation are significant if $p < 0.005$ and are not significant if $p > 0.005$ (Schober *et al.*, 2018).

3.19 Correlation of pesticides in different seasons per matrix

OCPs in soil during dry season had negative correlation with those in sediments and water for both seasons. However, it had a strong positive correlation of OCPs in soil during wet season and fish during both dry and wet seasons. This is as illustrated in Table A6.1, Appendix VI.

A positive correlation during wet season indicated that at high concentration, there is movement of OCPs from the soil to the sediment and water by run-off and leaching. Fish also get OCP residues from water and soil either through the food chain or by directly feeding on the same. OCPs are also released from the sediments to water by desorption and redistribution.

3.20 Correlation of pesticides across matrices

There were positive correlation coefficient values (p) of OCPs in water at 0.29 and 0.043 in sediments and fish respectively as illustrated in Table A6.1, appendix VI. This positive correlation could have resulted from run-off of pesticide residues from the surrounding agriculturally productive rice farms which may be aggravated by the same agricultural activities in coffee and tea farms upstream. These OCPs deposited are then transferred to the water medium through desorption. In addition, OCPs may also be released from the soil to the sediment since they have high affinity to organic matter which may be released from the soil to the sediment by run-off and leaching. Moreover, due to high volatility of OCPs, their residues may be drifted to the sediment and water by evaporation from the source where they may exist at high concentrations.

3.21 Correlation of heavy metals in different seasons per matrix

There was positive correlation between concentrations of heavy metals in soil during the dry season with those in soil during the wet season with a correlation coefficient of 0.955. This is as illustrated in Table A5.2, Appendix V. This may have been attributed to heavy metals being released from the soil to the sediment and water through discharge and surface run-off during the wet season.

3.22 Correlation of OCPs with heavy metals

OCPs had positive correlation with heavy metals with a positive coefficient correlation of 0.955. This was due to the fact that the heavy metals are discharged from the soil by desorption and re-suspension. They are also transferred to water medium by desorption (Table A5.2, appendix V).

CHAPTER FOUR

4. RESULTS AND DISCUSSIONS

4.1 Results of physical-chemical parameters in water, soil and sediment

4.1.1 Physical-chemical parameters of water

The physical-chemical parameters of water that were investigated included pH, temperature, TDS, electrical conductivity and TSS. Table 4.1 illustrates the composition of physicalchemical parameters in water for both dry and wet seasons.

Table 4.1: Physical-Chemical Parameters

SITE	SEASON	pH	TEMP ^{O}C	TDS (mg/L)	COND(μS/cm)	TSS (mg/L)
BRIDGE	DRY	6.82	22	190.0±0.0	274.0 ± 0.00	260.00 ± 0.00
	WET	7.2	23	90.0± 0.00	190.0± 0.00	46.60 ±0.00
EBENEZER	DRY	8.54	23	73.0 ± 0.00	104.0 ± 0.00	300.00± 0.00
	WET	7.8	22	420.0 ± 0.00	850.0 ± 0.00	75.30±0 0.00
ALAN	DRY	8.51	23	187.0 ± 0.00	333.0 ± 0.00	25.00 ± 0.00
	WET	7.6	22	150.0± 0.00	310.0 ± 0.00	13.40 ±0.00
LAWI	DRY	8.18	25	251.0± 0.00	392.0 ± 0.00	20.00 ±0.00
	WET	7.7	22	260.0 ± 0.00	530.0 ± 0.00	66.30 ±0.00
KASUKU	DRY	7.29	24	1.0 ± 0.00	154.0 ± 0.00	40.00 ± 0.00
	WET	8.6	22	610.0 ± 0.00	1220.0 ±0.00	303.0 ± 0.00

From Table 4.1 it can be deduced that the pH values of the ponds were within the range of 6.82 and 8.6. Most of the sites had pH within the desirable range of 6.5-8.5 (WHO, 2004). This was also consistent with the results of pH values of various water points along river Nyando in Muhoroni recorded by Owuor *et al*. (2019). However, the pH of the site number 5 (Kasuku) registered a pH value of 8.6 during the wet season which is slightly above the desirable range and if not checked may reach a level where it may be intolerable for the aquatic organisms especially fish. This may be attributed to the interplay between respiration during the night by underwater organisms (adding CO_2) and photosynthesis during the day (removing CO_2) (Oyewale, 2006). Therefore, if the pH goes beyond the desirable range, it signifies a situation where there is less production of CO_2 by underwater organisms which is expected to react with H^+ ions to form carbonic acid which is supposed to lower the pH. The temperature range was from 22 ^{o}C to 25 ^{o}C and from 22 ^{o}C to 23 ^{o}C for dry and wet seasons respectively suggesting that the temperature was well regulated in these environments. The TDS ranged between 1.0 mg/L and 251.0 mg/L during the dry season and between 90 mg/L and 610 mg/L during the wet season. High levels of TDS signify high amounts of dissolved ions and inorganic matter in the water ponds which also relate with electrical conductivity. For instance, the TDS of Ebenezer pond recorded 420.0 mg/L during the wet season which was comparatively high in relation to other sites, and also recorded a high electrical conductivity of 850 µS/cm for the same season. In addition, the highest TDS of 610.0 mg/L during wet season was recorded at Kasuku pond and the same site recorded the highest electrical conductivity of 1,220.0 µS/cm during the wet season. Generally, there was higher TDS, electrical conductivity and TSS in the water from fishponds during the wet season than what was recorded during the dry season. However, this was not very conspicuous as other sites registered higher TDS levels in dry season than during wet season. For instance, Bridge and Allan fishponds recorded higher TDS levels of 190.0 mg/L and 187.0 mg/L respectively in dry season than in wet season of 90 mg/L and 150 mg/L in the same order. Therefore, seasonal variation in TDS in these fishponds could not accurately be established probably due to anthropogenic and natural factors (Idoko, 2007 and Wadie, 2010).

TSS ranged between 20.0 mg/L and 260.0 mg/L in Lawi and Bridge ponds respectively during the dry season, while during the wet season, it varied from 13.40 mg/L to 303.0 mg/L in Allan and Kasuku ponds respectively. Generally wet season recorded higher TSS levels than in dry season. This was mostly attributed to surface run-off from nearby rice farms and discharge from Agro-chemicals and other factories like Chemelil and Muhoroni Sugar Factories which are situated along the River Nyando upstream. TSS less than 25 mg/L is considered low and between 25-100 mg/L is considered medium and above 100 mg/L is considered high (FAO, 2016). It therefore follows that Lawi pond registered a low TSS of 20 mg/L during the dry season while during the wet season it registered a medium TSS level of 66.3 mg/L. Allan pond also registered a low TSS level of 13.40 mg/L during the wet season but its TSS value was however medium at 25.0 mg/L during the dry season. This does not agree with higher values of TSS during wet seasons than during dry seasons (FAO, 2016). However, Kasuku pond registered the highest TSS value of 303.0 mg/L during the wet season. This is considered high (FAO, 2016). This may have been attributed to run-off and high discharge from nearby rice farms during the wet season as a result of anthropogenic activities.

4.1.2 Sediment Physical-chemical parameters

Physical-chemical characteristics of both sediments and soils was comprehensively carried out by the Kenya Agricultural & Livestock Research Organization (KALRO) (Table 4.2). The pH of the sediment samples from the fishponds in Ahero ranged from 5.89 to 7.44 for Ebenezer and Allan ponds, respectively. Majority of the sediment samples recorded pH values within the desirable range of 6.5-8.5 for the five sites (WHO, 2004). However, Ebenezer and Allan ponds recorded low pH values of 5.89 (moderately acidic) and 6.22 (slightly acidic), respectively. This may affect the growth and the productivity of the fish as they derive their food from the sediment.

Table 4. 2: Composition of sediments from different sites in Ahero fishpond for dry and wet seasons

s

Me% = percent mill equivalent

Note: Organic carbon content: <0.5% implies low while 0.5-7.5% implies medium/moderate/adequate.

	Sediment &Soil Analytical Data							
Field/Site	Allan		Allan		Bridge		Bridge	
Sample designation	Soil		Sediment		Soil		Sediment	
Lab. No/2018	2831		2832		2833		2834	
Soil depth cm	Sub		Sub		Sub		Sub	
Fertility results	Valu	Class	Value	Class	Value	Class	Value	Class
* Soil pH	6.72	slight acid	7.44	slight alkaline	7.80	Moderatealka	6.50	slight acid
Exch. Acidity me%								
* Total Nitrogen %	0.35	Adequate	0.05	Low	0.15	Low	0.35	Adequate
* Total Org. Carbon %	3.50	Adequate	0.52	Low	1.56	Moderate	3.58	Adequate
Phosphorus ppm	165	High	24	Low	16	Low	30	Adequate
Potassium me%	4.90	High	1.08	adequate	1.12	Adequate	1.77	High
Calcium me%	26.7	High	35.4	High	42.4	High	33.4	High
Magnesium me%	4.57	High	4.89	High	4.37	High	4.46	High
Manganese me%	1.40	Adequate	0.38	adequate	0.42	Adequate	1.02	Adequate
Copper 2pm	1.89	Adequate	1.81	adequate	3.08	Adequate	3.28	Adequate
Iron ppm	12.1	Adequate	14.4	adequate	22.0	Adequate	27.4	Adequate
Zinc ppm	1.6	Low	1.4	Low	62.22	Adequate	3.36	Low
Sodium me%	0.58	Adequate	1.42	adequate	0.76	Adequate	1.34	Adequate
Elect. Cond. mS/cm			1014µ		638µs			

Organic carbon ranged from 0.52 (low) to 3.58 (adequate) at Allan and Bridge ponds, respectively. There were high levels of potassium in most of the sediment samples with a few being low and moderate. Calcium, sodium and magnesium levels were high in all the sediment samples analysed. Table 4.2 shows different sediment properties in Ahero fishponds from KALRO. Further details on the range of essential elements and micronutrients are illustrated in the Table A6.2, Appendix VI.

4.1.3 Soil Physical-chemical parameters

Table 4.3 illustrates composition of different soil properties in some Ahero fishponds as analysed by KALRO. Further details. The soil pH ranged from 6.72 to 8.10 at Allan and Kasuku ponds, respectively.

Table 4.3 composition of soil from different sites in Ahero fishpond for dry and wet seasons

	Soil& soil analytical data							
Field/Site	Kasuku		Kasuku		Lawi		Ebenezer	
Sample designation	Soil		Sediment		Soil		Sediment	
Lab. No/2018	2835		2836		2837		2838	
Soil depth cm	Top		Sub		Top		Sub	
Fertility results	Value	Class	Value	class	Value	Class	Value	Class
* Soil pH	8.10	Moderate	6.22	slight acid	6.91	near neutral	5.89	moderate
Exch. Acidity me%								
* Total Nitrogen %	0.15	Low	0.25	Low	0.15	Low	0.15	Low
* Total Org. Carbon %	1.40	Moderate	2.29	Moderate	1.44	Moderate	1.48	Moderate
Phosphorus ppm	32	Adequate	40	adequate	35	Adequate	85	High
Potassium me%	1.57	High	2.15	High	2.11	High	1.87	High
Calcium me%	37.0	High	33.0	High	26.3	High	20.3	High
Magnesium me%	3.94	High	5.11	High	5.14	High	3.65	High
Manganese me%	0.26	Adequate	1.30	adequate	1.87	Adequate	0.71	Adequate
Copper ppm	2.81	Adequate	4.07	adequate	2.26	Adequate	5.21	Adequate
Iron ppm	14.3	Adequate	107.4	adequate	18.2	Adequate	152.0	Adequate
Zinc ppm	14.1	Adequate	36.1	adequate	10.03	Adequate	8.21	Adequate
Sodium me%	3.87	Adequate	3.11	adequate	1.30	Adequate	0.80	Adequate
Elect. Cond. µS/cm	0.07	Adequate						

Me% = percent mill equivalent

Note: Details of classification of essential elements and micronutrients are illustrated in Tale A6.2; Appendix VI

Total nitrogen was recorded low for all the sites while phosphorus was recorded adequate for most of the sites. Organic carbon was recorded as either moderate or adequate ranging from 1.4 (moderate) and 3.5 (adequate) at Kasuku and Allan ponds respectively. Potassium, calcium and magnesium levels were high in all the sites, while manganese, copper, sodium and iron were adequately present. Electrical conductivity was insignificant in most sites and therefore not recorded. It was however recorded 0.07 µS/cm and 638 µS/cm (high) at Kasuku and Bridge ponds, respectively.

4.2 Nutrients Analysis

4.2.1 Nitrites in Water

Nitrite concentration levels ranged from 0.01 (at Alan) to 0.02 mg/L (at Kasuku) and from 0.02 to 0.16 mg/L for dry and wet seasons, respectively. It was recorded that the concentration of nitrites was higher during wet season than during dry season. This may have been attributed to runoff from the nearby rice farms. Consequently, use of excessive animal manure in fishponds may also result into high levels of nitrite when there is inconsiderable oxidation of nitrite (NO_2) to nitrate (NO_3^-) by the nitrite oxidizing bacteria (Oyewale, 2006). Nitrite concentrations by WHO ranges from 0.005 to 0.50 mg/L (Singh, 2007) and therefore the concentrations recorded were within the allowable range. However, regular monitoring is of great necessity to ensure that it doesn't rise to the level which it may turn toxic to the fish in fishponds which may interfere with their productivity. Table 4.4 and Figure 4.1 show the concentrations of nitrites

from the fishpond sites for dry and wet seasons.

Table 4. 4: Nitrite concentrations for dry and wet seasons in mg/L

SITE	DRY (mg/L)	WET (mg/L)
BRIDGE	0.02 ± 0.01	0.25 ± 0.17
EBENEZER	0.02 ± 0.01	0.02 ± 0.01
ALAN	0.01 ± 0.01	0.08± 0.01
LAWI	0.02 ± 0.01	0.16 ± 0.01
KASUKU	0.02 ± 0.01	0.13 ± 0.02

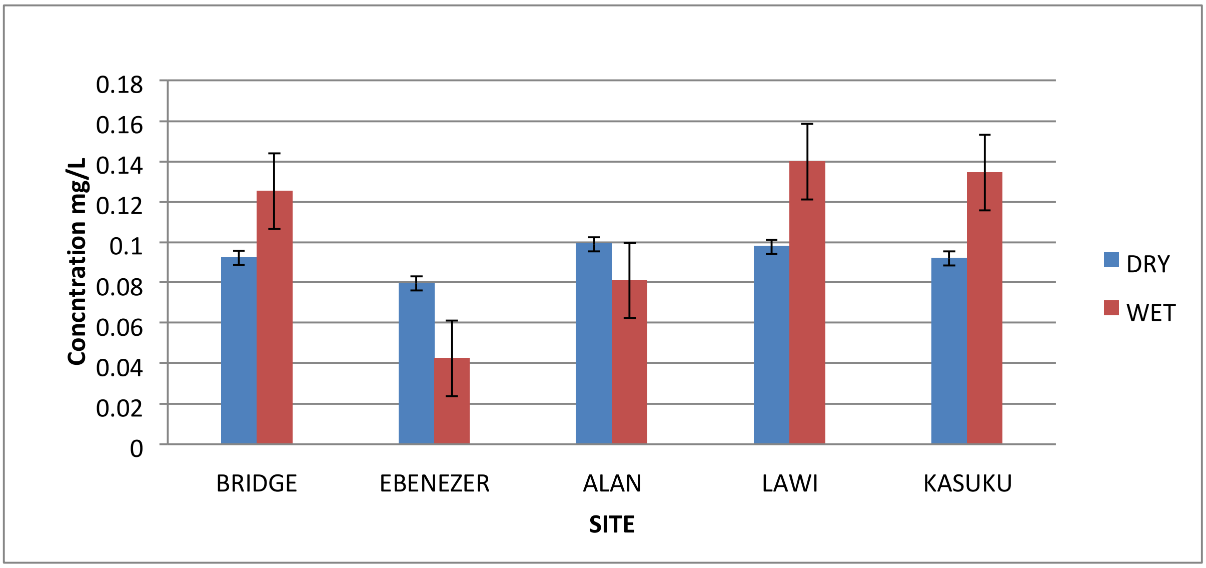


Figure 4.1: Average nitrite concentration in water during both dry and wet seasons

4.2.2 Phosphates in water

The concentrations of phosphates ranged from 0.63 ± 0.00 mg/L (Lawi pond) to 2.10 ± 0.00 mg/L (Kasuku pond) and from 2.70 ± 0.00 mg/L (Bridge) to 8.78 ± 0.00 mg/L(Kasukupond) for dry and wet seasons, respectively. There were notable higher concentrations during wet season than during dry season. This may be attributed to increase in water discharge loading in phosphate nutrients that occur upstream (Kericho, Nandi Highlands). Industrial discharge into River Nyando which is used as irrigation water in rice farms, which eventually reaches fishponds through surface run-off and adsorption, may also contribute to increase in levels of phosphate nutrients during wet season. However, the concentrations recorded were below 10 mg/l, which is the maximum level set by WHO, (2004). Table 4.5 and Figure 4.2 show the average concentration of phosphates during dry and wet seasons respectively.

Table 4. 5: Average concentration of Phosphates during dry and wet seasons in mg/L

SITE	DRY	WET
BRIDGE	0.91 ± 0.05	2.7 ± 1.51
EBENEZER	2.01 ± 0.23	6.41 ± 0.26
ALAN	1.34 ± 0.18	4.89 ± 0.24
LAWI	0.63 ± 0.45	4.23 ± 0.25

KASUKU	2.08 ± 0.12	8.78 ± 0.15

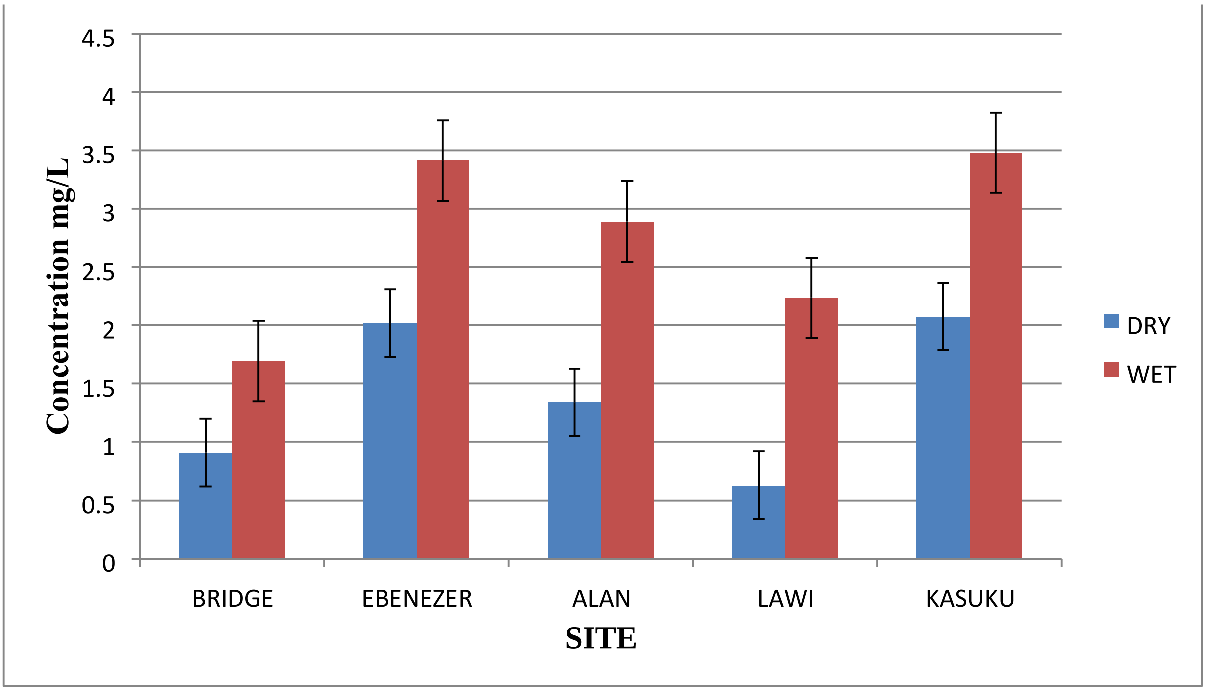


Figure 4.2: Variation in Phosphate concentration during dry and wet seasons

4.2.3 Nitrates in water

The nitrate levels varied from 0.01 ±0.00 mg/L at Alan to 0.06 ±0.00 mg/L at Kasuku pond and from 0.36 ±0.00 mg/L at Bridge to 1.44 ±0.00 mg/L at Kasuku ponds during dry and wet seasons, respectively. It is worth noting that the concentration of nitrates was higher during long rainy season than during short rainy season. The allowable range of nitrates is below 10 mg/l, according to WHO (2004). During wet season, there is considerable discharge from upstream waters which flows from farms where nitrate fertilizers have been used. This may contribute to higher levels of nitrates during wet season. In addition, use of animal manure in fishponds, excessive feeding of fish and use of fertilizers in agriculturally intensive regions easily makes its way into underground aquifers and surface waters, thereby increasing levels of nitrates in fishponds (Domagalski, 2012). Table 4.6 and Figure 4.3 show the average concentration of nitrates during short and long rainy seasons.

Table 4.6: Average nitrate concentrations (mg/L) for dry and wet seasons

SITE	DRY	WET
BRIDGE	0.02 ± 0.01	0.36 ± 0.02

EBENEZER	0.02 ± 0.01	0.53±0.01
ALAN	0.01 ± 0.01	1.24±0.03
LAWI	0.02 ± 0.01	1.24± 0.03
KASUKU	0.06 ±0.01	1.44± 0.02

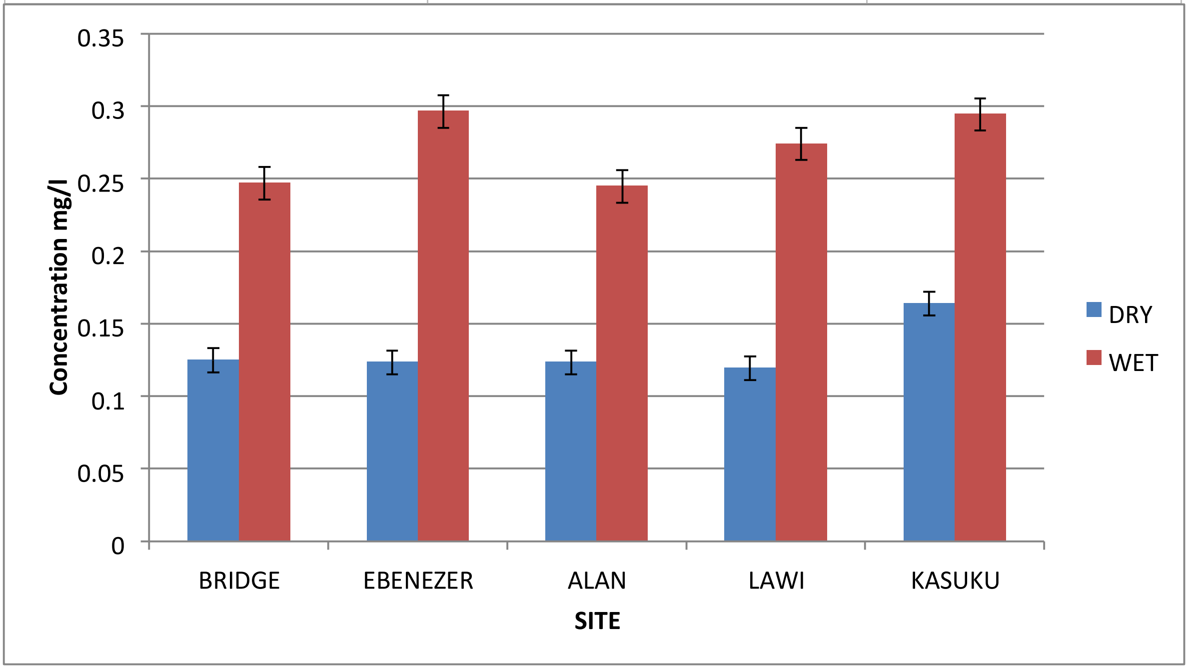


Figure 4.3: Variation in nitrate concentration during both dry and wet seasons

4.3 Heavy Metals Analysis

The concentration levels of cadmium, chromium, lead, zinc and copper were determined in the three matrices: water, soil and sediment, both in short and long rainy seasons from five sites using AAS.

4.3.1 Heavy metal levels in water

The presence of heavy metals in water during the dry season ranged from values below LOD for both Cu and Pb in all the sites to 7.24 ±0.01 mg/L for Cr in Alan pond (Table 4.7). During the wet season, the mean concentration of the heavy metals ranged from values below LOD for Pb in all the sites to 12.01 ±0.01 mg/L for Cr in Kasuku pond. There was notably higher mean concentration of heavy metals during the wet season as compared to the dry season as illustrated in Table 4.7.

Table 4.7: Heavy metals concentration in water during dry and wet seasons (mg/L)

Site		Chromium (Cr)	Cadmium (Cd)	Lead (Pb)	Zinc (Zn)	Copper (Cu)

BRIDGE	Dry	4.05 ±0.01	0.02 ± 0.00	<LOD	0.05 ± 0.01	<LOD
	Wet	9.73 ± 0.30	<LOD	<LOD	0.22 ±0.2	0.02 ±0.01
EBENEZER	Dry	4.42 ± 0.01	<LOD	<LOD	0.01 ±0.01	<LOD
	Wet	9.61 ± 0.50	0.01 ±0.00	<LOD	0.08 ±0.03	0.01 ±0.00
ALAN	Dry	7.24 ±0.01	0.06 ±0.01	<LOD	0.02 ±0.00	<LOD
	Wet	9.37 ± 0.80	0.02 ±0.00	<LOD	0.03 ±0.00	0.01 ±0.00
LAWI	Dry	6.54 ±0.01	0.09 ±0.01	<LOD	<LOD	<LOD
	Wet	11.41 ± 1.00	<LOD	<LOD	0.07 ±0.00	<LOD
KASUKU	Dry	5.41 ±0.01	<LOD	<LOD	<LOD	<LOD
	Wet	12.01 ± 0.01	0.30 ±0.00	<LOD	0.08 ±0.04	<LOD

Key: below limits of detection (<LOD)

4.3.1.1 Chromium

As observed from Table 4.7, mean concentration of Cr in water samples ranged from 4.05 ±0.01 mg/L (Bridge pond) to 7.24 ±0.01 mg/L (Alan pond) during dry season and from 9.37 ±0.8 mg/L (Alan pond) to 12.01 ±0.01 mg/L (Kasuku pond) during wet season. In *Ebenezer* fishpond, chromium levels ranged from 4.42 ± 0.01 to 9.61±0.5 mg/L. Chromium concentration in *Alan* fishpond ranged from 7.24 ±0.01 to 9.37 ±0.8 mg/L while in Lawi fishpond, chromium levels ranged from 6.54 ±0.01 to 11.41 ±1.00 mg/L. Finally, in *Kasuku* fishpond, the levels of chromium ranged from 5.41 ±0.01 to 12.01 ±0.01 mg/L. Chromium presence has been recorded in the previous studies around the Gulf of Lake Victoria as follows: Lake water; 0.23±0.04 mg/L to 0.79±0.02 mg/L and inflowing rivers into the lake recorded at below LOD to 50 mg/L (Mwamburi, 2016). Anthropogenic activities like burning of bushes, wastes from metallic industries, sludge from waste water, smoking and natural processes such as drifting of volcanic dust by air are responsible for chromium deposits in the environment (Tenai *et al*., 2016).

4.3.1.2 Cadmium

The highest concentration of cadmium was recorded in *Kasuku* fishpond at 0.30 ±0.00 mg/L for wet season, while for the dry season, it recorded values below LOD. Generally higher concentration was recorded during dry season. It was notable that the sites recorded low levels of Cd which may not be an environmental concern at the time. However, low levels may bioaccumulate over a period of time, and this may pose a serious threat to environment and human health. According to a research study in Nairobi, Faridah (2013), found levels of heavy metals including cadmium among factory workers' blood samples in production sections such as battery recycling, battery manufacturing, steel and scrap welding, paint manufacturing and pharmaceutical plants and they were found to be suffering from cardiovascular and respiratory diseases which were associated with their exposure on cadmium and other related heavy metals. Another research study (Tenai *et al*., 2016) in four Eastern Rift Valley Lakes (Oloidien, Crater, Elementaita and Nakuru), found out that there were low concentrations of chromium and cadmium in soil sediments from the four sites. The study also reported presence of cadmium in Lesser Flamingo blood tissues sampled, which was however found to be below toxicological levels that are reported harmful by the US Environmental Protection Agency (Tenai *et al*., 2016).

4.3.1.3 Lead

Lead concentration levels were not detected in all the sites during both dry and wet seasons. In one study on water quality in Nyando River in Muhoroni, Kenya, the concentration of lead was found to be below LOD (Owuor *et al*., 2019). In another study carried out to determine the levels of certain heavy metals, recorded mean concentration of lead at 12.00 ±14.24 mg/L and 14.24 ± 8.86 mg/L in Lakes Nakuru and Elementaita, respectively (Tenai *et al*., 2016). In the same study, there were no detectable levels of lead from Lakes Oloidien and Crater. Since Pb is not broken down, there is possibility of binding and eventual accumulation to levels that may turn out to be toxic to both the environment and human health and hence regular monitoring of traces of Pb in the environment and taking appropriate measures is very necessary (Tenai *et al*., 2016).

4.3.1.4 Copper

Copper levels registered during dry season were below LOD. Considerable low levels were recorded for wet season with the highest recorded at 0.02±0.01 mg/L from *Bridge* fishpond. In another study on water quality in Nyando River in Muhoroni, Kenya, there was low concentration of copper (Owuor *et al*., 2019). Increase in the levels of copper during wet season may have been attributed to agricultural activities that included use of insecticides, fungicides and fertilizers in the nearby farms (Solomon, 2007).

4.3.1.5 Zinc

Zinc average levels ranged from values below LOD at both *Lawi* and *Kasuku* fishponds to 0.01±0.01mg/L at *Ebenezer* fishpond for dry season and from 0.026±0.00 to 0.22±0.20 mg/L at *Alan* and Bridge fishponds respectively for wet season. This was consistent with another research study carried out along River Nyando, Muhoroni, Kenya on water quality that also recorded low levels of zinc (Owuor *et al*., 2019). Notably higher levels of zinc were recorded during wet season than during the dry season. This may have been attributed to discharge from both nearby rice farms and farms upstream due to fertilizers used and other anthropogenic activities (Owuor *et al*., 2019).

4.3.2 Average heavy metals concentrations in sediment

Heavy metals concentration in sediment was below LOD for Pb from the four sites, with one site *Kasuku* fishpond recording 13.73 ±0.00 mg/kg during dry season. Chromium in sediment ranged from 5.65 ±1.00 to 8.93 ±0.00 mg/kg while cadmium ranged from below LOD from the four sites to 0.02 ±0.02 mg/kg. For zinc the levels ranged from below LOD to 6.06 ±0.01 mg/kg. Copper levels ranged from below LOD to 0.47 ±0.01 mg/kg during dry season. Table 4.8 show the average concentrations of selected heavy metals in sediments during the dry and wet seasons.

Table 4.8: Average concentration levels of heavy metals in sediment during dry and wet seasons (mg/kg)

Site		Chromium (Cr)	Cadmium (Cd)	Lead (Pb)	Zinc (Zn)	Copper (Cu)
Bridge	Dry	5.65 ±1.00	0.02 ±0.00	<LOD	4.79 ±0.3	0.36 ±0.08
	Wet	17.65 ±0.3	0.02 ±0.00	0.01 ±0.00	3.13±0.8	0.04±0.04
Ebenezer	Dry	5.77 ±0.2	<LOD	<LOD	1.79±0.01	<LOD
	Wet	19.10±0.00	<LOD	<LOD	1.01±0.02	0.08±0.00
Alan	Dry	6.49 ±0.2	<LOD	<LOD	1.96 ±0.02	0.45 ±0.1
	Wet	19.65 ±0.8	<LOD	0.64 ±0.04	2.00 ±0.3	0.97 ±0.01
Lawi	Dry	7.33 ±0.00	<LOD	<LOD	2.23±0.8	0.38 ±0.2
	Wet	21.10±2.00	0.01 ±0.00	0.85 ±0.1	2.40 ±0.6	1.01 ±0.06
Kasuku	Dry	8.53 ±0.00	<LOD	13.73 ±0.00	2.37±0.4	0.47 ±0.08
	Wet	24.53 ±0.6	<LOD	0.26 ± 0.20	2.26 ±0.4	0.72 ±0.2

Key: below limits of detection (LOD)

During the wet season, the mean concentration of the heavy metals varied from 17.65 ±0.3 to 24.53 ±0.6 mg/kg for chromium in Kasusku pond. The concentration of cadmium ranged from values below LOD to 0.02 ±0.00 mg/kg while that of lead ranged from values below LOD to

0.64 ±0.04 mg/kg. Zinc levels ranged from 1.01 ±0.02 mg/kg to 3.13 ±0.8 mg/kg and that of copper ranged from 0.04 ±0.04 to 1.01 ±0.06 mg/kg.

4.3.2.1 Cadmium

The concentration of Cd ranged from below LOD to 0.17 ±0.01 mg/kg for dry season and from below LOD to 0.02 ±0.01 mg/kg for wet season. Considerably there were higher levels of Cd in wet season than in dry season. This may have been attributed to discharge from the river overflow, run-off and partly due to leaching (ECDG, 2012).

4.3.2.2 Chromium

The concentration of chromium ranged from 5.77 ±0.2 to 8.53 ±0.00 mg/kg and from17.65 ±0.3 to 24.53±0.6 mg/kg for dry and wet seasons, respectively. Chromium levels were considerably higher in wet season than in dry season. A study by Oyewale (2006) carried out to investigate the concentration levels of some selected heavy metals including Cr along the basin of Lake Kainji in Nigeria recorded the levels of Cr in sediment at 27 mg/kg. It was noted that the average concentration of Cr was medium (Oyewale, 2006). Also notable was that there were the highest levels of Cr in sediment among the three compartments: water, soil and sediment. This is significant as sediment acts as a sink for most of pesticide and heavy metal pollutants (Ozortuk *et al*., 2009). If fish and other aquatic organisms derive their food from the sediment deposits, then the status of heavy metals (Cr included) in their systems may pose a health risk to both the aquatic organisms and human beings who feed on fish (Samir, 2008).

4.3.2.3 Lead

Concentration levels of lead in sediment ranged from values below LOD (for four sites) to 13.73 ±0.00 mg/kg in Kasuku pond for dry season and from values below LOD to 0.85 ±0.1 mg/kg for wet season as illustrated in Tables A1.2 in appendix I. Ahero being situated on the busy Nairobi-Kisumu high-way, it may be the main source of lead residues being emitted by vehicles in the form of lead fumes, settling in soil and swept into the fishponds through discharge and runoff. Even though the Pb levels may have been low at the time of study, it has potential for great danger as it is highly toxic even at low levels. There is great potential for the level increasing as lead deposited bio-accumulate in the aquatic organisms and this is likely to pose great safety risk to aquatic environment and human health. There was considerable increase in the levels of lead from the dry season to the wet season. This was consistent with other recent studies done on lead and other heavy metals by Kabiro (2015). The study recorded average concentration levels of lead in sediment at 0.035± 0.02 and 0.068 ±0.03 mg/kg for dry and wet seasons respectively (Kabiro, 2015). This may have been attributed to high discharge and runoff during water overflow, industrial discharge and water from pipes during wet season (Tenai *et al*., 2016). However, in another study on effects of heavy metals pollution on omega3-Polyunsaturated fatty acid level in Tilapia from Winam Gulf of Lake Victoria, the presence of lead in sediment samples was found to be quiet high. This was attributed to the unsolved Pb in seawater being adsorbed by sediment (Muinde *et al*., 2013).

4.3.2.4 Copper

Copper concentration levels ranged from values below LOD to 0.47 ±0.08 mg/kg and from 0.04 ±0.04 to 1.01 ±0.06 mg/kg for dry and wet seasons respectively. The levels of copper was highest at 1.01 ±0.06 mg/kg in *Lawi* fishpond with notable higher levels recorded during the wet season than during dry season, being consistent with other selected analysed heavy metals in this study. This variation in levels of copper during wet season is attributed to agricultural activities that include use of insecticides, fungicides and fertilizers in the nearby farms that discharge into sediment fishpond through runoff, percolation or leeching (Solomon, 2007).

4.3.2.5 Zinc

Zinc levels in sediment ranged from 1.79 ±0.01 mg/kg to 4.79 ±0.3 mg/kg and from 1.01 ±0.02 to 3.13 ±0.8 mg/kg for dry and wet seasons respectively. This is as illustrated in Table A1.2 in appendix I. The highest levels were recorded at the *Bridge* fishpond for both dry and wet seasons. Just like other heavy metals analysis, there was general increase in the mean concentrations in wet season as compared to dry season.

4.4 Average heavy metals concentration in soil

During the dry and wet seasons, the average concentration of some selected heavy metals in soil samples, Cr ranged from 2.79 ±0.7 mg/kg in Ebenezer fishpond during the dry season to 15.09 ±0.7 mg/kg in Lawi fishpond during the wet season. Cd recorded values that ranged from below LOD in Kasuku fishpond during the wet season to 0.11 ±0.01mg/kg in Ebenezer fishpond during the dry season. Pb recorded values that ranged from below LOD in Alan, Lawi and Kasuku fishponds during the dry season to 6.38 ±0.00 mg/kg in Ebenezer during the dry season. Zn mean concentration ranged from 2.00 ±0.1 mg/kg in Alan fishpond during the dry season to 6.06 ±0.2 mg/kg in Bridge fishpond during the dry season. The mean concentration for Cu ranged from values below LOD in Ebenezer fishpond during the dry season to1.36 ±0.1 mg/kg in Bridge fishpond during the dry season. Higher mean concentration of heavy metals under investigation was recorded during dry seasons compared to wet seasons. Table 4.9 shows concentrations of some selected heavy metals in soil samples from five sites adjacent to the fishponds in Ahero irrigation scheme during both dry and wet seasons.

Table 4.9: Average concentration of heavy metals in soil during dry and wet seasons (mg/kg)

Metals Site		Chromium (Cr)	Cadmium (Cd)	Lead (Pb)	Zinc (Zn)	Copper (Cu)
Bridge	Dry	3.85 ±0.2	0.17 ±0.01	2.30±0.00	6.06 ±0.2	1.36±0.1
	Wet	10.33 ±0.2	0.01±0.00	0.58±0.04	4.34±0.06	1.20±0.08
Ebenezer	Dry	2.79 ±0.7	0.11 ±0.01	6.38±0.00	2.24±0.00	<LOD
	Wet	12.61 ±0.00	0.01 ±0.00	0.52±0.02	2.70 ± 0.2	0.35±0.03
Alan	Dry	5.89 ±0.3	0.09 ±0.01	<LOD	2.00 ±0.1	0.41±0.07
	Wet	13.45 ±0.2	0.01±0.00	0.37±0.3	3.21 ± 0.4	1.12±0.00
Lawi	Dry	5.29 ±0.2	0.03 ±0.01	<LOD	2.49 ±0.3	0.60 ±0.4
	Wet	15.09 ±0.7	0.01 ±0.00	0.41±0.02	3.24±0.06	1.18±0.04
Kasuku	Dry	6.01 ±0.8	0.02 ±0.01	<LOD	3.54±0.06	0.54 ±0.2
	Wet	15.01 ±0.3	<LOD	0.30±0.00	2.88±0.02	1.01±0.03

Key: < below limits of detection (LOD)

4.4.1 Chromium

As illustrated in Tables 4.9, the highest level of Cr in soil was recorded in Kasuku fishpond at 6.01 ±0.8 mg/kg and in Lawi fishpond at 15.09±0.7 mg/kg during dry and wet seasons respectively. The lowest average levels were recorded in Ebenezer fishpond at 2.79 ±0.7 mg/kg and from the Bridge fishpond at 10.33 ±0.2 mg/kg during short and long rainy seasons consecutively. There were recorded higher average levels of Cr during long rainy season than that recorded during short rainy season. This was consistent with the analysis of other heavy metals in the other two matrices: water and sediment. In another study on the presence of chromium in the Gulf of Lake Victoria, it's concentration in soil was from 6.7±1.1 to 11.8±2.0 mg/kg while other African top soils in the same study ranged from 1.0 to 6230 mg/kg and subsoils ranged from1.0 to 2140 mg/kg (Mwamburi, 2016). The study found the levels of chromium in the soil samples to be above the limit given by WHO of 0.1 ppm (0.1mg/kg) (Table A6.1, Appendix VI).The sites with high levels of Cr as has been recorded in other heavy metals analysis were attributed to anthropogenic activities due to increasing population in the urban towns (Mwamburi, 2016).

4.4.2 Cadmium

Cadmium concentration was recorded highest in Bridge at 0.17±0.01 mg/kg and 0.01±0.00 mg/kg for dry and wet seasons respectively. The lowest levels were recorded in Kasuku pond at 0.02 ±0.01 mg/kg and values below LOD for dry and wet seasons, respectively. There were notable lower levels of Cd during wet season than in dry season. This was not consistent with other heavy metals analysis whose levels were higher during wet season than during dry season. Rather than anthropogenic activities the source of Cd may have been due to geological activities causing its residues to discharge into the fishpond sites (Kabiro, 2015). Comparing the mean concentration of Cd with the limits recommended by the WHO, (2004) in soils for agriculture at 0.003 mg/kg, the study found the concentration of Cd to be higher.

4.4.3 Lead

The levels of lead ranged from values below LOD (for Kasuku, Lawi and Alan) ponds to 6.38 ±0.00 mg/kg in Ebenezer fishpond and from 0.30±0.00 to 0.58±0.04 mg/kg during dry and wet seasons respectively. This is as illustrated in Table A1.3 in appendix I. Ahero being situated on the busy Nairobi-Kisumu high-way, it may be the main source of lead residues being emitted by passing-by vehicles in the form of lead fumes, settling in soil and swept into the fishponds through discharge and run-offs. There were considerable higher levels of lead recorded during the wet or rainy season as compared to what was recorded during the dry or short rainy season. This may have been attributed to deposits of lead residues drifted by airborne dust from point source, or naturally occurring lead in soil and use of lead-based paint, and lead-acid accumulators (Kabiro, 2015, Ondiere, 2016 and *Nunda et al.*, 2018). In comparison to the recommended limits of Pb in soil at 0.1 mg/kg (WHO, 2004), Ebenezer fish pond was found to be having higher concentration of lead metal at 6.38 ±0.00 mg/kg and this poses an environmental concern. This may have been attributed to discharge of lead deposits from heavy trucks passing along the nearby busy Nairobi-Kisumu highway.

4.4.4 Zinc

Zinc levels ranged from 2.00 ±0.1 to 6.06 ±0.20 mg/kg and from 2.70 ±0.2 to 4.34 ±0.06 mg/kg for dry and wet seasons respectively. The highest levels were recorded in *Bridge* for both the dry and wet seasons as illustrated in Table A1.3 in appendix I. There was general increase in zinc levels in wet season as compared to dry season. This may have been attributed to discharge from both nearby rice farms and farms upstream due to fertilizers used in the farms.

4.4.5 Copper

Copper mean concentration ranged from values below LOD to 1.36 ±0.1 mg/kg and from 0.35 ±0.03 to 1.20 ±0.08 mg/kg for dry and wet seasons respectively. The highest levels were recorded in *Bridge* pond both for the dry and wet seasons. Notable higher levels of copper were recorded during the wet season than during dry season as illustrated in Tables A1.3 in appendix 1. This was attributed to use of fungicides and insecticides made from copper thereby discharging during overflows in wet seasons from the nearby rice farms and upstream. In comparison to other recent studies, there were higher levels of copper recorded in Lake Elementeita basin according to a study carried out on heavy metals analysis by Ondiere, (2016). The copper levels ranged from 2.96 ±0.3 to 865.83 ± 5.76 mg/kg for Mbaruk River, Mbaruk Lake recorded levels from 34.26 ± 17.26 to 454.76 ±34.58 mg/kg while Kikopey Spring registered copper levels ranging from 9.21 ± 2.08 to 518 ± 23.02 mg/kg. These levels of copper were far above the WHO standard limits of 100 mg/kg in soil (WHO, 2004). Consequently, at these levels, the life of aquatic organisms become intolerable due to toxicity of copper. This was due to release from the nearby industries using copper in their daily operations and release from agricultural activities (Ondiere, 2016 and Tenai *et al*., 2016). This study finds mean concentration of copper to be low as compared to other studies. However, the low levels have the potential of bioaccumulating in soil to toxic levels to the aquatic environment if not checked.

4.5 Organochlorine pesticide residue levels

A total of 17 organochlorine pesticides were analysed for residue levels in water, soil, sediment and fish samples. The pesticides included aldrin, dieldrin, heptachlor, heptachlor epoxide, endosulphan I, endoslphan II, endosulphan sulphate, endrin, endrin aldehyde, *p, p'*-DDT, *p, p'*DDD, methoxychlor, alpha-HCH, beta-HCH, gamma-HCH, delta-HCH.

4.5.1 Organochlorine pesticide mean concentrations in water samples

The average organochlorine pesticide concentrations in water samples from different sites during dry season ranged from values below LOD to 11.95±2.50 µg/L, with dieldrin recording the highest concentration levels at Ebenezer pond. This was followed by β-HCH (9.76 ±1.60 µg/L, Alan pond), methoxychlor (6.88 ±0.7 µg/L, Ebenezer pond), endosulfan sulfate (5.75±0.1 µg/L , Kasuku pond), heptachlor epoxide (4.63 ±0.02 µg/L , Lawi pond), αendosulfan (3.87 ±0.02 µg/L , Alan pond), α-HCH (2.95 ±0.05 µg/L, Bridge pond), aldrin (2.73 ±0.6 µg/L, Kasuku pond), *P, p'*-DDT (2.62 ±0.1µg/L, Kasuku pond), β-Endosulan (1.83 ±0.05 µg/L , Ebenezer pond), heptachlor-epoxide (1.75 ±0.01 µg/L, Bridge pond). The rest of the OCPs mean concentrations ranged between 0.00 and 1.00. DDE was not detected in all the sites and across all the matrices during the dry season. Possibly this was due to the fact that its parent compound, DDT had not degraded to release it to the environment (Osoro *et al*., 2016). In addition, higher levels of endosulphan sulphate over alpha and beta endosulphan suggest contamination from past use of the compound. This was also true in the case of dieldrin over aldrin, heptachlor epoxide over heptachlor (Abong'o *et al.*, 2015). OCPs mean concentrations during the dry season (December-February) are as shown in Figure 4.4 and further illustrated in Table A2.1 in Appendix II.

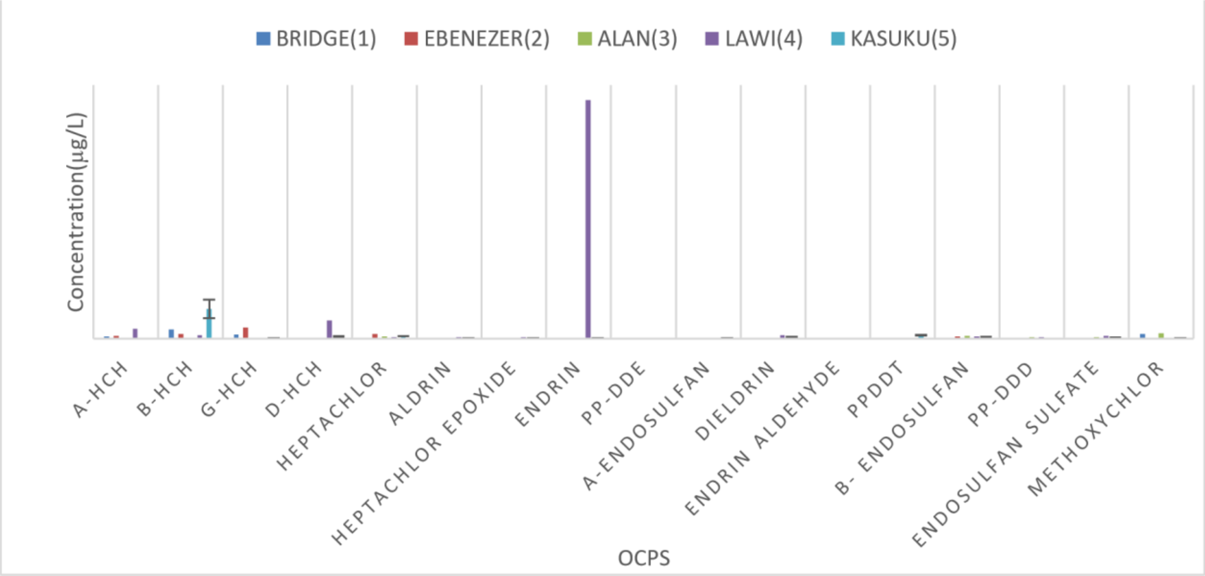


Figure 4.4: Average concentration of OCPs in water samples during dry season

The average levels of OCPs in water samples during the wet season (March- May) ranged from values below LOD to 13.16±0.00 µg/L. The highest level was recorded in endrin at Lawi pond. Methoxychlor was detected at 4.59 ±1.24 µg/L in Ebenezer fishpond. The study shows that endrin and methoxychlor were widely used compared to other OCPs around Nyando River basin and hence their high presence in the water fishponds. According to another study in

Nyando River catchment by Abong'o *et al*. (2015), methoxychlor pesticide was widely used in the area. The presence of DDT which has long-term chronic toxicity effects to the environment and human health and its use has been banned (Annex B of the Stockholm Convention, 2002) but restricted to use in malaria causing vector control by the Kenyan government (Abong'o *et al*., 2015), was recorded at 3.50 ±0.05 µg/L in Allan pond during the wet season (March-May). Compared to the dry season (December-February), DDT in water samples was recorded at 2.62±0.1 µg/L in Kasuku pond. However, in another study around the Lake Victoria basin, DDT recorded the highest at 0.830 ±0.02 µg/L in Mbita Iceplant during the short rainy season, (September) (Osoro *et al*., 2016). This study found the mean concentration of DDT high and this exceeds the DDT minimum acceptable limit in surface waters at 1.0 µg/L (WHO, 2004). There was a possibility of past application of DDT to the surrounding environment against mosquitoes causing malaria (Abong'o *et al*., 2015). Figure 4.5 and table A3.2 in appendix III show OCPs residue levels found in water samples from the five sites during the wet season. The high levels of DDT could be attributed to widespread application in the past against agricultural insect pests and in public health vector control of malaria. The *p,p'*-DDE levels were below LOD across all the matrices. The presence of HCHs could be attributed to the use *et al.*, 2015).

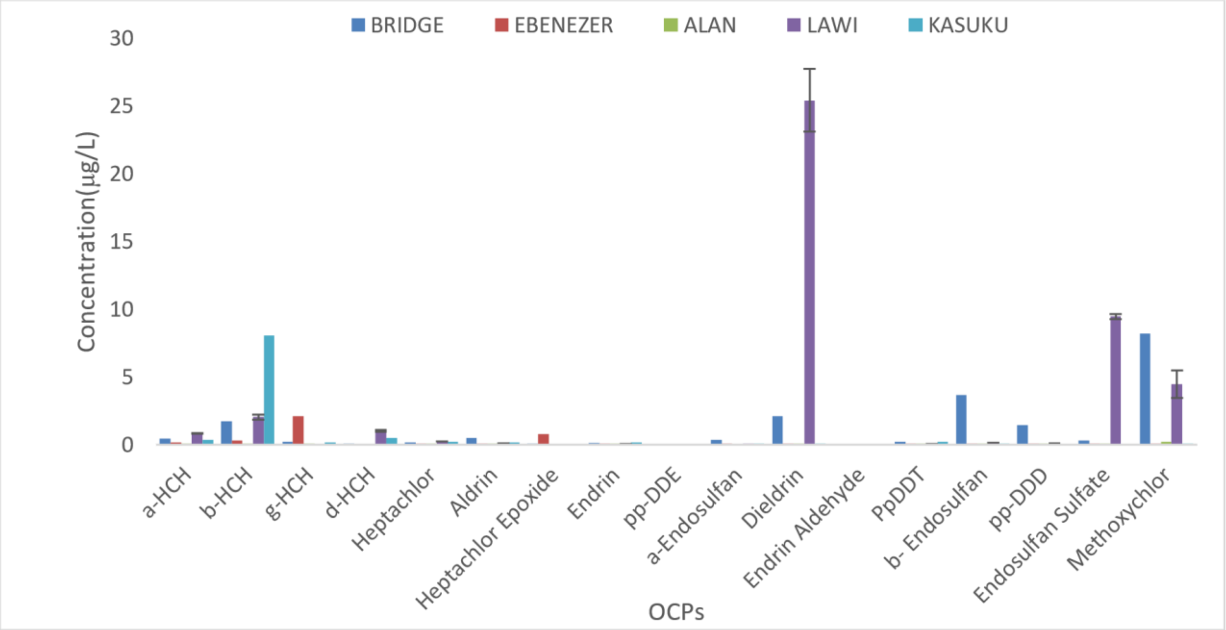


Figure 4.5: Average OCPs residue levels in water samples during wet season

of technical lindane which contains alpha, beta, gamma and delta HCH isomers. HCH was widely applied in Kenya for seed dressing against soil-based insecticides. However due to high persistence of the compounds in the environment, the residue levels are still detectable in water, soil and sediments. In addition, beta HCH is known to be more persistent in the environment hence accounting for its higher concentrations compared to the others HCH isomers (Abong'o

4.5.2 Average concentration of OCPs residues in sediment samples

The average concentration levels of OCPs in sediment samples during the dry season ranged from values below LOD to 25.40 ±2.31 µg/kg (Figure 4.6).

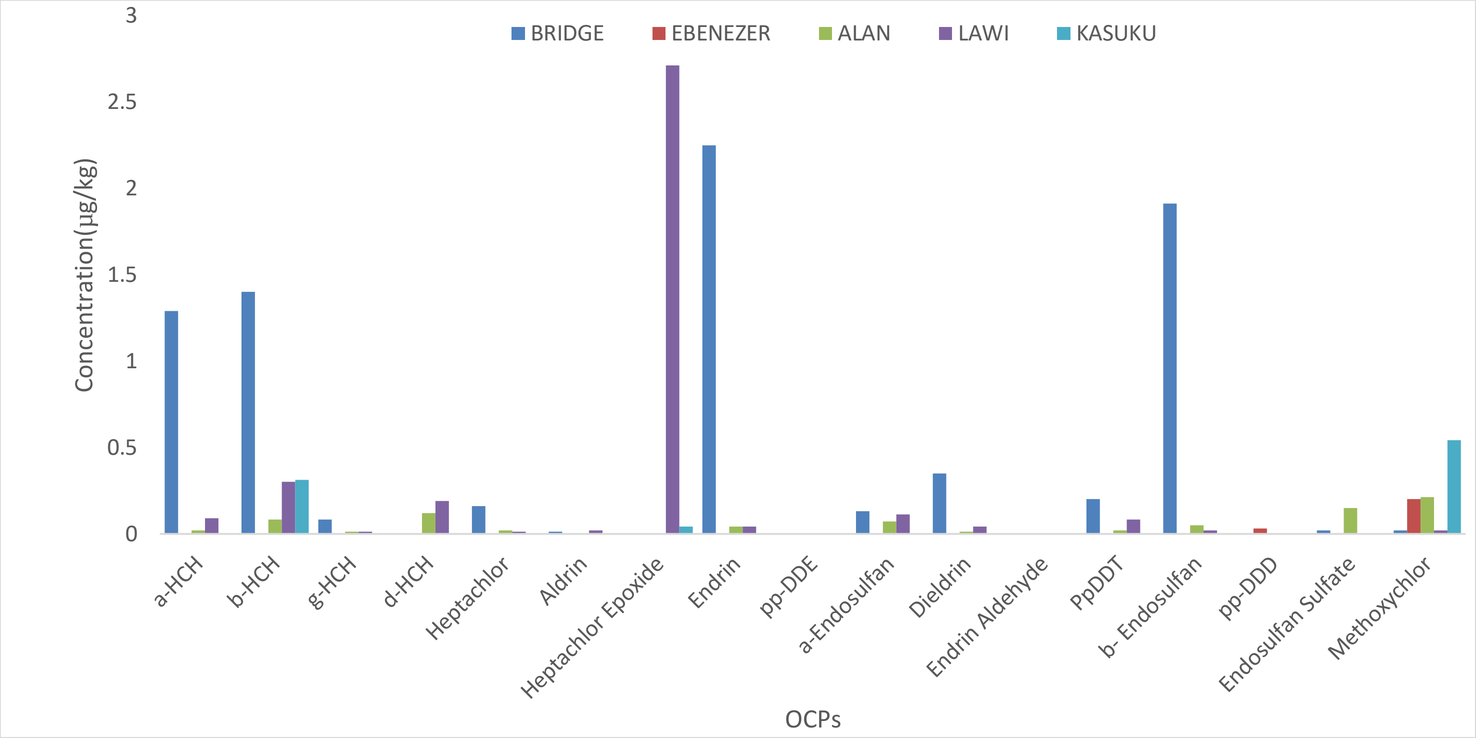


Figure 4.6: Average OCPs residue levels in sediment samples during dry season

The highest level was recorded in dieldrin at Lawi pond. Table A3.3 in the appendix III and Figure 4.6 illustrate the residue levels of OCPs in sediment samples from the five sites during the dry season. The highest OCPs recorded in sediments were endosulphan sulphate, betaHCH, dieldrin, beta endosulphan and methoxychlor. The high presence of endosulphan sulphate compared to alpha and beta endosulphan could be attributed to environmental degradation, since the later break down via epoxidation to endosulphan sulphate. Similarly high levels of dieldrin compared to aldrin could be attributed to environmental degradation of aldrin to dieldrin, or direct application of dieldrin from the past use cycles (Osoro *et al.*, 2016). The use of most of these POPs, particularly the use of DDT is restricted for the control of malaria spreading vectors (Abong'o *et al.*, 2015). Their presence in the environment could be attributed to environmental persistence, especially in cases where metabolites are detected at higher concentrations than the parent compounds (Abong'o *et al.*, 2015). According to Abong'o *et al.*, (2015), OCPs like aldrin, endrin and heptachlor were not detected in the soil samples along the Nyando River catchment area. However, this study has detected the presence of the same OCPs in small proportions across all the matrices.

The average OCPs concentrations for sediment samples during the wet season ranged from below LOD to 2.71 ±0.00 µg/kg. The highest level was recorded for Heptachlor epoxide pesticide at Lawi pond. There were generally higher levels of OCPs recorded in sediment samples compared to other matrices. In addition, there were higher levels of OCPs residues in sediments during wet season than during the dry season. This was attributed to adsorption and percolation from the water medium to the sediment (Ndunda *et al.*, 2018).

In another study on investigations of organochlorine pesticide residues in sediment and water from Nairobi River, Kenya on sediments registered α-HCH, β-HCH, γ-HCH, heptachlor epoxide and *ρ,ρ'*-DDD were detected in all the samples whereas α-HCH, γ-HCH, δ-HCH, heptachlor epoxide, endosulfan I and endrin in all water samples (*Ndunda et al.*, 2018). This was attributed to their persistence in the environment, unlawful use, leaching, or run-offs from contaminated soils and rocks (*Nunda et al.*, 2018).

The OCPs residue levels from five sites are as illustrated in Figure 4.7 and in Table A1.4 in appendix I. The highest OCPs detected in the sediments were dieldrin (11.95±2.5 µg/kg in Ebenezer pond) and b-HCH (9.76 ±1.60 µg/kg in Alan pond). The concentrations measured in the wet seasons were significantly higher than the concentrations measured in the dry season.

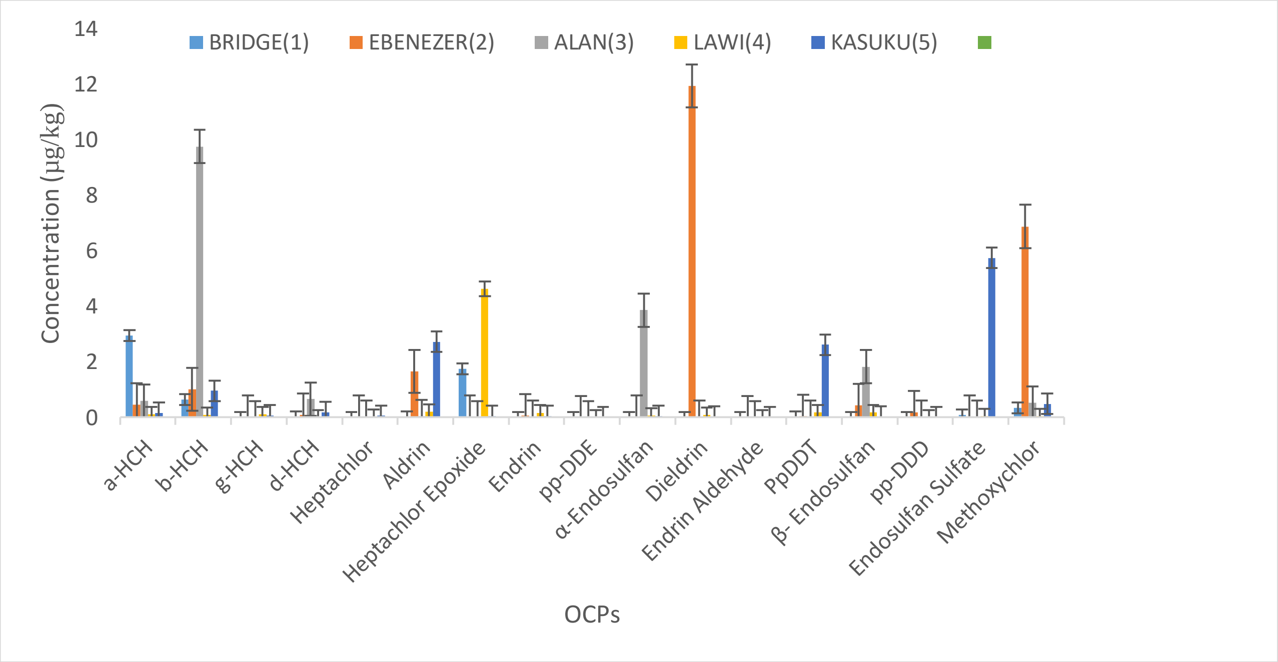


*Figure 4.7: Average OCPs levels in sediment samples during wet seaso*n

4.5.3 Average OCPs levels in soil samples

The average OCPs levels in soil samples during the dry season (December to February) ranged from values below LOD to 8.05 ±0.03 µg/kg. The highest level was recorded in β-HCH in Kasuku pond. In another study in Rusinga Island, α-HCH was found to be having the highest concentration at Mbita Iceland, around Lake Victoria basin, at the level of 32.91±3.84 µg/kg (Osoro *et al.*, 2016). This showed that the isomers of HCH are actively in use by farmers around the basin of Lake Victoria, with Nyando basin also actively involved as evidenced by a research study by Abong'o *et al.* (2015).

Figure 4.8 and Table A3.5 in appendix III show the residue levels of OCPs in soil samples from the five sites during dry season. The highest OCP residue levels in soil were recorded from Kasuku followed by Lawi, while the rest of the sites recorded concentrations below 1.0 µg/kg.The dominant OCPs measured in the soil samples were beta-HCH, dieldrin and endosulphan sulphate. Higher levels of endosulphan sulphate over endosulphan, and dieldrin over aldrin suggested that majority of the OCPs detected in the soil samples (between December and February) could be attributed to past applications of the compounds. Hence the metabolites levels were higher than the parent compounds (Abong'o *et al.*, 2015). Due to the tropical climate around the Nyando basin and its environs, the OCPs detected undergo relatively higher dissipation rate compared to other cooler regions like temperate countries. This therefore informs higher concentration of metabolite OCP residues compared to their parent compounds (Abong'o *et al.*, 2015).

The *p,p'*-DDT was relatively high compared to *p,p'*-DDD and *p,p'*-DDE. However, the presence of relatively high concentration of *p, p'*-DDD which is also a metabolite of *p, p'*-DDT could suggest past use of p, p'-DDT rather than any new applications of *p, p'*-DDT. The other possible cause of higher *p, p'*-DDT than the metabolites can be attributed to illegal use of DDT other than in the areas its use is restricted to (Abong'o *et al.*, 2015).

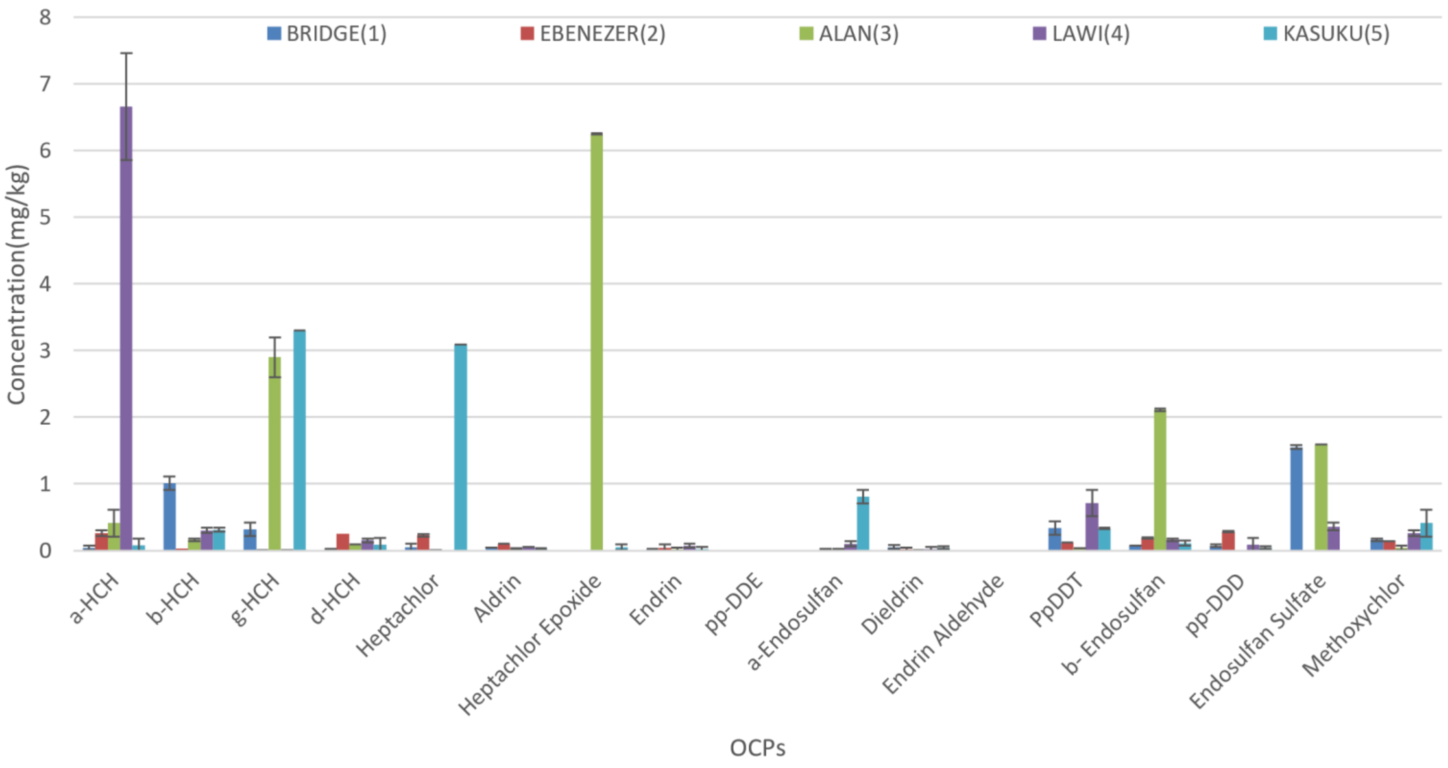


Figure 4.8: Average OCPs level in soil samples during dry season

The average OCPs levels in soil samples during wet season ranged from values below LOD to 6.66 ±0.8 µg/kg. Alpha-HCH recorded the highest concentration of all the isomers, which was recorded in fish from Lawi pond, and heptachlor epoxide in soil samples adjacent to Alan pond. The concentrations of OCPs in the wet season were relatively comparable to the levels recorded dry season. This may be attributed to the fact that no new applications of OCPs were made to the environment rather than the leeching and run-off from the agricultural fields from the previous contamination loads.

The OCPs residues obtained from five sites are represented in Figure 4.9 and in Table A3.6 in Appendix III. Dominant OCPs recorded in soil during the wet season were alpha HCH, heptachlor epoxide, gamma HCH, Heptachlor, beta endosulphan and endosulphan sulphate. Higher levels of endosulphan sulphate compared to the alpha and beta endosulphan suggested contamination from the past use of the chemicals in agriculture. The concentrations of the alpha HCH were also higher than the gamma isomer suggesting the breakdown of lindane to the alpha isomer, implying that the levels detected in the current research could be explained by the past use of technical HCHs in the region.

Other compounds that recorded the high concentrations were gamma-HCH, heptachlor, betaendosulphan, and endosulphan sulphate. The higher levels of endosulphan sulphate the alpha and beta isomers would suggest contamination from past applications due to higher metabolite than the parent compounds.

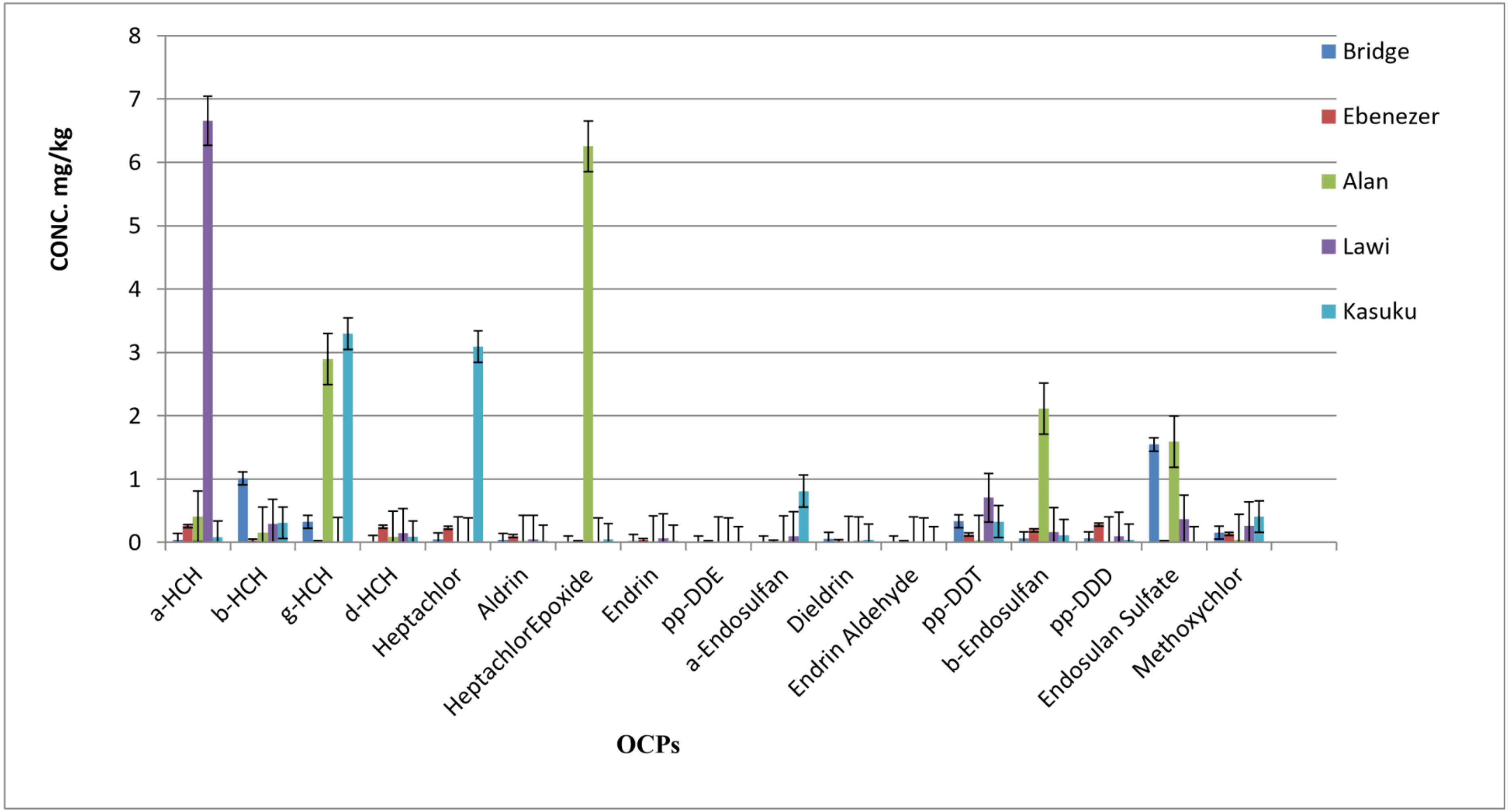


Figure 4.9: Average OCPs residue levels in soil samples during wet season

4.5.4 Average OCPs levels in fish samples

The concentration of OCPs from the fish samples during the dry season ranged from values below LOD to 5.81±0.00 µg/kg. The highest level of OCP recorded was Heptachlor epoxide in Kasuku pond. The OCPs levels in fish samples from the five sites are illustrated in Figure 4.10 and Table A3.7 in Appendix III.

Dominant OCPs in the fish samples were heptachlor epoxide and the gamma HCH. The concentrations of OCPs in fish were lower than 6.0 µg/kg suggesting much lower levels compared to the soil samples. DDTs, aldrin, dieldrin, and endosulphans were recorded at very low levels which suggested limited extent of contamination by these compounds. The ponds that recorded the highest levels of OCPs in the fish were Kasuku and Bridge, while the rest of the ponds had relatively lower concentrations below 1 µg/kg.

The presence of all isomers of HCHs in the fish samples suggested the use of technical lindane in the region, in the past applications. This was also evident in water, soil and sediment samples.

HCHs were dominated by delta-HCH, gamma-HCH and beta-HCH while alpha –HCH recorded the lowest levels among the HCHs. In other recent studies in the Lake Victoria basin by Osoro *et al*., (2016), found out α-HCH having average concentration of 7.023 ±0.01 µg/L and 22.624 ± 3.23 µg/kg in water and sediment samples respectively. This was followed by βHCH having a concentration of 2.96 ±0.97 µg/L and 21.94 ± µg/kg in water and sediment samples respectively. γ-HCH recorded the least concentration at 0.52 ±0.01 µg/L and 6.23±1.95 µg/kg in water and sediment samples respectively. In another study along River Nyando basin by Abong'o *et al.*, (2015), hexachlorohexane's presence in soil samples was investigated and γ-HCH was recorded in some of the sites (1, 26 and 33) in February with the highest mean concentration of 3.90 µg/kg in site 26. In September, site 1 recorded the highest mean concentration at 3.13 µg/kg. In the month of May, it was not detected in all the sampling sites, nevertheless, it was found in sites 4, 23 and 26 in December with site 4 recording the highest mean concentration at 4.493 µg/kg (Abong'o *et al*., 2015). It showed that the pesticide was in use by farmers in December. It was also evidenced that the pesticides varied in concentration with different points and seasons (pesticides concentration in various sites changing with short/long rains). The presence of OCPs in soil, water and sediment samples affect the aquatic environment particularly fish in fishponds through the food chain (Abong'o *et al*., 2015).

DDTs registered relatively low levels in the fish samples suggesting limited exposure or contamination to the pond fish, although the levels of *p, p'*-DDT was higher than the *p, p'*DDE and *p, p'*-DDD. Dieldrin was comparable to aldrin, while heptachlor epoxide was relatively higher than heptachlor. The trend suggested contamination of OCPs from past applications rather than new applications of OCPs whose use are either restricted or banned in the environment (Abon'go *et al.*, 2015).

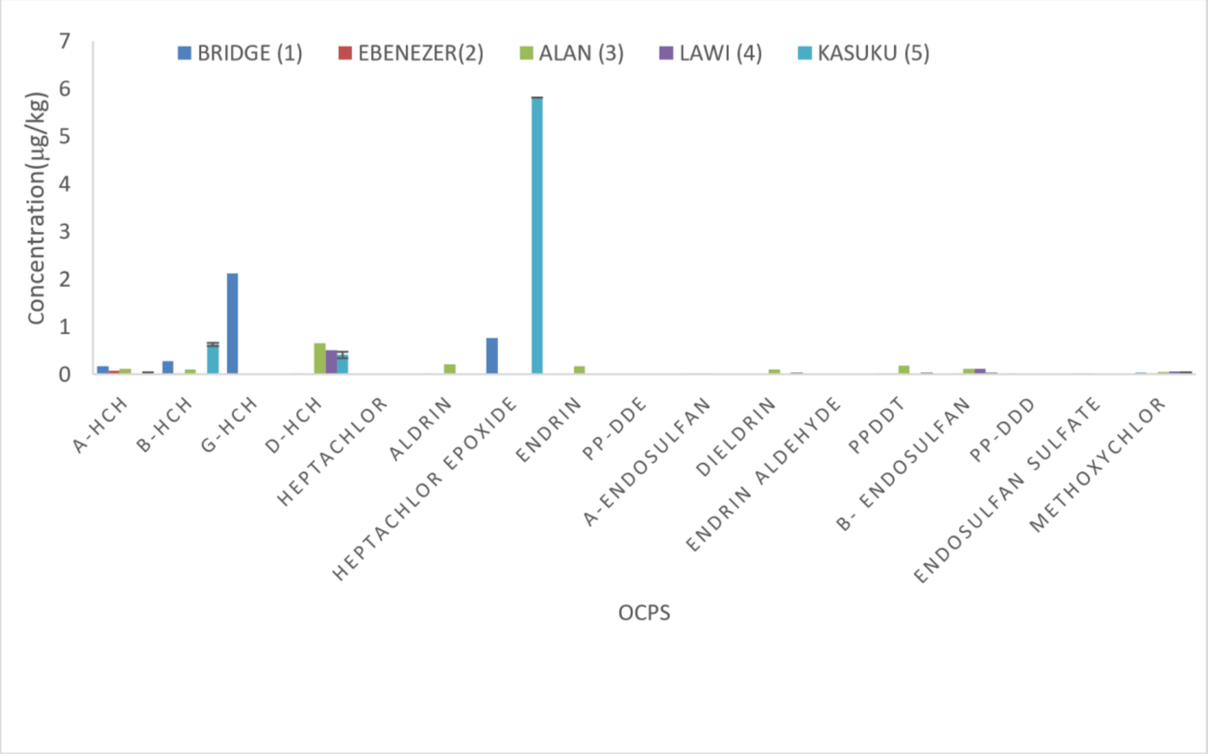


Figure 4.10: Average OCPs concentrations in fish samples during dry season

The average residue levels for OCPs in fish samples during wet season ranged from values below LOD to 10.10 ±0.30 µg/kg. The highest OCP levels recorded was beta-HCH, at Allan pond. In comparison, there were relatively higher levels of OCPs recorded during the wet season than during the dry season. This may have been attributed to overflow and leeching from the agricultural fields coupled with anthropogenic activities during the rainy season. Fish derive their food from the residues of plant materials and small organisms like worms in the water, which can also be contaminated by OCPs deposited in the sediment and adsorbed on suspended materials in water as some of the OCPs are hydrophobic. The OCPs residue levels were recorded in five sites as illustrated in Figure 4.11 and in Table A3.8 in the Appendix III. The dominant OCPs detected in the fish samples during the wet season were beta-HCH, alphaHCH, heptachlor, endrin, alpha-endosulphan and *p,p'*-DDT. Higher contaminations were registered in Alan, Ebenezer and Kasuku ponds compared to the other two ponds (Bridge and Lawi).

HCH contamination was dominated by alpha and beta- HCH isomers which tend to be more persistent than the gamma HCH. On the other hand higher levels of heptachlor, endrin, endosulphan and DDT registered relatively higher levels of the parent compounds than the metabolites, though at low levels. Other research studies have also shown higher concentration of aldrin and heptachlor than their metabolite products in soil, water and sediment samples (Abong'o *et al.*, 2015). This is an indication of the recent use of parent organochlorine pesticide compounds.

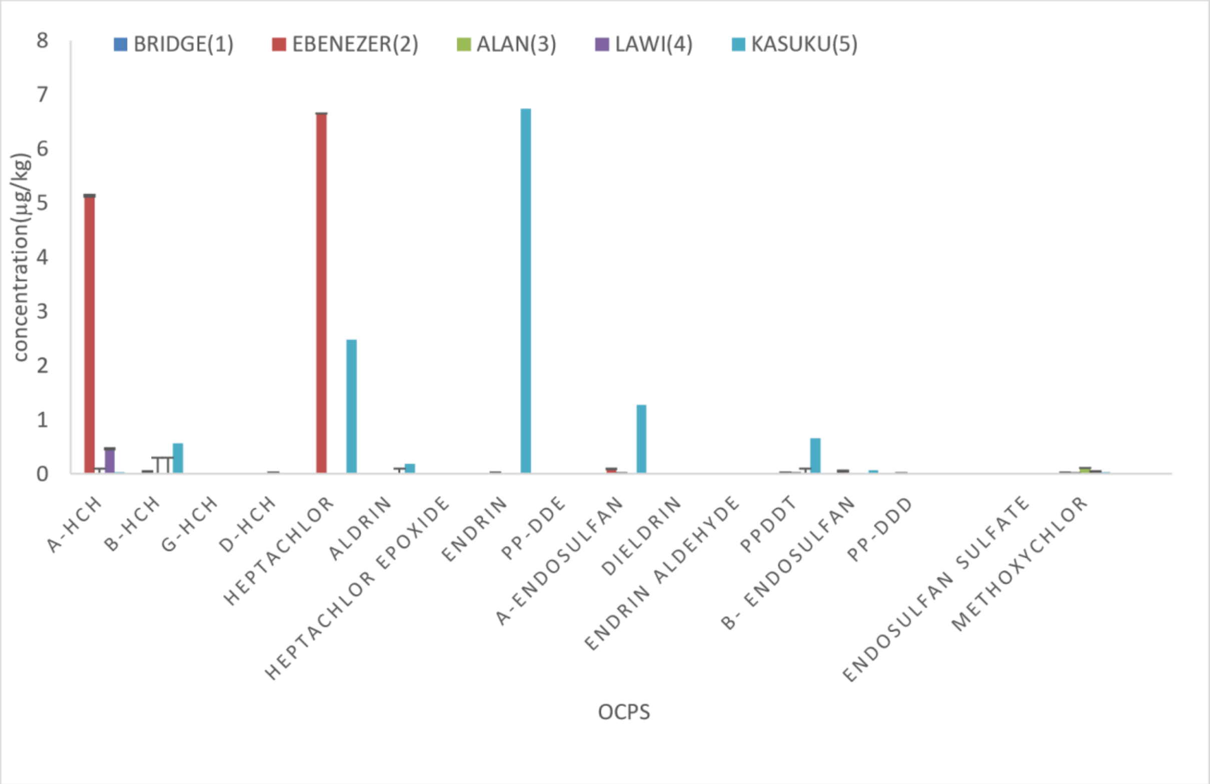


Figure 4.11: Average OCPs residue levels in fish samples during wet season

CHAPTER FIVE

5. CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

1) Organochlorine pesticide residues detected in Ahero fish pond soil, sediment, water and fish samples included α-HCH, β-HCH, γ-HCH, δ-HCH, heptachlor, aldrin, heptachlor epoxide, endrin, α-endosulfan, dieldrin, *p,p'*-DDT, β-endosulfan, *p,p'*-DDD, endosulfsulfate and methoxychlor. Endrin aldehyde and *p,p'*-DDE were detected at values below limits of detection across all the matrices. However, the low limits of detection have the potential for bioaccumulating thus threatening both aquatic organisms and human health.
2) The physical-chemical parameters of water were determined as TDS, TSS, pH, electrical conductivity and temperature. Those of sediment and soil samples were determined as, pH, total nitrogen, total organic carbon, phosphorus, potassium, calcium, magnesium, manganese, copper, sodium and iron. It was noted that there was significant correlation between physical-chemical parameters detected and the presence of OCPs in the sites of study.
3) From the results it was evidence that there was accumulation of nutrient levels and organic pollutants in fishponds and other aquatic ecosystems during both dry and wet seasons. This would negatively interfere with fish growth and their productivity in fishponds in Ahero irrigation scheme and the country at large.
4) The OCPs detected were in different concentrations which may have been affected by seasonal variations, location of the fishponds, anthropogenic activities in the region and physical and chemical properties of the OCPs. This also affected the mean concentration of pesticide residues in fish.

5.2 Recommendations

The study wishes to make the following recommendations based on its findings:

1) The presence of some POPs like DDT and its metabolites (DDD) whose use has been restricted for the control of vector causing diseases like mosquitoes is a concern that needs further interrogation as to whether it is used as per the laid guidelines by relevant agencies like NEMA and County Fisheries Department (CFD).

2) Due to the presence of physical-chemical parameters and their impacts on the presence of OCPs in water, soil, sediment and fish samples, the study recommends some level of controlled anthropogenic activities at the source of River Nyando and around the entire River Nyando basin. This should be coupled with regular monitoring of such levels to avoid scaling to higher levels that might pause health risks to the aquatic environment and human health.

3) The study recorded some levels of nutrients from fishponds which affected the growth and fish productivity. To mitigate this level of contamination, the study recommends stoppage of use of water from rice fields which has been found to be contaminated with residues of OCPs and other inorganic pollutants. Alternative source of clean water like rain water is highly recommended.

4) The study found the presence of levels of OCPs and other inorganic pollutants in water, soil, sediment and fish samples. These levels changed with seasonal variations due to anthropogenic activities. The study therefore recommends monitoring and regulation of anthropogenic activities which will go along way with reducing the impact of OCPs contamination in fish.

REFERENCES

Abong'o, D.A., S. Wandiga, I. Jumba, V.O.Madadi, Van den B., Nawaziro B.B.,Wafula Geodfrey, H. Kylin,Nkedi-Kizza P. (2015).Organochlorine Pesticide residue levels in soil from Nyando River Catchment, Kenya. *Africa Journal of Physical Sciences* 2(1): pp 18-32. ISSN 2313-3317 (https://www.researchgate.net/publication/28331219125/09/021).

Abong'o, D., S.Wandiga, I. Jumba, V.O.Madadi, H.Kylin (2014).Impact of Pesticides on Human Health and Environment in the River Nyando Catchment, Kenya. *IJHAMS 2(3): pp 1-14 ;(https://www.beta.diva.portal.org-10/07/2019).*

Abong'o, D. (2009). *Occurrence, distribution and environmental impact of Organochlorine Pesticide residues in Lake Victoria Catchment: A case study of River Nyando drainage basin of Winum Guff, Kenya.* PhD thesis, University of Nairobi, Nairobi, Kenya *(https://www.erepository.uonbi.ac.ke-10/07/2018).*

Aloyce R. Kaliba, Charles C Ngugi, John M.Mackambo, Kaiitanus O. Osewe (2007).Potential effect of aquaculture promotion on poverty reduction in Sub-Saharan Africa.

Aquaculture International 15 (6), 445-459. www.http://link.springer.com- *25th September, 2021).*

Adebeyejo, O.A., Clarke E.O., Olarinmoye, M.O. (2011). Organochlorine pesticide residues in water, sediment shell-fish samples from Lagos Lagoon Complex, Nigeria.

Researcher 3:38-45 https://www.futa.edu.ng-16/05/2019).

Agarry, S. E., Olu-Arotiowa, O.A., Aremu, M.O. and Jimoda, L.A., (2013). Biodegradation of Dichlorovos (organophosphate pesticides) in soil by bacterial isolates. *3 (8); 11-16 (https://www.core.ac.uk-11/05/2019).*

Aly M.M., Al-aidaroos B. and Alfassi F.A., (2017).Pesticides Characters, Importance and Microbial Degradation. *IOSR-JPBS,* Vol. 12, Issue 2, pp 20-28 (https://www.sciencedirect.com-20/05/2020).

Ashburner, J. and Friedrich, T., (2001). Improving handling of Pesticides Application equipment for the Safety of Applicators. *Journal of Pesticides Management;* Vol. 1, pp 9-11 (https://www.cabdirect.org-10/12/2020).

Baldwin, D.R. and W.J.Marsall, (2003). Heavy metals poisoning and its Laboratory investigations. *Analysis of Clinical Biochemistry*, vol.36, no.3, pp. 267-300 (https://www.journals.sagepub.com-12/05/2020).

Benedict P.Satia, (2016). An Overview of the large marine ecosystem programs at work in Africa today. *Environmental Development 17, 11-19 (www.http;//sciencedirect.com23/10/2021)*

Biego, H., G., (2014). Assessment of Organochlorine Pesticides in Fish sold in Abidjan Markets and Fishing Sites. *AJFA, Vol. 10, 3, pp 1-28 (https://www.researchgate.net05/06/2020).*

Curtis E. Lind, Randall E, Brummett, Raul W. Ponzoni, (2012). Participatory research, market access and small-scale commercial aquaculture in Central Cameroon*, 4 (3), 125-141.*

(www.http://onlinelibrary.wiley.com-25thSeptember, 2021)

Daly, H., (1998). Introduction to insect biology and diversity, 2nd ed. Oxford University Press, New York, *USA (https://www.cabdirect.org-20/05/2020).*

Domagalski, J. L. and Johnson, H., (2012). Phosphorus and groundwater: establishing links between agricultural use and transport to streams. *US Geological Survey Fact Sheet 3004 (https://www.pubs.usgs.gov-03/05/2020).*

ECDG, (2002). European Commission DG ENV. E3 Project ENV. E.3/ETU/0058. Heavy metals in waste water. Final report (https://www.researchgate.net-06/05/2017).

Ellsworth, P.C. and Jones, J.S., (2001). Cotton IPM in Arizona; A decade of Research, Implementation and Education. Cotton; A college of Agriculture Report. (http://www.iorsjournal.org-20th September, 2017)

FAO, (2020). The State of World Fisheries and Aquaculture. Rome. (http://www.fao.org-25th, Sept.2021).

FAO, (2014). The State of World Fisheries and Aquaculture. Rome. 223 pp. (htt: //www.fao.org/3/a-i3720;20/10/2021.)

FAO, (2016). The State of World Fisheries and Aquaculture- contributing to food security and nutrition for all. Rome. Pp 200. (www.fao.org/3/a-i5499-24/05/2019).

Farida, H. W., (2013). *Assessment of levels of selected heavy metals among industrial workers and related Occupational health effects in the city of Nairobi and Athi River Township.* PhD thesis, University of Nairobi, Nairobi, Kenya;s(https://www.erepository.uonbi.ac.ke-07/07/2020).

Gale, E.F., (1952). The Chemical activities of bacteria. New York, Academic Press; pages 234. (http://www.iorsjournal.org-20th September, 2017)

Ghorab, M.A. and Khalil, M.S., (2015). Toxicological Effects of organophosphates pesticides. *International Journal of Environmental Monitoring and Analysis 3:218-220 (https://www.researchgate.net-13/07/2020).*

Gillion, R.J., (2007). The Quality of our Nation's Water: Pesticides in the nation's streams groundwater. US Geological Survey (https://www.researchgate.net-14/08/2020).

Gitonga,N.K., Mbugua, H. and Nyandati, B. (2004). New approach to fish farming extension in Kenya. In Samaki News: A magazine of the Department of Fisheries of Kenya vol.3 No.1 Motif Creative Arts Limited, Nairobi, KE.pp 8-12 (http://dx.doi.org/10.5657/FAS.2014.0001-30/11/2021).

Helweg, C., (2003). Facts of Pesticides in Surface Waters, Laboratory and Field Experiments; Ministry of Environment, Danish Environmental Protection Agency, *Pesticides Research No. 68 (https://www.mst.dk-13/09/2020).*

Henry, L., (2003). Levels of some Pesticides in Environmental Samples from Southern Lake Victoria and its Catchment and their chemodynamics in Tilapia Species, Water and Sediments under Experimental Conditions, Tanzania *(https://www.41.86.178.5:8080/xmluihandle/123456789/12738-28/07/2020).*

Idoko, O.M. and Oklo, A., (2007). Seasonal Variation in Physico-chemical Characteristics of Rural Groundwater of Benue State, Nigeria. *Journal of Asian Scientific Research, 2 (10)-574-586 (https://www.researchgate.net-25/10/2020).*

Ize-Iyamu, O.K., I.O.Abia and P.A.Egwakhide, (2007). *Concentrations of Residues from Organochlorine Pesticides in Water and Fish. Edo State, Nigeria. Int. J. Physical SCi, 2: 237-41 (https://www.academic journals.org-27/10/2020).*

Kabiro, P.L., (2015). *Determination of Bacterial Composition, Heavy Metals Contamination and Physico-chemical Parameters of fishpond water in Abothuguchi Central, Meru County, Kenya.* Msc thesis, Kenyatta University, Nairobi, Kenya (https://www.ir.library.ku.ac.ke-24/02/2020).

Kegley, S. (1999). Disrupting the Balance, Ecological Impacts of Pesticides in Carlifornia, USA (https://www.pesticideresearch.com-24/09/2020).

Kerle, E. A, Jenkins, J. J. and Vogue, P.A., (2007).Understanding pesticide persistence and mobility for groundwater and surface water protection. Oregon State University Extension Service, EM8561-E (https://www.lir.library.oregonstate.edu-29/09/2020).

Laura Cal,Paula,S.B.,J.Miguel,Ingo B.,Josep R. (2017).Fish pigmentation and the melanocortin system*; Interactive Physiology 211,26-333. (http;//sciencedirect.com; 21/10/2021)*

LORENZ, E.S., (2009). “Potential Health Effects of Pesticides.” Ag Communications and Marketing. 1-8(https://www.books.google.com-29/10/2020).

Matthias Halwart, (2020). Fish farming on the global food system agenda in 2020.FAO Aquaculture Newsletter, II-III, 2020 (http://search.proquest.com;20/10/2021)

McIntyre, (2008). “Chemosensory Deprivation in Juvenile Coho Salmon Exposed to Dissolved Copper Under Varying Water Chemistry Conditions.” *Environmental Science Technology 42: 1352-1358 (https://www.pubs.acs.org-03/04/2021).*

Miller, G.T., (2004). Sustaining the Earth, 6th ed. Thompson hearing. Inc. pacific Grove, California, USA (https://www.scirp.org-05/06/2020).

Munguti,J.M., Jeong-D.K., Ochieng, O.O.(2014). An Over view of Kenyan Aquaculture: Current Status, Challenges and Opportunities for Future Development.*Fish Aquat Sci 17 (1), 1-11; eISSN: 2234-1757 (http://e-as.org;20/10/2021).*

Mwambur, J., (2016). Chromium Distribution and Spatial Variations in Finer Sediment Grain Size Fraction and Unfractional Suficial sediment in Nyanza Gulf of Lake Victoria (East Africa).*Journal of Waste Management;2016(1):1-5 (https;//doi.org/10.1155/2016/7528263-27th November,20121).*

NES, (2002). First National Communication of Kenya to the Conference of the Parties to the United Nation Framework Convention on Climate Change (UNFCCC), Nairobi, Kenya: National Environmental Secretariat (https://www.wedocs.unep.org25/07/2020).

Nesar Ahmed, James D. Ward, Christopher P. Saint (2014). Can integrated aquaculture-agriculture (IAA) produce “more crop per drop”? *Food security 6 (6), 767-779. (http:// www.springer.com-25th September, 2021).*

NES, (2006). National Impact Plan for Stockholm on Persistent Organic Pollutants, Nairobi, Organochlorine Pesticides in Water and Sediment from Rusinga Island, Lake Victoria; *Journal of Applied Chemistry (IOSR-JAC); ISSN:2278-5736. vol.9, Issue 9, pp 56-63;* (http://www.iorsjournal.org4thOctober,2021)*Kenya:NationalEnvironmentalSecretariat.EJEAFche8(11):12691274(https://www.researchgate.net-26/08/2020).*

Njanja, A., (2017). Zinc Deficiency prevalence high among children. Daily Nation (Business Daily 8th Aug. 2018; pp 6-8).

Ndunda, E.N., Madadi V.O., Wandiga, S.O., (2018). Organochlorine pesticide residues in sediments and water from Nairobi River, Kenya: levels, distribution and ecological risk assessment. *Environmental Science and pollution Research*; 25(34):34510-34518 (https://www.researchgate.net-27/06/2020).

Okeniyia, S.O., Eqwikhide, P.A., Akporhonore, E.E. and Obazed, E.I., (2009). Distribution of Organochlorine and Organochlorinated Pesticide residues in water bodies of some rivers in Northern Nigeria (https://www.ncbi.nlm.nih.gov-17/10/2020).

Ondiere, V.B., Vincent, M.O., Ochieng, A.A.and Oduor, F.D.O., (2017). Assessment of Heavy Metals Contamination in Lake Elementaita Drainage Basin, Kenya. *International* Journal of *Scientific Research in Science, Engineering and Technology. 2017; 3(5):283-289 (http://www.iorsjournal.org-6th November, 2020)*

Osoro E.M., Wandiga S.O., Abong'o D.A., Madadi V.O.and Macharia J.W., (2016). Organochlorine Pesticides Residues in Water and Sediments from Rusinga Island, Lake Victoria, Kenya. *IOSR Journal of Applied Chemistry (IOSR-JAC) e-ISSN: 2278-5736. Volume 9, Issue 9 Ver.II (September, 2016), pp 56-63 (www.iosrjournals.org23/07/2021).*

Owuor, J., Oindo, O.A., V.,Shikuku and G. Okowa, (2019). Assessment of Water quality of the Nyando River (Muoroni, Kenya) using the water quality index (WQI) method. *International Research Journal of Environental Science, 8(2); 27-33 (https://www.researchgate.net/pulication/332911928-25th November,2021).*

Oyewale, A.O. and Musa, I., (2006). Pollution assessment of the lower basin Lakes Kainji/Jebba, Nigeria: heavy metals status of the waters, sediments and fishes. *Journal of Environmental Geochemistry and Health, 28(3): 273(https://www.mindat.org-27/05/2020).*

Ozuturk, M., Ozozen, G., Minareci, O., Minareci, E., (2009). Determination of Heavy Metals in Fish, Water and Sediments of Avsar Dam Lake in Turkey. *Iran Journal of Environmental Health, Science and Engineering, 6(2): 73-80 (https://www.scirp.org11/01/2020).*

Randall E. Brummet, Jerome Lazard, John Moehl, (2008). *African aquaculture: Realizing the potential.Food Policy 33 (5), 371-385, 2008,* (http://www.sciencedirect.com-25th, September, 2021).

Reddy, G.V.P. and Baustista, J.R., (2012). Integration of the Predatory Mite Neoseiulus Californicus and Petroleum spray oil for control of Tetranychusmariane on eggplant. *Biocontrol Science and Technology: 22, 1211-1220. (http://www.iorsjournal.org-20th September, 2017)*

Rossel, G., Quero, C., Assessment of heavy metals pollution in water and sediments and their effect on Oreochromis niloticus in the Northern Delta Lakes, Egypt. 8th International

Symposium on Tilapia Aquaculture (https://www.scrip.org-19/10/2020).sColl, J. and

Geervo, A., (2008). Biorational Insecticides in Pest Management. *Journal of pesticide Science, Vol.33, No. 2, pp 103-121. (http://www.iorsjournal.org-20th September, 2017)*

Sacramento, C.A., (2008). Department of Pesticide Regulation. “What are the Potential Effects of Pesticides?” Community Guide to Recognizing and Reporting Pesticide Problems, 27-29 (https://www.springregulatorysciences.com-23/05/2020).

Samir, M.S. and Ibrahim M. S., (2008). Assessment of Heavy Metals Pollution of Some Water Resources and Their Effect on Oreochromis niloticus in the Nornthern Delta Lakes, Egypt.8th International Symposium on Tilapia in Aquaculture,Cairo,475-489 (http://www.scirp.org-23rd,July,2021).

Sauer, A.K. Stefanie P., Simone H., Laura T., Tarana Ann K., (2 017). Characterization of zinc amino acid complexes for zinc delivery in vitro using Caco-2 cells and enterocytes from

Biometals *30, 643-661. (http://www.springer.com-23rd, July 2021).*

Schober P.,Medstat, C.B.and L.A.Schwart, (2018). *Correlation coefficients; Appropriate use And Interpretation. Journal, Anesthesia & Analgesia 126.5(2018):1763-1768.* (https:www.researchgate.net/publication/323388613-25th November, 2021)

Singh B.K., Walker A., Alun J. Morgan W. & Wright D.J., (2004). Biodegradation of Chlorpyrifus by Enterobacter Strain B-14 and Its Use in Bioremediation of Contaminated Soils. *Journal of Appl. Environ Microbiol. 70, 4855-4863 (https://www.journals.asm.org-20/08/2020*).

Situma D., (2010). *Assessment of Polycyclic Aromatic Hydrocarbons in Air and Soil from selected sites in Nairobi.* Msc thesis, University of Nairobi, Kenya

(https://www.researchgate.net-28/04/2020).

Smith, K.R., Corvalan, C.F. & Kiellstorm, T., (2011). How much Global III Health is attributed to Environmental Factors? *Journal of Epidemiology 10 (5): 573-84* *(https://www.thelancet.com-25/06/2020).*

Solomon F., (2007). Toxic effects of Copper and other metals. University of British Columbia, Vancouver, B.C. (https://www.researchgate.net-19/08/2019).

Surekha, R., Lakshmi, P., S., Jyothi, K., Narasimha, G. and Venkateswarlu, K., (2008). Isolation and characterization of chlorpyrifos degrading bacterium from agricultural soil and its growth response. *Afr. J. Microbiol. Res., 2(1): 26-31(https://www.academicjournals.org-10/08/2021).*

Tano, Z.J. (**a**)**,** (2011). *Ecological Effects of Pesticides in the Modern World- Risks and Benefits. ISBN: 978-953-307-458-0,* In Tech. University of Dar es Salaam, Dar es Salaam, Tanzania (https://www.citeseerx.ist.psu.edu-16/09/2020).

Tano, Z. J. (**b**), (2011). Identifying Physical and Chemical Properties of Pesticides in the Mordern World-trend in pesticide analysis, (Margarita Stoytcheva,), Publisher: *In Tech, Croatia (https://www.citeseerx.ist.psu.edu-17/09/2020).*

Taub, Frieda, B., (2004). Biological Impacts of Pollutants on Aquatic Organisms. University of Washington, College of Ocean and Fishery Sciences, Sea H/g, W.A. (https://www.tandonline.com-20/09/2020).

Tenai, B.C., J.M. Mbaria., (2016). Assessment of heavy metals concentration in water, soil sediments and biological tissues of the Lesser Flamingoes in four Eastern Rift-Valley Lakes. African *Journal of Environmental Science and Technology; Vol. 10 (pp 1-6) No. 6 (https://www.ajol.info.com-08/10/2020).*

Tchounou, P.B., (2012). *Heavy Metals Toxicity and the Environment.* A Handbook of Environmental Health and Safety. Vols I & II, 3rd ed., CRC Press, Boca Raton, Florida., USA (https://www.linkspringer.com-17/09/2020).

UNEP, 2012. Stockholm Convention on Persistent Organic Pollutants (https://www.chmpops. Int.-20th February, 2018).

Muinde, V., R.Nthuribi,B.Munyali and J.Mmari, (2013). Effects of Heavy Metals Pollution on Omega-3-Polyunsaturated Fatty Acid Levels in Tilapia Fish from Winam Gulf of Lake Victoria. *ISNN: 1874-8295 (http://bentham.org/open/toenriej/index.htm;25th November, 2021).*

Wadie, A.S.T. and Abduljalil, G.A.D.S., (2010). Assessment of Hydrochemical Quality of Groundwater under Urban areas within Sana'a Secretariat. *Ecletica Quimica.. 35(1), pp 77-84. (https://www.SCIELO.BR/EQ; 20/07/2020)*

Wamanji, E., (2018). Why food safety is a major national issue: https://www.nationmedia.com- 20th *February, 2018.*

Wambwa, C.M., (2015). *Analysis of heavy metal concentrations in selected species of genus tephrosia in South Eastern and Coastal Regions, Kenya.* Msc Thesis, University of Nairobi, Nairobi, Kenya (https://www.ir-library.ku.ac.ke-18/09/2020).

Wang'ombe, G., (2014). *Risk of Agrochemicals in the Environment and Human Health in Mukaro Location, Nyeri County, Kenya;* Msc thesis, Kenyatta University, Nairobi, Kenya (https://www.ir-library.ku.ac.ke-/11/10/2020).

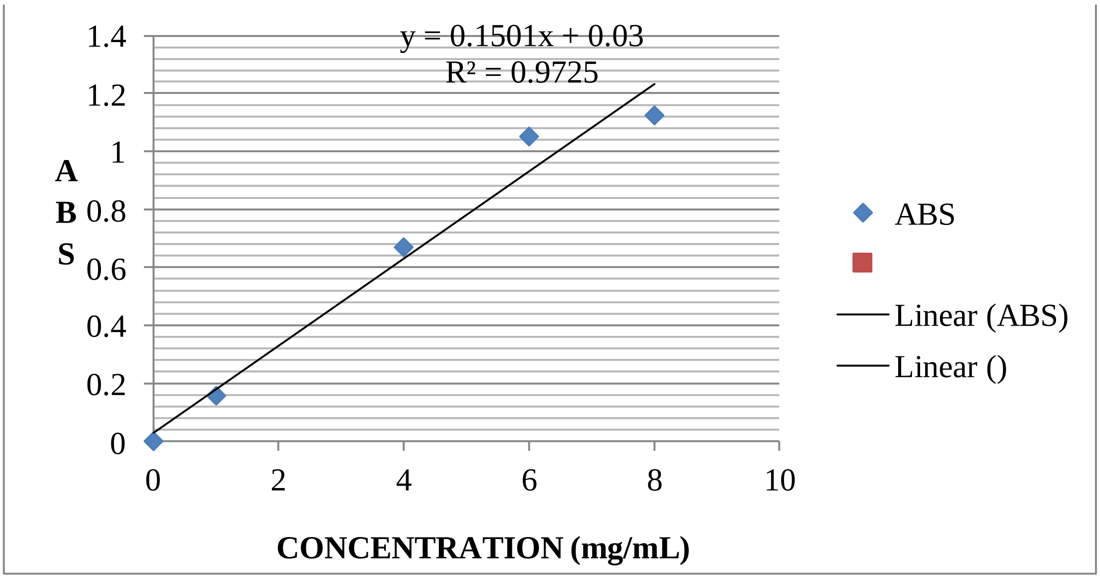
World Health Organization, (2004). Guidelines for drinking –water quality, 3rd edition, I: Recommendations. World Health Organization.World Health Organization, (2019). Food safety issues associated with heavy metals. Environmental International, vol.125, pp 399-417; (http://www.doi.org/10.1016/j.envint-19th, July 2019).

Wright, D. and P. Welbourn, (2002). Environmental Toxicology, Cambridge University Press, Cambridge; (http://www.dx.doi.org/10.1017/CBO9780511805998- 10th, July 2018) http://www.agritech.tnau.ac.in (20th October, 2021)

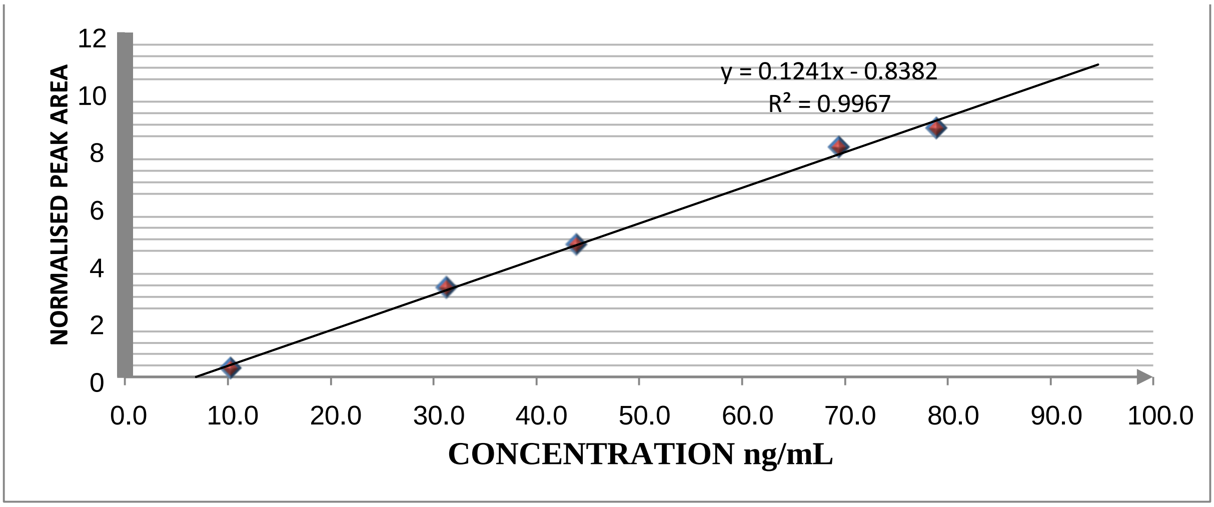
APPENDIX I

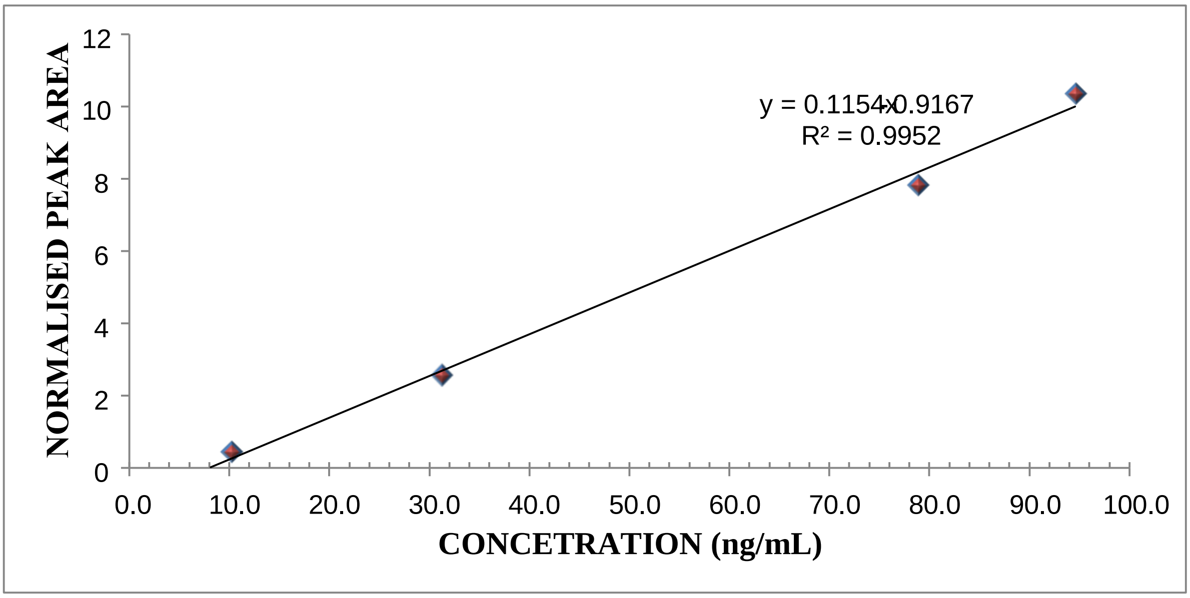
CALIBRATION CURVES

A2. 1: Calibration curve for phosphates

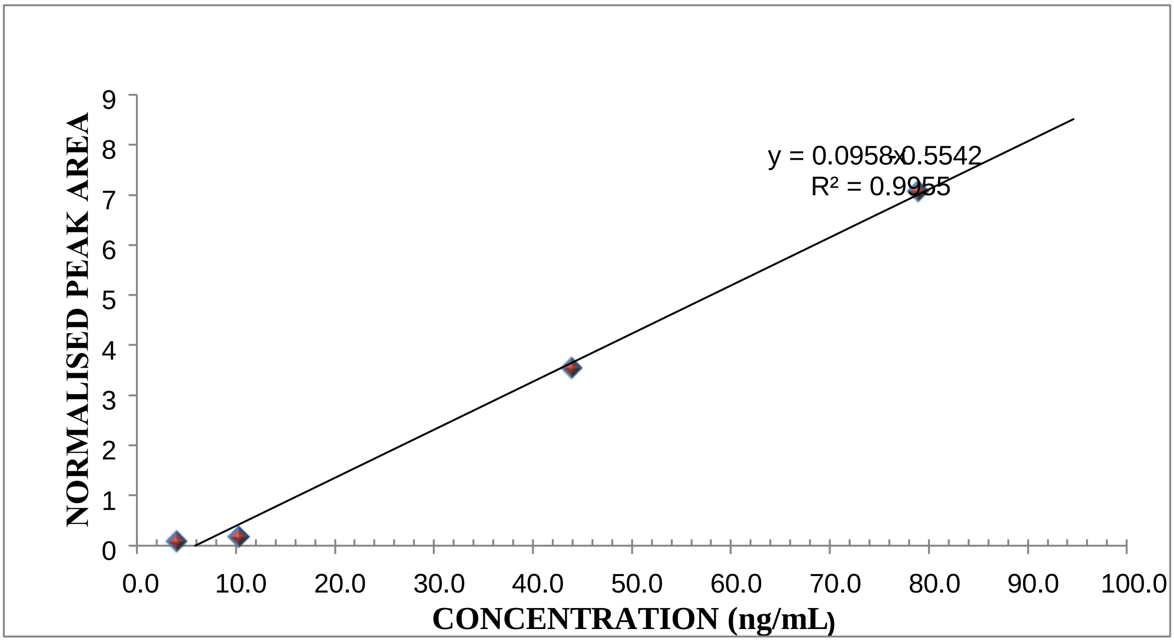


b) Calibration curves for OCPs

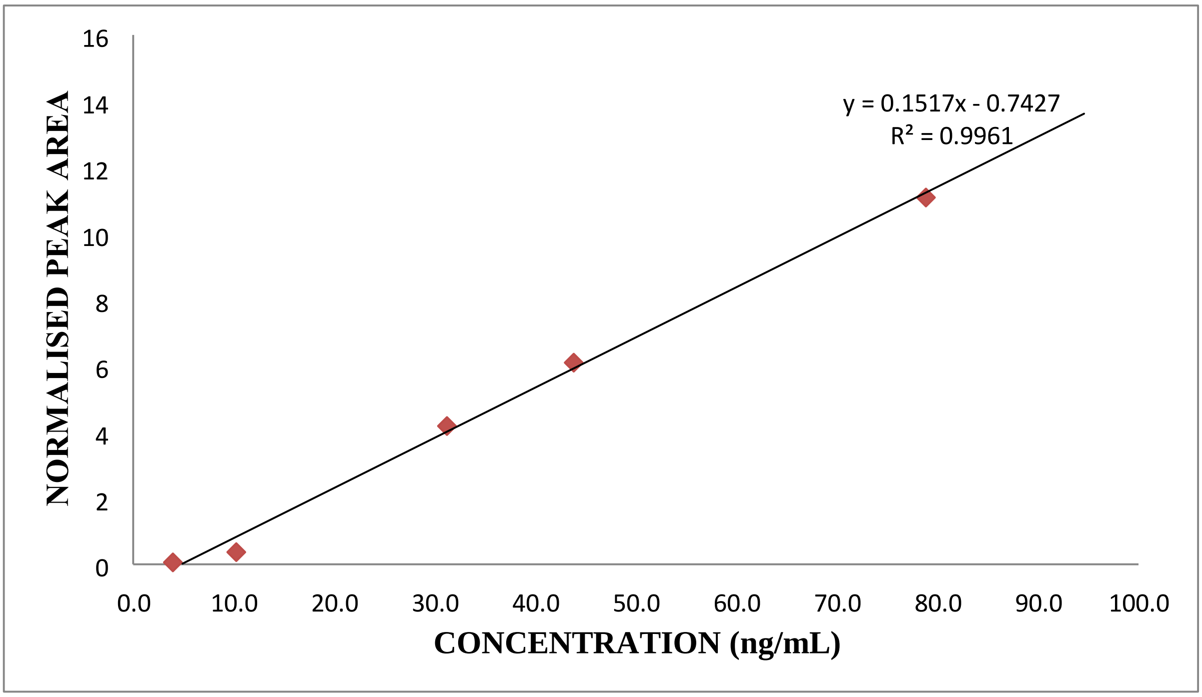




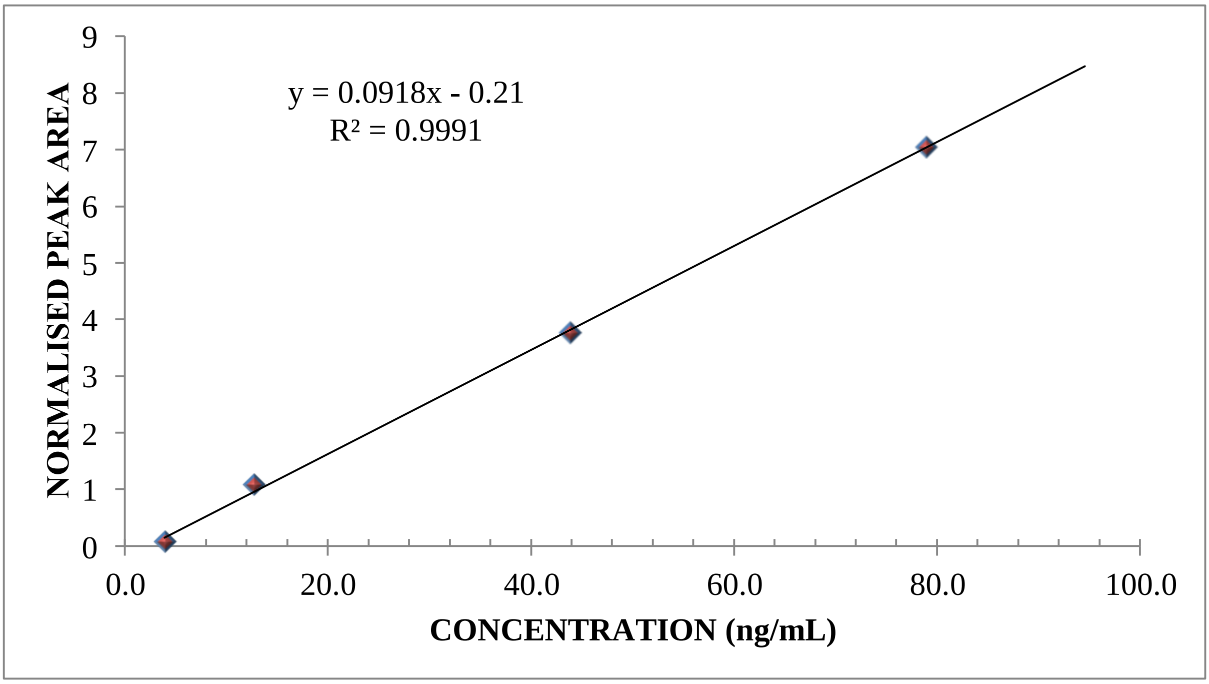
A2.2: b-HCH



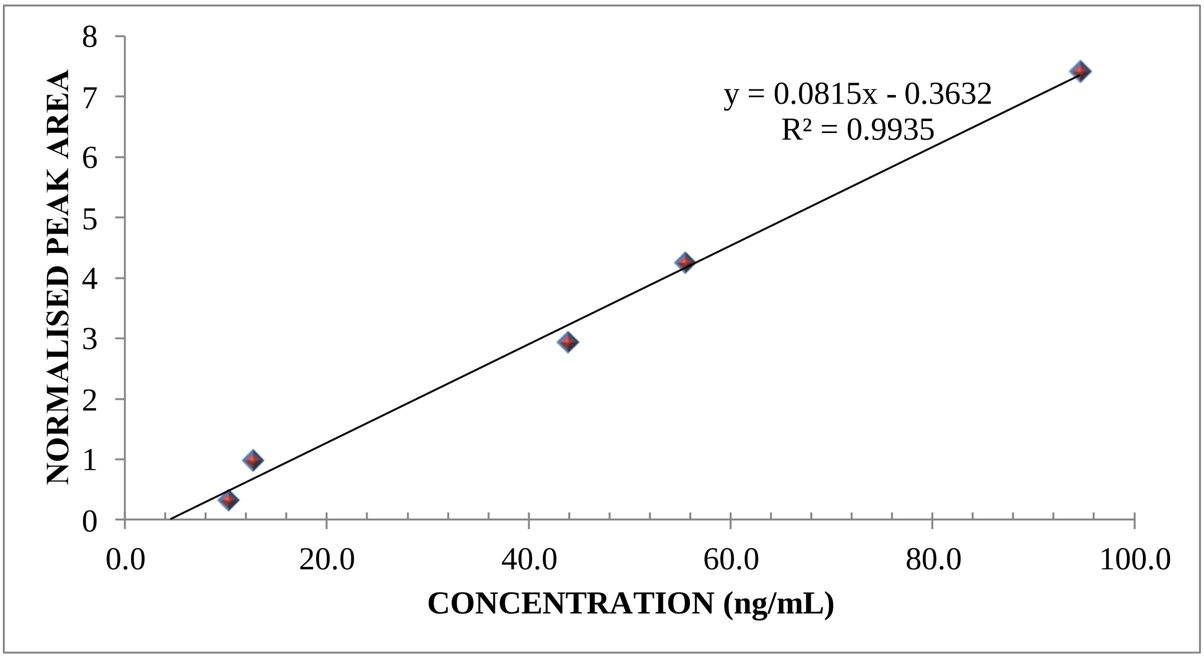
A2.3:d-HCH



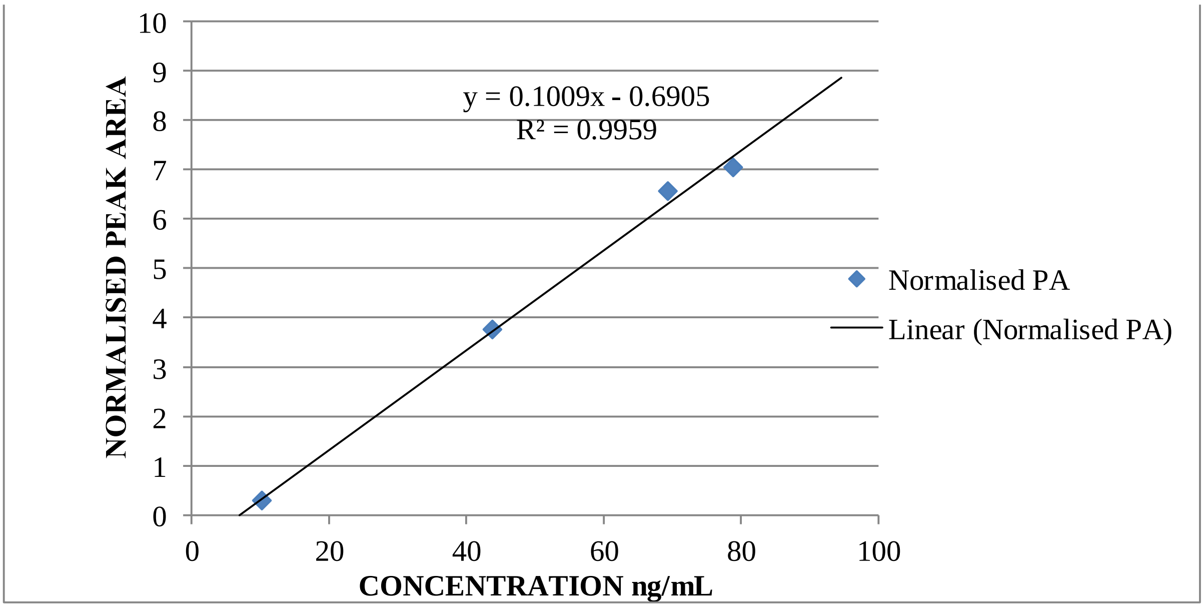
A2.4: g-HCH



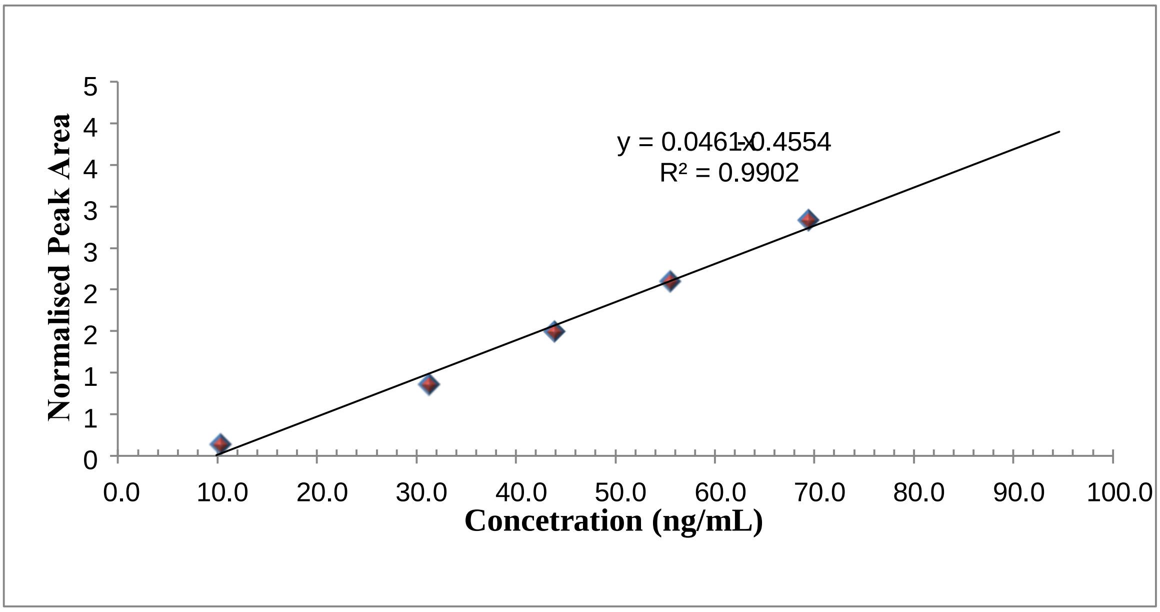
A2.5: Heptachlor



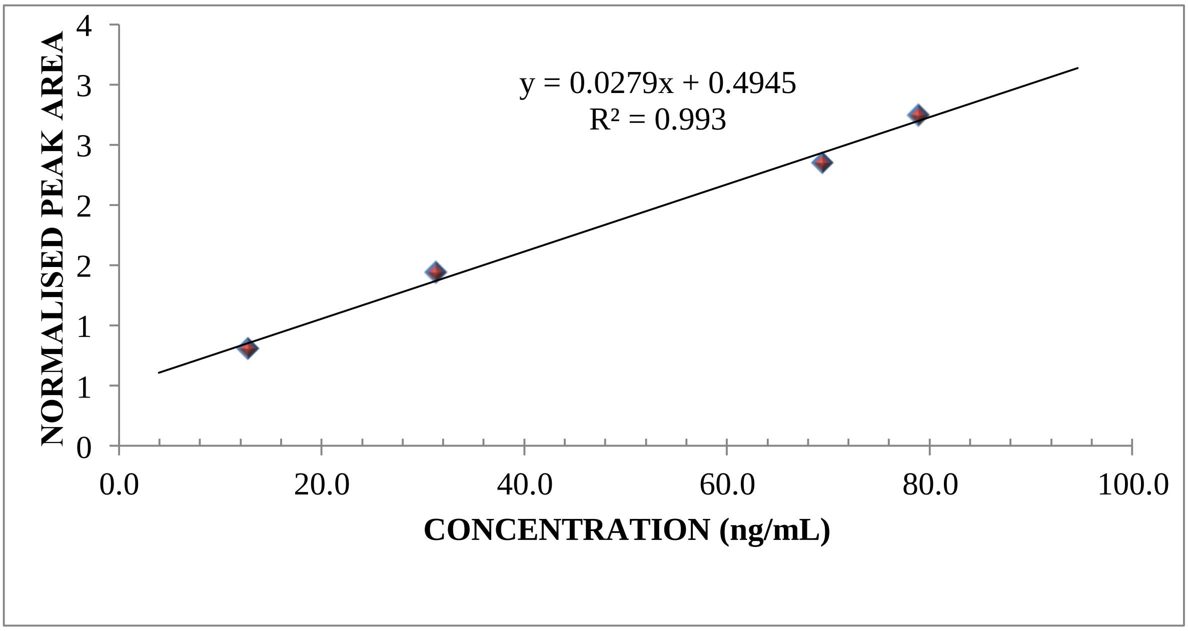
A2.6: Aldrin



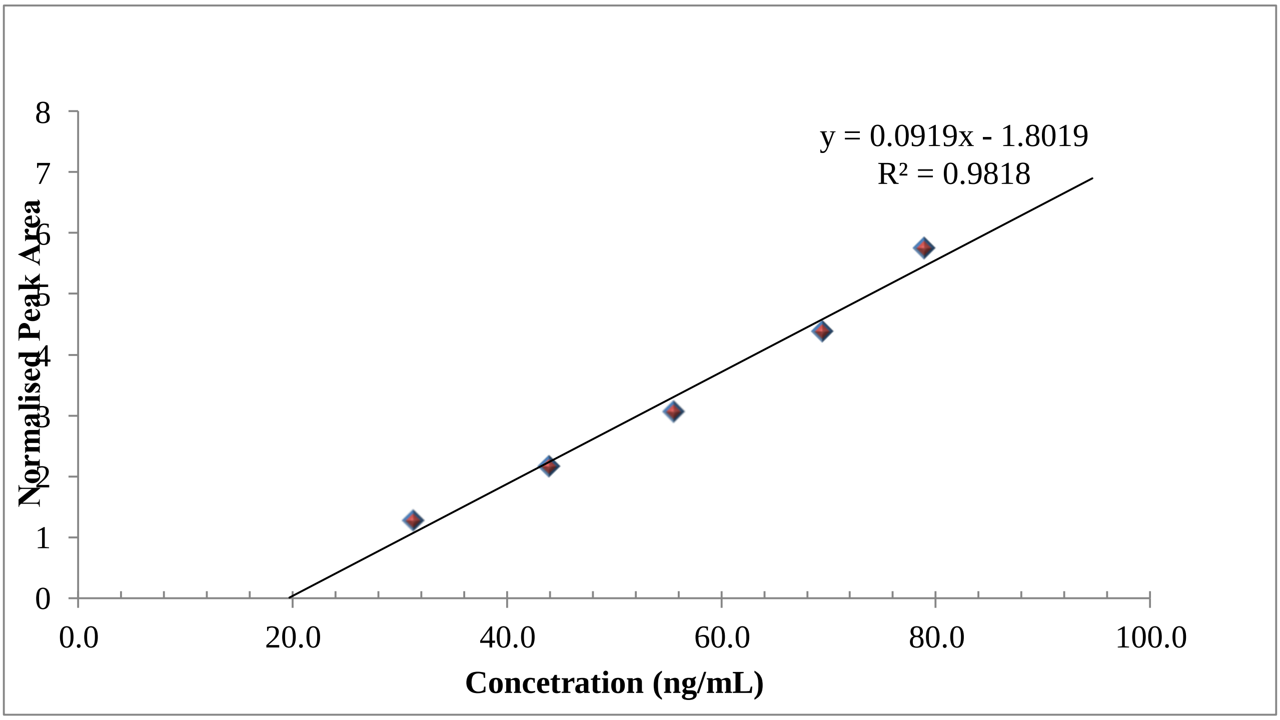
A2.7: Heptachlor Epoxide



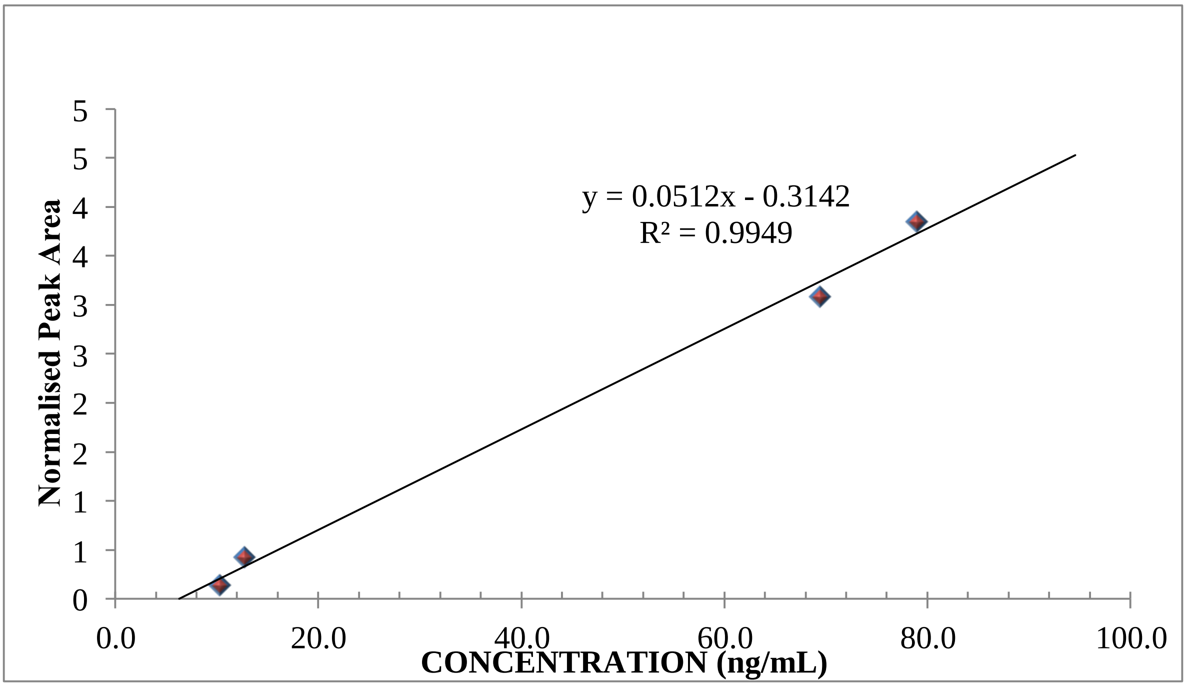
A2.8: Endrin



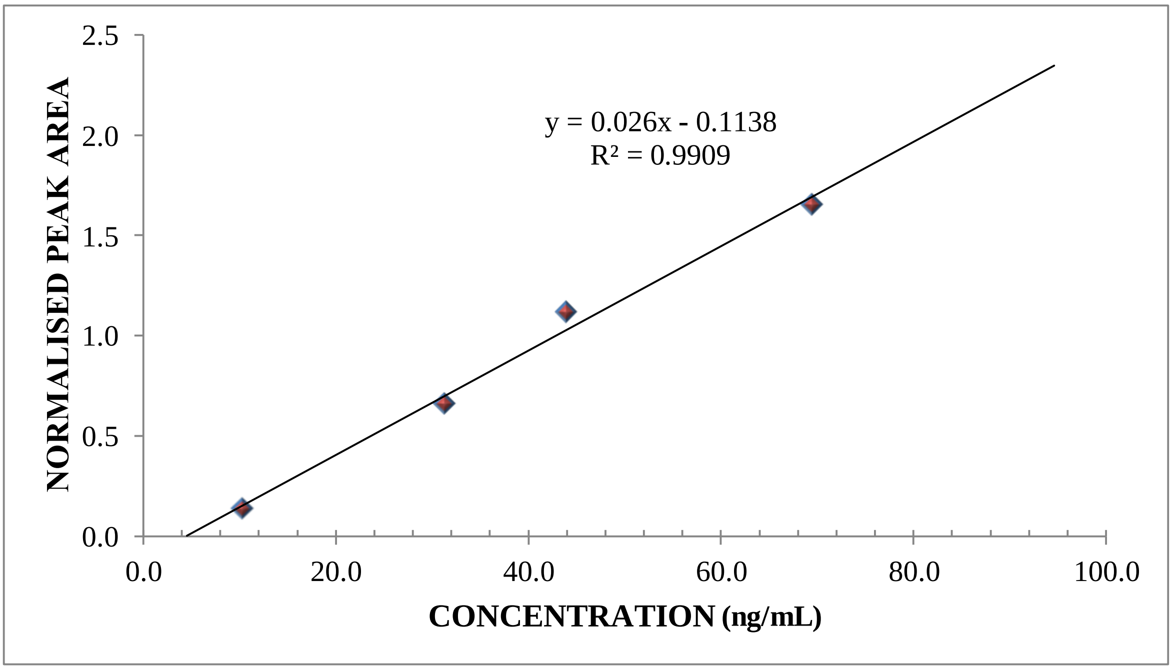
A2.9: Endosulfan I



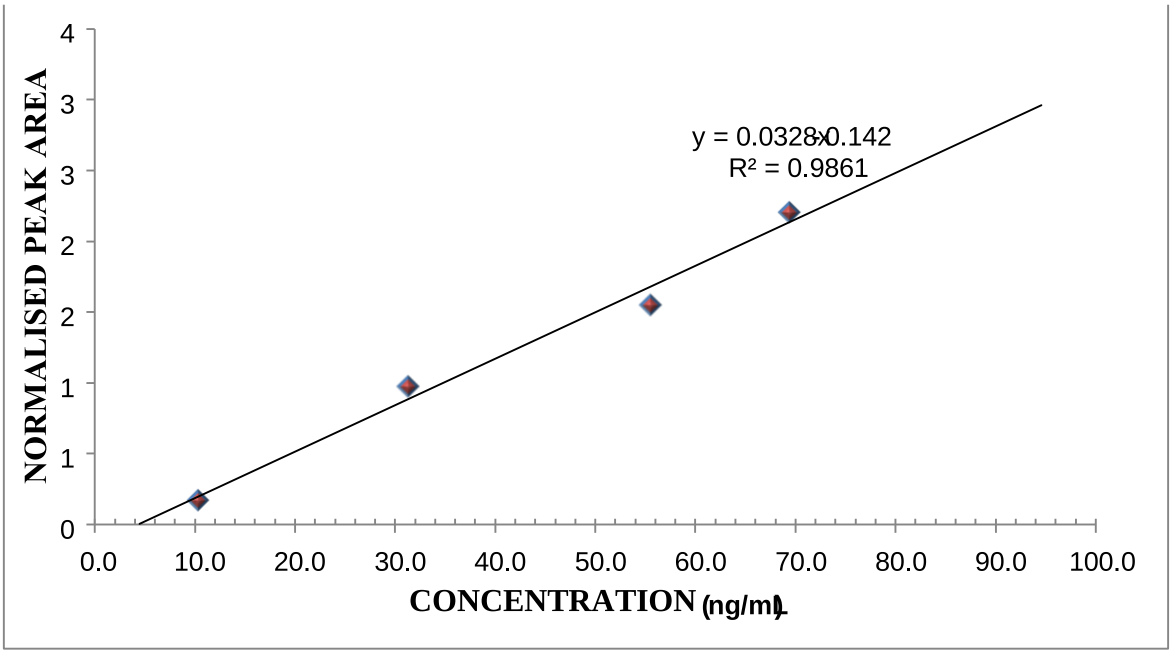
A2.10: Dieldrin



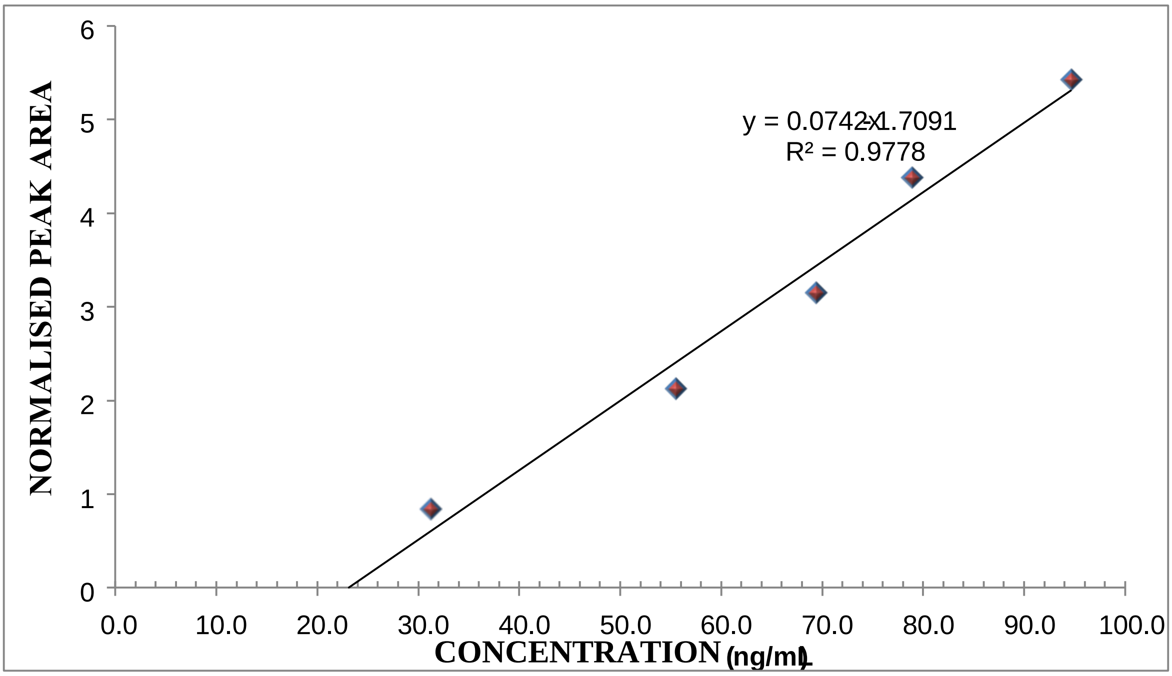
A2.11: Endrin Aldehyde



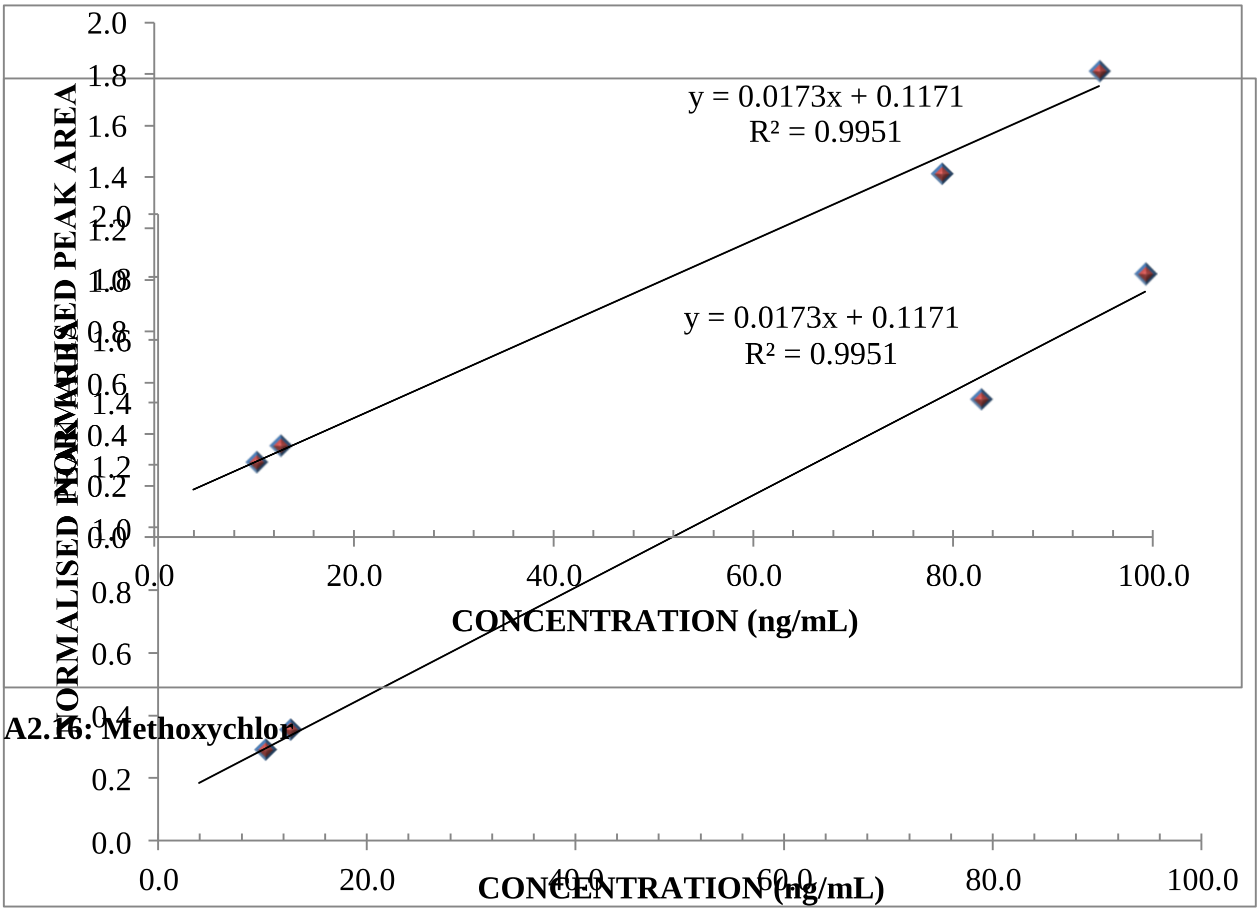
A2.12: DDT



A2.13:Endosulfan II



A2.14: DDD



A2.16: Methoxychlor

A2.15: Endosulfansulfate

APPENDIX II

CONCENTRATIONS OF OCPs

Table A2. 1: OCPs residue levels in water during dry season (µg/L)

Site/ Pesticide	BRIDGE(1)	EBENEZER(2)	ALAN(3)	LAWI(4)	KASUKU(5)
a-HCH	0.11 ±0.01	0.17 ±0.04	0.04 ±0.02	0.55 ±0.9	0.0
b-HCH	0.52 ±0.001	0.28 ±0.01	0.03 ±0.05	0.18 ±0.01	1.64 ±0.5
g-HCH	0.24 ±0.00	0.61 ±0.00	0.01 ±0.01	0 ±0.00	0.04 ±0.01
d-HCH	0.02 ±0.00	0.014 ±0.005	0.00 ±0.00	1.01 ±0.7	0.13 ±0.02
Heptachlor	0.0	0.28 ±0.04	0.13 ±0.01	0.10 ±0.00	0.15 ±0.00
Aldrin	0.05 ±0.003	0.03 ±0.003	0.03 ±0.02	0.10 ±0.005	0.05 ±0.002
Heptachlor Epoxide	0.02±0.004	<0	<0	0.08 ±0.004	0.04 ±0.003

Endrin	0.01±0.00	0.01 ±0.004	0.02 ±0.00	13.16 ±0.00	0.03 ±0.001
pp-DDE	< 0	< 0	< 0	< 0	< 0
a-Endosulfan	0.02 ±0.02	0.02 ±0.00	0.00 ±0.00	0.01 ±0.003	0.02 ±0.01
Dieldrin	0.01 ±0.003	0.07 ±0.06	0.04 ±0.01	0.19 ±0.03	0.10 ±0.004
Endrin Aldehyde	< 0	< 0	< 0	< 0	< 0
PpDDT	0.04 ±0.003	0.02 ±0.01	0.05.±0.01	0.02 ±0.00	0.19 ±0.15
b- Endosulfan	0.07 ±0.01	0.14 ±0.002	0.15 ±0.04	0.14 ±0.02	0.06 ±0.03
pp-DDD	0.01 ±0.00	0.02 ±0.002	0.1 ±0.00	0.09 ±0.3	0.00 ±0.00
Endosulfan Sulfate	0.01 ±0.00	0.015 ±0.00	0.09 ±0.00	0.16 ±0.1	0.07 ±0.01
Methoxychlor	0.26 ±0.02	0.044 ±1.24	0.3 ±0.19	0.06 ±0.03	0.039 ±0.08
∑OCP	1.39	1.723	0.98	15.75	2.559

Table A2

.2: OCPs residue levels in water samples during wet season (µg/L)

Site/ Pesticide	BRIDGE	EBENEZER	ALAN	LAWI	KASUKU
a-HCH	0.46 ±0.5	0.17 ±0.1	0.04 ±0.06	0.83 ±1.2	0.35 ±0.5
b-HCH	1.70 ±0.6	0.28 ±0.3	0.03 ±0.003	2.04 ±0.2	8.05 ±0.03
g-HCH	0.19 ±0.05	2.12 ±0.7	0.01 ±0.7	0±0.00	0.17 ±0.7
d-HCH	0.02 ±0.02	0.00	0.00	1.01 ±0.5	0.51 ±0.00
Heptachlor	0.14 ±0.05	0.01 ±0.00	0.02 ±0.00	0.22 ±0.1	0.19 ±0.006
Aldrin	0.48 ±0.3	0.02 ±0.00	0.03 ±0.004	0.10 ±0.1	0.16 ±0.00
Heptachlor Epoxide	0.02 ±0.01	0.76 ±0.4	< 0	< 0	< 0
Endrin	0.13 ±0.09	0.01 ±0.00	0.06 ±0.02	0.02 ±0.00	0.17 ±0.00
pp-DDE	< 0	< 0	< 0	< 0	< 0
a-Endosulfan	0.35 ±0.5	0.02 ±0.02	0.00	0.01 ±0.00	0.02 ±0.00
Dieldrin	2.11 ±1.4	0.07 ±0.005	0.02 ±0.00	25.40 ±2.31	0.04 ±0.05
Endrin Aldehyde	0	0	0	0	0
PpDDT	0.21 ±0.08	0.02 ±0.00	0.04 ±0.00	0.02 ±0.00	0.19 ±0.176
b- Endosulfan	3.68 ±1.24	0.01 ±0.7	0.02 ±0.01	0.14 ±0.1	0.06 ±0.01
pp-DDD	1.46 ±0.13	0.02 ±0.033	0.01 ±0.00	0.09 ±0.03	0±00
Endosulfan Sulfate	0.28 ±0.02	0.03 ±0.003	0.01 ±0.00	9.45 ±1.2	0.00
Methoxychlor	8.17 ±0.7	0.04 ±0.014	0.20 ±0.1	4.46 ±1.00	0.08 ±0.002
∑OCP	19.40	3.54	0.48	43.78	10.00

Table A2.3: OCPs residue levels in sediment samples during dry season (µg/kg)

Site/ Pesticide	BRIDGE	EBENEZER	ALAN	LAWI	KASUKU
a-HCH	1.29 ±0.17	0.0	0.02 ±0.02	0.09 ±0.01	0.0
b-HCH	1.40 ±0.03	0.0	0.08 ±0.01	0.30±0.04	0.31 ±0.03
g-HCH	0.08 ±0.01	0.00	0.01 ±0.00	0.01 ±0.00	0.00±0.00
d-HCH	0.00	0.00	0.12 ±0.1	0.19 ±0.01	0.00±0.00
Heptachlor	0.16 ±0.2	0.00	0.02 ±0.001	0.01 ±0.00	0.00±0.00
Aldrin	0.01 ±0.001	0.00	0.00	0.02 ±0.002	0.00±0.00
Heptachlor Epoxide	0.00	0.00	0.00	2.71 ±0.00	0.04 ±0.003
Endrin	2.25 ±0.00	0.0	0.04 ±0.01	0.04 ±0.03	0.0
pp-DDE	< 0	< 0	< 0	< 0	< 0
a-Endosulfan	0.13 ±0.2	0.00	0.07 ±0.00	0.11 ±0.08	0.00
Dieldrin	0.35 ±0.5	0.00	0.01 ±0.00	0.04 ±0.04	0.00
Endrin Aldehyde	< 0	< 0	< 0	< 0	< 0
PpDDT	0.20 ±0.03	0.00	0.02 ±0.002	0.08 ±0.00	0.00
b- Endosulfan	1.91 ±0.5	0.00	0.05 ±0.06	0.02 ±0.01	< 0
pp-DDD	0.00	0.03 ±0.04	0.00	0.00	0.00
Endosulfan Sulfate	0.02 ±0.01	0.00	0.15 ±0.07	0.00	0.00
Methoxychlor	0.02 ±0.01	0.20 ±0.01	0.21 ±0.06	0.02 ±0.01	0.54 ±0.03

Table A2

∑OCP	7.82	0.23	0.80	3.62	0.89

. 4: OCPs residue levels in sediment samples during wet season (µg/kg)

Site/ Pesticide	BRIDGE(1)	EBENEZER(2)	ALAN(3)	LAWI(4)	KASUKU(5)
a-HCH	2.95 ±0.05	0.45 ±0.02	0.59 ±0.04	0.12 ±0.01	0.17±0.1
b-HCH	0.64 ±0.003	1.01 ±0.05	9.76±1.60	0.10 ±0.006	0.96 ±0.02
g-HCH	< 0	0.03 ±0.07	<0	0.12 ±0.002	0.07 ±0.01
d-HCH	0.03 ±0.002	0.09 ±0.11	0.66 ±0.002	<0	0.18 ±0.02
Heptachlor	0.003 ±0.002	0.01 ±0.002	0.01 ±0.00	0.01 ±0.00	0.06 ±0.01
Aldrin	0.02 ±0.02	1.66 ±0.3	0.04 ±0.01	0.21 ±0.02	2.73 ±0.6
Heptachlor Epoxide	1.75 ±0.01	0.01 ±0.00	<0	4.63 ±0.02	0.05 ±0.01
Endrin	0.01 ±0.00	0.06 ±0.02	0.02 ±0.00	0.17 ±0.00	0.05 ±0.01
pp-DDE	<0	<0	<0	<0	<0
α-Endosulfan	0.01 ±0.01	0.03 ±0.006	3.87 ±0.02	0.06 ±0.02	0.05 ±0.03
Dieldrin	0.00	11.95 ±2.5	0.01 ±0.00	0.09 ±0.1	0.03 ±0.03
Endrin Aldehyde	< 0	< 0	< 0	<0	< 0
PpDDT	0.02 ±0.009	0.05 ±0.004	0.02 ±0.00	0.19 ±0.02	2.62 ±0.1
β-Endosulfan	0.01 ±0.01	0.43 ±0.2	1.83 ±0.1	0.19 ±0.08	0.02 ±0.02
pp-DDD	0.0	0.18 ±0.05	0.02 ±0.002	0.00	0.00
Endosulfan Sulfate	0.10 ±0.006	0.01 ±0.001	0.02 ±0.001	0.04 ±0.001	5.75 ±0.1
Methoxychlor	0.35 ±0.11	6.88 ±0.7	0.53 ±0.04	0.05 ±0.01	0.49 ±0.11

∑OCP	5.893	22.83	17.38	5.94	13.31

Table A2.5: OCPs residue levels in soil samples during dry season (µg/kg)

Site/ Pesticide	BRIDGE	EBENEZER	ALAN	LAWI	KASUKU
a-HCH	0.21 ±0.5	0.19 ±0.3	0.08 ±0.03	0.35 ±0.5	0.61 ±0.3
b-HCH	0.11±0.01	0.23 ±0.03	0.03 ±0.003	2.04 ±0.2	8.05 ±0.03
g-HCH	0.02 ±0.01	<0	0.01 ±0.7	<0	170 ±1.4
d-HCH	0	<0	0.00 ±0.005	0.91 ±0.9	1.55 ±0.4
Heptachlor	0.03 ±0.01	0	0.01 ±0.01	0.13 ±0.05	0.04 ±0.03
Aldrin	0.04 ±0.006	<0	0	0.08 ±0.02	2.73 ±0.64
Heptachlor Epoxide	0	<0	0	0.00 ±0.00	0.05 ±0.005
Endrin	0.14 ±0.2	0.02 ±0.02	0.01 ±0.01	0.10 ±0.01	0.79 ±0.3
pp-DDE	<0	<0	<0	<0	<0
a-Endosulfan	0.35 ±0.5	0.02 ±0.02	0.00 ±0.00	0.01 ±0.003	0.02 ±0.02
Dieldrin	2.11 ±1.4	0	0.02 ±0.00	0.13 ±0.00	0.04 ±0.13
Endrin aldehyde	0	0	0	0	0
Pp-DDT	0.06 ±0.001	0.04 ±0.001	0.02 ±0.00	0.19 ±0.2	2.62 ±0.1
b- Endosulfan	0.04 ±0.005	0.07 ±0.005	0.02 ±0.007	0.04 ±0.05	0.84 ±0.4
pp-DDD	0.03 ±0.01	0.13 ±0.01	0	0	0.09 ±0.02
Endosulfan Sulfate	0.01 ±0.01	0.04 ±0.04	0.02 ±0.00	0.04 ±0.001	5.75±1.00
Methoxychlor	0.05 ±0.7	0.55 ±0.002	0.03 ±0.02	0.14 ±0.02	0.49 ±0.1
∑OCP	3.2	1.3	0.26	4.17	25.34

Table A2

.6: OCPs residue levels in soil samples during wet season (µg/kg)

Site/ Pesticide	BRIDGE(1)	EBENEZER(2)	ALAN(3)	LAWI(4)	KASUKU(5)
a-HCH	0.04 ±0.03	0.26 ±0.04	0.41 ±0.2	6.66 ±0.8	0.08 ±0.1
b-HCH	1.01 ±0.1	0.03 ±0.01	0.16 ±0.02	0.30 ±0.04	0.31 ±0.03
g-HCH	0.32 ±0.1	0.0	2.90 ±0.3	0.01 ±0.001	3.30 ±0.00
d-HCH	0.01±0.01	0.25 ±0.005	0.09 ±0.003	0.15 ±0.03	0.09 ±0.1
Heptachlor	0.05 ±0.05	0.23 ±0.02	0.01 ±0.004	0.0	3.09 ±0.00
Aldrin	0.04 ±0.003	0.10 ±0.004	0.02 ±0.01	0.05 ±0.002	0.03 ±0.002
Heptachlor Epoxide	0.0	0.0	6.25 ±0.01	0.0	0.05 ±0.04
Endrin	0.02 ±0.00	0.04 ±0.05	0.02 ±0.02	0.07 ±0.03	0.02 ±0.03
pp-DDE	< 0	< 0	< 0	< 0	< 0
a-Endosulfan	0.0	0.01 ±0.01	0.02 ±0.00	0.10 ±0.04	0.81 ±0.1
Dieldrin	0.05 ±0.03	0.02 ±0.02	0.01 ±0.004	0.02 ±0.03	0.04 ±0.02
Endrin Aldehyde	< 0	< 0	< 0	< 0	< 0
PpDDT	0.34 ±0.1	0.12 ±0.005	0.03 ±0.002	0.71 ±0.2	0.33 ±0.01
b- Endosulfan	0.07 ±0.00	0.19 ±0.01	2.11 ±0.02	0.16 ±0.02	0.11 ±0.04
pp-DDD	0.07 ±0.02	0.28 ±0.01	0.0	0.09 ±0.1	0.04 ±0.02
Endosulfan Sulfate	1.55 ±0.03	0.0	1.59 ±0.00	0.36 ±0.06	0.0
Methoxychlor	0.16 ±0.02	0.14 ±0.002	0.04 ±0.03	0.26 ±0.04	0.41 ±0.2
∑OCP	3.71	1.41	13.64	2.26	8.30

Table A2

.7: OCPs residue levels in fish samples during dry season (µg/kg)

Site/ Pesticide	BRIDGE (1)	EBENEZER(2)	ALAN (3)	LAWI (4)	KASUKU (5)
a-HCH	0.17 ±0.14	0.08 ±0.03	0.12 ±0.16	< 0	0.04 ±0.05
b-HCH	0.28 ±0.3	0.03 ±0.003	0.10 ±0.03	< 0	0.63 ±0.003
g-HCH	2.12 ±0.7	0.0	0.01 ±0.002	< 0	0.0
d-HCH	0.02 ±0.02	0.0	0.66 ±0.7	0.51 ±0.05	0.41 ±0.07
Heptachlor	0.0	0.01 ±0.01	0.01 ±0.00	< 0	0.0 ±0.002
Aldrin	0.02 ±0.004	0.0	0.21 ±0.09	< 0	0.0
Heptachlor Epoxide	0.76 ±0.4	0.0	0.01 ±0.005	< 0	5.81 ±0.00
Endrin	0.0	0.01 ±0.01	0.17 ±0.18	0.0	0.0
pp-DDE	< 0	< 0	< 0	< 0	< 0
a-Endosulfan	0.02 ±0.02	0.02 ±0.01	0.03 ±0.02	< 0	0.0
Dieldrin	0.01 ±0.005	0.01 ±0.01	0.1±0.1	0.0	0.01 ±0.01
Endrin Aldehyde	< 0	< 0	< 0	< 0	< 0
PpDDT	0.02 ±0.004	0.02 ±0.00	0.18 ±0.07	0.0	0.01 ±0.004
b- Endosulfan	0.01 ±0.7	0.02 ±0.01	0.12 ±0.1	0.12 ±0.005	0.01 ±0.00
pp-DDD	0.02 ±0.03	0.0	0.0	0.0	0.0
Endosulfan Sulfate	0.03 ±0.003	0.02 ±0.00	0.01 ±0.001	0.0	0.0
Methoxychlor	0.04 ±0.01	0.03 ±0.04	0.05 ±0.01	0.06 ±0.005	0.04 ±0.005
∑OCP	3.50	0.15	1.83	0.69	6.97

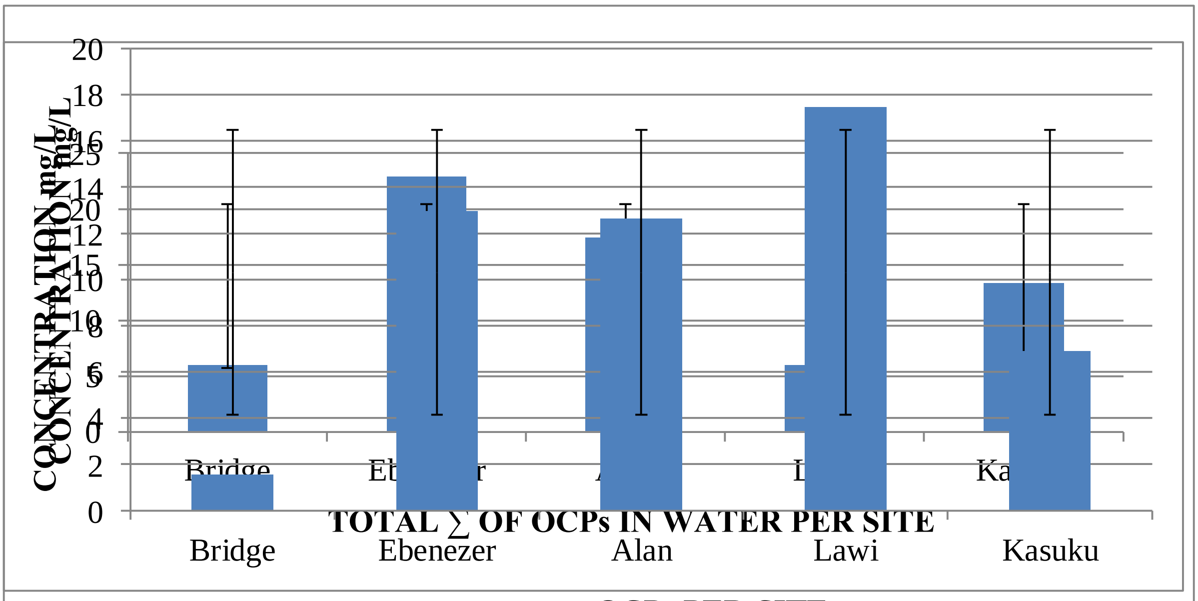
Table A2

.8: OCPs residue levels in fish during wet season (µg/kg)

Site/ Pesticide	BRIDGE(1)	EBENEZER(2)	ALAN(3)	LAWI(4)	KASUKU(5)
a-HCH	0.00±0.00	5.13 ±0.02	0.44 ±0.6	0.46 ±0.07	0.03 ±0.01
b-HCH	0.0	0.04 ±0.01	10.10 ±0.3	< 0	0.56 ±0.3
g-HCH	0.0	< 0	0.0	< 0	< 0
d-HCH	< 0	< 0	0.69 ±0.03	0.0	< 0
Heptachlor	< 0	6.65 ±0.00	0.41 ±0.007	< 0	2.47 ±0.00
Aldrin	< 0	< 0	0.02 ±0.002	< 0	0.19 ±0.1
Heptachlor Epoxide	< 0	0.0	0.04 ±0.00	< 0	0.0
Endrin	0.0	0.03 ±0.03	0.02 ±0.02	0.0	6.74 ±0.00
pp-DDE	< 0	< 0	< 0	< 0	< 0
a-Endosulfan	0.0	0.09 ±0.09	0.03 ±0.03	0.0	1.27 ±0.00
Dieldrin	0.0	0.0	0.15 ±0.2	0.0	0.0
Endrin Aldehyde	0.0	0.0	0.0	0.0	0.0
PpDDT	0.0	0.02 ±0.00	0.58 ±0.01	0.0	0.66 ±0.8
b- Endosulfan	0.0	0.05 ±0.03	0.07 ±0.003	0.0	0.07 ±0.07
pp-DDD	0.0	0.01 ±0.00	0.01 ±0.002	0.0	0.0
Endosulfan Sulfate	0.0	0.0	0.0	0.0	0.0
Methoxychlor	0.02 ±0.01	0.01 ±0.004	0.11 ±0.005	0.04 ±0.01	0.03 ±0.01
∑OCP	0.03	5.38	12.67	0.50	12.02

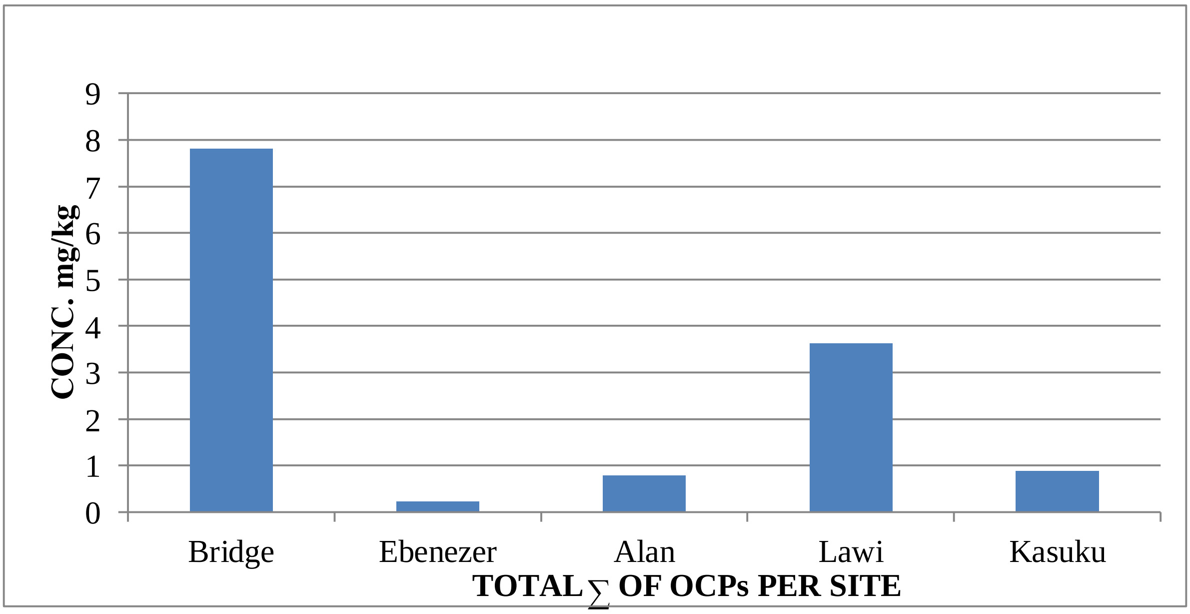
APPENDIX III

SUMMATION OF OCPs LEVELS PER SITE

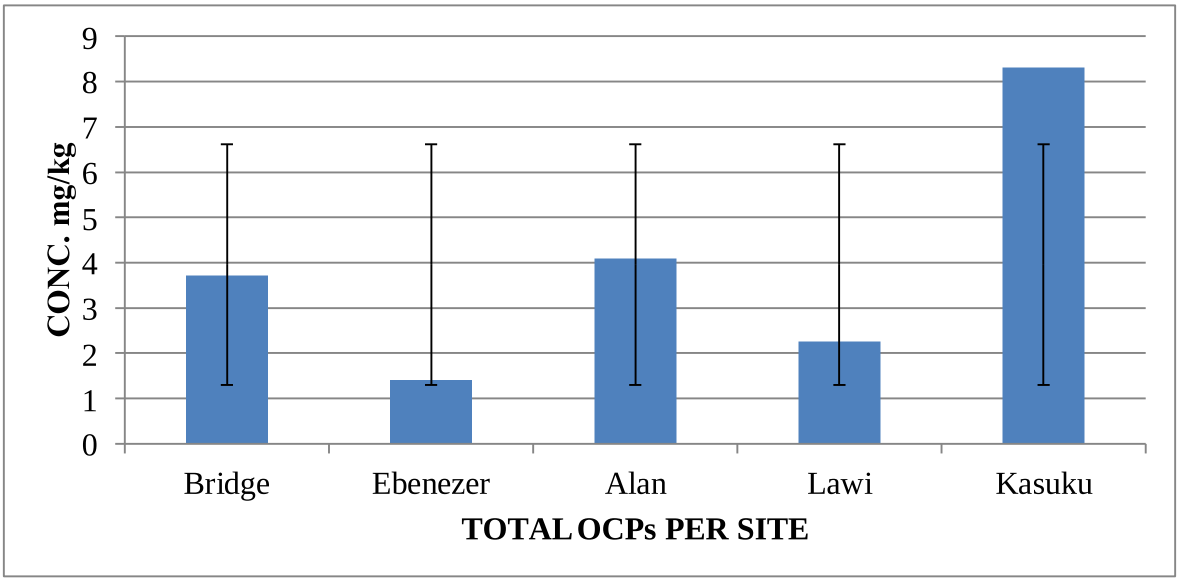


A3.1: **Summation of OCPs in water samples per site during dry season**

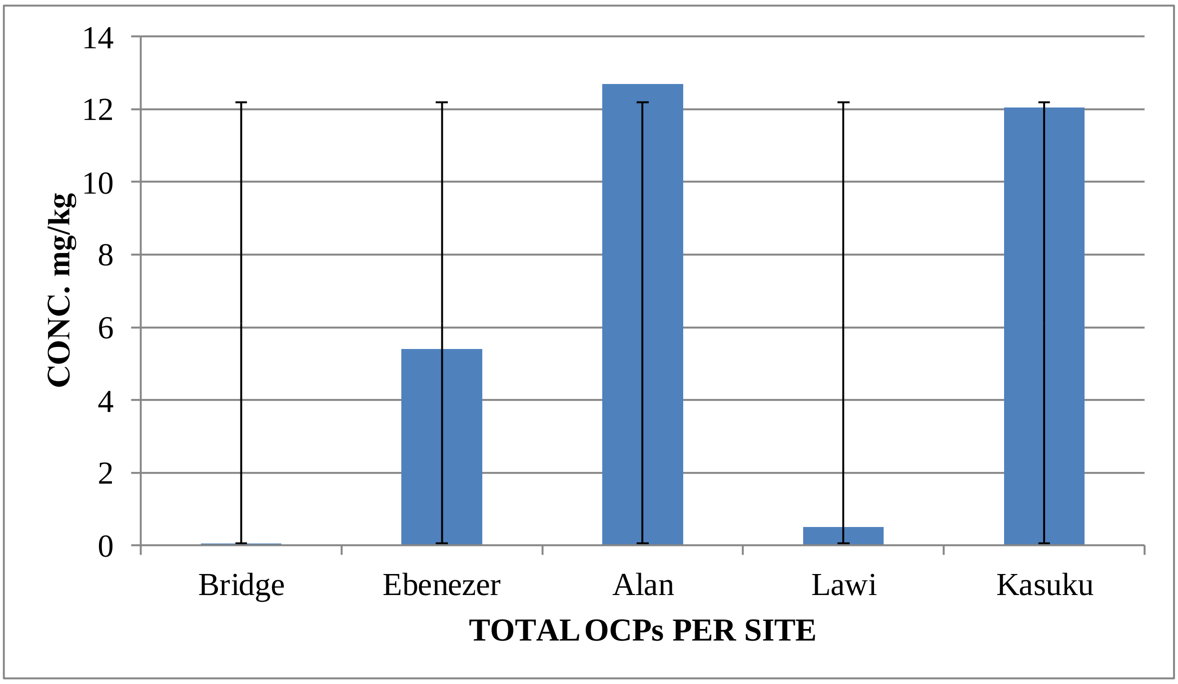
A3.2: Summation of OCPs in water samples per site during wet season



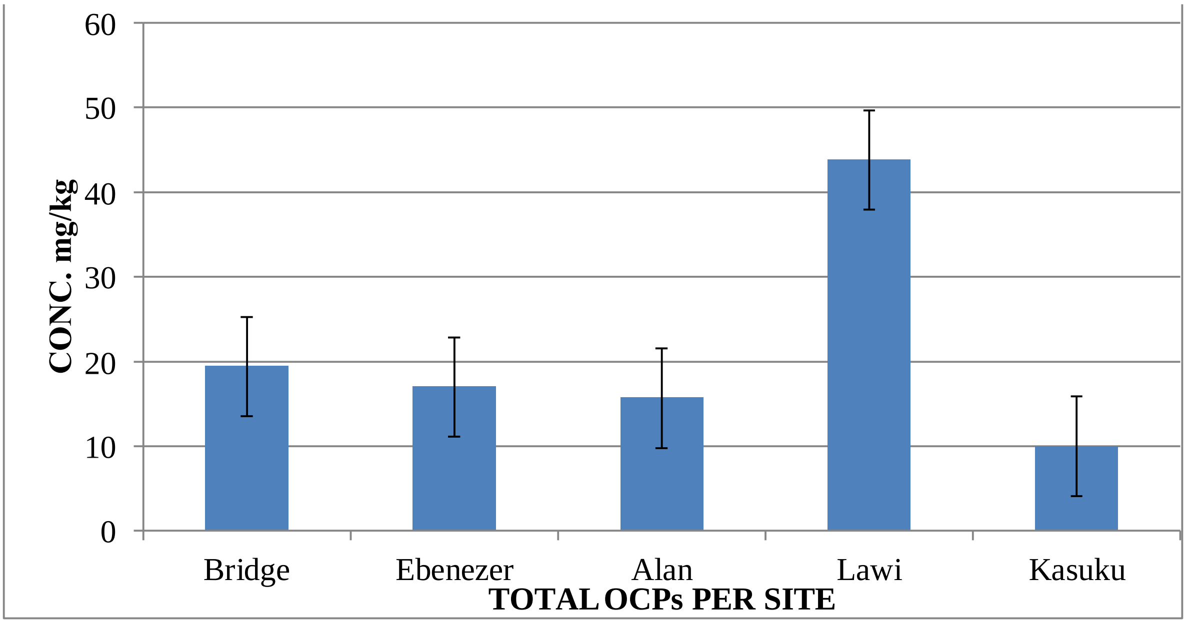
A3.3: Summation of OCPs in sediment samples per site during dry season



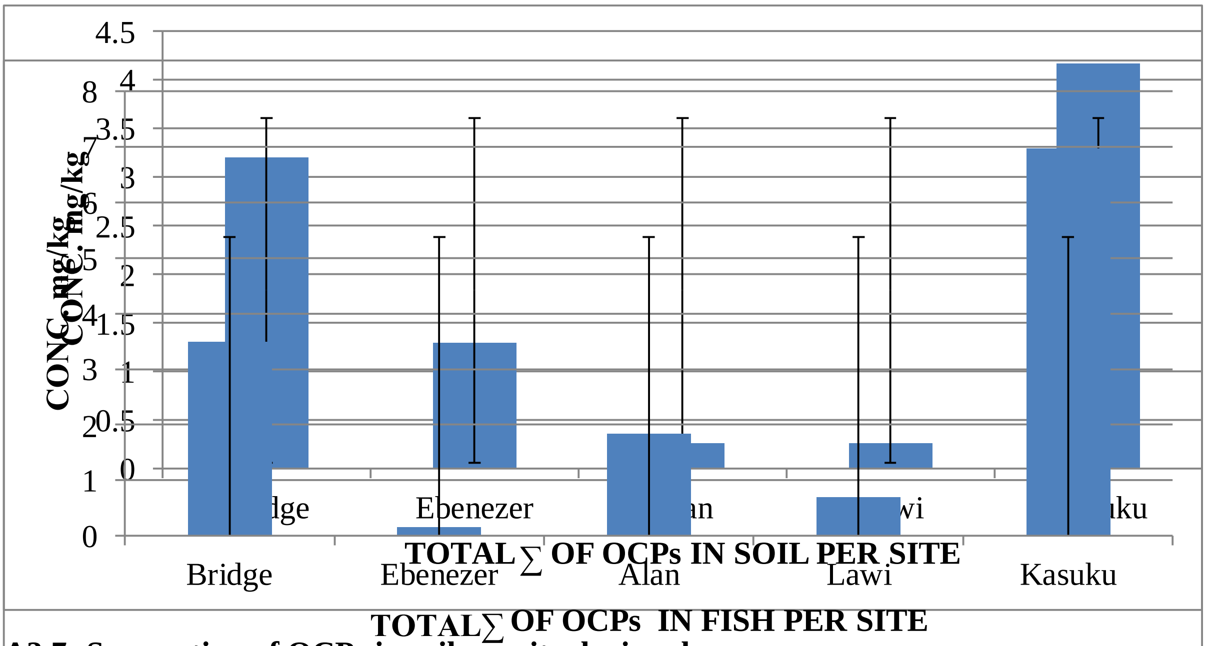
A3.4: Summation of pesticides in soil per site during wet season



A3.5: Summation of pesticides in fish per site during wet season



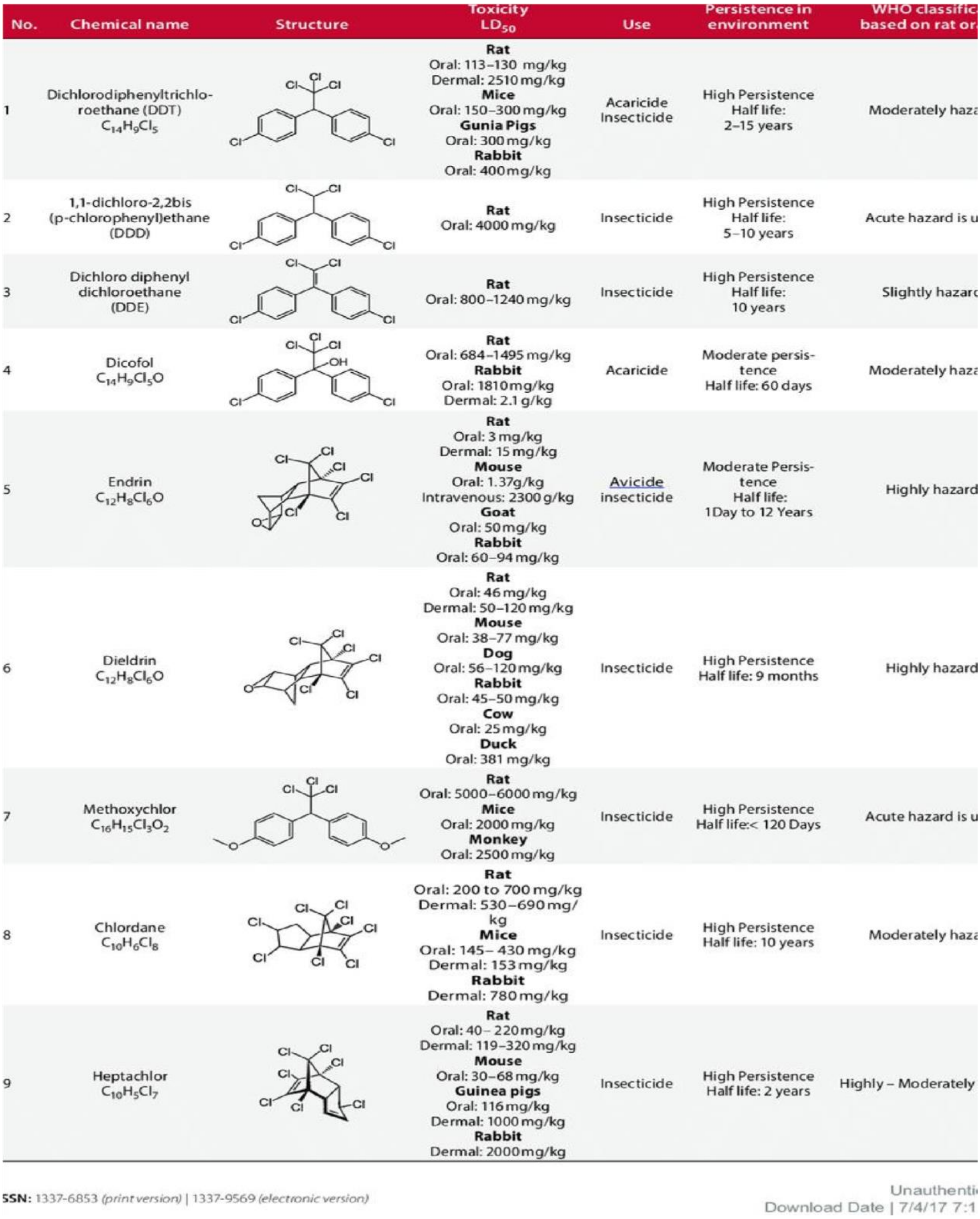
A3.6: Summation of OCPs in sediments per site during the dry season



A3.7: Summation of OCPs in soil per site during dry season

A3.8: Summation of OCPs in fish per site during the dry season **APPENDIX IV**

STRUCTURES OF SOME OF THE ORGANOCHLORINE PESTICIDES



No.	Chemical name	Structure	Toxicity LD$_{50}$	Use	Persistence in environment	WHO classific based on rat or
1	Dichlorodiphenyltrichloroethane (DDT) $C_{14}H_9Cl_5$		**Rat** Oral: 113–130 mg/kg Dermal: 2510 mg/kg **Mice** Oral: 150–300 mg/kg **Gunia Pigs** Oral: 300 mg/kg **Rabbit** Oral: 400 mg/kg	Acaricide Insecticide	High Persistence Half life: 2–15 years	Moderately haz
2	1,1-dichloro-2,2bis (p-chlorophenyl)ethane (DDD)		**Rat** Oral: 4000 mg/kg	Insecticide	High Persistence Half life: 5–10 years	Acute hazard is u
3	Dichloro diphenyl dichloroethane (DDE)		**Rat** Oral: 800–1240 mg/kg	Insecticide	High Persistence Half life: 10 years	Slightly hazar
4	Dicofol $C_{14}H_9Cl_5O$		**Rat** Oral: 684–1495 mg/kg **Rabbit** Oral: 1810 mg/kg Dermal: 2.1 g/kg	Acaricide	Moderate persistence Half life: 60 days	Moderately haz
5	Endrin $C_{12}H_8Cl_6O$		**Rat** Oral: 3 mg/kg Dermal: 15 mg/kg **Mouse** Oral: 1.37g/kg Intravenous: 2300 g/kg **Goat** Oral: 50 mg/kg **Rabbit** Oral: 60–94 mg/kg	Avicide insecticide	Moderate Persistence Half life: 1Day to 12 Years	Highly hazard
6	Dieldrin $C_{12}H_8Cl_6O$		**Rat** Oral: 46 mg/kg Dermal: 50–120 mg/kg **Mouse** Oral: 38–77 mg/kg **Dog** Oral: 56–120 mg/kg **Rabbit** Oral: 45–50 mg/kg **Cow** Oral: 25 mg/kg **Duck** Oral: 381 mg/kg	Insecticide	High Persistence Half life: 9 months	Highly hazard
7	Methoxychlor $C_{16}H_{15}Cl_3O_2$		**Rat** Oral: 5000–6000 mg/kg **Mice** Oral: 2000 mg/kg **Monkey** Oral: 2500 mg/kg	Insecticide	High Persistence Half life:< 120 Days	Acute hazard is u
8	Chlordane $C_{10}H_6Cl_8$		**Rat** Oral: 200 to 700 mg/kg Dermal: 530–690 mg/kg **Mice** Oral: 145– 430 mg/kg Dermal: 153 mg/kg **Rabbit** Dermal: 780 mg/kg	Insecticide	High Persistence Half life: 10 years	Moderately haz
9	Heptachlor $C_{10}H_5Cl_7$		**Rat** Oral: 40– 220 mg/kg Dermal: 119–320 mg/kg **Mouse** Oral: 30–68 mg/kg **Guinea pigs** Oral: 116 mg/kg Dermal: 1000 mg/kg **Rabbit** Dermal: 2000 mg/kg	Insecticide	High Persistence Half life: 2 years	Highly – Moderately

SSN: 1337-6853 *(print version)* | 1337-9569 *(electronic version)*

APPENDIX V

DATA CORRELATION

A5.1: Correlation of concentration of OCP in water, sediment and soil both in dry and wet seasons

	water dry	water wet	sediments dry	sediments wet	soil dry	soil wet	fish dry	fish wet
water pearson correlation dry sig (2 tailed) N	1 5	0.260 0.673 5	-0.805 0.100 5	-0.818 0.091 5	-0.107 0.864 5	-0.119 0.849 5	-0.231 0.708 5	0.595 0.290 5
water pearson correlation wet sig (2 tailed) N	0.260 0.673 5	1	0.279 0.649 5	-0.553 0.333 5	0.311 0.611 5	-0.476 0.417 5	-0.655 0.230 5	0.043 0.945 5
sediments pearson correlation dry sig (2 tailed) N	-0.805 0.100 5	0.279 0.649 5	1 5	0.519 0.371 5	-0.036 0.954 5	-0.241 0.696 5	-0.178 0.774 5	-0.721 0.169 5
Sediments Pearson correlation Wet sig (2 tailed) N	-0.818 0.091 5	-0.553 0.333 5	0.519 0.371 5	1 5	-0.213 0.731 5	-0.137 0.825 5	0.065 0.918 5	-0.752 0.143 5
Soil Pearson correlation Dry sig (2 tailed) N	-0.107 0.864 5	0.311 0.611 5	-0.036 0.954 5	-0.213 0.731 5	1 5	-0.137 0.825 5	0.065 0.918 5	-0.752 0.143 5
Soil Pearson correlation Wet sig (2 tailed) N	-0.119 0.849 5	-0.476 0.417 5	-0.241 0.696 5	-0.137 0.825 5	0.891 0.043 5	1 5	0.965 0.008 5	-0.612 0.273 5
Fish Pearson correlation Dry sig (2 tailed) N	-0.231 0.708 5	-0.655 0.230 5	-0.178 0.774 5	0.065 0.918 5	0.885 0.046 5	-0.965 0.008 5	1 5	0.423 0.477 5

Fish	Pearson correlation	0.595	0.043	-0.721	-0.752	0.424	0.612	0.423	1
Wet	sig (2 tailed)	.290	.945	.169	.143	.477	.273	.477	
	N	5	5	5	5	5	5	5	5

***Correlation is significant at the 0.05 level (2-tailed)**

****Correlation is significant at the 0.01 level (2-tailed)**

A5.2: Correlation of concentration OCPs with selected heavy metals

		Soil Dry	Soil Wet	Sediment Dry	Sediment Wet	Water Dry	Water Wet
Soil Dry	Pearson Correlation	1	-0.783	-0.035	-0.595	-0.938	-0.262
	Sig (2-tailed)		0.118	0.955	0.290	0.018	0.670
	N	5	5	5	5	5	5
Soil Wet	Pearson Correlation	0.783	1	0.448	0.908	0.708	0.745
	Sig (2-tailed)	0.118		0.449	0.035	0.181	0.149
	N	5	5	5	5	5	5
Sediment Dry	Pearson Correlation	-0.035	0.448	1	0.782	-0.075	0.817
	Sig (2-tailed)	0.955	0.449		0.118	0.905	0.092
	N	5	5	5	5	5	5
Sediment Wet	Pearson Correlation	-0.595	0.904	0.782	1	0.489	0.881
	Sig (2-tailed)	0.290	0.035	0.118		0.403	0.049
	N	5	5	5	5	5	5
Water Dry	Pearson Correlation	-0.938	0.708	-0.075	0.489	1	0.080
	Sig (2-tailed)	0.018	0.181	0.905	0.403		0.899
	N	5	5	5	5	5	5

APPENDIX VI

LIMITS OF SELECTED HEAVY METALS, ESSENTIAL ELEMENTS AND MICRONUTRIENTS

Table A6.1: Limits of selected heavy metals in drinking water, soils and vegetables by WHO, Kenya, USA EPA

Organization/country	Variables whose standards were reviewed	Recommended limits for studied heavy metals (ppm)				
		Cd	Pb	Cr	Zn	Cu
WHO	Drinking water	0.005	0.01	0.1	NG	NG
	Soil or Agriculture	0.003	0.1	0.1	NG	NG
KENYA(NEMA,KEBS)	Drinking water	0.01	0.01	NG	NG	NG
	Soils for Agriculture	NG	NG	NG	NG	NG
	Plants/Vegetables	0.05	0.3	NG	NG	NG

Ppm refers mg/kg or mg/L, NG…means not given

Source: http://www.agritech.tnau.ac.in

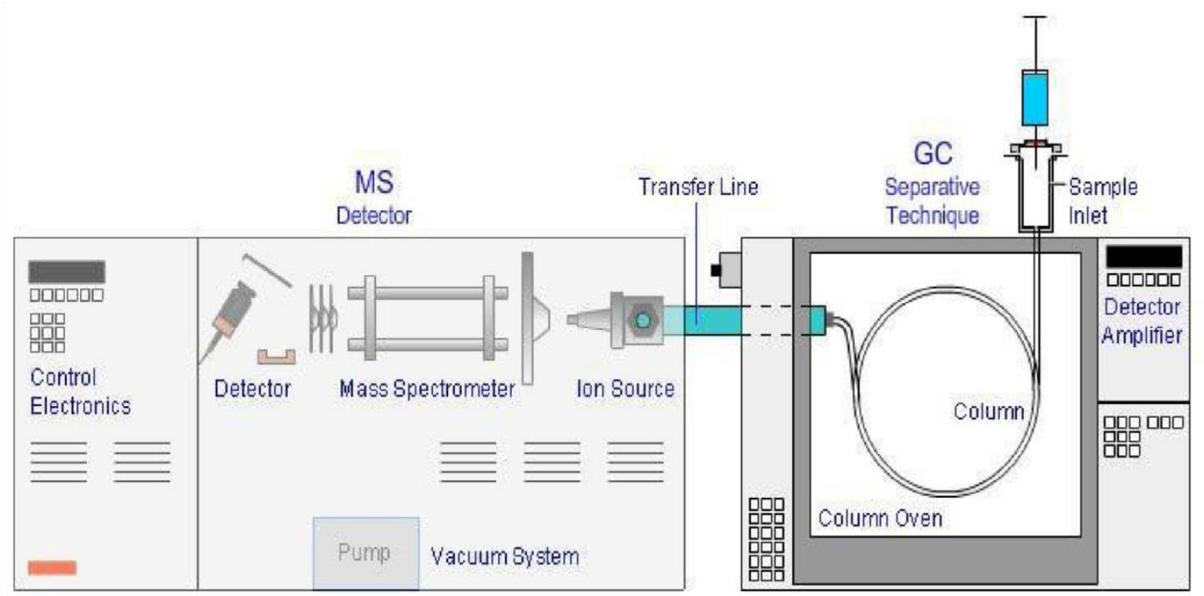
A6.2: Ranges of essential elements and micronutrients in Soil

Essential elements	% Deficient	% Sufficient or normal	% Excessive or Toxic
Major Elements			
Nitrogen (N)	< 2.50	2.50-4.50	> 6.00
Phosphorus (P)	< 0.15	0.20-0.75	> 1.00
Potassium (K)	< 1.0	1.50-5.50	> 6.00
Calcium (Ca)	< 0.50	1.00-4.00	> 5.00
Magnesium (Mg)	< 0.20	0.25-1.00	> 1.50
Sulfur (S)	< 0.20	0.25-1.00	> 3.00
Micronutrients	**ppm**	**Ppm**	**ppm**
Boron (B)	5-30	10-200	50-200
Chlorine (Cl)	< 100	100-500	500-1,000
Copper (Cu)	2-5	5-30	20-100
Iron (Fe)	< 50	100-500	> 500
Manganese (Mn)	15-25	20-30	300-500
Molybdenum (Mo)	0.03-0.15	0.1-2.0	>100
Zinc (Zn)	10-20	27-100	100-400

Source: http://www.agritech.tnau.ac.in

APPENDIX VII

COMPONENTS OF GC-MS MACHINE



A5.1 Schematic diagram of GC-MS

APPENDIX VIII

PICTORIAL REPRESENTATION OF THE STUDY SITES

A8.1: Catching fish samples in one of the fishpond sites

A8.2: With KEMFRI staff investigating some of the water parameters usingYSI Multi Parameter.

A8.3: Illustrating storage of samples in a freezer after sample collection in KEMFRI Lab