UNIVERSITY OF NAIROBI

ASSESSMENT OF ORGANOCHLORINE PESTICIDE RESIDUES IN WATER, SEDIMENT, SOIL AND KHAT (*Catha edulis*) IN IGEMBE SOUTH, MERU COUNTY, KENYA

BY

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DECLARATION

This thesis is the original work of the author except where due references are made. It has not been submitted partially or wholly for the award of a degree to this or any other institution of learning

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DEDICATION

In memories of my mother Rael Mpekethu who taught me discipline and hard work and led by example for all the years.

ACKNOWLEGMENT

ABSTRACT

Organochlorine pesticides (OCPs) are highly persistent in the environmental media including soil, water, and air, and are also widely detected in food materials. High levels of OCPs are associated with diverse ill health effects that include carcinogenicity, teratogenicity, endocrine disruption, immune system suppression, and environmental degradation. There is inadequate data on the extent of OCPs contamination in Igembe South sub county. Hence, the aim of this study was to determine the organochlorine pesticide residues levels in water, sediments, soil and khat from selected points in Igembe south in Meru County where khat has been cultivated over the years. The study was guided by interviews using structured questionnaires to gain data on the kind of pesticides applied in the area. Thereafter, field sample collection and testing of khat, sediments, water, and soil samples to determine organochlorine pesticide residue levels was carried out. Soil and khat were sampled from farms where khat is grown, while sediments and water sampling done from the Ura river traversing the farms. Soxhlet method was applied during extraction of pesticides from soil, sediments and khat samples while solvent-solvent extraction method applied to extraction from the water samples. The extracts were cleaned by eluting with HPLC grade n-hexane through preconditioned aluminum oxide chromatographic column and concentrated using a rotary evaporator and further concentrated under a stream of nitrogen to 500 µL. Samples were analyzed for presence of 17 OCPs using a gas chromatograph equipped with an electron capture detector. The mean values of physicochemical parameters of River Ura water ranged between 6.7±0.04 and 7.8±0.04 for pH, 48±0.58 to 167±1.15 µS/cm for electrical conductivity and 25±1.15 to 88±1.00 mg/L TDS levels. The mean residue levels of organochlorine pesticides in the soil samples collected ranged from <0.001± 0.00 - 197.07±36.47 µg per kg with the highest recorded in soil samples from Anchenge sampling site in March 2016. In water, pesticide residue levels varied from <0.001± 0.00 to 5.64±0.99 µg/L with the highest levels recorded in water samples collected from Kiiji site in March. The sediment samples had pesticide residue levels varying from <0.001 to 134.96±24.36 µg/kg and the highest concentration was in sediment samples from Ikandu site collected in March. In the khat samples, concentrations ranged between <0.001 - 110.11±5.31 µg/kg. According to the findings, environmental samples from the Igembe South sub-county still contain DDT and its metabolites, heptachlor, aldrin, dieldrin, endrin, lindane, and other pesticides that have been banned. Organochlorine pesticide concentrations varied widely in water, soil, sediment, and khat. The variances were caused by differences in the site's locations, human activities, seasonal variations and environmental factors.

Key words: Organochlorine pesticides, Igembe South, soil, water, sediments, khat.

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ACRONYMS AND ABBREVIATIONS

ATSDR	Agency for Toxic Substances and Disease Registry
BDL	Below Detection Limit
CDC	Centers for Disease Control
DDE	Dichlorodiphenyldichloroethylene
DDT	Dichloro-diphenyl-trichloroethane
EPA	Environmental Protection Agency
FAO	Food and Agriculture Organization
GC-ECD	Gas Chromatography with an Electron Capture Detector
GOK	Government of Kenya
GPR	General purpose reagent
HCB	Hexachlorobenzene
HCH	Hexachlorocyclohexane
HPLC	High-performance liquid chromatography
IARC	International Agency for Research on Cancer
IUPAC	International Union of Pure and Applied Chemistry
KALRO	Kenya Agricultural and Livestock Research Organization
KMS	Kenya Meteorological Society
KNBS	Kenya National Bureau of Statistics
LOD	Limit of detection
NRC	Norwegian Refugee Council
OCPs	Organochlorine pesticides
Ops	Organophosphates
PCPB	Pest Control and Products Board
POPs	Persistence Organic Pollutants
SPSS	Statistical Package for Social Scientists
TDS	Total Dissolved Solid
UNEP	United Nations Environment
USEPA	U.S. Environmental Protection Agency
WHO	World Health Organization

UNITS OF MEASUREMENTS

μg/Kg	micrograms/Kilogram
μg/L	micrograms/Litre
μL	microliter
μS/cm	micro-Siemen per centimetre
mg/L	milligrams per Litre
ppm	parts per million

CHAPTER ONE

1. INTRODUCTION

1.1 Background information

Khat is a product of shrubs known as *Catha edulis*, consisting of leaves and shoots. It is perennial and cultivated mainly in Kenya, Ethiopia and Yemen (Simmons, 2008). Its leaves contain cathinone and cathene and are chewed to give the stimulant effects like that produced by tea, coffee and amphetamines (Yusuf, 2011). Cathinone and cathene are part of a category of organic substances known as phenylalkylamines (Wabe, 2011). The desirable effects after khat use are; alertness, anorexia and euphoria (Kalix, 1988). In the United Kingdom, there are two known types of khat, the Kenyan type called Miraa and the Ethiopian type called Harari. Miraa is thought to have a stronger effect than Harari (Al-Motarreb, 2002). It is also thought to have detrimental effects on society when used; hence the UK banned its imports (Kassim, 2015). Apart from the social disadvantages, it has been thought to have potential health effects on daily users like blurred vision, oral cancer, and risk of stroke, gastrointestinal diseases, hypertension and tachycardia (Hassan *et al.,* 2007).

There is a study that has also associated chewing of khat with low serum albumin and protein in the blood of the users (Al-Ashwal *et al.,* 2013). In addition, some levels of pesticides used in khat farming are thought to contaminate khat products (Ashraf *et al.,* 2016). The concern is that people do not wash khat before chewing hence ingesting some pesticide residue levels, which may lead to cancer of the digestive tract or kidney failure (Stuyt, 2011). According to Date *et al.* (2004), there are a number of deaths reported caused by ingestion of poisonous chemicals (pesticides) used in khat farming.

The Ethiopian were khat samples analyzed revealed the presence of pesticide residue levels in some areas. Diazinon residual levels ranged from 173.9-751.4 µg/kg of khat compared to the EU recommended levels for fruits and vegetables of 10 µg/kg. DDT and its products ranged from 709.0 ±457.9 µg/kg to 755.57±394.0 µg/kg compared to the European Union guideline for

vegetables and fruits of 0.05 µg/kg (Daba, 2011), while aldrin concentrations in the khat samples, were below the threshold for detection. The presence of organochlorine pesticides used in khat farming has been connected to oesophageal and oral cancers among the consumers of the product (Al-Hadrani, 2000). In addition, organochlorine pesticides are of environmental concern worldwide because of their persistence, tendency to build up in biota, chronic toxicity and potentially harmful effect on humans and other animals. Consequently, trading and application of several organochlorine pesticides has been declared illegal worldwide, including Kenya. However, several are being used illegally since they are cheap and effective. Environmentalists have also shown that once pesticides are applied to the crop in the field, the activity may be transferred to the surrounding environment, such as water, soil, air sediments and other non-target plants and animals (Ravindran *et al.,* 2016).

In Kenya, Miraa is commonly grown in Meru County, particularly in the former Meru North (Nyambene) region, which includes Igembe North, Igembe South, Igembe Central and Tigania East Sub Counties. Khat is the one crop known to boost the economy of these communities. The outstanding cash crop is of great benefit to farmers because it is grown for the domestic and export markets (Carrier, 2005a; Carrier, 2005b; Klein *et al.,* 2009). Moreover, earlier, in the export market, tonnes of khat were sold abroad; in Amsterdam, London and also Somalia, while a good amount was sold in the local market (Mwagha and Ntong'ondu, 2014).

Pesticides are widely applied in khat farming to prevent insect pests attack and fungal infections and is usually carried out on a monthly basis immediately after harvesting. Consequently, the focus of the current research was to establish the residual quantities of pesticides with organochlorine compounds in the environment and the produce of miraa farming.

Farmers apply pesticides on khat to curb pests and fungal diseases that reduce growth and production of the plants (Daba, 2011). However, those who consume or chew khat that has been treated with a variety of pesticides may develop acute adverse signs such as stomach irritation, dryness of mouth, swollen belly, headaches and loss of appetite (Klein *et al.,* 2009). Also, little has been done on the social and public health impacts of the production, marketingand use of khat (Kassim, 2015).

1.2 Statement of the problem

Organochlorine pesticides are potentially carcinogenic, neurotoxic and immune-toxic substances (Taiwo, 2019; Ravindran *et al.,* 2016). They are also implicated health challenges such as low sperm count, birth defects, reproductive malfunctions and deformities, Parkinson's disease (Leena *et al.,* 2012; Sosan, *et al.,* 2008;), endocrine disruption, and many other developmental disorders. OCPs are environmentally persistent, bioaccumulate in fat cells, and biomagnify in food chain (Schecter *et al.,* 2010; Ravindran *et al.,* 2016). Hence OCPs are compounds of international concern (Karlaganis *et al.,* 2001).

Previous research has indicated the existence of OCPs with regard to the environment media such as air, water, soil, sediments and fish due to previous use among other factors (Wandiga *et al.,* 2002; Abong'o *et al.,* 2018; Madadi, 2006). Data regarding OCPs residues is lacking in Igembe South despite having been widely used in the area in the past. Hence, investigating the kind of pesticides employed in khat cultivation together with the OCP environmental residues quantities in water, soil, sediments and khat was necessary to provide missing data on potential human health and environmental risks of exposure.

1.3 Hypotheses

There is no environment contamination as a result of pesticides applied during khat cultivation.

1.4 Objectives

1.4.1 Overall objective
To determine the extent of environmental contamination by the organochlorine pesticides residue levels in khat farming areas, Igembe South Sub County, Meru County.

1.4.2 Specific objectives
1.Identify the type of pesticides used in khat farming in Igembe South Sub County, Meru County.

2.Determine the residue levels of the selected organochlorine pesticides (OCPs) in soil, water and sediments from Ura River in Igembe South Sub County.

3.Determine the organochlorine pesticide residue levels in khat sold in selected markets in Igembe South sub-County.

4.Determine seasonal variation in the levels of OCPs in khat from local markets, soil, water and sediments from Ura River in Igembe South Sub County.

1.5 Justification

Despite the immense importance of the use of pesticides, the contamination may also come due to poor knowledge of the harm the chemicals are likely to bring to the environment on or after uncontrolled use. This include; soil and surface water contamination in areas where there is the heavy and persistent application of pesticides (Aktar *et al.,* 2009). Other effects may be poisoning plus bad health implications for the immediate users on exposure if good handling methods are neglected or unknown (Drum, 1980). This poisoning by any type of hazard is estimated by toxicity, dose and duration of exposure to the pesticide (USEPA, 2006). Furthermore, the target pests can develop resistance after wrong or long use of a certain chemical /pesticide leading to constant change in the type of chemicals used. The pesticide residues in human and animal food products can translate to transfer and also bio magnifications along the entire food chain (Arias-Estévez *et al.,* 2008).

Organochlorine insecticides were often used by farmer previously for khat and other crops to keep plants safe from insects and disease. It is possible that these pesticides are widely dispersed and deposited into the environment affecting non-target organisms (Arias-Estévez *et al.,* 2008; Marete *et al.,*2021). Pesticide residues may also remain in the plant materials that are consumed (Bhattacharjee, 2013). No information about OC pesticide residue levels on the environment and the consumed Khat plant parts from Igembe South, hence the need to conduct this research.

CHAPTER TWO

2. LITERATURE REVIEW

2.1 Pesticides

Pesticides are a group of chemicals that help in controlling pests and their effects by either attracting and killing or repelling them to minimize their detrimental effects (Taylor *et al*., 2003). They help in downsizing or complete removal of the negative impacts of pests/ parasites so as to improve and maintain the quality and quantity of the farm produce (FAO, 1989). According to WHO/UNEP (1990), pesticides are chemicals made to kill vectors and pests in agriculture and also at the domestic level. Apart from farms, pesticides are also used in homes, hospitals, and recreational and industrial areas (Tano, 2011). Pests are known to compete for nutrients with plants or animals and hence affecting their health and productivity.

2.2 Agriculture and pesticides

The application and using pesticides in farming dates back to the agrarian revolution. The pesticide industry grew over the years as more demand for crop production surfaced and soil fertility went down (Muir, 2002). However, unlike the first generation of pesticides, modern pesticides date back to the 19th century. The first generation included the highly toxic arsenic compounds, hydrogen cyanide and Bordeaux mixture (copper sulphate) (IUPAC, 2010). The second generation had synthetic organic compounds as pesticides, with the 'miraculous' dichlorodiphenyltrichloroethane (DDT) in 1873 being the first in the category to be synthesized (WHO, 1995). DDT was effective because it had a wider spectrum of action and cheaper. However, it was later known to be troublesome and dangerous because of its bio-magnifications in the biota (Briggs, 1992). Apart from DDT, other pesticides are known to be useful but with also undesirable implications that accompany their use (Aktar *et al.,* 2009).

2.3 Identification and classification of pesticides

Pesticide formulation usually includes carrier/diluents, binders, dispersants, active ingredients and preservatives (Tano, 2011). Mostly, pesticides have their active ingredients referred to by common names depending on the manufacturer. They are also identified using the systematic name to show their chemical nature. There are many ways of classifying pesticides, but in chemistry, classification by chemical structure is the most important (Buchel, 1983). Based on their chemical nature, pesticides are in two main classes; organic and inorganic pesticides.

Inorganic pesticides contain cyanide, arsenic, mercury and sulphur, which makes them able to persist in the ecosystem (Hassall, 1990). Contrarily, organic pesticides may be natural or synthetic (Unsworth, 2010; Hay, 2012). Natural organic pesticides are mainly from plants, while syntheticpesticides usually are either aromatic or aliphatic hydrocarbon groups, which are; organophosphorus, organochlorine, pyrethrins and carbamates. This classification depends onthe active group in the main hydrocarbon system.

2.3.1 Organophosphorus pesticides

Organophosphorus insecticides contain a phosphate group in their formula: R1 PO (OX) R2, R groups are ethyl or methyl groups, and O on the OX groups may be replaced with S, and the X group takes a wide range of forms (Balali-Mood *et al.,* 2012). They act as cholinesterase inhibitors causing nervous impulses to fail hence involuntary muscle twitching, paralysis and death depending on the exposure. Whereas organochlorine compounds are persistent, organophosphates readily break down in the environment (Martin, 1968). Routes of exposure include dermal, ingestion and inhalation (Balali-Mood *et al.,* 2012). The breakdown of both OPs and carbamates is catalyzed by pH, temperature or both, and their existence in the environment ranges from days to months (Arias-Estévez *et al.,* 2008). The major organophosphorus pesticides include; acephate, azamethiphos, azinphos ethyl azinphosmethyl, bromophosethyl, dimethoate, diazinon, phosmet, fenitrothion, chlorpyrifos, ethyl, dichlorvos, menazon, dioxathion, chlormephos, malathion, adifenphos, ethion, ethopropos, etrimfos, dimethoate, parathion-methyl, trichlorfon, methidathion, naled, famphur,

oxydemeton-methyl parathion among others (Richardson and Seiber, 1993).

2.3.2 Organochlorine pesticides

They are usually chlorinated compounds made for the purpose of killing or deterring pests and are known to be persistent in different environmental compartments. They were used for a number of years in the past but due to their nature of slow degradation, they have been detected in soil, water sediment and also plants. This is years later after they were banned. Persistent organochlorine pesticides contain chlorinated hydrocarbon components, and as a result, they breakdown slowly and build up in the animal's fatty tissues (Schecter *et al.,* 2010).

Due to their intrinsic toxicity and frequent links to detrimental health effects on non-target organisms and the environment, the majority of organochlorine pesticides are prohibited. They conducted a study on human serum for people from Dallas, Texas. Among the organochlorine pesticides examined, lindane, oxychlordane, *p,p'*-DDT and trans-nonachlor were frequently observed in the human serum of all the individuals involved (Schecter *et al.,* 2010). To safeguard people and the ecosystem against POPs, the Stockholm Convention considered several OCPs as part of POPs. Aldrin, endrin, heptachlor epoxide, dieldrin, chlordane, mirex, Hexachlorobenzene (HCB), dichlorodiphenyltrichloroethane (DDTs),toxaphene, heptachlor, and Hexachlorocyclohexane (HCHs) are a few examples (Schecter *et al.,* 2010).

The OC pesticide structure consists of chlorinated aromatic rings/hydrocarbon chain andcarries features of bioaccumulation, toxicity and persistence. When a material has a half-life insediment or soil that is longer than six months or two months in water, it is said to be persistent.The other conspicuous characteristic is their lipophilic nature and tendency to bio-accumulate in the fatty tissues. They are also water-insoluble, a property that enables them to be easily carried by wind over a long distance (Wania & Mackay, 1995).

2.3.2.1 Lindane

Lindane, also known as gamma hexachlorocyclohexane (ɤ-HCH), is an organochlorine pesticide that was used in seed treatment before being banned in the United States in 1984. The

Stockholm Conventionprohibits it in the majority of countries around the world. When it enters the soil, it adheres strongly and has a 3–6-year half-life (Sang *et al.,* 1999). HCH is not soluble in water and cansettle to the bottom and becomes part of the sediments, hence it accumulates in aquatic life andbiomagnifies up the food chain (Bhattacharjee, 2013). Finally, it typically does not evaporate in the atmosphere, but if it does, it can be transported by wind. HCH may enter the human bodythrough, breathing low levels of it in the air, consuming contaminated foods and drinking polluted water. Babies are also highly vulnerable to the chemical from breast feeding contaminated milk. HCH has been linked with liver disease, harming the immune system,and damaging the nervous system, kidneys, blood, bones, thyroid gland, and endocrine system (Sohail *et al.,* 2004; Kaiser, 2000).

2.3.2.2 Mirex

Mirex was produced in 1940 and had been in the market as a pesticide from 1955, but banned in the USA around 1978. It was mainly used to control fire ants and in paint, rubber, plastic and electrical goods as fire accelerants. Mirex is not easily degradable once it enters the atmosphere (Zhang *et al.,* 2008). It strongly binds to both the soil and sediment particles. It is also insoluble in water, so it will settle to the bottom once it enters a water body. Due to its longhalf-life, it builds up in fish and other aquatic organisms, which feed on organisms that use sediments as food and biomagnifies up the food chain (Zhang *et al.,* 2008). Although it is still unclear what the health effects of mirex are on people, we can conclude with absolute certaintyof the effects it has on humans because of a similar compound found in Chlordecone, which has effects on the skin, liver, nervous system, and the male reproductive system. Hooker Chemical manufactured mirex as a chlorinated fire-resistant.

2.3.2.3 Aldrin and its analogues

Aldrin and its analogues were famous from the 1950s up to the 70s. Aldrin was first produced in 1948 but was manufactured in 1950. An oxygenated metabolite of Aldrin is dieldrin, which is its pesticide product (WHO, 2003). Aldrin is rarely detected in the environment because it easily degrades into dieldrin (NRC, 1982). Endrin, a stereoisomer of dieldrin, is said to have

been popular in cotton farming. These groups of chemicals were banned for agricultural use in most countries or prevented from non-agricultural applications with the US implementing the ban in 1987 (ATSDR, 2002). Acute exposure to endrin causes dizziness, nausea, headaches, confusion, and vomiting. Endrin is not classified as a carcinogen. Endrin can also be transmitted to babies through breastfeeding (Mueller *et al.,* 2008). Figures 1.1-1.3 below show the structures of aldrin, endrin and dieldrin respectively.
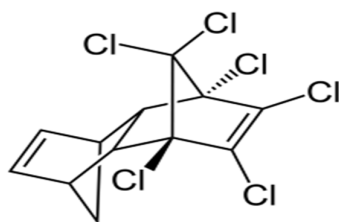
Figure 1.1: Aldrin
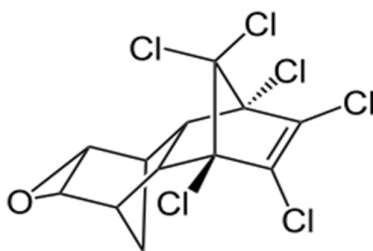
Figure 1.2: Endrin
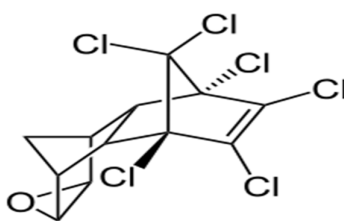
Figure 1.3: Dieldrin

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2.3.2.4 Dichlorodipenyltrichloroethane (DDT)

DDT was widely used for agriculture in World War II but was banned in 1972. One of its analogues, *p,p'*-DDE, is estimated to have a half-life of above seven years in humans. Studies have shown this pesticide in the blood serum of people exposed to it directly and indirectly (Subramaniam & Solomon, 2006). It has been suspected that DDT is a possible mutagen, carcinogen and teratogen. High exposure to DDT has been found to cause egg thinning in birds. DDT is also highly toxic to aquatic life (Jiang *et al.,* 2009). Rusiecki *et al.* (2008) study looked at DNA methylation levels in a human population and environmental exposure to organochlorine persistent pollutants like DDT and concluded that global methylation levels were adversely correlated with blood plasma levels. Figure 1.4 show structures of DDT and
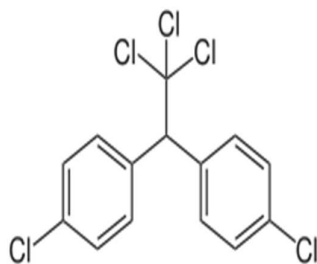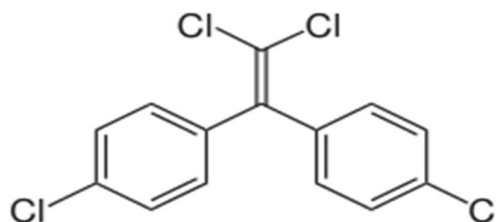
    4,4'-Dichlorodiphenyltrichloroethane   *4,4'*-Dichlorodiphenyldichloroethene

Figure 1.4: Structures of DDT and its metabolite p,p'-DDT respectively

According to WHO, DDT has been a great help to public health, particularly in the fight against malaria (WHO/UNEP, 1990). However, because of its persistence in the environment and subsequent bioaccumulation in plants and animals, there has been widespread concern. DDT is not easily degradable due to its stability, so it has been found in the environment long after its use was discontinued. Though not immediately toxic, DDT and its metabolite cause deposition and accumulation primarily in adipose tissues, resulting in carcinogenic and neurological effects (van-Wendel *et al.,* 2001) and premature births (Turusov *et al.,* 2002) as well as defective births long after years of exposure (IARC, 1991) and (Kabasenche and Skinner, 2014). DDE which is a metabolite of DDT is known to be more potent than the parent compound as it is more persistent due to the long half-life in organisms and also the environment (Torres-Sánchez *et al.,* 2009).

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It has even been known that DDT and its metabolites have a high potential for adsorption in soil, a property linked to the soil's organic matter composition (Boul, 1995).

2.3.2.5 Endosulfan

Endosulfan's hazard is extremely concerning. This is due to the fact that it lasts a long time in the environment and contaminates human food after bio-accumulating in both plants and animals (Briz *et al.,* 2011). It works by having an impact on the nerve system. Endosulfan's gastrointestinal absorption is typically fairly high, but it was discovered that its acute inhalation toxicity was larger than its cutaneous toxicity (USEPA, 2010). Figure 1.5 shows the chemical structure for endosulfan.
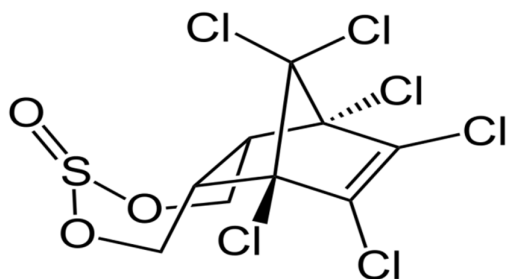
Figure 1.5: The Structure of endosulphan

2.3.2.6 Chlordane

Chlordane was introduced in 1948 as a pesticide. It was used for domestic and agricultural purposes (USEPA, 2016). Chlordane has a long half-life and may stay for over 20 years in soil particles. Its main mode of leaving the soil is through evaporation into the air (WHO/UNEP, 1990). Because it is difficult to dissolve in water, it builds up in adipose tissues of living things, both aquatic and terrestrial (ATSDR, 2013). Chlordane is highly toxic to earthworms, bees, fish, and aquatic life. The EPA ceased chlordane usage in 1978 and all uses were banned after 1988 (USEPA, 2016).

2.3.3 Carbamates

The general formula for carbamates contains the carbamic acid: R_1OOCNR_2 (Hassall, 1990). In this case the toxicity of both the aryl carbamates and oximes is important in the effectiveness of the pesticide (De Bleecker, 2008). The difference between the action of OPs and carbamates is that of the carbamate's inhibition is reversible while that of OPs is irreversible (Drum, 1980).

2.3.4 Pyrethrins

Pyrethrins are a group of pesticides whose origin is natural unlike the other classes of pesticides. Although there are synthetic pyrethrins, the original structure of the group is from the product the flowers of pyrethrum (Gunasekara, 2004). They are good because they act fast, are biodegradable and less toxic to human compared to other pesticides (ATSDR, 2003). Synthetic pyrethrins are made through modification of the original structure of pyrethrin; introducing a biphenoxy and halogens replace hydrogen to increase stability (Gunasekara, 2004). Some of the common pyrethrins are deltamethrin, cypermethrin and permethrin.

2.4 Possible pathways of pesticides in the environment.

When pesticides are applied, they can stay in the environment for a short while or for a long time, and in certain situations, they can travel to locations that are far from the original application site (Tiryaki & Temur, 2010). They can consequently be found in rivers/streams and also in groundwater (USEPA, 2006). This risk is usually related to farming and application techniques plus the natural conditions and processes like climate and soil properties, among others (USEPA, 2016). Other routes of exposure include accidental inhalation, especially in the surrounding where the pesticides are being applied (ATSDR, 2013).

Food chains can also be possible routes of exposure (Simcox, 1995). Ways of their dispersion include wind, air and water. They can also get adsorbed onto plants, soil, and structures and later washed into water sources or go into the water directly when it rains (USEPA, 2006). They may also fall from the field to streams or macropore flow-rapid passage into groundwater This dispersion is affected by the soil properties and composition. For example, microcavities in the

soil can delay their breakdown (Tiryaki & Temur, 2010). Also, soil composition and properties vary depending on geological origins, position in the landscape, climatic zone and the different cropping and soil management practices used (Arias-Estévez *et al.,* 2008). The risk of leaching increases if the binding is weak due to lack of organic matter in the soil (von der Ohe & Goedkoop, 2013; USEPA, 2006).

2.5 Pesticide regulation in Kenya

Pesticides were specifically addressed in the Food, Drugs and Chemical Substances Act of 1965 (Cap 254). Since then, parliament has passed the Forest Act, Cap. 318, the Water Act, Cap. 389, the Animal Food Act, Cap. 345, and the Agriculture Act, Cap. 318, all of which have an impact on pesticide application, dissemination and control.

The law that governs information on pesticides in Kenya is the Pest Control Product Act, which went into effect in 1983 (GOK, 1985). The law's main goal was to govern and manage the importation, production, distribution, and exportation of items used for pest control and the routine application of pesticides. The Act's creation, the Pest Control Products Board (PCPB), went into operation in 1984. The responsibilities of the PCPB outlined below.

2.5.1 Regulatory
Pest Control and Products Board (PCPB) controls the supply and distribution of pest control goods, analyze all pesticides and recommend them for use. It also Inspects and analyze any facility meant for manufacturing and storing pesticides and approve or register pesticides.

2.5.2 Technical

The technical duties of the PCPB include gathering and deciphering information about pesticides from important organizations including the UNEP, FAO, and EPA, as well as analyzing data from manufacturers on the benefits of pesticides.

2.5.3 Training
The training functions of the PCPB are to educate people about the risk of pesticides or pest

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control products and the impact of the use of pesticides.

2.6 Effects of pesticide use

Pesticides enable the farmers to get high yields due to less or no interference from pests. This, in turn, leads to an economic boost for the community or the person using the pesticides (Kishimba *et al.,* 2004). But the increased yield is directly proportional to the amounts of pesticides used per hectare. However, this is accompanied by bad environmental and public health effects like in the case of DDT, but later also proven to be of environmental health concern (Hay, 2012). Before its negative effect was known, the livelihood of many people was boosted because there were fewer deaths or sicknesses due to vector-borne diseases like malaria and also increased crop yield (WHO, 1995). However, it came with an effect on the environment due to their transfer and persistence in the environment.

2.6.1 Adverse health effects associated with pesticides

Among the many contaminants in the environment, pesticides hold a conspicuous place owing to their unique properties of acute and chronic toxicity and high biological activity (Alavanja *et al.,* 2014). They can be classified as biocides which can hurt other organisms apart from the target (Hatcher, 2008).

2.6.2 Effects related to organophosphate (OPs) exposure

The USEPA classifies organophosphate (OPs) as either moderately toxic or highly toxic substances (USEPA, 2006). They work by interfering with the nervous system through the inhibition of acetylcholinesterase (Hatcher, 2008). In case of acute exposure, symptoms such as nausea, twitching, headache, excessive salivation and tearing, convulsions and death are exhibited.

2.6.3 Developmental effects;

Due to their effects on the neurological system, the OPs affect behavioral development and cognitive function negatively (WHO, 2008).

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2.6.4 Reproductive effects

Since they interfere with the endocrine system, they lead to a significant twist in the reproductive system of human beings. There has been a relationship between the presence of organophosphate metabolites in humans with reduced levels of sex hormones including testosterone (Sheiner, 2003). Some epidemiologic research on Chinese workers in a pesticide factory showed that organophosphate exposure contributed to reduced concentration of sperms and high percentage of sperm mortality in semen (Padungtod *et al.,* 2000). The study also revealed a negative relationship between OP exposure and testosterone (Padungtod *et al.,* 1998) and increased sex chromosome aneuploidy in sperm (Padungtod *et al.,* 1999).

2.6.5 Cancer

Most reports delink OPs with cancer, but CDC reports several studies linking exposure to OP and lymphoma and/or leukemia (Eskenazi *et al.,* 1999). Another possible carcinogenic OP is dichlorvos (USEPA, 2006).

2.6.6 Parkinson's Disease

Parkinson's condition is a human neurological disease, and since OPs act by affecting the nervous system and the brain, there is a link between the two. There is an increased risk of Parkinson's disease for those who live close to applications of Dimethoate, Diazinon and chlorpyrifos (Hatcher, 2008).

2.7 Effects related to Organochlorine exposure

2.7.1 Diabetes

There is an alarm at the rate of diabetes cases arising worldwide in recent years (King, 1998). Some types of diabetes like type 2- diabetes have been linked to Organochlorine pesticide exposure in a study comparing levels of some OCPs in serum and cases of type 2 diabetes in America. The pesticides considered in the study were oxychlordane and trans–nonachlor (Lee, 2011). A similar study was done by Cox and others (Cox *et al.,* 2007) with similar results. In a research study done in Korea, diabetes was still associated with Organochlorine exposure (Son, 2010). There was another study that revealed *p, p'*-DDE association with diabetes in fish

consumers over a decade from 1994 to 2005 (Turyk, 2009).

2.7.2 Hormonal cancers, Breast and prostate Cancer

According to Snedeker (2001), epidemiologic evidence on the link between organochlorine exposure and hormone malignancies is insufficient and inconsistent. More research is being conducted to investigate the link between exposure and breast cancer cases in Japanese women. The serum concentrations of Hexachlorocyclohexane, dieldrin, and trans-nonachlor were associated to prostate cancer in a 1999-2004 survey data comparison between prostate and breast malignancies and serum concentrations of Organochlorine pesticides (Xu *et al.,* 2010).

2.7.3 Thyroid Hormonal Imbalance

Thyroid inactivity has been linked to most organochlorine pesticides (Meeker *et al.,* 2007), and an imbalance of thyroid hormones can affect maternal thyroid hormone levels during pregnancy. Autoimmune related issues on humans have also been reported as a result of exposure to the organochlorine pesticides (Sinaii *et al.,* 2002). However, Hagmar *et al.* (2001) indicated a negative association between *p,p'*-DDE and thyroid hormones in their studies. Exposure to *p,p'*-DDE to children was linked to lead to hyperactivity disorder (Sagiv *et al.,* 2010) confirming the neurotoxicity of DDT and its analogues. Mathew (2012), also linked organochlorine pesticides pollution to Parkinson's disease from epidemiology research.

2.7.4 Effects on human sperm production and count.

In South Africa, Limpopo province, where DDT is applied annually to prevent malaria, a study on the correlation between DDT exposure and the quality of semen in young men indicated that the quantities of *p,p'*-DDE in blood was inversely proportional to spermatozoa production and sperm mobility (Anneck, 2007). In another investigation, overall levels of *p,p'* -DDE and *p,p'*-DDT were linked to low sperm concentration, high sperm mortality, and sperm morphology in men in United States of America (Messaros *et al.,* 2009). Exposure to organochlorines and other PCPBs is also a neurotoxic and affects development of fetus during pregnancy (Jurewicz & Hanke, 2008).

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2.8 Related research on pesticides in Kenya and other East African countries

Various related research studies haves been previously conducted about the use of pesticides and their contamination of the environment. More emphases are on organochlorine pesticides because of the fact that they are persistent in the nature. Abong'o *et al.* (2015) did an analysis of levels of OC contamination in soil samples from the river Nyando catchment area between 2005 and 2006 in agricultural farms. The highest levels detected in soil were methoxychlor at 20.00±1.52 µg/kg, endosulphan at 30.27± 2.10 µg/kg and 18.32± 0.28 µg /kg of aldrin. The results indicated that the mean concentrations of methoxychlor (8.82± 0.0020 g/l) in water, silt (92.89 ±3.76 g/kg), and aquatic weeds (39.64± 3.05 g/kg) were higher. Additionally, the weed plants showed tendency to build up the aldrin (15.52 ±3.76 g/kg), according to Abong'o *et al*. (2018). Each and every targeted OCPs were found in the study. These studies revealed the presence of all the targeted OCPs. A study on sediments from lakes Natron and Bogoria and some acacia leavesfrom plants around the lakes, showed DDT residues even *p, p'*-DDT and *p, p'*-DDE (Bettinetti *et al.,* 2011). Although most of the organochlorine pesticides like DDT and other related compounds are banned, they are still detectable in the environmental samples. This is attributed to previous use, persistence, obsolete stocks, spreads from contaminated sites and also illegal use. (Macharia *et al.,* 2016; Wandiga *et al.,* 2002; Abongo *et al.,* 2018; Madadi *et al.,* 2006).

CHAPTER THREE

3. MATERIALS AND METHODS

3.1 Description of the study area.

The research was carried out in Meru County, Igembe South Sub-County (Figure 3.1), which houses the Nyambene forest. The forest is a major source of rivers in the area that provides Water to many households. Ura River is the main river in the area and cuts across the sub-county into the Meru National Park to join the Tana River (Trust for African rock art, 2008). Igembe's south area is in the South Eastern marginal mixed farming zone of the Tana River Basin in Kenya, and Ura River is used largely by khat farmers close to it for irrigating their farms for more crop yields (Baker *et al.,* 2015). Its tributaries, Mboone, Mwaamba and other rivers, are also used for the same purpose. The study area, lies within coordinates 0° 7' 30'' N -0° 15'0'' N and 37° 50'0'' E –38° 0' 0'' E. The land area of the sub-county is 255.2 km^2 and its population is 161,646 (KNBS, 2019).
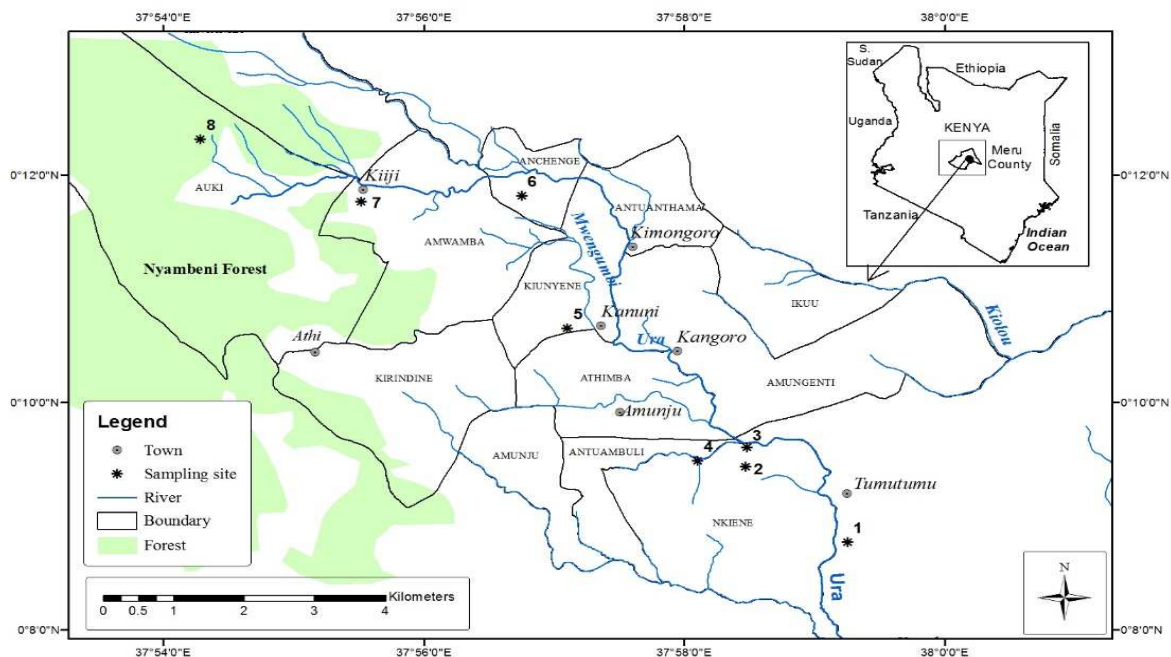
Figure 3.1 A map of Igembe south sub-county showing sampling sites

Eight sites were selected in the study area for sampling purpose (Table 3.1). The area has varied seasons, the driest being; January- March and August -September; the short rains come from October and November and the long rains in April and May as given by Kenya Meteorological Services (KMS, 2015).

Table 3.1:*Local names and description of the sampling sites*

Coded site	Sampling site	Coordinates	Altitude (m)	Human activities
1	Nyambene forest	037°54'17''E 00°12'19''N	1670	Forest, zero grazing, tea and khat along the forest boundaries,
2	Kiiji	37°55'31'' E 00°11'46'' N	1498.2	khat, tea, bananas, maize, beans, potatoes, yams, coffee and zero grazed animals
3	Anchenge	37°56'45'' E 00°11'49'' N	1392.11	khat, maize, beans, bananas and tea
4	Ikandu	37°57'06'' E	1256.6	khat, maize, beans, bananas, coffee

		00°10'39'' N		farming
5	Ikurone	37°58'06'' E 00°09'29'' N	1091.7	khat, maize, beans, bananas farming
6	Ntherone tributary	37°58'27'' E 00°09'29'' N	989.4	khat, beans, maize, mangoes farming
7	Ntherone	37°58'27'' E 00°09'30'' N	1011.7	khat, beans, maize, mangoes farming
8	Tumu- Tumu	37°59'15'' E 00°08'46'' N	947	khat, maize, beans, sorghum, green grams, millet, pigeon peas farming

3.1.1 Land use and sampling sites selection

The major activity in Igembe south sub-County is food and cash crop farming. The area has varied physical and climate conditions (Mwoga, 2014). A major part of Nyambene hills and forest, is a catchment area of rivers that join the Tana River in the sub-county. The rivers provide Water for domestic and agricultural use (Baker *et al.,* 2015). Ura River enters Meru National Park where it joins the Tana River. The uplands of Igembe South have tea, khat and food crops while low lands have most khat with maize, beans, bananas and vegetables. Though not much now, coffee was a major cash crop in the 1950-80s but was replaced by khat farming (Harrison *et al.,* 2019). Along the Ura River, eight sampling locations (Table 3.1) and eight farms adjacent to the river were chosen (Figure 3.1).

3.2 Socio - economic surveys about the pesticides use in khat farming

In order to acquire data on the types of pesticides used in the study region, frequency of application, and level of awareness, among other things, field-structured questionnaires were used to conduct a survey in the study area. This was accomplished by giving the questionnaires to a total of 50 respondents at random. Additionally, general information on the interviewees' gender, age, education, and occupation was gathered. Appendix 1 is a sample of the questionnaire that was utilized.

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3.3. Reagents, apparatus and instruments

Prior to usage, general purpose reagents (GPR) n-hexane, acetone, and dichloromethane (DCM) underwent triple distillation. HPLC grade isooctane was obtained from local vendors in Nairobi. Among the analytical grade chemicals utilized were hydrochloric acid of analytical grade from Panreac Ltd, Nairobi, sodium chloride, sodium hydroxide anhydrous sodium sulphate and dipotassium hydrogen phosphate, as well as activated charcoal from Lobe Chemie Pvt Ltd. High purity helium (99.99 percent purity) was supplied by BOC Kenya Ltd in Nairobi, while high purity white spot nitrogen (99.99 percent purity) wasacquired from Gas Labs Ltd in Nairobi. A highly-pure pesticide standard combination was provided by Sigma Aldrich Ltd. To concentrate the sample extracts, nitrogen was used. The Water used to rinse glassware and for use in the actual analysis was distilled at the University of Nairobi, Department of Chemistry laboratories.

3.3.1 Equipment and apparatus

All general-purpose grade solvents were triple distilled using a fractional distiller. Soil, khat plant material, and sediment samples were extracted using a Soxhlet setup consisting of heating mantles, Soxhlet thimbles, extractors, and condensers, while water, was extracted using a technique of solvent-solvent extraction utilizing a 2.0 L separation funnel. Stuart rotary evaporator was used to concentrate sample extracts. For clean-up of the samples, columns of glass material, length of 20 cm, with inner diameter of 2 cm and packed with alumina were used.

Total dissolved solids and electrical conductivity were assessed using Scientific Martin MI 306 instruments. The pH level of the water was determined with an IQ 150 pH meter. A Fisher ScientificA-160 weighing balance that had been calibrated with certified weights was used to ascertain the weights of all the samples. All glassware for the analysis was carefully cleaned, chromic acid soaked for almost 2 hours, and rinsed with normal tap water before being rinsed once more with distilled water and then methanol. In a BINDER E28#04-71528 oven, the moisture levels in the soil, plant matter, and sediments was measured using a gravimetry technique. Meanwhile,cleaned glassware was dried for five hours at 105 ºC in a laboratory oven before being cooled in a desiccator.

Samples were kept in a lab-line refrigerator with an explosion-proof door after extraction and before analysis. Additionally, samples were kept in a deep freezer until extraction. An Agilent GC system 6890N fitted with an electron capture detector (ECD) was employed to measure the amounts of organochlorine pesticide residues levels in sample extracts. Desiccators, beakers, glass vials (10 mL), autosampler vials (1.5 mL), pasteur pipettes, measuring cylinders (1000 mL, 100 mL), micro syringes (10, 25, 50, 100 mL) and Whatman filter sheets (No. 42) were also used.

3.3.2 Reagents preparation

The preparation of anhydrous sodium sulphate was done by baking in the oven at 200 ° C for 16 hours to basically purify and activate it (USEPA, 2007). The activated alumina for clean-up was prepared by drying overnight at 200 °C before being deactivated with 8% water. In order to deactivate 92 g of activated aluminium oxide in a 250 mL round-bottomed flask, 8 mL of HPLC grade water was added, the mixture was shaken to remove any lumps, and the mixture was then baked at 200 °C for an overnight period. The pH 7 phosphate buffer was done by combining 50 mL of 0.2 M dipotassium hydrogen phosphate with 29.6 mL of 0.2 N HCl., Acetone, hexane and dichloromethane underwent three separate distillations to remove contaminants and impurities. Prior to usage,10 mL of 10% HCl and 0.5–1 g of copper were mixed together for 5 minutes to activate. After centrifuging the copper- acid mixture for one minute at 300 rpm to allow separation of the copper powder from hydrochloric acid which then was disposed. Clean methanol was added, the mixture was thoroughly agitated, and centrifugation was performed once more.

3.4 Sample collection, preservation and storage

3.4.1 Soil collection

Eight farms from the study were selected along the Ura River and its tributaries. At each sampling point, using a spotless stainless-steel shovel, the soil samples were dug 25 cm deep from five places, thoroughly mixed, and a composite of three 200 g soil samples each taken, wrapped in clean sterilized aluminium foils, then into bags that were self-sealing, put in a cool

box and delivered to the laboratory (Cox, 2002). When the samples arrived in the laboratory, they were well preserved in a deep freezer set at -19 °C, awaiting extraction, clean-up and analysis. For soil samples, pesticides were extracted within 10 days of each sampling period.

3.4.2 Water and sediment collection

Grab water samples were taken from the Ura River near the selected Khat farms. They were then put in amber glass bottles of 2.5 L capacity that was previously been cleaned with tap water, liquid detergent and rinsed with distilled water, followed by dichloromethane, and allowed to dry overnight (USEPA, 2001). Each water sample was labelled suitably before being subjected to a 100 g sodium chloride treatment to purposefully dehydrate microbes capable of degrading pesticides.

Six cores of sediment samples were taken from the left bank, midstream, and right river banks at a depth of 5 and 10 cm using a clean stainless-steel shovel. The samples were well mixed before being taken in 200 g triplicates in sterile aluminium foils (Clement, 1992). After that, they were labelled, put in self-sealing bags, and kept in polyurethane cool boxes until they were taken to the University of Nairobi's Department of Chemistry lab for extraction clean-up and analysis.

Coleman cooler boxes were used for packaging and transportation to the lab immediately. The water samples were stored in the lab refrigerator at a 4-degree Celsius temperature. Prior to extraction and analysis, the sediment samples were kept in the freezer at -19 °C (Cox, 2002). Within 10 days of the sampling, pesticides were extracted from water and sediment samples.

3.4.3 Khat (miraa) collection

Khat samples from eight different markets in the area of study (Figure 3.1) were collected randomly, buying three bundles, each weighing 200 g from eight markets (Table 3.1). All of the samples were packaged in sterile, clean self-sealing bags with labels and maintained frozen at - 4 °C up to the time of extraction and testing (Cox, 2002). The samples were transported to the lab in cool polyurethane storage containers. In five days of the sample's collection, pesticides residues extraction from the khat samples was done.

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3.5 Determination of physicochemical properties of water

3.5.1 pH of the water

A scientific pH meter Model IQ 150 pH meter was used on-site to assess the pH of 50 cubic centimetres of water samples from Ura River sample locations. The pH meter was calibrated using various buffer solutions with pH values of 4.0, 7.0, and 10.0.

3.5.2 Electrical conductivity and the total dissolved solids

Electrical conductivities and total dissolved solids of the 50 ml water samples were obtained in the field by measuring with a scientific Martin instrument model MI 306. A single- point procedure was used to calibrate the equipment by selecting the EC range and then pressing the CAL key. Deionized water was used to clean and rinse the instrument's probe. The sleeve holes of the clean probe were completely submerged as it was inserted deep into the fluid. To release every air bubble that had become trapped inside the sleeve, the probe was repeatedly tapped. The dry probe was left in the air when the calibration process began at zero. The required buffer value was chosen, and "REF" and "CAL" indicators showed on the screen. The calibration was checked by pressing the SHIFT+CFM keys. When everything was in order, the meter presented the message "Store Good" and went back into measurement mode.

3.6 Physicochemical properties of soil and sediment determination

To establish a baseline understanding of the soil in concern, the samples were analysed at Kenya Agricultural and Livestock Research Organization's Food Crops Research Centre for physical-chemical parameters such as pH and moisture retention, total organic carbon and texture composition (Avery & Bascomb, 1982).

3.7 Sample preparation

3.7.1 Water samples extraction

Water samples in triplicates were subjected to extraction by a solvent-solvent technique to USEPA method 3510C (USEPA, 1996). 2 L of water was transferred into a 3-litre beaker, and

the pH was measured. Following the addition of 50 mL of the buffer solution (0.2 M dipotassium hydrogen phosphate), the level of pH was brought back to neutral by addition of 0.1 MHCl and 0.1 M NaOH. A weight of 100 g of sodium chloride being added to the mixture in a 2 L separating funnel as a quencher's salt to help extract analytes into the organic solvent. A volume of 60 mL of dichloromethane (DCM) distilled thrice was added to the sample, and the mix was well shaken for two minutes, three rounds to complete the extraction (with venting intervals to release pressure). Each time, the mixture was given 30 minutes to settle before being partitioned, and the three organic layer extracts were collected into a 500 mL conical flask. After that, activated drying agent, anhydrous sodium sulphate was applied to the pooled extract to get rid of water traces. The sample extract free of water was combined with the 2 mL isooctane, which was then underwent concentration to 3 mL by a laboratory rotary evaporator. The extracts were transferred into 10 mL glass vials, closed with screw-caps and kept in the refrigerator at 4 °C until clean-up.

3.7.2 Soil and sediment extraction

Pesticide residues in soil and sediment were extracted using a Soxhlet technique according to EPA method 3540. Before extraction, soil and sediment samples from the deep freezer at -19 °C were thawed overnight. After thawing, the samples were air dried.

Large lumps and stones were removed from the samples, and the remainder was crushed into fine particles with a clean mortar and pestle before being carefully mixed for homogeneity. The exact weights of 10 g of finely milled sample were recorded in triplicates. Prior to transferring the sample to the Soxhlet extraction thimbles, 10 g of activated sodium sulfate that was anhydrous was measured and added to the sample for drying. As an internal reference, 100 µL of 0.1 ppm isodrin solution was added. The samples were then Soxhlet extracted using 200 mL of hexane: acetone in a 3:1 ratio in a 500 mL extraction flask for 16 hours.

The extracts were concentrated to around 3 mL using the rotary evaporator to prevent analytes loss after adding 2 mL of isooctane. The extract was then put into 10 mL glass vials with covers and kept in the refrigerator at 4 °C up until cleanup was done.

3.7.3 Khat extraction process

Plant samples that had been stored at $\leq$ -19 $^{\circ}$C were thawed overnight before extraction and were air-dried after thawing. Triplicate khat samples were equally cut into small pieces with clean scalpels for each sample and crushed to a homogeneous sample using mortar and pestle. The extraction process, which used USEPA method 3510, used 10 g of the crushed sample. It was mixed with 10 g activated anhydrous sodium sulphate and placed in the Soxhlet extraction thimble. The extraction process took 16 hours and used a combination of 3 parts hexane and 1 part acetone totalling to 200 mL. To prevent analyte loss, extracts were reduced to about 3 mL using an evaporator after adding 2 mL of isooctane. The extract was then moved to 10 mL glass vials using pasture pipettes, capped and stored at 4 $^{\circ}$C.

3.7.4 Water, soil, sediments and khat samples clean up

The concentrated water, soil, khat, and sediment sample extracts were cleaned using multi-layered glass columns with a bottom made of sintered glass that were 25 cm long and 2 cm in diameter. A layer of baked-out anhydrous Na_2SO_4 measuring 1 cm thick, 15 g of deactivated alumina, and a final layer of baked-out Na_2SO_4 measuring 1 cm thick were all placed inside the column. To remove chlorophyll (discoloration) from khat extracts, an additional 1 centimetre of activated charcoal was placed on top.

The column was pre-conditioned by passing 15 mL of HPLC-grade hexane through it before the concentrated extract was added and the organochlorine pesticides (OCPs) were eluted using 165 mL of HPLC-grade hexane. Khat and water eluents from cleanup were concentrated in isooctane using a rotary type of evaporator to a volume of 1 mL, then moved to pre-weighed auto vials, where they were further evaporated to a volume of around 0.5 mL for GC analysis. The soil and sediment eluents were concentrated to 3 mL using the same technique as the khat and water in order to prepare them for sulphur removal.

3.7.5 Sulphur removal from soil and sediment extracts

After cleaning, one (1) gram of copper metal powder, freshly activated, was introduced into the extract to create copper sulphide, which is a black-coloured substance (USEPA, 2001). The

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extracts were filtered through glass wool, 2 g baked dry sodium sulphate, preconditioned with 5 mL triple-distilled hexane in a glass funnel. The extracts were filtered into a clean round-bottomed flask and then eluted three times with 20 mL of hexane. The sulphur-free extracts were mixed with 2 mL of isooctane and then evaporated again to roughly 2 mL using a rotating evaporator. The extracts were once again cleaned with alumina before being concentrated in isooctane to 1 mL on the same evaporator. All extracts were put into clean, accurately weighed auto vials and concentrated up to about 0.5 mL with a nitrogen stream for automated GC-ECD analysis.

3.8 Calibration curve for OC pesticides analysis

Calibration standards were prepared using the stock solution, which contained 17 OCPs. The standards, which consisted of 9 levels, were obtained through various dilutions of the stock solution. To reduce error of carry over, serial dilution was avoided. These solutions were prepared in autosampler vials directly. The concentrations were determined by precisely weighing all stock solution additions as well as isooctane. The OCPs mixture contained heptachlor, aldrin, heptachlor epoxide, and α-, β-, δ-, γ-HCH, dieldrin, endrin, α -Endosulphan, p, p'-DDD, endrin aldehyde, p,p'-DDT, β -Endosulphan, p,p'-DDE, endosulphan sulphate and methoxychlor. The concentration of the reference standards ranged from 3.92 ng/mL - 94.60 ng/mL.

The peak areas of each analyte in the standard mixture, as well as the different concentration levels, were used to generate calibration curves with the best fit lines in the form Y= MX+ C.

All of the calibration curves had a regression factor (R^2) greater than 99 %, implying a strong relation between peak area (instrument response factor) and analyte concentration.

The concentration of standards was determined by interpolation of the graph of the equation Y= MX + C where Y is the peak area/instrument response, x stands for the standard concentration, m and c represent gradient and a constant, respectively. The sample analytes concentrations were also obtained through a similar procedure.

3.9 Quality control and assurance

It was accomplished by introducing isodrin as an internal standard into each sample prior to extraction. This was critical in determining the method's recovery and efficiency. The tests were carried out in triplicate. In addition, anhydrous sodium sulphate and distilled water were used as field blanks. In order to detect any contamination, if any, the blanks were brought to and from the field during sampling. They underwent the same procedures as the samples.

3.10 GC analysis

All samples were tested for the presence of organochlorine pesticides (OCPs) using a gas chromatogram (Agilent 6890N), an autosampler (Agilent 7683 series injector), and an electron capture detector (Agilent ECD). While the injector was kept at 250 °C, the detector was kept at 300 °C. The carrier gas was helium, which had a purity of 99.99%, and the makeup gas was nitrogen, which had a purity of 99.99. Helium's gas flow rate was constantly at 2 mL/min.

The following temperature protocols were used for the injection: 90 °C for 3 minutes, 90 °C to 200 °C (at 30 °C/min and a 15-minute hold time), and 200 °C to 275 °C (at 30 °C/min and a 5-minute hold time). The injector was configured to pulse splitless injection mode with a 1μL injection volume. High-performance capillary column fused with DB-5 silica, the GC column had a length of 30 m, internal diameter of 0.25 mm, and film thickness of 0.25 μm. Chemstation software was used to process the data.

3.11 Limits of detection (LOD) of organochlorine pesticides residue level

According to Miller and Miller (2010), the detection limit of an analytical procedure is the concentration of an analyte that gives a signal in the instrument different from that of the background blank. In other words, the smallest value of concentration that a method can reliably detect compared to the blank of the procedure.

The relationship adapted from the equation below was used to determine the detection limit of each of the seventeen OCPs based on the lowest concentration of the calibration standards

injected and the related noise signals.

LOD = (3 x Noise peak area x concentration of standard injected (ng))
       Analyte the response in the lowest calibration point

In this case, the LOD of the target Organochlorine pesticides was from 1.10 ng/L for α- HCH to 3.60 ng/L for aldrin. The various LOD for the Organochlorine pesticides determined is in Table 3.2

Table 3.2: Limit of detection values for various pesticides (mean± s.d)

Pesticides	LOD (ng/L)	Pesticides	LOD (ng/L)
α –HCH	1.1±0.1	Endosulphan sulphate	2.1±0.1
β- HCH	1.6±0.1	Aldrin	3.6±0.1
γ- HCH	1.6± 0.1	Dieldrin	3.1±0.1
δ –HCH	4.0±0.1	Endrin	2.2±0.1
p,p,'- DDT	1.7± 0.1	Endrin aldehyde.	2.2±0.1
p,p,'- DDE	1.8± 0.1	Heptachlor	1.1±0.1
p,p,'- DDD	1.6±0.1	Heptachlor epoxide	1.1± 0.1
α- Endosulphan	1.1±0.1	Methoxychlor	1.6±0.1
β-Endosulphan	1.5±0.1		

3.12 Organochlorine pesticide recovery levels

The average percentage recoveries of the 17 pesticides in water, sediments, soil and khat was in the range of 70.01±4.21% for endrin and 114.83± 3.33% for dieldrin, respectively. The other targeted OCPs had recovery values, as summarized in Table 3.3 The recoveries were within the acceptable range, and hence there were no corrections (EURL, 2013).

Table 3.3: Percentage recoveries of OCP residue in water, sediment and soil

Pesticide	Recovery(%±S.D) in water	Recovery (%±S. D) in sediment	Recovery (%±S. D) in khat	Recovery (%±S. D) in soil
α-HCH	94.82±8.31	88.43±7.60	98.22±4.67	99.21±7.87
β-HCH	87.52±4.09	79.43±2.94	83.46±4.78	80.99±22.32
γ-HCH	92.06±9.58	94.23±9.44	89.06±7.40	89.22±6.87
δ-HCH	82.54±6.95	78.46±8.21	83.81±3.57	82.46±12.35
p, p'-DDT	99.89±3.41	92.03±7.42	92.87±5.29	94.08±6.35
p, p'-DDE	78.35± 5.12	86.74±6.53	76.56±8.06	76.33±7.14
p, p'-DDD	99.31±2.84	94.08±4.85	89.61±2.45	96.81±2.84
α- Endosulphan	102.58±4.95	97.93±3.68	98.12±6.27	101.21±10.34
β-Endosulphan	93.23±7.13	83.40±5.34	83.05±7.30	79.21±6.56
Endosulphan sulphate	78.25± 6.00	81.63±6.76	80.46±8.84	77.11±8.54
Aldrin	94.26±5.23	91.48±5.22	92.31±2.91	79.22±11.02
Dieldrin	114.83±3.33	98.42±3.76	97.44±4.92	92.99±4.58
Endrin	70.01±4.21	79.76±3.54	84.85± 6.28	76.31±9.87
Endrin aldehyde.	77.81±8.63	89.06±4.32	82.52±4.62	92.16±31.44
Heptachlor	92.08±4.56	96.18±2.69	93.36±4.35	79.23±5.68
Heptachlor epoxide	98.35±2.45	93.57±3.64	92.47±4.66	91.71±13.15
Methoxychlor	88.23±6.86	89.56±3.85	85.46±8.42	88.36±3.58

Average = mean± S.D

3.13 Data analysis

The data was analyzed using Microsoft Excel. The Statistical Package for Social Scientists (SPSS, 22) was used to analyse the association between seasonal fluctuations and the levels of pesticide residue that were found. In addition to showing how other factors, such as pH, TSS, TDS, electrical conductivity, and sample type, related to the levels of pesticide residue, the results were displayed using graphs and statistical tables.

CHAPTER FOUR

4. RESULTS AND DISCUSSION

4.1 Survey on pesticides in the Igembe south sub- county

Field questionnaires were administered to 45 khat farmers within Igembe Sub County. Filled questionnaires were analysed and the results presented in Tables 4.1, 4.2, Figures 4.1 and 4.2 below.

4.1.1 Types of pesticides used in khat farming

The regularly used pesticides by farmers in Igembe south sub county include; organophosphates, carbamates, neonicotinoids and pyrethrins.

Table 4.1: Types of pesticides used in khat farming

Pesticide trade name	Active ingredient	Classification	% of farmers using the pesticide
Manik	Acetamiprid	Neonicotinoid	42
Agrinate	Methomyl	Carbamate	56
Asataf	Acephate	Organophosphate	40
Cyclone	Chlorpyrifos + Cypermethrin	OP & Pyrethroid	32
Sulban	Chlorpyrifos	Organophosphate	10
Contaf	Hexaconazole	Fungicide	14
Thunder	Imidacloprid+ Beta cyfluthrin	Neonicotinoid+ Pyrethrin	26
Lannate	Methomyl	Carbamate	4
Dithane	Mancozeb	Carbamate	8
Diazate and Diazol	Diazinon	Organophosphate	8

Most farmers recorded use of organophosphates pesticides on their khat plants followed by carbamates pesticides while pyrethrins and neonicotinoids had an equal percentage on the popularity of the pesticides used in khat farming in Igembe South. The finding of this survey corresponds to one carried out in river Nyando catchment area where farmers confirmed to be commonly using organophosphates in their farming activities (Abong'o *et al.,* 2014). On the

contrary, studies have recorded use of organochlorine pesticide in Meru County, including heptachlor, endrin and dieldrin among others (Marete *et al.,* 2021). This indicates illegal use of the banned pesticides by the farmers creating high health risk to the residents and consumers of the farm produce. Joyce (2013) also analysed for organochlorine residue in upper Tana region and detected levels of DDT together with its metabolite to levels above 100 µg/L among others.

The pesticides listed in Table 4.1 are registered in Kenya by the Pest Control and Products Board (PCPB, 2015) and are used for khat farming. Although in the list of PCPB (2015) the use of the pesticides in khat is not mentioned, the farmers claimed that the pesticides are useful in protecting their crops for pests and diseases. Most farmers recorded use of a combination of two or more of the types of the pesticides listed here for better effectiveness.

Although organochlorine pesticides were not listed among the ones used by the farmers various research conducted in different parts of the country on soil, water, sediments and aquatic weeds, show significant levels in the environment because of their persistence, obsolete stocks, spreads from contaminated sites and also illegal use (Wandiga *et al.,* 2002; Kishimba & Mihale, 2009; Abong'o *et al.,* 2015; Abong'o *et al.*, 2018). Other studies in Hyderabad city revealed considerable levels of organochlorine pesticides from dump sites of obsolete or banned pesticides (Alamdar *et al.,* 2014).

4.1.2 Frequency of pesticide applications by the farmers

Most farmers (78%) apply pesticides once a month, while 18% in a fortnight. Few farmers (2%) apply the pesticides before and after harvest and 2% after three weeks (Figure 4.1).
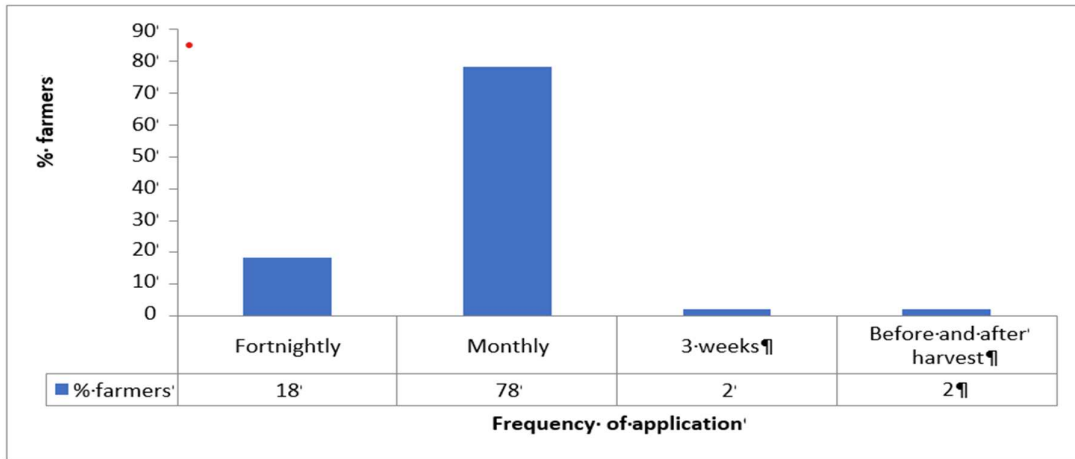
Figure 4.1 Frequency of pesticide application on the khat crop

This is comparable to the results of a research carried out in Netherlands. On the most intensively treated crops, the most popular insecticide and fungicide chemicals were applied on average between 10 and 20 times annually (Van Drooge *et al.,* 2001).

4.1.3 Amounts of pesticides applied by the farmers per annum

All the respondents used pesticides in khat growing but most farmers (78%) use 2 kg on their farms every year while 19% of the farmers use 1kg of pesticides. 1% of the farmers use 10 kg, 1% of the farmers use 5 kg of the pesticides and 1% of the farmers use less than 0.5 kg of pesticide every year. Figure 4.2 below shows the amounts of pesticides used by farmers.
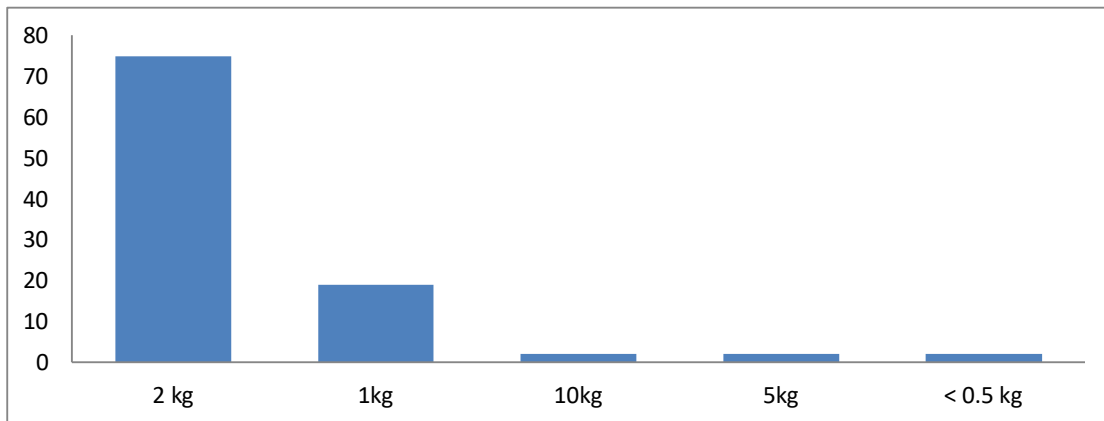
Figure 4.2 Annual pesticides used by each farmer

4.1.4 Gender of the farmers

Table 4.2 reveals that men made up 89% of the respondents (farmers), while women made up 11%. As a result, men are substantially more likely than women to be respondents who are khat farmers. This was in line with a survey from Ghana by Danso *et al.* (2002), who discovered that 27% of respondents were women and 73% of respondents were male farmers. However, it was contrary to studies done in Uganda and Kenya which reported female farmers number exceeding that of males in urban areas. Particularly, it was found out that 80% and 56% of farmers in urban areas to be women in Uganda and Kenya, respectively (Jones *et al.,* 2009).

4.1.5 Age brackets of the farmers

several of the respondents were between 31-34 years (38 %), followed by 20-24years (36%), 35 - 39 years (11%), above 40 years (15 %) and whereas no respondents that where in the age of 15 – 19 years (Table 4.2).

Table 4.2: Socio demographic data of the farmers

Farmer's information	Frequency	Percentage
Gender		
Male	40	89
Female	5	11
Total	45	100
Age brackets		
15-19	0	0
20-24	16	36
30-34	17	38
35-39	5	11
40 and above	7	15
Totals	45	100
Level of education		
No education	3	7

Primary	26	58
Secondary	15	33
Tertiary	1	2
Total	45	100
Knowledge on the safe handling of the agrochemicals		
Trained	9	20
Untrained	36	80
Total	45	100

4.1.6 Level of education of the farmers

Results on the education level showed that the highest numbers of farmers were those with primary levels of education (58%), followed by the secondary (33%), tertiary (2%) and without education (7%) (Table 4.2). In general, the results indicate that the khat farmers in Igembe have different levels of literacy. These findings were similar with those from other studies on level of education of the farmers involved in urban agriculture in Ghana by Danso *et al.* (2002) which showed that 23% of farmers lack any formal education while 33% had primary, 37% secondary and 6% with tertiary education.

4.1.7 Number of trained and untrained farmers

From Table 4.2, 80% of the farmers were Not trained in the proper handling of agricultural chemicals like pesticides while 20% had been trained. This implies that a higher percentage of khat farmers in Igembe Sub-County have not been trained on the careful use and handling of the agrochemicals. The majority of khat farmers do not wear protective gears when using pesticides or reading the instruction labels on the pesticide containers on the use of pesticides and their disposal procedures. This corresponds with a study conducted in Sagana Nyeri County on the safety in handling pesticides by the small-scale farmers (Mureithi *et al.,* 2011) and tomatoes farmers in Mwea Irrigation Scheme, Kirinyaga County (Momanyi *et al.,* 2019).

4.1.8 Other information from the survey

The vast majority of farmers (71%) harvest their crop within thirty days after pesticide treatment, 22% after two weeks, and 2% after three weeks. A lot of pesticides are used during

the dry season because that is when pests and diseases are most prevalent. Pesticides have been used by the majority of farmers for more than ten years.

4.2 Physical- chemical parameters of water, sediments and soil

4.2.1 pH of the water samples from Ura river during wet and dry seasons

Table 4.3 show the overview of the levels of pH recorded in the wet and dry seasons across the sampling sites.

Table 4.3: pH levels of the water in wet and dry seasons

Sampling sites	Wet season	Dry season
Site 1	7.19±0.03	7.45±0.03
Site 2	7.03±0.03	7.61±0.02
Site 3	6.89±0.02	6.95±0.01
Site 4	6.62±0.51	7.86±0.01
Site 5	6.93±0.01	7.26±0.02
Site 6	6.95±0.02	7.86±0.02
Site 7	6.91±0.01	7.21±0.02
Site 8	7.15±0.01	6.91±0.02

Dry season in March showed higher pH values in all the sampling sites than the wet season (October). Ikandu and Ntherone sampling sites showed the highest pH value of 7.8 followed by Kiiji at 7.6 in March 2016. Table 4.3 displays the water samples' pH values, collected for analysis on both seasons and their variation. According to WHO standard, the pH guideline for drinking water should be below 8 (WHO, 1997). Hence all the water samples collected complied. The variation in the pH levels during the dry and wet seasons (Figure 4.3) could be due to the dilution of the water by the heavy rains in the month of October 2015. The high pH levels at Ikandu and Ntherone sampling sites could be attributed to the location, which is the mid-stream and the many agricultural activities that are upstream and also around the said sampling locations. Figure 4.3 shows variation of pH levels in water.
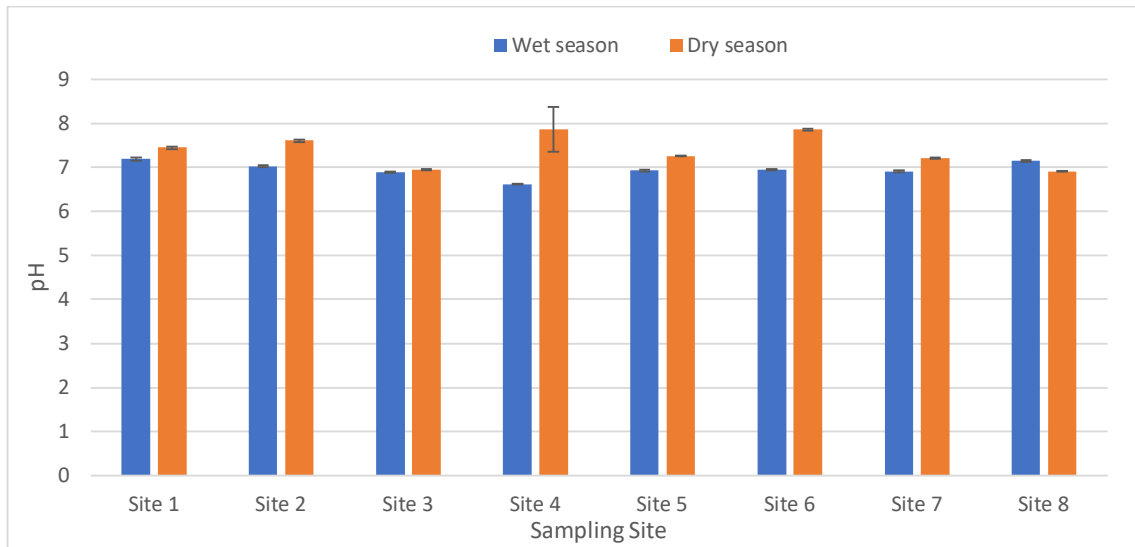
Figure 4.3 Variation of P^H in the water samples in wet and dry seasons

4.2.2 TDS of the water samples collected in wet and dry seasons.

The amounts of total dissolved solids (mg/L) in water samples taken in the months of March and October as the dry and wet seasons respectively are displayed in Table 4.4.

Table 4.4:Total dissolved solids levels of water in wet and dry seasons

TDS (mg/L)	Wet season	Dry season
Site 1	31.59±0.08	28.31±0.02
Site 2	26.84±0.12	82.48±0.30
Site 3	25.49±0.04	48.70±0.01
Site 4	36.05±0.14	61.18±0.09
Site 5	31.50±0.03	81.20±0.10
Site 6	34.67±0.11	46.49±0.10
Site 7	26.42±0.07	70.13±0.15
Site 8	33.79±0.10	56.20±0.10

The term "total dissolved solids" (TDS) refers to the inorganic salts and minute amounts of organic matter that are dissolved in water. Usually, cations of magnesium, calcium, potassium, and sodium are present together with anions of carbonates, hydrogen carbonates, sulfate, nitrate, and chloride. Dissolved solids may influence the flavour of water. According to TDS levels,

excellent drinking water has less than 300 mg/L, good water has between 300 and 600 mg/L, fair water has between 600 and 900 mg/L, poor water has between 900 and 1,200 mg/L, and unsatisfactory water has more than 1,200 mg/L (WHO, 2003).

In general, the TDS levels in the water samples were within the approved WHO drinking water recommendations. According to the WHO (2003), the river Ura water's values ranged from 25.49±0.04 mg/L to 82.48±0.30 mg/L, with values below 300 mg/L signifying excellent taste. Additionally, it was discovered that the samples of water had more TDS during the dry season than the wet season (Figure 4.4). This difference could be explained by the river's and its tributaries' slower flow and smaller volume of water giving it more time to interact with the rocks and soils around and within it, resulting in more dissolved solids. In Nyambene, it was only lower during the dry season.
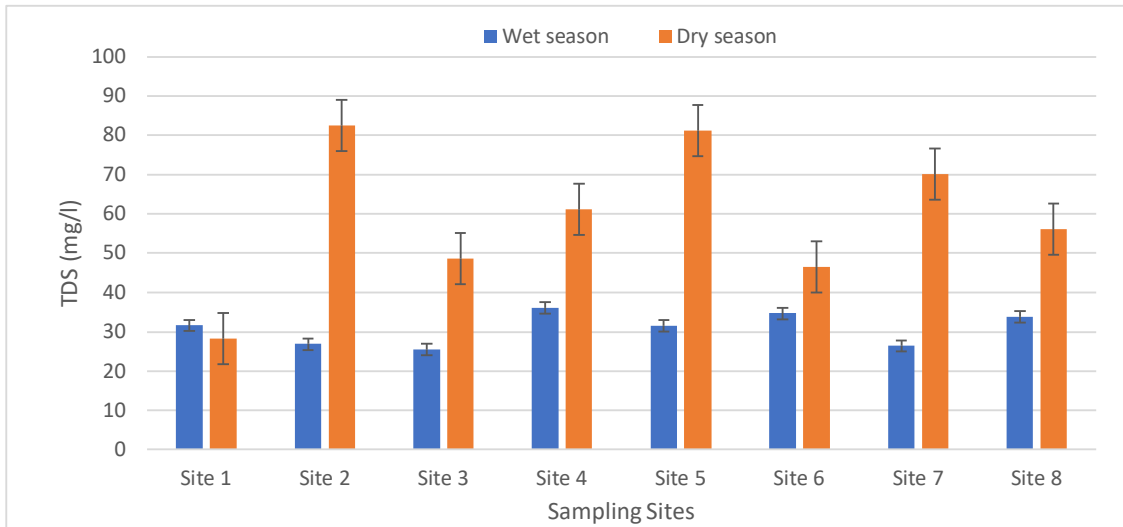
Figure 4. 4 Variation of the TDS in the water samples in wet and dry seasons

4.2.3 Electrical conductivity of the water from Ura river

Table 4.5 and Figure 4.5 show the levels of electrical conductivity (µS/cm) of the water samples collected for analysis during the month of October 2015 and March 2016.

Table 4.5: Electrical conductivity levels in the water in wet and dry seasons

Sampling sites	Wet season (µS/cm)	Dry season (µS/cm)
Nyambene	62.45±0.05	58.20±0.02
Kiiji	53.04±0.02	164.79±0.02
Anchenge	50.17±0.01	98.19±0.02
Ikandu	72.12±0.02	122.50±0.05
Ikurone	63.63±0.17	161.90±0.05
Ntherone	69.59±0.02	93.10±0.10
Ntherone Tributary	56.28±0.03	140.08±0.26
Tumu Tumu	67.40±0.05	113.40±0.02
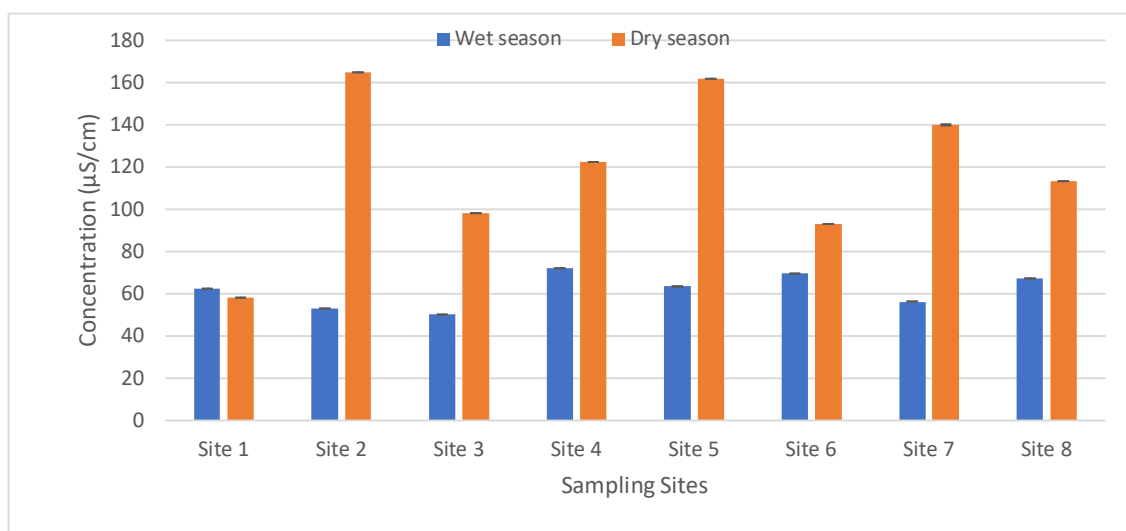
Figure 4. 5 Electrical conductivity levels for the water samples in wet and dry seasons

4.2.4 Physico-chemical parameters of sediment from Ura River

The sediments from the Ura River ranged in pH levels from 8.30±0.00 to 9.9±0.00, which is mildly basic. Notably, pH is a measure that represents soil physicochemical characteristics, discharge of nutrients conditions, and hazardous substances affects (Sharma *et al.,* 2013). The levels obtained were within the range of lake sediments that had pH between 4 and 9 (Boyd, 1995).

Additionally, the sediments contained significant amounts of organic carbon, up to 1.9±0.01%. The macronutrients (nitrogen, phosphorus, and potassium) were also abundant in the samples, with mean concentrations as high as 1.50±0.02%, 45.00±0.02 ppm, and 3.70±0.00 ppm, respectively. Farm runoff may be partially responsible for such (Rozpondek *et al.,* 2017; Junakova and Balintova, 2012).

The concentration of Iron was highest in Tumu Tumu (635.00±4.60 ppm), this was followed by Nyambene with value of 601.00±1.00 ppm. According to Ogbeibu *et al.* (2014), the EPA levels of copper and zinc should not exceed 25 ppm and 90 ppm respectively hence the sediments from Ura river complied to this guideline.

Table 4. 6: Physico-chemical properties of sediment from sampling sites

Parameters	Nyambene	Kiiji	Anchenge	Ikandu	Ikurone	Ntherone	Ntherone tributary	Tumu-Tumu
pH	9.90±0.00	9.90±0.00	9.50±0.00	8.30±0.00	9.60±0.00	9.20±0.01	8.30±0.01	9.60±0.01
Conductivity (μS/cm)	3.30±0.01	3.90±0.01	3.20±0.01	3.50±0.01	3.00±0.00	2.90±0.01	3.10±0.01	1.60±0.01
Total N%	0.10±0.01	0.30±0.01	0.10±0.02	1.20±0.01	1.50±0.02	1.10±0.01	1.00±0.03	0.60±0.03
Total OC%	1.60±0.02	1.90±0.01	1.60±0.03	1.30±0.01	1.80±0.01	0.20±0.02	1.30±0.01	1.90±0.02
P (ppm)	20.40±0.02	33.20±0.10	20.50±0.01	33.00±0.06	33.00±0.06	55.00±0.06	45.00±0.01	45.00±0.02
K (ppm)	3.40±0.01	3.30±0.01	3.30±0.01	3.70±0.00	3.30±0.01	2.30±0.03	4.00±0.01	2.90±0.01
Ca (ppm)	15.40±0.01	17.60±0.01	1.40±0.02	1.40±0.02	15.50±0.02	5.10±0.02	15.30±0.01	12.50±0.02
Mg (ppm)	2.50±0.01	2.50±0.01	2.50±0.02	1.70±0.01	2.10±0.02	3.00±0.03	1.20±0.04	2.00±0.04
Mn (ppm)	2.00±0.02	1.80±0.04	1.90±0.01	1.50±0.03	1.20±0.01	0.80±0.02	1.10±0.03	1.20±0.04
Cu (ppm)	1.80±0.02	1.40±0.03	1.10±0.04	1.30±0.03	1.40±0.03	2.00±0.01	1.80±0.02	1.70±0.03
Fe (ppm)	601.00±1.00	485.00±2.50	523.00±0.00	500.00±3.60	400.00±2.70	352.00±2.70	356.00±1.00	635.00±4.60
Zn (ppm)	3.60±0.02	3.90±0.01	3.30±0.01	3.40±0.04	3.50±0.02	3.40±0.01	3.50±0.02	3.10±0.03
Na (ppm)	1.90±0.60	1.10±0.01	1.10±0.17	1.90±0.02	1.90±0.00	0.90±0.04	1.00±0.01	1.20±0.02

4.2.5 Physical-chemical parameter of soil from the sampling sites

Table 4.7:Physico-chemical properties of soil samples

Parameters	Nyambene	Kiiji	Anchenge	Ikandu	Ikurone	Ntherone	Ntherone tributary	Tumu Tumu
Soil pH	6.54±0.02	5.58±0.00	5.79±0.03	6.62±0.02	6.28±0.03	5.82±0.01	5.16±0.00	6.11±0.03
Conductivity µS/cm)	2.36±0.03	1.23±0.03	3.26±0.05	2.65±0.10	1.84±0.03	2.65±0.03	1.56±0.01	1.86±0.00
Total N%	0.45±0.03	0.96±0.03	0.14±0.02	0.29±0.03	0.87±0.02	0.06±0.02	0.59±0.01	1.02±0.01
Total OC%	0.87±0.01	0.56±0.03	0.36±0.01	0.96±0.02	0.66±0.02	0.45±0.03	0.35±0.04	0.69±0.01
P (ppm)	45.00±0.01	42.36±0.02	28.00±0.01	34.81±0.01	44.50±0.00	20.20±0.16	28.32±0.01	55.00±0.01
K (ppm)	0.52±0.02	0.72±0.01	0.34±0.02	0.72±0.03	0.54±0.01	1.32±0.02	0.42±0.02	0.45±0.03
Ca (ppm)	9.64±0.02	8.59±0.01	8.55±0.02	8.58±0.02	8.56±0.03	9.62±0.03	8.56±0.03	10.14±0.02
Mg (ppm)	2.47±0.03	2.18±0.02	2.26±0.01	2.73±0.02	2.73±0.03	2.71±0.02	2.72±0.00	3.41±0.02
Mn (ppm)	2.01±0.01	1.56±0.02	1.13±0.00	1.51±0.01	1.71±0.02	1.43±0.00	1.96±0.03	1.35±0.03
Cu (ppm)	9.77±0.01	9.71±0.01	10.75±0.03	10.24±0.04	9.96±0.02	9.18±0.02	9.06±0.01	9.81±0.00
Fe (ppm)	402.00±1.00	326.00±1.73	356.00±1.00	306.00±1.73	393.00±1.00	389.00±1.53	409.00±0.58	345.00±1.73
Zn (ppm)	7.70±0.01	7.70±0.01	8.23±0.01	7.60±0.01	7.40±0.01	6.25±0.01	7.84±0.02	7.80±0.01
Na(ppm)	0.93±0.01	0.64±0.04	0.9±0.01	1.23±0.02	0.66±0.03	0.45±0.03	0.96±0.03	0.96±0.03

The table 4.7 reveals an overview of the nature of the soil being analysed; characteristic to the farms in the study region. Among the physico-chemical parameters that influence transportation and bioavailability of organochlorines and other pesticides in soil includes the soil P^H. The soil's PH in the research region ranged from 5.16±0.00 to 6.54±0.02, which indicates a mild acidity. This may be as a result of natural soil weathering processes, the levels of nitrogen application of ammonium fertilisers and low levels of calcium, magnesium and Sodium in the soil. (Aiyesanmi & Idowu, 2012).

On determination of conductivity in the soils, the levels ranged from 1.23±0.03 to 3.26±0.01 (µS/cm) across the sites. Just as organic matter holds nutrients in soil systems, it has also been linked with the dynamics and distribution behaviour of pesticides, inorganic and other organic pollutants (Spark and Swift, 2002). The organic carbon percentage in the area of study

fluctuated across the area with values between 0.35±0.04 to 0.96±0.02. The values are relatively small probably because of top soil erosion due to the topography of the area (Baker *et al.,* 2015).

4.3 Determination of organochlorine residue levels in environmental samples

4.3.1 Organochlorine (OC) pesticides levels in water from Ura river

Water samples from eight sampling locations along the Ura River were analyzed, and the results revealed the presence of all the organochlorine pesticide in question in different concentrations, from <0.001±0.00 µg/L to 5.64±0.99 µg/L. Water samples collected in October 2015 from Kiiji site had the highest concentration of OCPs (Table 4.9).

4.3.1.1 OC pesticides residue levels in water samples during the wet season

The results of first sampling during the wet season (October 2015) showed presence of organochlorine pesticides at varying concentrations in the range from <0.001 to 2.76±0.05 µg/L. Methoxychlor was the highest with concentration of 2.76±0.05 µg/L at Kiiji. The OCPs in water samples collected during the wet season are presented in Table 4.10. The average values of hexachlorocyclohexane isomers were between *α*-HCH (<0.001 to 0.05 ±0.00 µg/L), *β*-HCH (<0.002 to 0.01±0.00 µg/L), *δ* –HCH (<0.004 to 0.23 ±0.00 µg /L) and *γ* –HCH was not detected in any of the sites. For *p,p'*- DDT, the concentration varied from <0.002 to 0.73 ±0.01 µg /L while the analogue *p,p'*-DDD ranged from <0.002 - 0.07 ±0.00 µg/L and *p,p'*-DDE analogue was not detected in any sampling site.

The mean concentration of aldrin, heptachlor, endrin, endrin aldehyde and dieldrin were detected across the range of <0.004 to 0.41±0.00 µg/L; <0.001 to 0.20±0.00 µg/L, <0.002 to 0.05±0.00 µg/L; <0.002 to 0.34 ±0.03 µg/L and <0.003 to 0.03 ±0.00 µg/L respectively. The mean concentration of endosulphan sulphate ranged from <0.001 to 2.73 ±0.01 µg/L and *β*– endosulphan from <0.001 to 0.14 ±0.00 µg/L. Methoxychlor showed values with range (<0.001 to 2.76 ±0.05 µg/L). Heptachlor epoxide and α-endosulphan were not detected in any of the water samples collected during wet season (Table 4.8).

Table 4.8: OCP residue levels in water samples in (µg/L) during the wet season

Pesticide /Site	Nyambene	Kiiji	Anchenge	Ikandu	Ikuronee	Ntherone	Ntherone tributary	Tumu Tumu
α-HCH	0.01±0.00	0.05±0.00	<0.001	0.04	0.03±0.00	0.03±0.00	<0.001	<0.001
β-HCH	<0.002	<0.002	<0.002	<0.002	<0.002	0.01±0.00	<0.002	<0.002
γ-HCH	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002
δ-HCH	<0.004	<0.004	<0.004	<0.004	0.01±0.00	<0.004	<0.004	0.24±0.00
Heptachlor	0.01±0.00	0.08±0.00	0.01±0.00	0.20±0.00	0.05±0.00	0.01±0.00	0.01±0.00	0.01±0.00
Aldrin	<0.004	<0.004	<0.004	<0.004	<0.004	<0.004	<0.004	0.41±0.00
Heptachlor epoxide	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
α- Endosulphan	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
p, p'-DDE	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002
Dieldrin	<0.003	<0.003	<0.003	0.03±0.00	<0.003	<0.003	<0.003	<0.003
Endrin	<0.002	<0.002	<0.002	0.05±0.00	<0.002	<0.002	<0.002	<0.002
β- Endosulphan	<0.001	0.14±0.00	0.05±0.00	0.08±0.00	0.06±0.00	0.04±0.00	<0.001	<0.001
p, p'-DDD	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	0.07±0.00
Endrin aldehyde	<0.002	0.34±0.03	0.28±0.00	0.30±0.00	0.05±0.00	0.09±0.00	<0.002	0.08±0.00
p, p'-DDT	<0.002	0.73±0.01	<0.002	<0.002	0.06±0.00	<0.002	<0.002	0.08±0.00
Endosulphan sulphate	2.73±0.01	0.86±0.00	<0.002	<0.002	<0.002	<0.002	<0.002	<0.00
Methoxychlor	1.80±0.00	2.76±0.05	1.27±0.03	2.24±0.08	0.58±0.00	0.90±0.00	<0.002	0.89±0.00

Concentration= Mean ± S.D
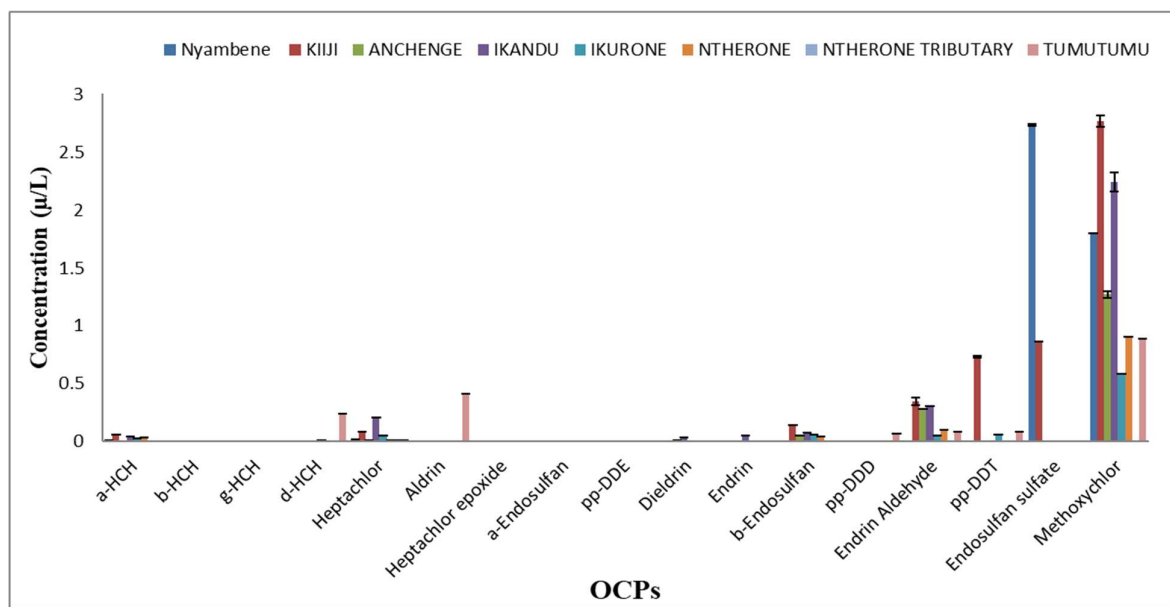
Figure 4.6 Organochlorine pesticide residue levels in water in wet season

From Figure 4.6 the highest pesticide residue detected was Methoxychlor (2.76±0.05 µg/L) at Kiiji, and Methoxychlor (2.24±0.08 µg/L) at Ikandu farm followed by endosulfan sulfate (2.73±0.01 µg/L) at Nyambene. Lindane (ɤ-HCH) was below detection limit but its isomers; δ-HCH was detected as 0.01 µg/L- Ikurone site and 0.24 µg/L at Tumutumu which are sampling sites at the mid and downstream reaches of the river respectively. *β*- HCH was also detected at a level of 0.01±0.00 µg/L at Ntherone. *α*- HCH was more frequent in most of the water samples collected. The levels ranged from <0.001 to 0.05± 0.00 µg/L. This distribution would suggest breakdown of lindane which was used years back, or deposition after long distance transportation. The findings slightly differed with the result of a study of HCH in Delhi, where five out of nine of the same matrices of mineral water contained *γ* - and *β*-HCH and all drinking water samples confirmed the presence of *α*-HCH and *δ*-HCH residues. The research in this case attributed HCH presence in the water to arise from the ground water processed to drinking water (Prakash *et al.*, 2004).

Heptachlor was also detected in all the sites in small quantities from 0.01± 0.00 µg/L - 0.20± 0.00 µg/L. Ikandu which is mid-stream recorded the highest level. There was no heptachlor epoxide detected suggesting scanty illegal use of heptachlor. *p,p'*-DDT levels were from <0.002

to 0.73 ± 0.01 µg/L at Kiiji site. Other sites that showed levels of *p,p'*-DDT were Ikurone 0.06 ± 0.00 µg/L and Tumu Tumu 0.08 ± 0.00 µg/L. This may indicate gradual degradation of *p,p'*-DDT in the environment or there could be current illegal use of the pesticide. *p,p'*-DDE was not detected and *p,p'*-DDD was only detected at Tumu Tumu 0.07 ± 0.00 µg/L further proving slow break down of *p,p'*-DDT in the area.

Although *α*-endosulphan was not found, *β*-endosulphan, which is more persistent in the ecosystem, was found with levels at Kiiji, Anchenge, Ikandu, Ikurone and Ntherone. Endosulphan sulphate was detected at Nyambene 2.73 ± 0.01 µg/L and Kiiji 0.86 ± 0.00 µg/L. All other sites did not record any levels. It is usually a result of breakdown of the endosulphan.

Very small levels of endrin were detected only in Ikandu water samples 0.05 ± 0.00 µg/L and its degradation product endrin aldehyde was predominant in water samples collected from six sites meaning previous use of endrin and slow breakdown to endrin aldehyde.

Methoxychlor seemed to be the major contaminant in the river water because all the samples except one from Ntherone tributary showed significant levels up to 2.76 ± 0.05 µg/L at Kiiji (Figure 4.6). This finding corresponds to the higher concentrations of methoxychlor recorded in water samples from Karun River comparing with the other organochlorine pesticide residues (Behfar *et al.,* 2013). The quantities found, however, were all still within the 20 g/L WHO drinking water guideline standards (WHO, 2011).

Aldrin was only detected in Tumutumu water sampling site as 0.41 µg/L which suggests contamination from long distance transportation and deposition. Dieldrin, a byproduct of aldrin degradation, was found in trace levels in the water samples from Anchenge. Aldrin concentrations in Tumutumu were at 0.41 ± 0.00 µg/L above the 0.03 µg/L WHO recommended limits, whereas dieldrin concentrations in water from Anchenge were just on the border of the limit (WHO, 2011). The other residues found in the water tested had all been below WHO drinking water limits (IUPAC, 2003).

Generally, Ura river appeared to be contaminated by small levels of OCPs. This is probably due to dilution by the heavy rains and the water running off at a very high rate (volume per seconds). It can clearly be seen from Table 4.8 that Kiiji indicated the highest level of OCP residue pollution detected among all the sampling sites. The low levels of concentration are attributable

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to dilution factor in the water bodies and also the hydrophobic nature of the compounds (Ravindran *et al.,* 2016).

4.3.1.2 OC pesticides residue levels in water samples during dry season

Results of the samples collected in dry season (March, 2016) showed presence of organochlorine pesticides at varying concentrations in the range of <0.001± 0.00 µg/L to 5.64±0.99 µg/L. The most abundant chemical found in Kiiji was methoxychlor (Table 4.9). Table 4.9 displays the OCPs in all of the water test samples taken in March from the various sites.

The average concentration of hexachlorocyclohexane (HCH) and its analogues ranged from below the detection threshold (<0.002 µg/L) for gamma-HCH to 0.56±0.00 µg/L. <0.002 ±0.00 µg/L to 0.56±0.01 µg/L of *beta*-HCH and δ-HCH from <0.004 to 0.13 ± 0.00 µg/L. *Alpha*-HCH was below detection limit of 0.001± 0.00 µg/L. *p,p'*-DDT was not detected and its analogue *p,p'*-DDE concentration was between <0.002 to 0.16± 0.00 µg/L .At each of the eight sampling sites, *p,p'*-DDD was below the detection threshold of 0.002 ± 0.00 µg/L (Table 4.9).

The mean levels of heptachlor, aldrin, heptachlor epoxide ranged between <0.001 to 0.15 ±0.00 µg/L; <0.004 to 0.11 ±0.00 µg/L and <0.001 to 0.03 ± 0.00 µg/L, respectively. While dieldrin and endrin were not detected, endrin aldehyde was between <0.002± 0.00 µg/L to 0.34 ± 0.00 µg/L. α–endosulphan gave a range between <0.001 to 0.15±0.00 µg/L while *β*–endosulphan and endosulphan sulphate were below detection limit.

Methoxychlor again was the most dominant OCP during the dry season of March 2016, with concentrations from <0.002 to 5.64±0.99 µg/L.

Table 4.9:OCP residue levels in water samples (µg/l) during dry season

Pesticide /Site	Nyambene	Kiiji	Anchenge	Ikandu	Ikurone	Ntherone	Ntherone tributary	Tumu Tumu
α-HCH	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
β-HCH	<0.002	0.56±0.01	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002
γ-HCH	<0.002	0.56±0.00	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002
δ-HCH	<0.004	0.13±0.00	<0.004	<0.004	<0.004	<0.004	<0.004	<0.004
Heptachlor	<0.001	0.15±0.00	<0.001	<0.001	0.01±0.00	<0.001	<0.001	<0.001
Aldrin	<0.004	0.11±0.00	<0.004	<0.004	<0.004	<0.004	<0.004	<0.004
Hepltachlor epoxide	<0.001	0.03±0.00	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
α-endosulphan	<0.001	0.15±0.00	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
p, p'-DDE	<0.002	0.16±0.00	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002
Dieldrin	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003
Endrin	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002
*β-e*ndosulphan	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
p, p'-DDD	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002
Endrin ldehyde	<0.002	0.34±0.00	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002
p, p'-DDT	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002
Endosulphan sulphate	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002
Methoxychlor	<0.002	5.64±0.99	3.09±0.06	1.21±0.01	1.61±0.02	0.90±0.00	1.81±0.02	1.27±0.01

Concentration= Mean ± S.D   n=8
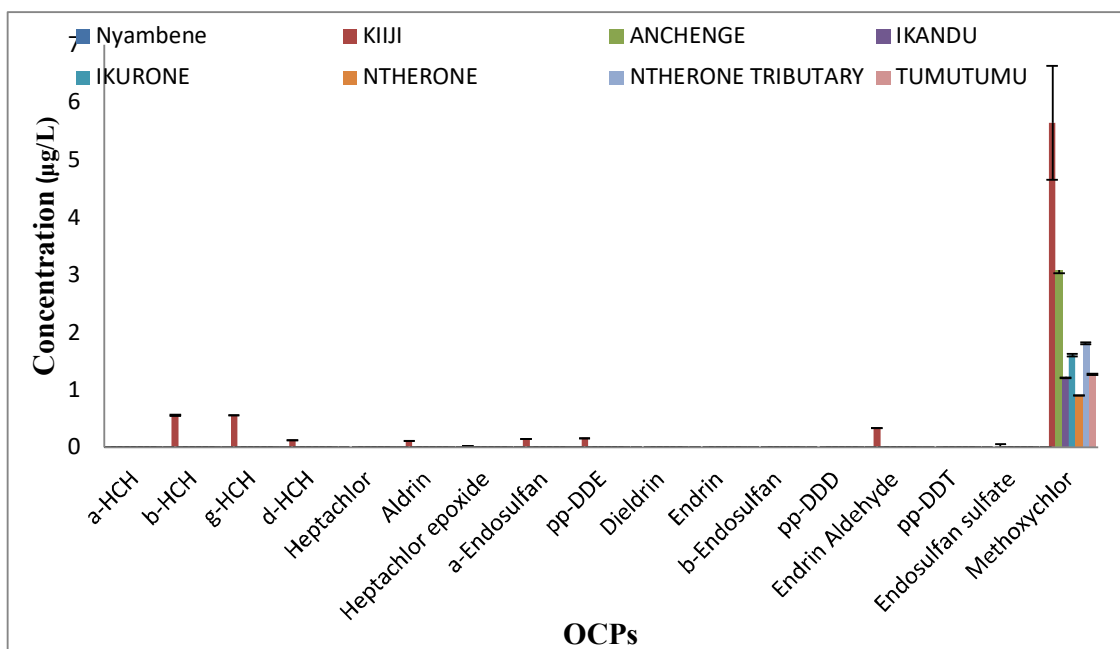
Figure 4.7 Organochlorine pesticides residue levels in water in dry season

During the month of March (dry season), the OCP residues levels in the water samples was lower (Figure 4.7), than the amounts detected in the rainy season (Figure 4.6). Lindane (γ- HCH) was only detected at Kiiji 0.56 ±0.00 µg/L. β and δ –HCH residue levels detected was 0.56±0.01 µg/L and 0.13 ±0.00 µg/L (Table 4.9) suggesting recent illegal use of lindane and slow degradation into its by products; β and δ –HCH or long-distance transportation and deposition.

Heptachlor was also detected at Ikurone (0.01±0.00 µg/L) and its breakdown product heptachlor epoxide (0.03±0.00 µg/L) at Kiiji. No levels of *p,p'*-DDT and *p,p'*-DDD were found in the water test samples. *p,p'*-DDE (0.16 ±0.00 µg/L) was detected at Kiiji indicating slow breakdown of *p, p'*-DDT or contamination from long distance deposition. While α-endosulphan (0.15 ±0.00 µg/L) was found in Kiiji, no endosulphan sulphate was found in any of the samples that were taken.

Kiiji water test samples also contained Endrin aldehyde, with concentrations of 0.34 ±0.00 µg/L implying previous use of endrin in the area or deposition after long distance transportation either by soil erosion or through the air. The pattern of low OCP residue quantities in samples of water when compared to other matrices such sediments and plants or animals are comparable to the

findings of a study conducted in Lake Nakuru. There, samples of water were examined, and it was discovered that OCP ranged from below the threshold of detection limit to 7.44 µg/L (Nantongo *et al.,* 2023).

Methoxychlor was often found among all the targeted OCPs in all the water collected except Nyambene water which is the sampling site next to the forest. The highest concentration of methoxychlor was recorded at Kiiji with 5.64 ±0.99 µg/L (Table 4.9). Generally, Kiiji sampling site predominantly shows the highest levels of contamination with lindane, *p,p'*-DDE, *α*-endosulphan, endrin aldehyde, aldrin and methoxychlor. Figure 4.7 shows the OCPs residue levels in March 2016. These findings are not unusual as several OCPs have already been found in other surface water studies as well (Zhou *et al.,* 2006). Here, the residues reported were up to 0.27 µg/L in Qiantang River water.

4.3.2 Concentration of OCP in sediment

All of the analytes targeted were present in the samples of sediment obtained from the eight sampling locations along the river Ura variably. According to the research, organochlorine pesticide residues (Table 4.10) ranging from <0.001 to 71.13 ±8.45 µg/kg of methoxychlor in sediment samples in wet season from Ntherone tributary sampling site were found.

4.3.2.1 Organochlorine pesticide residue levels in sediments from Ura River in wet season

Results from the samples collected in the wet season (October 2015), demonstrated that OCPs were present with varying levels in the range of <0.001 to 71.13±8.45 µg/kg. Among all the analytes, methoxychlor was the most at Ntherone tributary site.

The HCH isomers' average concentration ranged from $α$-HCH (<0.001 to 3.71±0.02 µg /kg), $β$-HCH (<0.002 to 0.44±0.00 µg/kg), $δ$-HCH (<0.004 to 22.60±0.85 µg/kg) and $γ$-HCH (<0.002 to 7.97±1.06 µg/kg). *p,p'*-DDT levels varied between <0.002 to 29.84±1.73 µg/kg) and its analogue (*p,p'*-DDD) ranged between (<0.002 to 19.09±2.85 µg/kg) and the range of *p,p'*-DDE between (<0.002 to 2.52±0.05 µg/kg).

Typically, the concentration of aldrin, heptachlor, heptachlor epoxide, endrin, endrin aldehyde and dieldrin ranged between, <0.004 to 46.44±2.49 µg/kg; <0.001 to 8.26±0.97µg/kg; <0.001 to 6.33±0.25 µg/kg; <0.002 to 3.61±0.00 µg/kg; <0.002 to 10.85±0.04 µg/kg; and <0.003 to

4.21±0.09 µg/kg, respectively (Table 4.10). Endosulphan isomers and metabolite ranged from α -endosulphan (<0.001 to 16.69±0.87 µg/kg); β-endosulphan (<0.001 to 35.91±4.82 µg/kg); endosulphan sulphate <0.002 to 51.96±2.76 µg/kg and methoxychlor <0.002 to 71.13±8.45 µg/kg (Table 4.10).

Table 4.10: OCP residue levels in sediment samples (µg/kg) in wet season

Pesticide / Site	Nyambene	Kiiji	Anchenge	Ikandu	Ikurone	Ntherone	Ntherone Tributary	Tumu Tumu
α-HCH	<0.001	<0.001	0.36±0.00	<0.001	0.57±0.01	0.03±0.00	3.71±0.02	<0.001
β-HCH	<0.002	<0.002	<0.002	<0.002	<0.002	0.43±0.00	0.45±0.00	<0.002
γ-HCH	<0.002	<0.002	<0.002	<0.002	<0.002	7.97±1.06	1.53±0.20	<0.002
δ-HCH	6.00±0.36	<0.004	22.60±0.85	<0.004	0.71±0.00	<0.004	11.60±1.34	<0.004
Heptachlor	<0.001	<0.001	0.14±0.00	<0.001	8.26±0.97	6.01±0.00	1.56±0.00	6.75±0.25
Aldrin	<0.004	<0.004	46.44±2.49	<0.004	4.93±0.00	15.99±1.46	19.34±0.85	19.46±1.72
Heptachlor epoxide	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	6.33±0.25
α-Endosulphan	6.04±0.00	<0.001	<0.001	<0.001	<0.001	<0.001	3.16±0.07	16.69±0.87
p p'-DDE	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	2.52±0.05	<0.002
Dieldrin	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	4.21±0.09	<0.003
Endrin	<0.002	<0.002	<0.002	0.05±0.00	<0.002	3.61±0.00	<0.002	<0.002
β- Endosulphan	35.91±4.82	<0.001	23.07±0.00	<0.001	<0.001	<0.001	8.45±1.01	12.45±0.89
p p'-DDD	<0.002	<0.002	<0.002	<0.002	0.28±0.00	6.72±0.95	19.09±2.85	<0.002
Endrin aldehyde	<0.002	<0.002	2.44±0.00	<0.002	1.09±0.00	10.85±0.04	10.20±0.09	14.25±0.70
p p'-DDT	<0.002	<0.002	14.69±1.53	<0.002	4.43±0.85	29.84±1.73	28.38±1.43	25.52±0.65
Endosulphan sulphate	<0.002	<0.002	31.12±0.89	<0.002	2.93±0.26	42.23±2.91	51.96±2.76	16.62±1.58
Methoxychlor	<0.002	<0.002	36.49±1.73	<0.002	0.75±0.07	65.63±5.63	71.13±8.45	54.78±7.20

Concentration (µg/kg) = Mean ± S.D   n=8
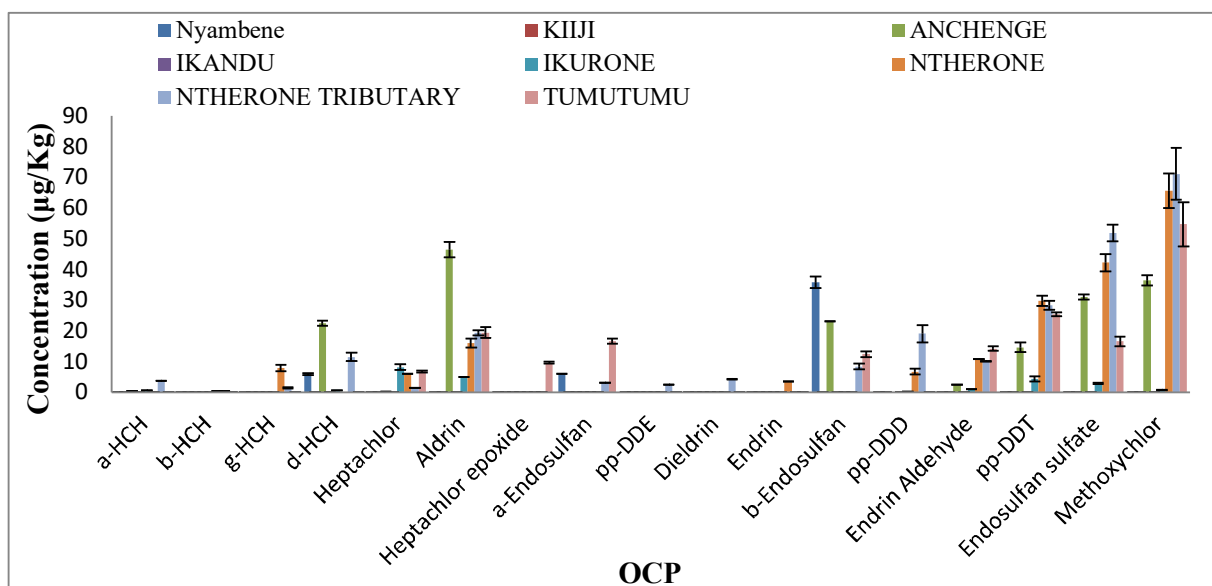
Figure 4.8 OCP residue levels in sediment samples (µg/kg) in wet season

Lindane (γ-HCH) and its isomers were detected in a number of the sediment samples collected (Figure 4.8). δ- HCH was detected in samples from four sites namely; Nyambene (6.00±0.36 µg/kg), Anchenge (22.60±0.85 µg/kg), Ikurone (0.71±0.00 µg/kg) and Ntherone tributary (11.59±1.34 µg/kg). Among all the other isomers in this group, it was the most abundant. γ-HCH which is known to be the most persistent of the isomers was observed at Ntherone 7.97±1.06 µg/kg and Ntherone tributary 1.53±0.20 µg/kg. Similarly, β-HCH was found in the two sites though in smaller quantities. Ntherone (0.43±0.00µg/kg) and the sediments from its tributary (0.45±0.00 µg/kg). α-HCH was detected in four sites; Anchenge (0.36±0.00 µg/kg), Ikurone (0.57±0.01 µg/kg), Ntherone (0.03±0.00 µg/kg), Ntherone tributary (3.71±0.02 µg/kg). The current study displays less quantities of HCH in Ura river sediments as opposed to the amounts in estuaries of rivers on the northern side of Bohai Sea that yielded up to 1964.97 µg/kg (Hu *et al.,* 2010). However, Lans-Ceballos *et al.* (2018) analyzed for HCHs in sediment samples from Sinú, a river in the Caribbean and reported levels of up to 7.57 µg/kg, similar to the findings in the Ura river sediments.

This whole distribution indicates either recent scanty use of γ-HCH, or its long-term degradation or atmospheric degradation to produce its breakdown products (α-HCH, β-HCH and δ-HCH). Heptachlor levels was detected at Ikurone (8.26±0.97 µg/kg) and its product heptachlor epoxide was only detected at Tumutumu (6.33±0.25 µg/kg). The sites upstream did not show any of the two so being a rainy season this would suggest the sediments were contaminated by heptachlor and heptachlor epoxide might have been from the erosion of the soils from farms into the river. This further suggests that there could be current use of heptachlor pesticides in the farms.

Aldrin was more predominant in a number of sites than its breakdown product dieldrin which was only detected at Ntherone tributary (4.21±0.09 µg/kg). The abundance of aldrin at Anchenge (46.44±2.49 µg/kg) as shown in Table 4.10, could indicate some recent illegal use of the chemical. Endrin was very scanty being observed in sediments from Ntherone only. On the other hand, endrin aldehyde appears many times in most sites except the two upstream sites, indicating slow decomposition of endrin along the river from mid-stream downwards. In sediments from five of the eight sampling sites, p,p'- DDT was found. The concentrations varied from midstream and downstream. The levels were much higher compared to those of p, p'- DDD (<0.00-19.09±2.85 µg/kg) and p,p'-DDE which was only detected at Ntherone tributary (2.52±0.05 µg/kg), implying illegal use of p,p'-DDT in the area or deposition after long distance transportation. β-endosulphan was more abundant than α- endosulphan because the latter is thought to be less tenacious in the natural environments. Their break down product, endosulphan sulphate was also detected at the sites where p,p'-DDT was detected but at much higher values (29.84±1.73 µg/kg) from Ntherone site.

However, it was noted that no levels were detected in sediments from the upstream sites indicating that contamination began in the mid-stream section. Levels of methoxychlor in Anchenge, Ikurone, Ntherone, Ntherone tributary and Tumutumu, which ranged from 0.75±0.07 µg/kg - 71.13±8.45 µg/kg in the sediments, could mean deposition form eroded soils into the river due to the heavy rainfall in the month of October (Figure 4.8). Generally, quite a number of OCPS were detected from Ura River sediment majorly due to erosion of soil from various places into the river during the heavy rains. This study confirms presence of organochlorine contaminants in the environment because it compares to similar findings in

sediments from Nairobi River, that were analyzed contained up to 41.9 µg/kg of OCPs (Ndunda *et al.,* 2018).

4.3.2.2 Organochlorine pesticide residue levels in sediments from Ura River in dry season

The samples collected in the dry season (March, 2016) showed presence of organochlorine pesticides at varying concentrations in the range from <0.001 to 134.96±24.36 µg/kg of *p,p'*-DDT at Ikandu (Table 4.11). The OCPs in sediment from the 8 sampling locations in March are shown in Table 4.11.

Average residues of hexachlorocyclohexane (HCH) isomers were α-HCH (<0.001 to 0.42 ±0.00 µg /kg), β-HCH (<0.002 to 6.75 ±0.97µg /kg), γ-HCH (<0.002 to 4.21 ±0. 01 µg /kg) and δ-HCH was not found at every site (Table 4.11).

The *p,p'*-DDT concentration varied between (< 0.002 to 134.96±24.3 6µg/kg) and its analogue (*p,p'*-DDD) ranged between (<0.002 to 16.22±1.54 µg/kg) while the *p,p'*-DDE analogue was from <0.002 to 0.32 ± 0.00 µg/kg. Average levels of heptachlor and endrin aldehyde ranged between <0.001 to 3.22±0.67 µg/kg and <0.002 to 48.27±4.88 µg/kg. Aldrin, endrin, heptachlor epoxide, endrin and dieldrin were all below the limit of detection in the eight sites (Table 4.11).

The range of average endosulphan isomer and levels of metabolites was α-endosulphan. (<0.001 to 16.03±1.54 µg/kg); β-endosulphan (<0.001 to 13.34±1.24 µg/kg); endosulphan sulphate <0.002 to 108.74±20.2 6µg/kg and methoxychlor <0.002 to 84.18±13.87 µg/Kg (Table 4.13).

Conclusively, the concentrations of OCP in the sediments during the dry season varied from <0.001 to 134.96±24.36 µg/kg of *p,p'*-DDT at Ikandu. The Table 4.11 and Figure 4.9 show the details.

Table 4.11: OCP residue levels in sediment samples (µg/kg) in dry season

Pesticide /Site	Nyambene	Kiiji	Anchenge	Ikandu	Ikurone	Ntherone	Ntherone tributary	Tumu Tumu
α-HCH	<0.001	0.42±0.00	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
β-HCH	<0.002	<0.002	1.14±0.00	6.75±0.97	<0.002	<0.002	2.15±0.08	<0.002
γ-HCH	<0.002	<0.002	<0.002	4.21±0.01	<0.002	<0.002	<0.002	<0.002
δ-HCH	<0.004	<0.004	<0.004	<0.004	<0.004	<0.004	<0.004	<0.004
Heptachlor	<0.001	3.22±0.67	1.34±0.06	0.29±0.00	<0.001	2.64±0.03	1.47±0.00	<0.001
Aldrin	<0.004	<0.004	<0.004	<0.004	<0.004	<0.004	<0.004	<0.004
Hepltachlor epoxide	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
α- Endosulphan	<0.001	16.03±1.54	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
p, p'-DDE	<0.002	0.32±0.00	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002
Dieldrin	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003
Endrin	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002
β- Endosulphan	<0.001	<0.001	<0.001	<0.001	6.09±0.87	<0.001	<0.001	13.34±1.24
p, p'-DDD	<0.002	<0.002	<0.002	<0.002	<0.002	16.22±1.54	<0.002	<0.002
Endrin ldehyde	<0.002	15.13±2.39	34.90±6.89	48.27±4.88	<0.002	<0.002	18.22±0.98	20.59±0.96
p, p'-DDT	<0.002	65.02±5.45	35.73±5.34	134.96±24.36	<0.002	<0.002	21.65±1.55	12.92±0.08
Endosulphan sulphate	<0.002	15.58±1.64	51.97±10.07	<0.002	<0.002	108.74±20.26	59.48±2.96	80.70±7.79
Methoxychlor	<0.002	62.25±8.79	72.81±6.43	40.37±11.35	<0.002	84.18±13.87	67.51±8.26	54.37±6.58

Concentration (µg/kg) = Mean ± S.D   Limit   n=8
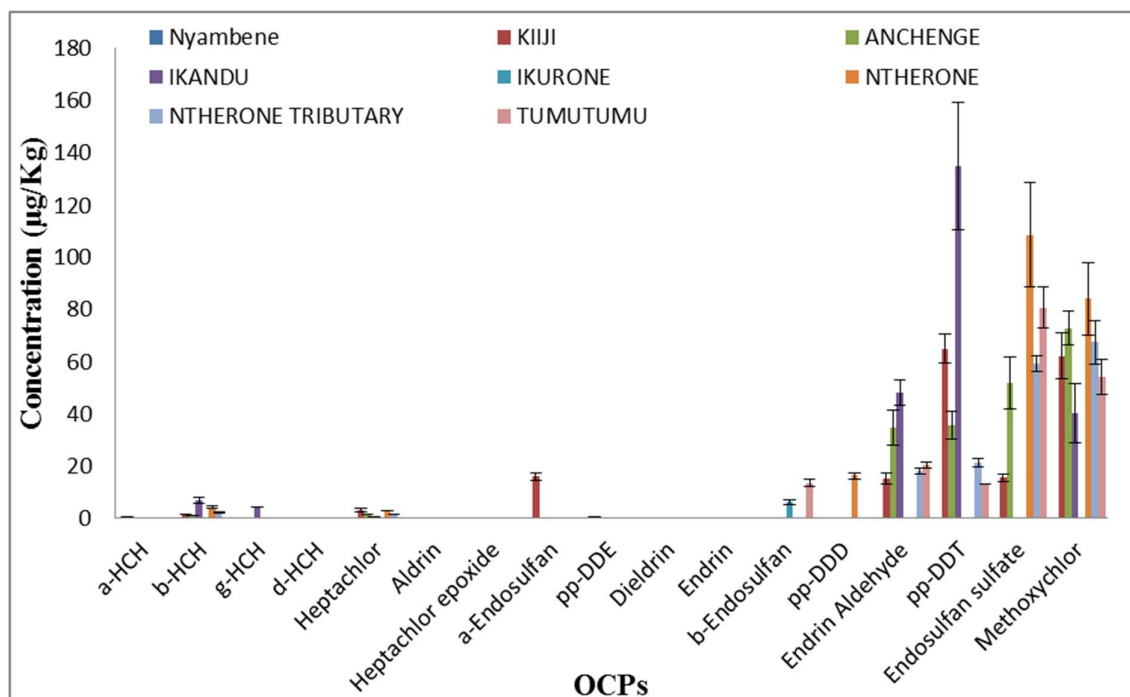
Figure 4. 9 OCP residue levels in sediment samples (µg/kg) in dry season

During the month of March 2016, a dry season, lower distribution with higher levels of OCPs (Figure 4.9) are listed in the sediments compared the rainy season (October 2015) season. Small quantities of ɤ-HCH were detected in the sample from Ikandu and Ntherone. Its β-HCH breakdown product was the most frequently detected in the various sites while α-HCH was very minor and only at Kiiji. δ- HCH was not detected in all the eight sites.

Heptachlor seemed still to be dominant though in small quantities with it's by product heptachlor epoxide not detected in all the sites. This was an indication of recent illegal use of heptachlor as a pesticide in the area. Presence of endrin aldehyde in the sample is an indication of previous use of endrin, which is not present in any of the samples in the sediments of Ura River.

The majority of the sediment samples had *p,p'*-DDT, Ikandu sample recording the highest level of 134.96 ±24.36 µg/kg. There was no evidence of its by products, *p,p'*-DDD and *p,p'*-DDE. This indicates recent illegal use of *p,p'*-DDT in the area or long-term accumulation or long-distance transportation and deposition. The results of DDT in sediment samples from Ura river

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were comparable to the levels detected in samples from Malaysia's Cameron highlands which were between 0.025 µg/kg and 23.24 µg/kg on surface sediment samples (Saadati *et al.,* 2012).

Endosulphan sulphate and methoxychlor appeared to be a bit high in concentration levels with endosulphan sulphate indicating previous use of *α* and *β*–endosulphan in the area which are slowly degrading into endosulphan sulphate in the sediments.

In an over view, it is observed that most of the concentrations of the detected OCP were below the sediment quality guidelines as per the probable effect limits (PEL) (Burton, 2002). Even so constant monitoring of the residues and public awareness on use of these PCBs is important.

4.3.3 OCPs residue levels in soil samples

The examination of soil samples revealed amounts of the seventeen target pesticide residues at various locations. Average concentration was from <0.001 to 197.07±36.47 µg/kg. Soil samples collected from Anchenge in March had the most concentration.

4.3.3.1 Organochlorine pesticide residues in soil samples in wet season

The samples collected in the wet season (October, 2015) revealed the presence of pesticides made from organochlorine compounds at various levels of quantities. That is <0.001 to 99.57±5.87 µg/kg (Table 4.12). Methoxychlor was notably the highly detected at Nyambene area. Table 4.12 shows levels of organochlorine residues levels in samples of soil collected in rainy season at different locations.

Hexachlorocyclohexane was from <0.002 to 9.78±1.63 µg/kg for *γ*-HCH, *δ*-HCH (<0.004 to 14.50 ±0.33 µg/kg), *β*-HCH (<0.002 to 4.64 ±0.72 µg /kg), and *α* -HCH 0.62±0.00 µg/kg to 12.34 ±0.61 µg/kg). The average amount of *p,p′*-DDT was from 1.06±0.00 µg/kg to 28.89±0.83µg/kg) and its analogue (*p,p'*-DDE) lie from (<0.002 to 1.76 ±0.00 µg/kg) while *p, p'*-DDD ranged between (<0.002 to 12.40±1.85 µg/kg (Table 4.12).

The mean concentration of endrin aldehyde, aldrin, heptachlor, endrin, dieldrin and heptachlor epoxide ranged between <0.002 to 44.64±7.92 µg/kg, <0.004 to 3.79 ±0.00 µg/kg; <0.001 to 63.02±8.30 µg/kg; <0.002 to 4.64±0.11 µg/kg; <0.003 to 18.86±0.00 µg/kg and <0.001 to 37.09±2.85 µg/kg, respectively. The mean concentration of endosulphan isomers and

metabolite ranged between β-endosulphan <0.001 to 19.18±2.22 µg/kg; α-endosulphan <0.001 to 27.59±3.17 µg/kg; endosulphan sulphate <0.002 to 78.23±6.23 µg/kg and methoxychlor <0.002 to 99.57±5.87 µg/kg.

Table 4.12: Organochlorine pesticide residues in soil(µg/kg) during the wet season

Pesticide /Site	Nyambene	Kiiji	Anchenge	Ikandu	Ikurone	Ntherone	Ntherone tributary	TumuTumu
α-HCH	5.61±0.22	12.34±0.61	4.42±0.26	1.43±0.54	0.62±0.00	2.64±0.86	1.44±0.84	6.43±0.04
β-HCH	<0.002	1.39±0.24	0.31±0.09	1.49±0.09	<0.002	4.12±1.19	1.03±0.03	4.64±0.72
γ-HCH	<0.002	9.78±1.63	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002
δ-HCH	1.76±0.00	1.78±0.28	0.57±0.02	1.36±0.42	1.28±0.81	1.50±0.23	14.5±0.33	<0.004
Heptachlor	0.23±0.00	<0.001	<0.001	3.99±0.45	1.61±0.80	41.69±2.61	<0.001	63.02±8.30
Aldrin	<0.004	<0.004	<0.004	3.66±0.57	2.73±0.00	<0.004	<0.004	3.79±0.00
Hepltachlor epoxide	<0.001	1.11±0.00	<0.001	<0.001	1.83±0.54	<0.001	<0.001	37.09±2.85
α- Endosulphan	<0.001	27.59±3.17	<0.001	3.89±0.01	6.39±0.96	0.94±0.63	0.37±0.25	0.42±0.00
p, p'-DDE	<0.002	<0.002	0.68±0.00	<0.002	1.76±0.00	<0.002	<0.002	<0.002
Dieldrin	<0.003	<0.003	2.73±0.59	15.91±0.96	18.86±0.00	6.33±0.22	3.14±0.00	<0.003
Endrin	<0.002	<0.002	4.64±0.11	<0.002	1.43±0.00	3.25±0.00	1.87±0.00	<0.002
β-Endosulphan	<0.001	<0.001	7.71±1.80	2.70±0.00	8.74±1.87	<0.001	19.18±2.22	1.90±0.00
p,p'-DDD	0.74±0.00	<0.002	7.26±0.75	3.29±0.00	8.07±1.75	12.40±1.85	8.48±2.38	4.59±0.00
Endrin aldehyde	24.97±3.56	10.58±0.00	6.31±0.29	5.50±1.02	6.69±0.44	44.64±7.92	8.55±0.84	7.20±1.41
p,p'-DDT	12.84±0.00	1.06±0.00	22.54±1.43	16.04±0.00	28.89±0.83	24.89±6.32	23.25±1.89	19.80±0.99
Endosulphan sulphate	0.03±0.00	9.38±0.65	<0.002	29.78±0.64	24.85±0.56	36.76±0.00	78.23±6.23	46.45±13.85
Methoxychlor	99.57±5.87	95.03±5.14	60.67±5.7	18.10±0.79	35.21±1.77	38.93±2.34	77.84±5.32	27.76±0.25

Concentration(µg/kg) = Mean ± S.D   n=8
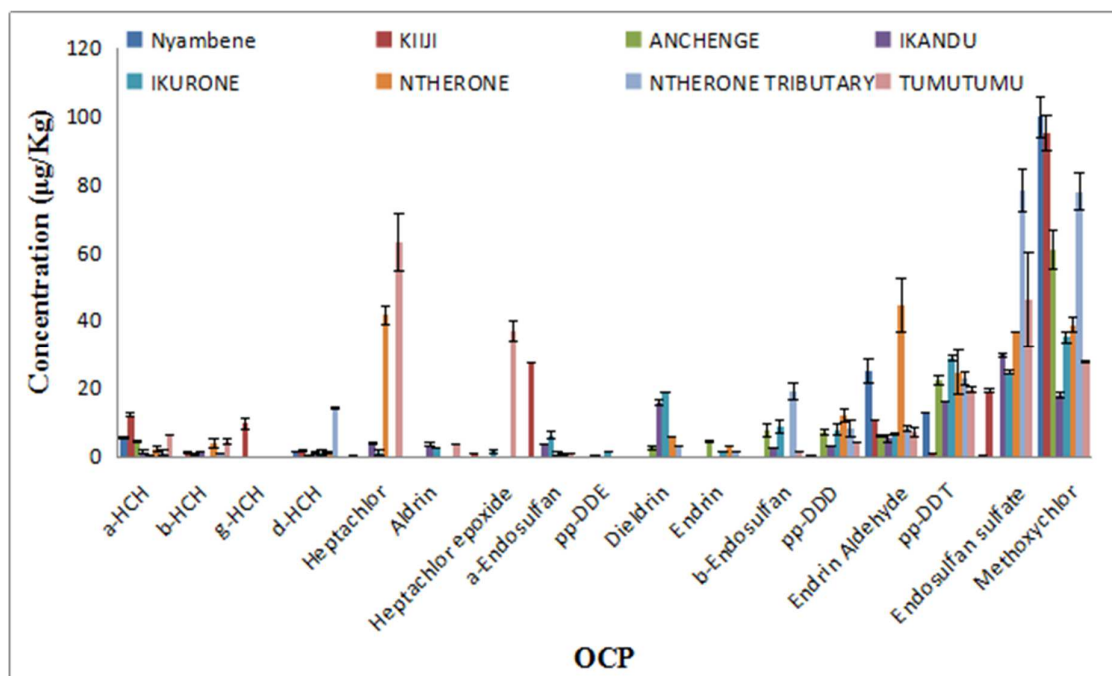
Figure 4.10 Organochlorine pesticide residue levels in soil samples in wet season

Kiiji sampling site had soil samples contaminated with all the isomers of HCH (Figure 4.10). α- HCH had high concentration 12.34 ± 0.61 µg/kg among all the isomers followed by γ-HCH 9.78 ± 1.63 µg/kg then β-HCH 4.64 ± 0.72 µg/kg and δ-HCH recorded the least concentration 1.78 ± 0.28 µg/kg. This distribution indicates some recent illegal use of lindane in the area and subsequent gradual degradation. Other sites recorded levels of contamination with α-HCH and β-HCH also detected at Anchenge, Ikandu, Ntherone, Ntherone tributary and Tumutumu (Figure 4.10). The amounts of HCH isomers detected in the current study exhibited lesser levels compared to those obtained from agricultural soils analyzed in Delhi, India ranging between 0.04 µg/kg and 458.00 mg/kg of soil (Prakash *et al.,* 2004).

Heptachlor had the highest distribution across most samples' sites with the highest level 63.02 ± 8.30 µg/kg at Tumutumu within the downstream portion of the study region. Heptachlor epoxide is correspondingly high at Tumutumu recording up to 37.09 ± 2.85 µg/kg (Figure 4.10). This implies slow degradation of heptachlor. Other sites that gave high levels of heptachlor

were from Ntherone (41.69±2.61 µg/kg) while other sites recorded relatively low concentration. Heptachlor which was usually used to control ants and termites is detectable in soil 14 years after it is applied. Its epoxide is even more stable. Hence the need to monitor it in the soil. A study carried out in Togo had 74% of the soil samples showed evidence of heptachlor epoxide (Mawussi *et al.,* 2014). This confirms residue of use and remains of heptachlor in the environment. The study of heptachlor and its epoxide in soils from farms in Igembe south confirms contamination with this kind of pesticide to levels up to 63.02±8.30 µg/kg.

Soil tests of farm located at the Kiiji sampling area had the highest content of *α*-endosulphan. with an average level of 27.59±3.17 µg/kg. It was also distributed in other sites recording up to 6.39±0.96 µg/kg at Ikurone but soils from Nyambene and Anchenge recorded below detection limit (<0.001 µg/kg). *β*-endosulphan was most in soils from Ntherone tributary 19.18± 2.22 µg/kg while soil samples from Ntherone, Nyambene and Kiiji recorded below detection limit of <0.001µg/kg. Endosulphan sulphate was abundant in all soil samples except from Anchenge site (Figure 4.10). Highest concentration was recorded at Ntherone tributary showing up to78.23±6.23 µg/kg. High concentration of endosulphan sulphate was also seen in soils from Tumutumu (46.45± 13.85 µg/kg), Ntherone (36.76±0.00 µg/kg), Ikandu (29.78±0.64 µg/kg), Ikurone (24.85± 0.56 µg/kg) and Kiiji (19.38±0.65 µg/kg). The distribution indicates some use of endosulphan sulphate in the environment. A similar detailed analysis of OCP residues in soils from Europe can be used to compare to the results of this study (Tzanetou & Karasali, 2022). There, 43.5% of soil samples tested positive for endosulphan sulphate while 87.5% of samples from Igembe south did show endosulphan sulphate. This is attributed to previous application of endosulphan based pesticides.

In every soil sample, there was indication of *p,p′*-DDT and the amounts ranged from 1.06±0.00 µg/kg at Kiiji to 28.89±0.83 µg/kg at Ikurone. Other high levels were recorded at Ntherone (24.89±6.32 µg/kg), Ntherone tributary (23.25±1.89 µg/kg), Anchenge (22.54±1.43 µg/kg), Nyambene (12.84±0.00 µg/kg), Tumutumu (19.80± 0.99 µg/kg) and Ikandu (16.04 ±0.00 µg/kg). This clearly indicates that across the farms in the area, there is use of *p,p'*-DDT which takes time to degrade into its metabolites, *p,p'*-DDD which is additionally well distributed. *p,p'*-DDE was scantly distributed. From a similar study by Mahugija *et al*. (2018), it was recommended that high level monitoring of use and residues of DDT and its analogues would

be necessary. This was after assessing their levels in soil samples from east of Lake Tanganyika and the analysis revealed presence of DDT and analogues to levels from 7.50 µg/kg to 564.20 µg/kg dry weight. In another case of past use of DDT in agriculture as well as malaria control in Mexico, 0.001 mg/kg to 0.79 mg/kg of DDT and 0.001 mg/kg to 0.64 mg/kg of DDE were detected in fields soil samples (Martinez *et al.,* 2011). These are causes of alarm that would direct further objective monitoring of DDT and the residues that result from its degradation in soils used for farming for safety of life.

Aldrin was detected in small quantities at Ikandu and Tumutumu while its breakdown product dieldrin appeared quite a number of times in levels ranging from (2.73±0.59 µg/kg to 18.86± 0.00 µg/kg) at Anchenge, Ikandu, Ikurone, Ntherone and Ntherone tributary. It was noted that soils from some sampling sites in Igembe south displayed levels of dieldrin corresponding to research done on European soils which indicated 18 µg/kg (Tsiantas *et al.,* 2021). Even soil samples from cocoa farms in Ghana had dieldrin as the frequently detected (0.005–0.02 mg/kg) by Fosu-Mensah *et al.* (2016). Endrin was also detected up to 4.64±0.11 µg/kg at Anchenge site but endrin aldehyde was much more suggesting active breakdown of endrin in the farms.

Just like in sediments, methoxychlor had the highest degrees of concentration in comparison to the rest of the OCPs targeted. Highest was recorded at Nyambene (99.57 ± 5.87 µg/kg) and the lowest at Ikandu (18.10± 0.79 µg/kg). The reason could be due to its availability in the market and hence usage in farms.

Wasswa, (2008) attributes the levels of pesticides in sediments to their hydrophobicity. As a result, they settle and accumulate in the sediments of water bodies. The sediments from Lake Victoria-Uganda contained a total of 18 pesticide residues and metabolites, with endosulfan sulfate accounting for 42% of all pesticide residue detections and chlorpyrifos recording the highest mean value at 4.18 g/kg (dry weight). Additionally, pesticide residues that were not authorized for usage in Uganda were also found by the study.

4.3.3.2 Organochlorine residue levels in soil during dry season

The concentration of OCPs in soil test samples obtained from eight sites varied from <0.00 to 197.07±36.47 µg/kg (Table 4.13). Endosulfan sulphate had the highest level at Anchenge

sampling site. Table 4.13 shows the mean concentration of OCPs residue levels in dry season (March, 2016).

Table 4.13:Organochlorine pesticides residues in soil (µg/kg) during dry season

Pesticide/ Site	Nyambene	Kiiji	Anchenge	Ikandu	Ikurone	Ntherone	Ntherone tributary	TumuTumu
α-HCH	0.74±0.00	<0.001	76.42±4.19	<0.001	<0.001	36.01	<0.001	<0.001
β-HCH	2.30±0.06	3.37±0.32	24.14±1.64	3.79±0.68	9.59±1.54	8.25±0.05	2.56±0.02	<0.002
γ-HCH	<0.002	2.22±0.00	20.65±2.76	2.93±0.02	2.42±0.01	2.72±0.01	1.69±0.00	<0.002
δ-HCH	<0.004	<0.004	<0.004	<0.004	<0.004	<0.004	<0.004	<0.004
Heptachlor	2.53±0.65	5.44±1.07	2.05±0.32	0.12±0.00	2.93±0.00	6.14±0.08	2.54±0.33	0.37±0.00
Aldrin	<0.004	<0.004	<0.004	<0.004	<0.004	<0.004	<0.004	<0.004
Heptachlor epoxide	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
α-Endosulphan	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
p, p'-DDE	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002
Dieldrin	<0.003	<0.0033	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003
Endrin	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002
β- Endosulphan	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
p, p'- DDD	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	9.31±1.06	<0.002
Endrin aldehyde	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002
p, p'-DDT	11.61±0.64	48.37±5.94	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002
Endosulphan sulphate	20.04±2.34	140.50±20.95	197.07±36.47	<0.002	52.72±2.45	<0.002	<0.002	<0.002
Methoxychlor	152.98±8.72	152.32±16.88	108.66±21.45	62.41±9.49	102.86±10.89	147.75±22.78	176.26±18.24	63.85±5.44

Concentration= Mean ± S.D   <n -Below detection limit   n=8
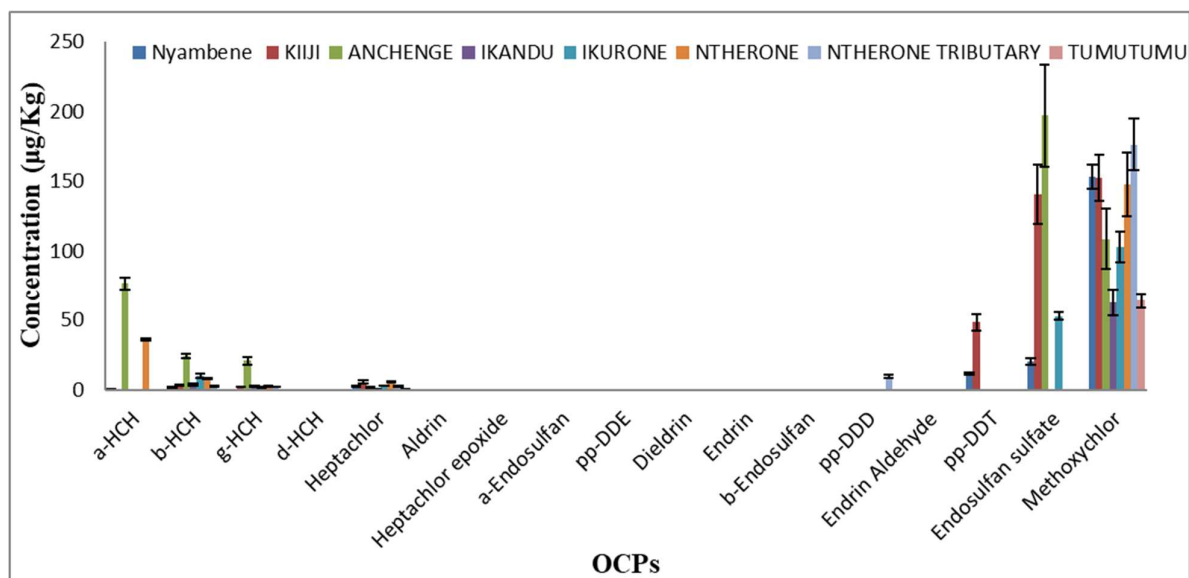
Figure 4. 11 Distribution of OCP in soil samples (µg/kg) in dry season

Samples of soil taken in March during the dry season (Figure 4.11) showed lower concentrations of organochlorine pesticides than in October (Figure 4.10).

γ-HCH and all isomers of HCH were detected at various points except δ-HCH. β- HCH was the most, followed by γ-HCH then α-HCH. Highest concentration of the total γ-HCH and its isomers was at Anchenge, followed by Ntherone, Ikurone, Kiiji, Nyambene and Ntherone tributary. Tumutumu did not record any amounts of these isomers (Figure 4.11). This may indicate recent illegal use of γ-HCH and deposition after long distance transportation.

Heptachlor was detected in all the soil samples though in small amounts from (0.37 ±0.00 µg/kg - 6.14 ± 0.08 µg/kg). Heptachlor epoxide was below detection the detection threshold across the sites.

p,p' -DDT was only recorded in samples of soil from Nyambene (11.61 ±0.64 µg/kg) and Kiiji (48.37±5.94 µg/kg) while its product metabolite *p,p'*-DDD was only detected at Ntherone tributary 9.31±1.06 µg/kg and *p,p'*-DDE was below 0.001±0.00 µg/kg at all the locations.

Endosulphan sulphate gave levels at Nyambene 20.04 ± 2.34 µg/kg, Kiiji 140.50±20.95 µg/kg, Anchenge 197.07±36.47 µg/kg and Ikurone 52.72±2.45 µg/kg. This suggests use of

endosulphan which is breaking slowly into endosulphan sulphate. There could also be contamination from deposition after long distance transportation.

In all of the soil test samples, methoxychlor was the most prevalent element, with amounts that varied from 62.41±9.49 µg/kg to 176.26±18.24 µg/kg suggesting illegal use of the chemicals in the farms. Abong'o *et al.* 2015 also assessed soil samples from Nyando river catchment area and detected methoxychlor levels in the range of the findings of the current study. Another study of OCPs in soil from farms near lake Naivasha also indicated levels of methoxychlor and others up to 104.17 µg/kg (Okworo, 2017). Due to the low moisture level of the soil test samples during the dry season compared to the rainy season, the amounts of residues of pesticides were greater.

4.4 OCPs residue levels in khat

The analysis of khat (miraa) samples from eight sampling sites showed presence of varying concentrations of different target organochlorine residues levels with a range from <0.001±0.00 µg/kg to 110.11±5.31 µg/kg.

4.4.1 Organochlorine pesticide residue levels in khat during wet season

The concentration of OCPs in khat samples collected from eight sampling sites ranged from 0.001±0.00 µg/kg to 110.11±5.31 µg/kg (Table 4.14). Methoxychlor was the highest detected at Ntherone tributary sampling site. Table 4.14 shows the mean concentration of OCPs during the wet season in October 2015.

Table 4.14: Organochlorine pesticide residues in khat (µg/kg) during wet season

Pesticide/ Site	Nyambene	Kiiji	Anchenge	Ikandu	Ikurone	Ntherone	Ntherone Tributary	Tumu tumu
α-HCH	<0.001	<0.001	<0.001	<0.001	<0.001	3.79±0.36	<0.001	<0.001
β-HCH	<0.002	<0.002	30.69±1.47	<0.002	6.74±1.34	68.68±13.47	<0.002	27.76±7.87
γ-HCH	0.14±0.00	43.61±5.36	19.31±4.32	0.13±0.00	68.83±10.36	67.04±7.68	29.72±0.68	14.58±1.78
δ-HCH	<0.004	47.27±0.79	61.02±9.85	<0.004	42.87±1.86	54.23±1.58	0.87±0.00	91.40±4.36
Heptachlor	<0.001	<0.001	24.38±0.71	<0.001	33.17±3.23	15.91±0.09	3.49±0.00	47.16±1.05
Aldrin	77.97±1.46	11.38±0.35	60.55±9.98	53.67±16.75	59.37±9.37	87.53±2.39	27.40±1.14	89.28±6.74
Heptachlor epoxide	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	101.49±1.14	<0.001
α- Endosulfan	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
p, p'-DDE	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002
Dieldrin	3.64±0.00	4.37±0.00	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003
Endrin	<0.002	1.71±0.01	<0.002	<0.002	<0.002	<0.002	2.03±0.00	<0.002
β-Endosulphan	35.91±1.46	<0.001	23.07±0.08	<0.001	<0.001	<0.001	8.45±1.68	12.45±0.08
p, p'-DDD	14.02±0.96	11.94±0.89	2.27±0.00	4.14±0.03	3.42±0.00	8.93±0.46	10.58±0.07	5.89±0.05
Endrin aldehyde	22.20±0.25	28.76±1.16	2.05±0.00	7.16±0.69	3.14±1.09	1.81±0.00	7.56±0.01	4.02±0.05
p, p'-DDT	64.83±15.36	62.89±16.38	43.66±8.72	101.70±8.77	25.83±7.23	38.67±8.65	98.54±9.12	34.77±1.54
Endosulphan sulphate	33.25±1.84	<0.00	27.96±0.85	37.82±1.85	16.19±0.00	40.95±0.77	100.17±2.01	10.79±0.00
Methoxychlor	31.85±5.13	62.83±6.35	53.42±4.41	48.26±8.64	29.60±1.59	27.74±6.16	110.11±5.31	44.67±9.00

Concentration= Mean ± S.D   n=8
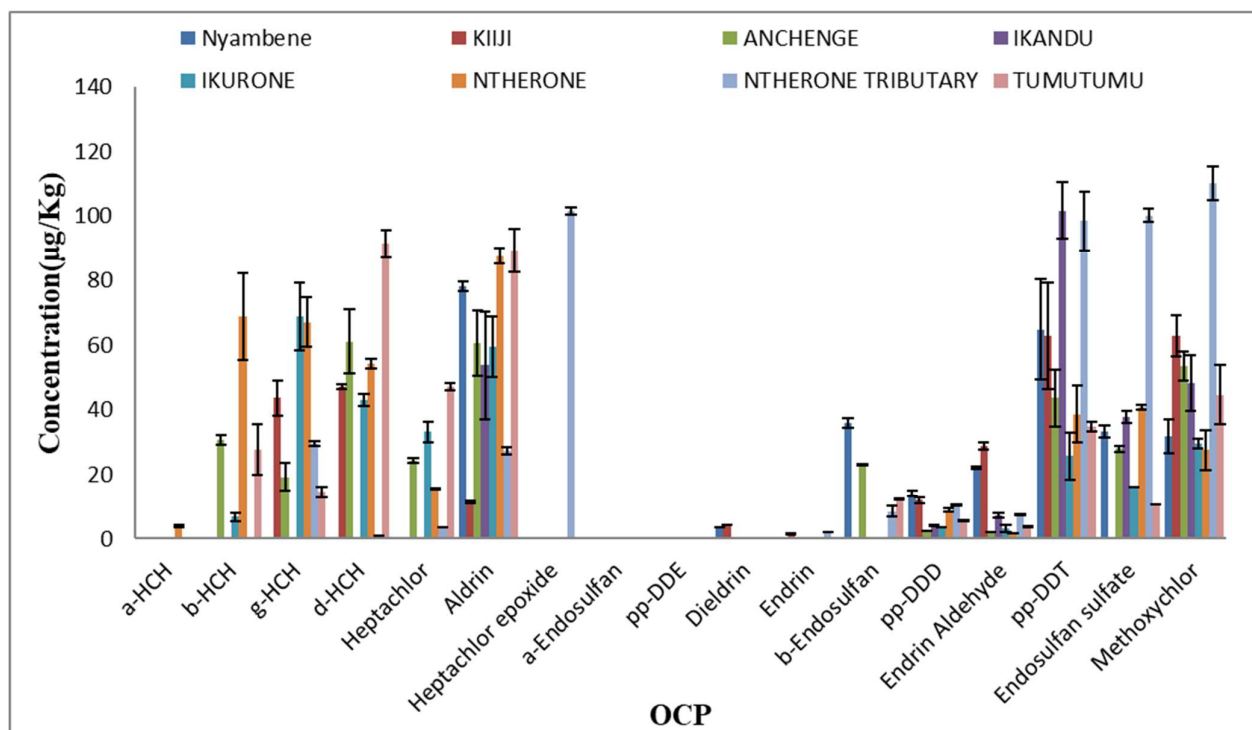
Figure 4.12 Organochlorine pesticide residue levels in khat samples in wet season

In October 2015, at the onset of heavy rainfall, khat samples collected from different small markets along Ura River showed quite a wide distribution of the targeted compounds in the samples (Figure 4.12). Hexacyclohexane was detected with γ-HCH having the most frequency in all the samples from the different markets with a range from 0.13±0.00 µg/kg to 68.83±10.36 µg/kg at Ikurone (Table 4.14). β- HCH was second most abundant missing in samples from only two sites followed by δ-HCH and α-HCH was the least and only in one site, Ntherone with 3.79±0.36 µg/kg.

In the same samples, heptachlor showed levels up to 47.16±1.05 µg/kg at Tumutumu (most downstream site) while its degradation product heptachlor epoxide was only seen at Ntherone tributary with an average level of 101.49±1.14 µg/kg. Presence of heptachlor in khat samples from Anchenge, Ikurone, Ntherone, Ntherone tributary and Tumutumu indicates a probability of recent use of the pesticide in khat production.

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α- endosulphan was not detected in any of the khat samples analysed while *β*-endosulphan appeared in khat from four out of eight (8) sites including Nyambene with 35.91±1.46 µg/kg, Anchenge 23.07±0.08 µg/kg, Ntherone tributary 8.45±1.68 µg/kg and 12.45±0.08 µg/kg at Tumutumu. Khat from two farms near up-streams showed high levels of OCPs while other samples reduced gradually as we went down stream. *β*-endosulphan was more dominant in the khat than *α*-endosulphan because it is more persistent in the environment. When *β*-endosulphan breaks down it forms endosulphan sulphate which appeared to be prevalent in all khat samples except from Kiiji market.

The highest concentration of endosulphan sulphate can clearly be seen in samples from farms near Ntherone tributary and Ntherone at 100.17±2.01 µg/kg and 40.95±0.77 µg/kg respectively while Nyambene (most upstream) had levels up to 33.25±1.84 µg/kg. All the other khat samples which showed levels of *β*-endosulphan also gave higher concentrations of endosulphan sulphate, a clear indication of past use of endosulphan based pesticides in khat farming and thereafter, a slow break down into its by product endosulphan sulphate.

Small levels of endrin in khat samples was only detected in samples from Kiiji and Ntherone tributary at levels of 1.70±0.01 µg/kg and 2.03± 0.00 µg/kg, respectively, while endrin aldehyde appeared in sample from all the market with levels ranging from 1.81±0.00 µg/kg to 28.76±1.16 µg/kg at Kiiji market. Generally, there is an indication of previous use of endrin in the farms and subsequent slow breakdown into endrin aldehyde, long distance transportation and distribution in the environment.

All of the samples contained considerable amounts of *p,p'*-DDT, with quantities varying from 25.83±7.23 µg/kg to 101.70±8.77 µg/kg in samples from Ikandu area farms. This indicates recent illegal use of *p,p'*-DDT, because *p,p'*-DDD is also as well distributed in every khat sample as *p,p'*-DDT (Figure 4.12). Though in smaller amounts as opposed to *p,p'*-DDT, presence of *p,p'*-DDD shows slow breakdown of *p,p'*-DDT to *p,p'*-DDD in the plant materials. *p,p'*-DDE was below 0.002±0.00 µg/kg in all the khat samples.

Woldetsadik *et al.* (2021) conducted research on DDT and HCH exposure and potential health concerns connected with khat intake in Southern Wollo, Ethiopia, where khat chewing is common. According to their findings, even low amounts of OCPs can be harmful to public

health. The examined samples contained β-HCH in excess of the European Commission's maximum residue level. The β-HCH/total HCH ratio ranged from 0.56 to 0.96, indicating a previous use of technical HCH. They also reported that, presuming an everyday consumable quantity of 100 grams, the adult dietary intakes of p,p'-DDT, total DDT and total HCH fluctuated between 3.12 to 57.9, 6.49 to 80.2, and 39.2 to 51.9 ng/kg in body weight in a day, correspondingly.

The β-HCH levels found in Wollo samples were significantly greater than those found in Ura River samples. However, the p,p'- DDT levels are the same as those found in Ura River samples. These are examples of OCP usage. As khat is chewed without any treatment, they relatively reveal a significant risk of cancer illnesses in terms of OCP levels, thus the intakes are of great concern.

Presence of aldrin in khat sample from all the markets suggests that the farmers could be using it in the production of khat. Its concentration in this season ranged from 27.40±1.14 µg/kg to 89.28±6.74 µg/kg. On the other hand, dieldrin (a breakdown product of aldrin) appeared to be very scanty in the samples analysed (Figure 4.12).

Analysis of methoxychlor gave values ranging from 27.74±6.16 µg/kg to 110.11±5.31 µg/kg (Table 4.14). All the khat samples collected from the various markets had some levels of methoxychlor indicating probable use of the pesticide in the area.

4.4.2 OCPS residues levels in khat samples during dry season

The concentration of OCPs residue levels in khat samples from the eight sampling sites ranged from <0.001±0.00 µg/kg to 95.31±8.21µg/kg. Methoxychlor was the highest detected at Ikurone sampling site. Table 4.15, shows the mean concentration of OCPs residue levels in khat in dry season (March, 2016).

March was generally a dry season and the khat samples collected had low levels of OCPs than in October 2016 (wet season). From the study hexacyclohexane was detected with α-HCH isomer being the most frequent as opposed to samples collected in October 2015 that contained more γ-HCH (Figure 4.12). β-HCH was second most frequent and two samples from Nyambene and Anchenge recorded some levels of δ-HCH. γ-HCH (lindane) was below detected limit. The

distribution above shows conversion of γ-HCH into its isomers in the samples and mostly to α-HCH (Figure 4.13).

Heptachlor epoxide was not detected in any sample but its mother compound heptachlor was seen in samples from Anchenge at 92.58±9.19 µg/kg, Ntherone tributary at 0.10 ± 0.00 µg/kg and Tumutumu at 1.54±0.07 µg/kg implying scanty application of heptachlor-based pesticides in khat production (Figure 4.13).

Table 4.15: OCPs residues in khat (μg/kg) during the dry season

Pesticide /Site	Nyambene	Kiiji	Anchenge	Ikandu	Ikurone	Ntherone	Ntherone tributary	TumuTumu
α-HCH	13.90±0.99	<0.001	9.34±0.65	23.73±3.13	49.75±2.54	12.78±0.36	3.64±0.46	10.56±1.65
β-HCH	2.97±0.00	48.75±6.73	53.11±4.77	50.66±2.78	0.51±0.16	3.60±0.00	<0.002	<0.002
γ-HCH	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002
δ-HCH	48.07±5.63	<0.004	12.20±0.23	<0.004	<0.004	<0.004	<0.004	<0.004
Heptachlor	<0.001	<0.001	92.58±9.19	<0.001	<0.001	<0.001	0.10±0.00	1.54±0.07
Aldrin	<0.004	<0.004	<0.004	<0.004	<0.004	<0.004	<0.004	<0.004
Heptachlor epoxide	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
α-endosulphan	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
p, p'-DDE	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002
Dieldrin	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003
Endrin	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002
β -endosulphan	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.0011	<0.00
p, p'-DDD	<0.002	<0.002	34.25±3.56	<0.002	36.54±3.65	<0.002	76.90±14.96	12.38±1.07
Endrin aldehyde	<0.002	<0.002	28.95±1.68	56.10±4.23	93.31±9.77	<0.002	56.83±11.24	<0.002
p, p'-DDT	10.58±0.87	<0.002	56.30±4.16	<0.002	<0.002	<0.002	<0.002	<0.002
Endosulphan sulphate	13.98±1.21	<0.002	60.20±6.25	27.46±0.97	20.90±1.47	22.11±1.49	<0.002	<0.002
Methoxychlor	16.87±1.88	<0.002	35.62±4.99	87.40±15.82	95.31±8.21	19.39±1.23	75.17±19.83	89.51±22.35

Concentration= Mean ± S.D   Limit n=8

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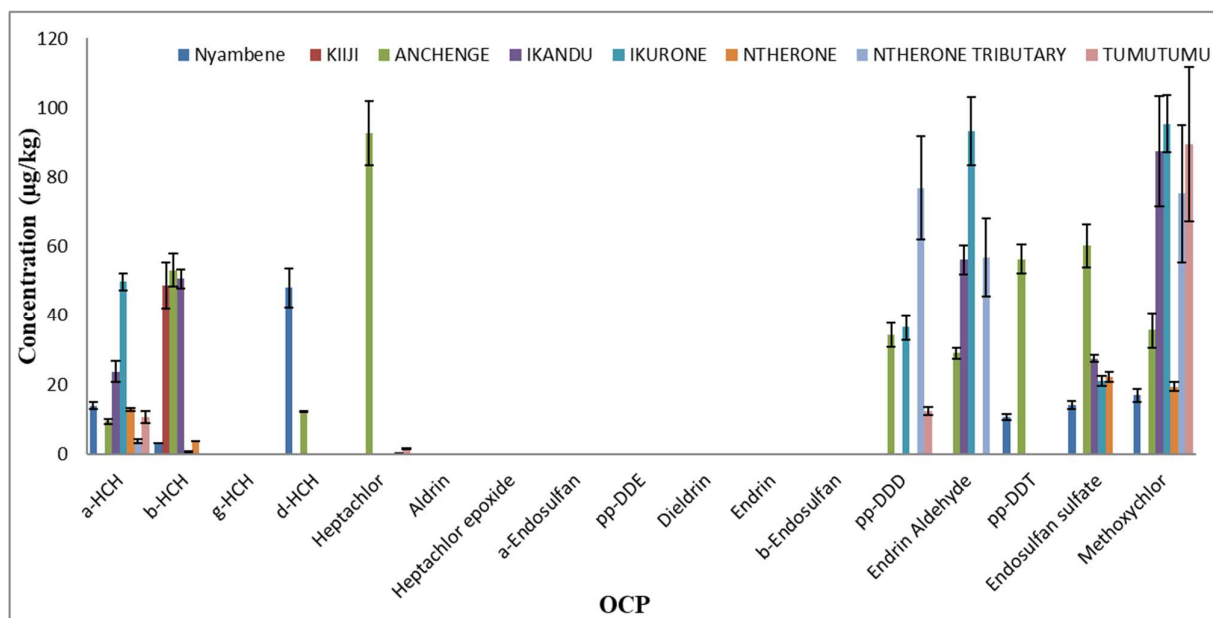
Figure 4.13 OCPs residue levels in khat samples in dry season

Neither *α* nor *β*-endosulphan sulphate was detected its breakdown compound endosulphan sulphate appeared in most samples in notable amounts ranging from <0.002±0.00 µg/kg to 60.20±6.25 µg/kg, a clear indication of past use of endosulphan and subsequent slow degradation in the environment (Figure 4.13).

Aldrin and dieldrin were below detection limit of <0.004 and <0.003± 0.00 µg/kg respectively in all the khat samples in March 2016. Endrin was not also seen but its breakdown product endrin aldehyde appeared in a number of samples from Anchenge (28.95±1.68 µg/kg), Ikandu (56.10±4.23 µg/kg), Ikurone (93.31±9.77 µg/kg) and Ntherone tributary (56.83±11.24 µg/kg).

p,p'-DDT was only seen in samples from Nyambene area market 10.58±0.87 µg/kg and Anchenge (56.30±4.16 µg/kg) but its metabolite *p,p'*-DDD had a higher frequency of appearance in samples from four out of eight markets with levels ranging from 12.38±1.07 µg/kg to 76.90 ±14.96 µg/kg (Figure 4.13). Again, even in this season, *p,p'*-DDE was not detected in any of the khat samples. The distribution suggests slow break down of *p,p'*-DDT to *p,p'*-DDD. Ligani and Hussen (2014) observed residues of *p,p'*-DDT and *p, p'*-DDE from recent pesticide applications in chewable parts of khat in Southern Ethiopia in levels of 10.8-19.7 and 3.5-18.6 g/kg, respectively, in their research on the presence of organochloride pesticides in

chewable portions of khat. The expressed daily uptake was 0.03 and 0.07 μg/kg, respectively, which was lower than the FAO/WHO criteria. However, their ongoing eating would not be safe because the DDT application extended to vegetables that are widely consumed in the region and whose cumulative use could be injurious. Notably, agricultural use of DDT in the country has been prohibited, but detection of this residue demands community education. In relation to our research, the *p, p′*-DDE levels found in the tested samples taken along the Ura River during the wet season were much below 0.002±0.00 μg/kg, making them inconsequential. However, *p, p′*-DDT residue levels ranged from 25.83 to 101.70 μg/kg across the seasons, which is substantially greater than the residue levels identified in Southern Ethiopia, implying increased consumption of the same by chewers and increased health hazards with sustained use. This will result in greater absorption of the same through crops planted along the Ura River, which is a key practice.

According to Mekonen *et al.* (2017), South Western Ethiopian farmers utilized a lot of pesticides in their khat farming. Khat is widely used on a regular basis in South Western of Ethiopia, the existence of residues in the chewed leaves could constitute a possible health concern to the unwary people. Their investigation attempted to evaluate the concentration of OCPs residues on khat leaf samples and estimate the potential health risk to users from ongoing exposure.According to their findings, DDT and its related compounds were present in 80% of the samples, with several of them above FAO/WHO maximum levels. Khat contained quantities of *p′p*-DDE and *p′p*-DDT of 0.033-0.113 and 0.010-0.026 mg/kg, respectively. After intake, this exposes people to the effects of DDT and its metabolites. Comparable residues were found in the studies conducted on samples that were collected along the Ura River in the drier months, and these results are comparable to the ones that were done in this study.

Despite being prohibited since the 1970s, some parts of the world continue to use DDT., notably in underdeveloped nations like Ethiopia, to prevent malaria because of its efficiency and low cost. The study sites near the Ura River, where agricultural production and the usage of pesticides are common, is likely to have an identical occurrence.

On the other hand, methoxychlor gave the most concentrations in all the samples collected along the river with an exception only at Kiiji. The levels were as high as 95.31±8.21 μg/kg in Ikurone

samples. Frequent occurrence of methoxychlor in the samples suggests common use of the pesticide in the area.

While the majority of khat research has concentrated on the pharmacological, psychotic and drug elements of the plant, the political, socioeconomical, and cultural history and advancement of the Horn of Africa, more study is required to determine the health risks connected to the illegal use of OCP in khat cultivation and, consequently, the hazards connected with its use (Ligani and Hussen ,2014).

4.5 Seasonal variation of pesticides residue levels in water, sediment, soil and khat

4.5.1 Seasonal variation of OCPs residue in water samples in the wet and dry seasons.

From Figure 4.14 in Nyambene site the water concentration of 14 out the 17 OCPs analysed were below detection limit in the dry (March, 2016) and in wet seasons (October 2015), α – HCH, heptachlor and Methoxychlor were higher.

Kiiji site, the concentration of heptachlor epoxide, HCH isomers, aldrin, and α –endosulphan were frequent in the dry season compared to rainy season while the concentration of endrin aldehyde, p,p'-DDT, endosulphan sulphate, α -HCH and heptachlor were high in wet as compared to the levels in the dry season. All the other 6 OCPs analysed were below limit of detection (<0.001± 0.00µg/L) during the wet and dry season.

In contrast to the wet season, the dry season at the Anchenge site had higher levels of methoxychlor, while the wet season had higher levels of heptachlor, dieldrin, β-endosulphan, and endrin aldehyde. Across both of the sampling times, none of the further 12 OCPs examined were found.

In Ikandu site the concentration of dieldrin, endrin, β-endosulphan, endrin aldehyde, methoxychlor, heptachlor and α-HCH were higher during the wet season while all than all the other. 10 OCPs analysed were not detected during the wet and dry season.

In Ikurone, the levels of methoxychlor were high during the dry month, while that of β-endosulphan, endrin aldehyde, p, p'-DDT, heptachlor, and HCH were prevalent within the rainy season. None of the other 10 OCPs that were analyzed were found during either of the two

seasons. At Tumutumu site, the concentration of *p,p'*-DDD, endrin aldehyde, *p,p'*-DDT, methoxychlor, *δ*-HCH, heptachlor and aldrin was high during the wet season and all 10 OCPs analysed were not detected.

Averagely, OC pesticides were in the water samples, the highest being methoxychlor at Kiiji at 5.64±0.99 µg/L. The frequent concentration of OCPs during the wet season at the eight sampling sites could be attributed to the surface run off and soil erosion and the high levels in the dry season (March) is attributed to their use for farming. Again, the low quantities but frequent or absence of pesticides in river water is attributable to dilution factor the in the river water. This kind of distribution of pesticides is not an isolated case but other studies of residues in ground and surface water display similar trends (Székács *et al.,* 2015). In this case monitoring was done on Hungarian water samples for a period of fifteen years and the report indicates that very few samples analysed displayed levels below the detection limits which were mostly in ng/L. Another study done on streams in Germany showed that farming activities using pesticides cause a threat on the water and the biodiversity in the streams. It further recommended continuous monitoring on the same (Szöcs *et al.,* 2017).
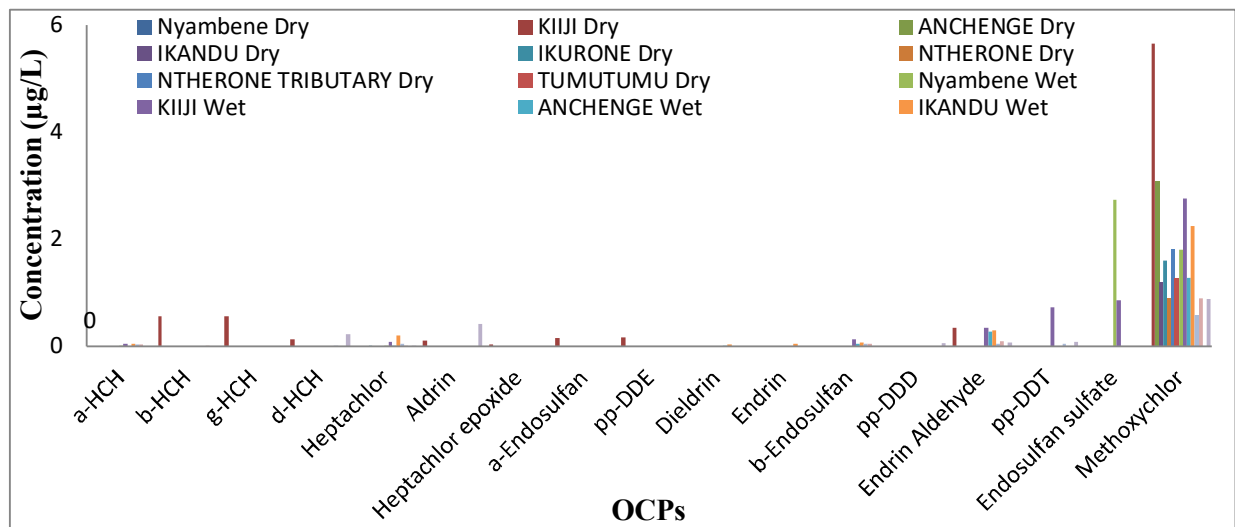
Figure 4.14 Seasonal variation of OCPs levels in water samples in wet and dry seasons

4.5.1.1 Average distribution of OCPs residue levels in water from the eight sampling sites

The Figure 4.15 below has the mean concentration of organochlorine pesticides residual amounts in each of the eight water test samples that were taken. Methoxychlor was most

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frequently found in the river water samples in Kiiji, but dieldrin, endrin, and *p, p′*-DDD were below $0.00 \pm 0.00\mu g/L$ (Figure 4.15).
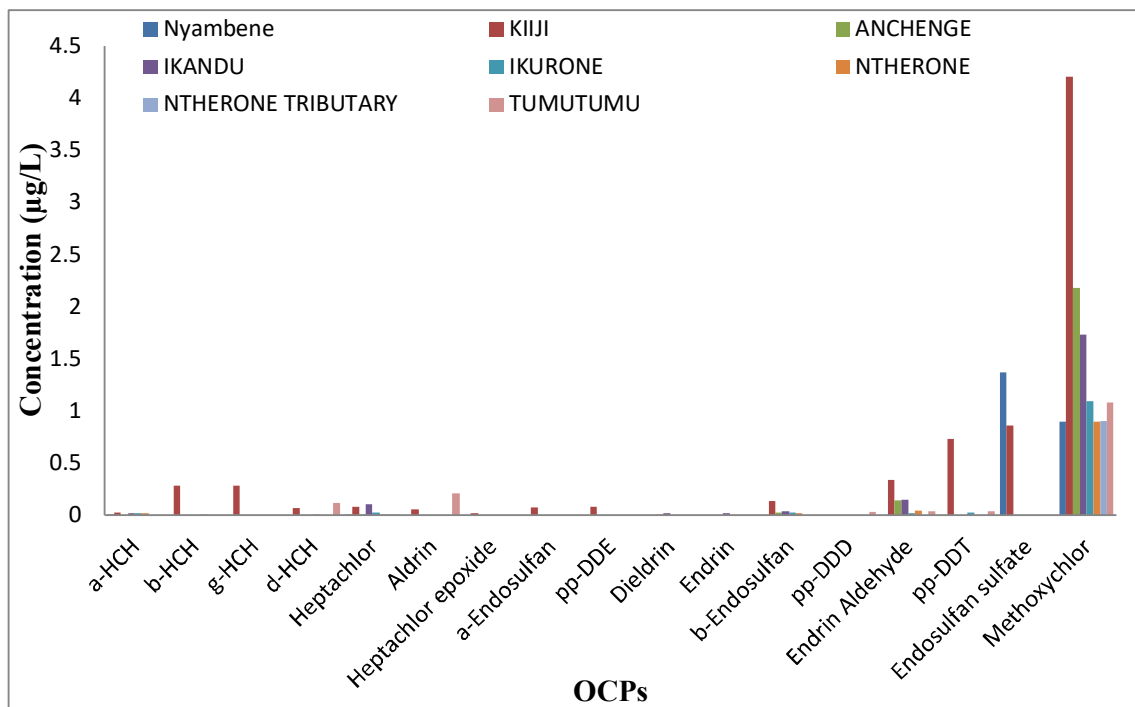
Figure 4.15 Average OCPs residue levels in water in wet and dry seasons

4.5.2 Seasonal variation of OCPs residue levels in sediment samples in wet and dry seasons

In Nyambene, the concentrations of all 14 OCPs were below detection limits during the rainy season while the concentrations of δ-HCH, α-endosulphan, and β-endosulphan were higher during the dry season. At the Kiiji sampling site the concentration during the wet season of 17 OCPs analysed were below $0.001\pm 0.00\mu g/L$ in all the points while in the dry season, β-HCH, α -HCH, heptachlor, α–endosulphan, *p,p'*-DDE, *p,p'*-DDT, aldrin aldehyde, endosulphan sulphate and methoxychlor were high.

Endrin aldehyde, *p,p′*-DDT, endosulphan sulphate, methoxychlor, and β-HCH concentrations were high at the Anchenge site during the dry season, whereas δ-HCH, heptachlor, aldrin, and α-HCH levels were high during the wet season. During the two sampling periods, none of the other 8 OCPs that were analyzed were found.

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In Ikandu site the levels during the wet season of 17 OCPs analysed were below the detection limit in all the sites while during the dry season the levels of β-HCH, p,p'-DDT, heptachlor, endrin aldehyde, δ–HCH and methoxychlor were high and all the other 11 OCPs analysed were not detected in the two seasons (Figure 4.16).

Only β-endosulphan was found in the Ikurone site, whereas the other 16 OCPs were below the detection threshold during the dry season (March). Endrin aldehyde, p,p'-DDT, p,p'-DDD, endosulphan sulphate, α-HCH, δ-HCH, heptachlor, and aldrin concentrations were high during the wet season, while the other 9 OCPs examined during that season were not found.

p,p'-DDT, endrin aldehyde, endosulphan sulphate as well as methoxychlor concentrations at the Ntherone site were considerable in the dry season, whereas the four isomers of hexachlorohexane ($\alpha, \beta, \delta, \gamma$), aldrin, and heptachlor were high during the wet season. In the two seasons, none of the other 7 OCPs that were analyzed were found in the sediment samples.

From the Ntherone tributary sampling site the concentration of p,p'-DDT, endosulphan sulphate, endrin aldehyde and also methoxychlor quantities appeared significant in the dry period, whereas the levels of hexachlorohexane isomers, α and β-endosulphan, endrin, dieldrin, heptachlor epoxide and heptachlor, aldrin, p,p'-DDE and p,p'-DDD were high during the wet season.

At Tumutumu site the concentration of p,p'-DDT, endrin aldehyde and p,p'-DDD, Methoxychlor, δ-HCH, heptachlor and aldrin was high during the wet season and all 10 OCPs analysed were not detected (Figure 4.16).
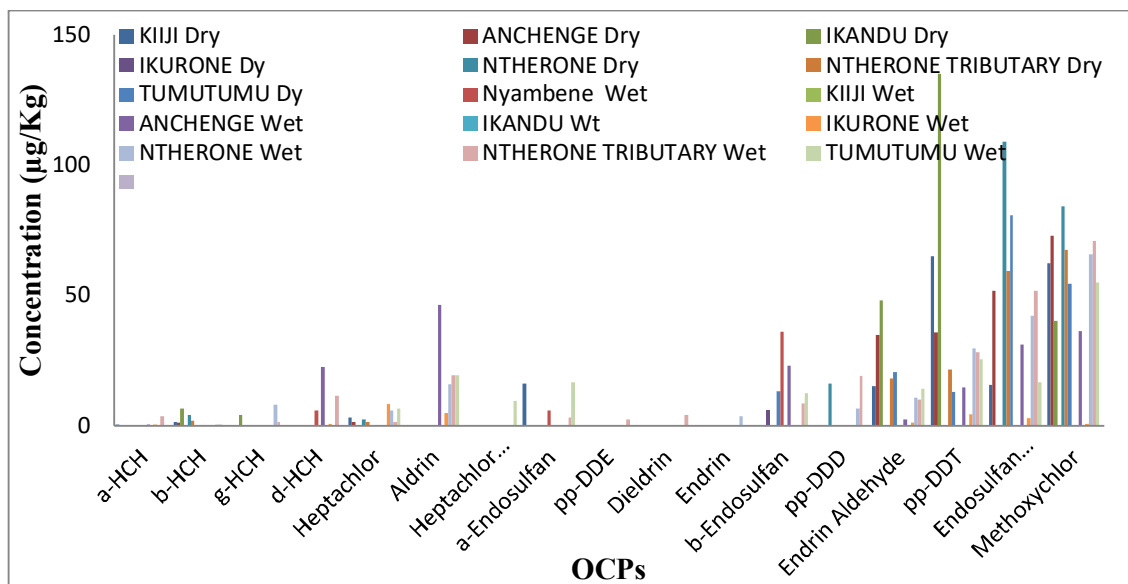
Figure 4.16 Seasonal variation of OCPs in sediment samples in wet and dry seasons

4.5.2.1 Average distribution of OCPs in sediment samples from the eight sampling sites

The average organochlorine levels throughout the sediments collected out of the eight locations of sampling are shown in Figure 4.17. It was noticed that the most concentration of the targeted analytes in the river sediments was endosulphan sulphate at Ntherone sampling site while heptachlor epoxide was absent from all of the sediment sampled from the Ura river except at Tumutumu that recorded 6.33±0.25 µg/kg in the wet season only (Figure 4.17).
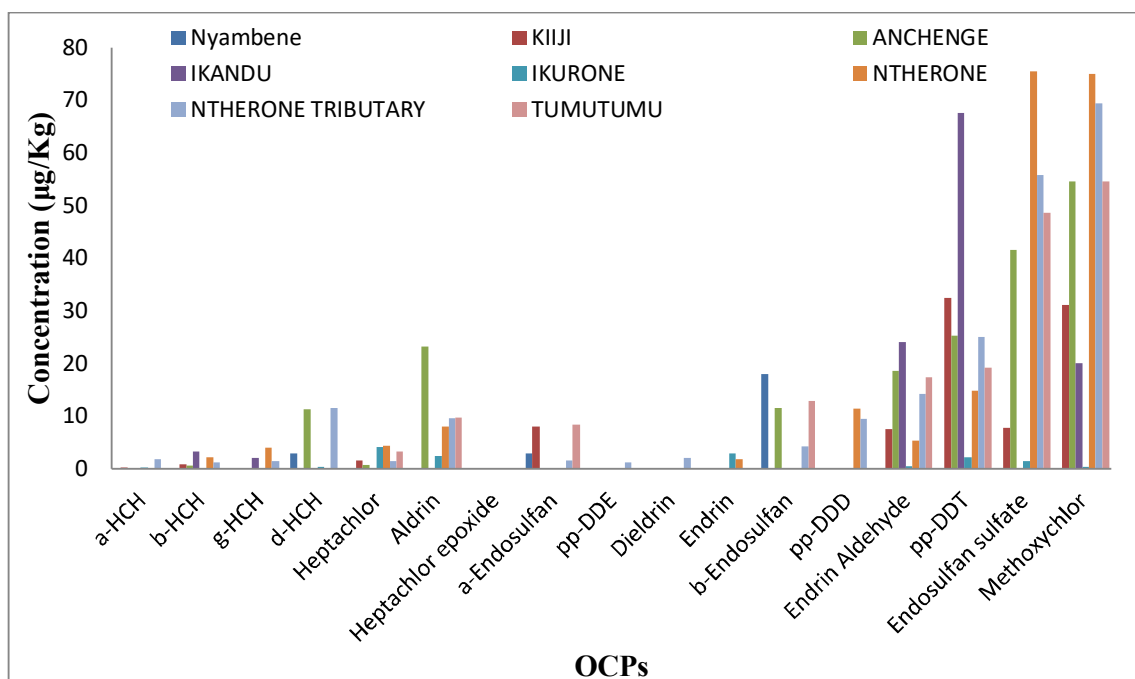
Figure 4.17 Average OCPs residue levels in sediment samples from the eight sampling sites

4.5.3 Seasonal variation of the OCP residue levels in soil in dry and wet seasons.

In Nyambene soil samples, the concentration of *p,p'*-DDT, endosulphan sulphate and methoxychlor were high during dry season while in the wet season δ–HCH, γ–HCH and β – HCH were higher and all the other 11 OCPs were below detection limit (Figure 4.18).

From the Kiiji sampling site, the concentration of *p,p'*-DDT, endosulphan sulphate, methoxychlor and α-HCH were high during the dry season while the concentrations of heptachlor epoxide, β-HCH, γ-HCH and α-HCH, aldrin were high during the wet season. All the other 8 OCPs analysed were below detection limit in the two sampling seasons.

The Anchenge site displayed concentrations of heptachlor, (α-, β and γ)-HCH, endosulphan sulphate and methoxychlor being high during the dry season while those of *p,p'*-DDE, dieldrin, endrin, β-endosulphan, *p,p'*-DDD, endrin aldehyde and *p,p'*-DDT gave higher concentrations during the wet season. All the other 4 OCPs analysed were below detection limit in the two sampling seasons.

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At Ikandu site, the concentration of β-HCH, γ-HCH and methoxychlor were high during the dry season while the concentration of α-HCH, heptachlor, aldrin, α-endosulphan, dieldrin, β-endosulphan, p,p'-DDD, endrin aldehyde and p,p'-DDT yielded higher values during the wet season. All the other remaining 5 OCPs analysed were below detection limit during the two seasons.

In Ikurone site the concentration of β-HCH, γ-HCH, heptachlor, endosulphan sulphate and methoxychlor were high during the dry season while the concentration of α-HCH, heptachlor, aldrin, endrin aldehyde, p,p'–DDT, α-endosulphan, heptachlor epoxide, β- endosulphan, p,p'-DDD, dieldrin, endrin and p,p'-DDE were high during the wet season and only δ-HCH was below detection limit during the two seasons (Figure 4.18).

For Ntherone site, the concentration of $\alpha,\ \beta,\ \lambda$-HCH and methoxychlor were high during the dry season while the concentration of heptachlor, aldrin, p,p'-DDE, endrin, β-endosulphan, $p,\ p$'-DDD and p,p'-DDT were high during the wet season. All the other 6 OCPs were below detection limit during the two seasons. On the other side, at Ntherone tributary site, the concentration of β-HCH, γ-HCH and methoxychlor were high during the dry season while the concentration $of\ \delta$-HCH, p,p'-DDE, endrin, p,p'-DDD, endrin aldehyde, α-endosulfan, β-endosulfan, p,p'-DDT, and endosulfan sulphate were high during the wet season.

Tumutumu site recorded high concentration of methoxychlor during the dry season However, the concentration of α and β-HCH, heptachlor, aldrin, heptachlor epoxide, α and β-endosulfan, p,p'-DDD, endrin aldehyde, p,p'-DDT and endosulfan sulfate were high during the wet season. All the other 4 OCPs analysed were below detection limit in the two seasons (Figure 4.18).

Distribution of the analytes like α-HCH, p,p'-DDE and other DDT metabolites in soil samples just like in the current study have been seen in other areas of the globe. An example of soil samples from Costa Rica (Daly *et al.,* 2007). In Kenya, research carried by Mungai and Wang (2019), illustrates a trend of soil contamination with HCHs and DDT in samples collected from Kapsabet, Nyeri and Voi. In their findings, they reported HCHs being dominant in the soils as compared to DDT. The HCH levels were up to 52.7 µg/kg in soil from Kapsabet. This is

comparable to the findings of the current study during the dry season where HCHs were detected to levels of up to 76.42 ± 4.19 µg/kg and α-HCH being the highest.

Miglioranza *et al.* (2003) have also proved soil contamination with organochlorine residues in a study they carried out on surface soil samples from Argentina. The highest levels of the detected OCP were at 656.1 ng/g dry weight. They attributed this amount to the characteristic considerable levels of organic matter in the area.
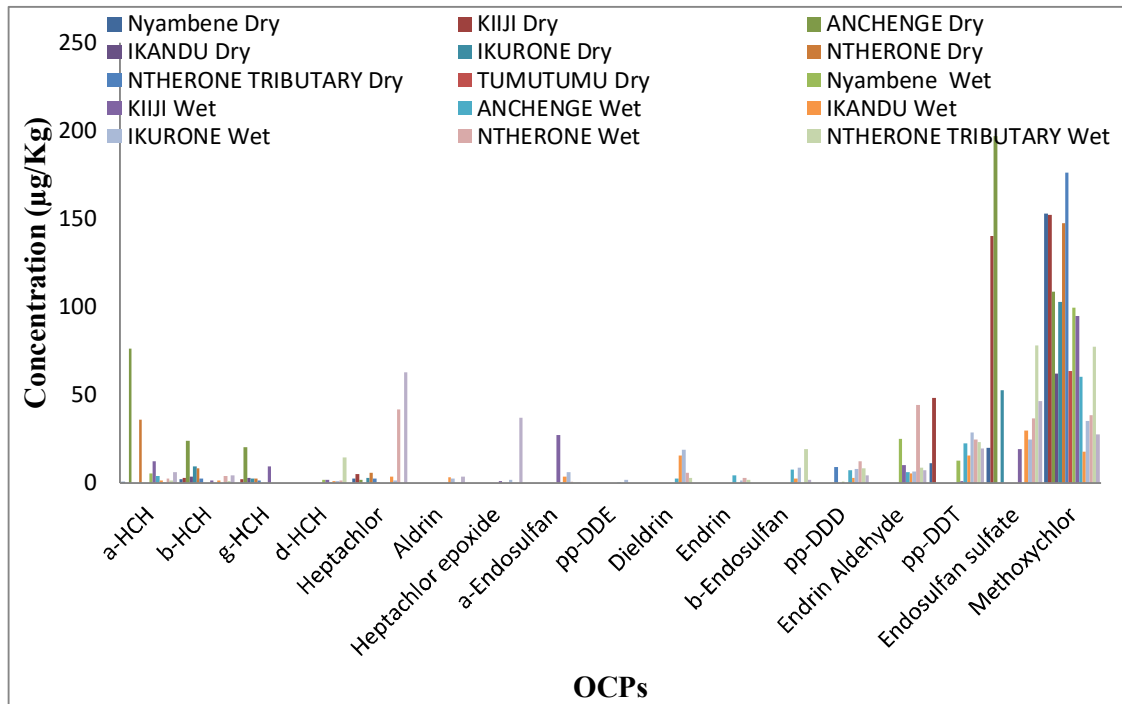
Figure 4.18 Seasonal variation of OCPs residue levels in soil samples in wet and dry seasons

While the frequency of pesticides was more during the wet season, the concentrations were higher in the dry season. These widely detected pesticides with lower concentrations in the soil samples collected during the rainy season would be due to dilution by the high moisture content in the soil. In addition, the rain water soaking soils increases availability and movement of the previously used pesticides in the soil matrix and therefore increasing the frequency of their detection (Jablonowski *et al.,* 2012). The rain water is known to take in the soluble organic matter in the soil which in turn allows transport of organic pollutants within the matrix and ground water (Reemtsma *et al.,* 2003; Chiou *et al.,* 1986).

4.5.3.1 Average distribution of OCPs in soil samples from the eight sampling sites.

The average organochlorine pesticides levels are shown for the soil samples collected from all the eight sampling sites. It was clear that methoxychlor was the highest in all the OCPs at Nyambene sampling Site (Figure 4.19).
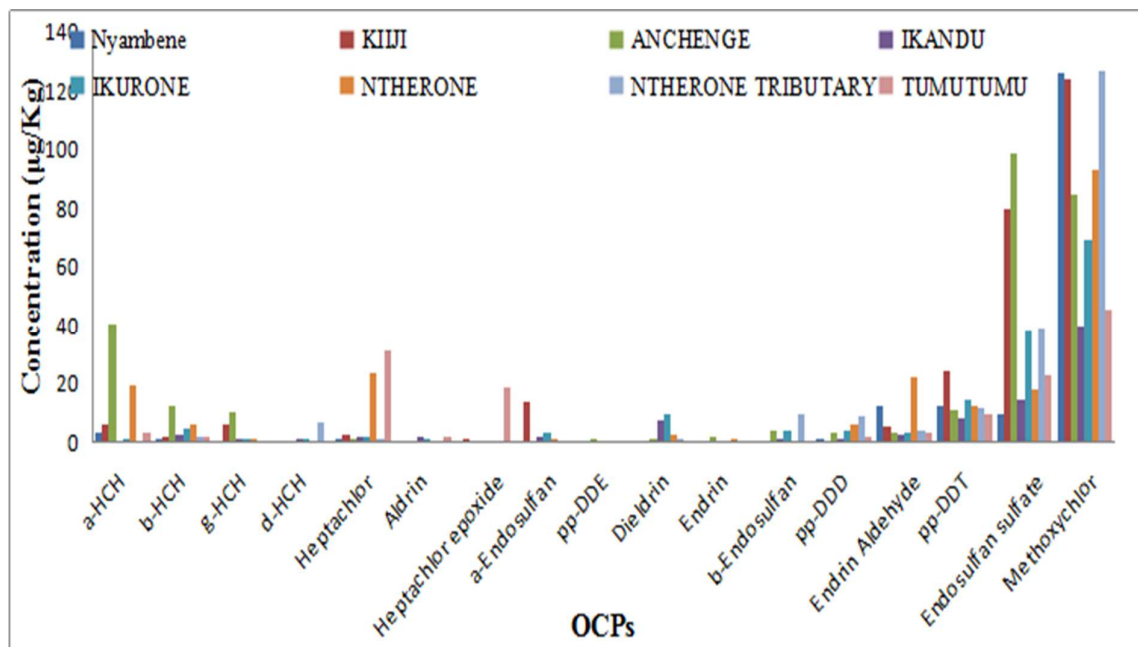
Figure 4.19   Average distribution of OCPs residue levels in soil from the eight sampling sites

The high concentration of methoxychlor in comparison to the rest of the analytes would due to current use. It has been similarly detected in other cases of soil studies in Kenya (Abong'o *et al.,* 2015; Okworo, 2017).

4.5.4 Seasonal variation of OCP residue levels in the khat samples in wet and dry season

From Figure 4.20, Nyambene khat the concentration of *p,p'*-DDT, endosulphan sulphate and methoxychlor were high during wet season while during the dry season δ–HCH, α and β –HCH were higher and all the other 11 OCPs were below detection limit.

Kiiji site the concentration of *p,p'*-DDT, endosulfan sulphate, methoxychlor and α-HCH were high during the dry season while the concentration of r, β and α-HCH, heptachlor epoxide and

aldrin were high during the wet season. All the other 8 OCPs analysed were below detection limit in the two seasons (Figure 4.20).

 Anchenge site, the concentration of endosulfan sulphate, heptachlor, α-HCH, β-HCH, γ-HCH and methoxychlor were significant over the dry season while the amounts of $p,\ p'$-DDE, dieldrin, endrin, β-endosulphan, p,p'-DDD, endrin aldehyde and p,p'-DDT were high during the wet season. All the other 4 OCPs analysed were below detection limit in the two sampling seasons. From Ikandu area, the level of β-HCH, γ-HCH and methoxychlor were high during the dry season while the concentration of α-HCH, heptachlor, aldrin, α-endosulphan, dieldrin, β-endosulfan, p,p'-DDD, endrin aldehyde and p,p'-DDT were high in the wet month. All the other remaining 5 OCPs analysed were below detection limit during the two seasons.

At Ikurone sampling location, the concentration of β-HCH, γ-HCH, heptachlor, endosulfan sulphate and methoxychlor were considerable in the dry season while the quantities of α-HCH, heptachlor, aldrin, α and β-endosulphan, p,p'-DDE, dieldrin, endrin, heptachlor epoxide, p,p'-DDD, endrin aldehyde and p,p'-DDT were high during the wet season and only δ-HCH was below detection limit during the two sampling seasons (Figure 4.20).

Ntherone point revealed the results of β, γ and α-HCH and methoxychlor that were higher during the dry period while the concentration of heptachlor, aldrin, p,p'-DDE, endrin, β-endosulphan, p,p'-DDD and p,p'-DDT were high during the wet season. All the other 6 OCPs were below detection limit during the two seasons. Around Ntherone tributary, the concentration of β-HCH, γ-HCH and methoxychlor were during the time of year when it's dry higher while the concentration of δ-HCH, α-and β-endosulfan, p,p'-DDE, endrin, p,p'-DDD, endrin aldehyde, p,p'-DDT and endosulphan sulphate were high during the wet season.

Khat samples obtained from Tumutumu site gave the concentration methoxychlor that was high in the dry season. The concentration of β- and α-HCH, α and β-endosulphan, heptachlor, aldrin, heptachlor epoxide, p,p'-DDD, endrin aldehyde, endosulfan sulfate and p,p'-DDT were high during the wet season. All the other 4 OCPs analysed were below detection limit in the two seasons (Figure 4.20).

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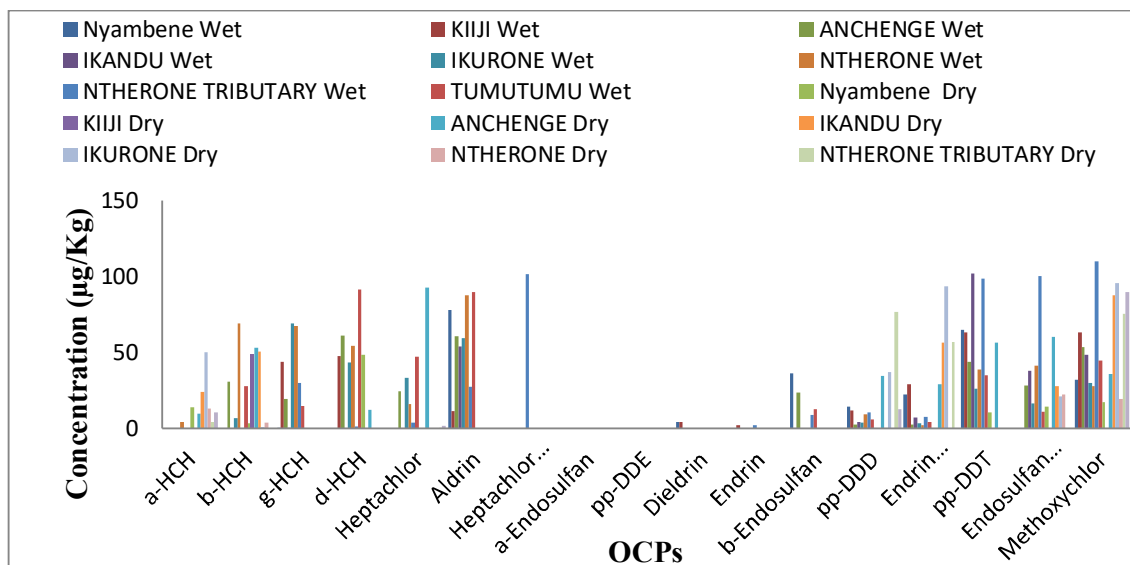
Figure 4.20 Seasonal variation of OCPs residue levels in khat from the eight sampling sites

4.5.4.1 Average distribution of OCPs residues levels in khat from the eight sampling sites

The Figure 4.21 below indicate the mean levels of OCPs in the khat samples collected from the eight markets. Endosulphan sulphate was clearly the highest detected in khat samples collected from the market near Nyambene sampling site.
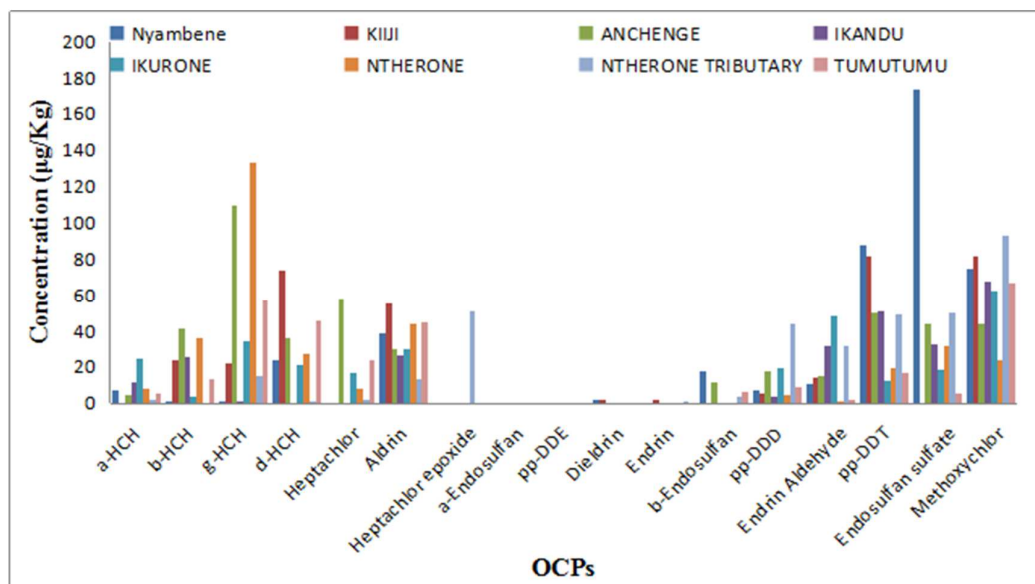
Figure 4.21 Average distribution of OCPs residue levels in khat from eight sampling sites

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4.6 Correlations

The subsections that follow show the correlation of OCPs concentration across matrix and with the physical chemical parameters.

4.6.1 Correlation of the OCPs with physical chemical parameters in the water samples

There was a direct proportionality between the OCPs residue levels in water with conductivity, pH, and TDS as shown by a positive R^2 value (p = 0.01) of 0.527, 0.738 and 0.682, respectively (Table 4.16). This suggests that different physicochemical parameters weakly influence the concentrations of some OCPs in the water.

Table 4.16: Correlation of OCPs residue levels and physico-chemical parameters in water

Correlations		OCPs in water	Water pH	Water TDS	Water conductivity
OCPs in Water	Pearson Correlation	1	.264	.141	.173
	Sig. (2-tailed)		.527	.738	.682
	N	8	8	8	8
Water pH	Pearson Correlation	.264	1	.254	.263
	Sig. (2-tailed)	.527		.544	.529
	N	8	8	8	8
Water TDS	Pearson Correlation	.141	.254	1	.999[**]
	Sig. (2-tailed)	.738	.544		.000
	N	8	8	8	8
Water Conductivity	Pearson Correlation	.173	.263	.999[**]	1
	Sig. (2-tailed)	.682	.529	.000	
	N	8	8	8	8
**. Correlation is significant at the 0.01 level (2-tailed).					

4.6.2 Correlation of OCPs across matrices

The amounts of OCPs in water had a direct correlation with soil, sediment and khat as indicated by a positive positive R^2 value (p = 0.01) of 0.258, 0.518, and 0.665 respectively (Table 4.17)

Table 4.17: Correlation of OCPs across matrices

		OCPs in Water	OCPs in Soil	OCPs in Sediment	OCPs in khat
OCPs in water	Pearson Correlation	1	.454	-.270	.183
	Sig. (2-tailed)		.258	.518	.665
	N	8	8	8	8
OCPs in soil	Pearson Correlation	.454	1	.296	.690
	Sig. (2-tailed)	.258		.477	.058
	N	8	8	8	8
OCPs in sediment	Pearson Correlation	-.270	.296	1	.030
	Sig. (2-tailed)	.518	.477		.944
	N	8	8	8	8
OCPs in khat (Miraa)	Pearson Correlation	.183	.690	.030	1
	Sig. (2-tailed)	.665	.058	.944	
	N	8	8	8	8

4.6.3 Correlation of OCPs in sediment with physico-chemical parameters

A direct relationship was seen between the OCPs concentration in sediment with organic carbon, nitrogen, conductivity and phosphorous in sediment as shown by a positive r value of 0.490, 0.396, 0.217 and .014, respectively.

Table 4.18: Correlation of OCPs residues with physico-chemical parameters in sediments

Correlations		pH of sediment	Total % nitrogen in sediment	Total % organic carbon in sediment	Phosphorous in sediment	Conductivity	OCPs in sediment
pH of sediment	Pearson correlation	1	-.523	.391	-.335	-.138	-.342
	Sig. (2-tailed)		.184	.338	.417	.745	.407
	N	8	8	8	8	8	8
Total %nitrogen in sediment	Pearson correlation	-.523	1	-.378	.552	-.142	.396
	Sig.(2-tailed)	.184		.356	.156	.737	.332
	N	8	8	8	8	8	8
Total % organic carbon in sediment	Pearson correlation	.391	-.378	1	-.581	-.050	.490
	Sig. (2- tailed)	.338	.356		.131	.907	.217
	N	8	8	8	8	8	8
Phosphorus in sediment	Pearson correlation	-.335	.552	-.581	1	-.441	.014
	Sig.(2-tailed)	.417	.156	.131		.274	.974
	N	8	8	8	8	8	8
Sediment conductivity	Pearson correlation	-.138	-.142	-.050	-.441	1	.217
	Sig.(2-tailed)	.745	.737	.907	.274		.605
	N	8	8	8	8	8	8
OCPs in sediment	Pearson correlation	-.342	.396	.490	.014	.217	1
	Sig.(2-tailed)	.407	.332	.217	.974	.605	
	N	8	8	8	8	8	8

4.6.4 Correlation of OCPs in soil with physico-chemical parameters

There was a direct relationship between the OCPs concentration in soil nitrogen, conductivity and phosphorous in soil as indicated by a positive r value of 0.14 and 0.01, respectively.

Table 4.19:Correlation of OCPs residue levels with physic-chemical parameters in soil

Correlations		Soil pH	Total %Nitrogen in Soil	Total %Organic carbon in soil	Phosphorous in Soil	Soil conductivity	OCPs in Soil
Soil pH	Pearson Correlation	1	-.081	.894**	.428	.372	-.151
	Sig. (2-tailed)		.848	.003	.290	.364	.722
	N	8	8	8	8	8	8
Total %Nitrogen in soil	Pearson correlation	-.081	1	.147	.815*	-.847**	.143
	Sig. (2-tailed)	.848		.729	.014	.008	.736
	N	8	8	8	8	8	8
Total %Organic carbon in soil	Pearson correlation	.894**	.147	1	.556	.030	-.022
	Sig. (2-tailed)	.003	.729		.153	.943	.959
	N	8	8	8	8	8	8
Phosphorous in soil	Pearson Correlation	.428	.815*	.556	1	-.470	.010
	Sig. (2-tailed)	.290	.014	.153		.240	.981
	N	8	8	8	8	8	8
Soil conductivity	Pearson Correlation	.372	-.847**	.030	-.470	1	-.384
	Sig. (2-tailed)	.364	.008	.943	.240		.348
	N	8	8	8	8	8	8
OCPs in soil	Pearson Correlation	-.151	.143	-.022	.010	-.384	1
	Sig. (2-tailed)	.722	.736	.959	.981	.348	
	N	8	8	8	8	8	8
**. Correlation is significant at the 0.01 level (2-tailed).							
*. Correlation is significant at the 0.05 level (2-tailed).							

CHAPTER FIVE

5. CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusion

Currently used pesticides in Igembe South are organophosphates, carbamates, neonicotinoids and pyrethroids. Banned OCPs are not currently used in agriculture by the farmers.

Most of OCPs under investigation were detected in water, soil and sediments at varying levels. The levels could be due the past use because of their low dissipation rate in the environment, or illegal applications.

Dominant OCPs in khat samples collected from the market were *p,p'*-DDT, *p,p'*-DDD, endosulphan sulphate, methoxychlor, beta, gamma and delta-HCH, aldrin and heptachlor.

OCP levels in khat were higher in wet season than in dry season, with cumulative levels in the wet season ranging from 252.88 μg/kg to 500.41 μg/kg, while in dry season ranged between 48.74 μg/kg and 382.56 μg/kg.

OCPs levels in soil, water and sediments were recorded at higher frequency in wet season than dry season, while the dry season recorded higher concentrations for most of the compounds compared to wet season.

5.2 Recommendations

1) Legislation should be set to control the indiscriminate use of pesticides within Igembe South Sub County, including trainings and sensitization on safe handling and use of the various pesticides.

2) Further research should be carried out on human beings and livestock to determine the levels of exposure to pesticides contamination.

3) Additional research should be carried out to determine the presence and levels of other type of pesticides such as organophosphates in soil, khat, river water and sediments.

4) There is need to set limits for pesticide residues in khat sold in the markets, as well as regular monitoring of pesticide residues in khat products.

REFERENCES

Abong'o, D., Wandiga, S., and Jumba, I. (2018). Occurrence and distribution of organochlorine pesticide residue levels in water, sediment and aquatic weeds in the Nyando River catchment, Lake Victoria, Kenya. *African Journal of Aquatic Science*, *43*(3), 255–270.

Abong'o, D.A., Wandiga, S.O., Jumba, I.O., Van den, B.P.J., Nazariwo, B.B., Madadi, V.O., Wafula, G.A., Kylin, H., and Nkedi-Kizza, P. (2015). Organochlorine pesticide residue levels in soil from the Nyando River catchment, Kenya. *African Journal of physical sciences,* 2(1)**:**18-32.

Abong'o, D.A., Wandiga, S.O., Jumba, I.O., Madadi, V.O., Kylin, H., (2014). Impacts of pesticides on human health and environment in the river Nyando catchment, Kenya. *International Journal of Humanities, Arts, Medicine and Sciences,* ISSN 2348-0521, *2*(3) ISSN (E) 2: 2348-0521.

Aiyesanmi, A.F., and Idowu, G.A. (2012). Organochlorine pesticides residues in soil of cocoa farms in Ondo state central district, Nigeria. *Environment and Natural Resources Research*, *2*(2), 1–9.

Aktar, W., Sengupta, D., and Chowdhury, A. (2009). Impact of pesticides use in agriculture: their benefits and hazards. *Interdisciplinary Toxicology*, 2(1), 1–12. https://doi.org/10.2478/v10102-009-0001-7.

Alamdar, A., Syed, J. H., Malik, R. N., Katsoyiannis, A., Liu, J., Li, J., Zhang, G., and Jones, K. C. (2014). Organochlorine pesticides in surface soils from obsolete pesticide dumping ground in Hyderabad City, Pakistan: Contamination levels and their potential for air–soil exchange. *Science of the Total Environment*, 470–471, 733–741.

Alavanja, M.C.R., Hofmann, J.N., Lynch, C.F., Hines, C.J., Barry, K.H., Barker, J. (2014). Non-Hodgkin lymphoma risk and insecticide: Fungicide and fumigant use in the agricultural health study. PLoS ONE 9(10): e109332.

Al-Hadrani, A.M., Thabet, A.M.M. (2000). Acute adverse health effects of pesticides sprayed on khat trees. *Journal of Pesticide Control and Environmental Sciences,* 8 (1), 97-106.

Al-Motarreb, A., Baker, K., and Broadley, K.J. (2002). Khat: pharmacological and medical aspects and its social use in Yemen. *Phytotherapy Research*, *16*(5), 403–413. https://doi.org/10.1002/ptr.1106.

Aneck, H., Natalie, H., Gloria, W., Schulenburg, M. S., Bornman, P. F., and Christian, D. (2007). Impaired semen quality associated with environmental DDT exposure in young men living in a malaria area in the Limpopo Province, South Africa. *J Androl* 28, 423-434.

Al-Ashwal, R.H., Al Maqtari, M.A., Naji, K.M., Al-wsabai, N. A., and Al Hazmy, S. M. (2013). Potential health effects of daily khat leaves chewing: Study on the biochemical blood constituents changes among adults in Sana'a city, Yemen. *International Journal of Biochemistry and Biotechnology, 2*(6), 416–463.

Arias-Estévez, M., López-Periago, E., Martínez-Carballo, E., Simal-Gándara, J., Mejuto, J.C., and García-Río, L. (2008). The mobility and degradation of pesticides in soils and the pollution of groundwater resources. *Agriculture, Ecosystems and Environment*,123(4),247–260. https://doi.org/10.1016/j.agee.2007.07.011

Ashraf, H., Saleh, A., Ibrahim, K., Magbool, O., Ghassam, S., Mohsen, F., and Fawaz, A. (2016). Health impact of khat chewing and pesticides: Detection of 8 pesticides multi-residues in khat leaves (*Catha edulis*) From Jazan Region, KSA. *Advances in Environmental Biology*,*10*(8),30–36.

ATSDR, (2013). Addendum to the toxicological profile for chlordane. Agency for toxic substances and disease registry division of toxicology and environmental medicine Atlanta, GA 30333.

ATSDR, (2003). Toxicological profile for Pyrethrins and pyrethroids. Atlanta, GA. Department of health and human services: Public Health Service.

ATSDR, (2002). Toxicological Profile for Aldrin/Dieldrin. Atlanta, GA: U.S. Department of health and human services: Public Health Service.

Avery, B.W., and Bascomb, C.L. (1982). Soil Survey Laboratory Methods. Harpenden, UK.

Baker, T., Kiptala, J., Olaka, L., Oates, N., Hussain, A., McCartney, M., (2015). Baseline review and ecosystem services assessment of the Tana River Basin, Kenya. Colombo, Sri Lanka: International Water Management Institute (IWMI). 107. (IWMI Working Paper 165). Doi: 10.5337/2015.223.

Balali-Mood, M., Balali-Mood, K., Moodi, M., and Balali-Mood, B. (2012). Health aspects of organophosphorous pesticides in Asian countries. *Iranian Journal of Public Health,* 41(10), 1–14.

Behfar, A., Nazari, Z., Rabiee, M. H., Raeesi, G., Oveisi, M. R., Sadeghi, N., and Jannat, B. (2013). The organochlorine pesticides residue levels in Karun River water. *Jundishapur Journal of Natural Pharmaceutical Products*, 8(1), 41–46. https://doi.org/10.17795/jjnpp-6783.

Bettinetti, R., (2011). A Preliminary evaluation of the DDT contamination of sediments in Lakes Natron and Bogoria (Eastern Rift Valley, Africa). *Springer,* 40(4), 341–350.

Bhattacharjee, D and Das, S., (2013). Toxicity of organochlorine pesticide, lindane to fish: A review Department of Life Science and Bioinformatics, Assam University, Silchar, India *Journal of Chemical and Pharmaceutical Research*, 5(4),90-96.

Boul, H.L. (1995). DDT residues in the environment—A review with a New Zealand perspective. *New Zealand Journal of Agricultural Research,* 38(2): 257-277.

Boyd, C.E. (1995). Bottom soils, sediment, and pond aquaculture, Chapman and Hall, London, UK, 1995.

Briggs, S.A. (1992). Basic guide to pesticides and their characteristics and hazards. Rachael Carson Council, Washington DC, USA.

Briz, V., Molina-Molina, J.M., Sánchez-Redondo, S., Fernandez, M.F., Grimalt, J.O., Olea, N., Rodríguez-Farré, E., Suñol, C. (2011). Differential estrogenic effects of the persistent organochlorine pesticides dieldrin, endosulfan and lindane in primary neuronal cultures. *Toxicological Sciences,* 120 (2): 413–27.

Buchel, K.H. (1983). Chemistry of pesticides, John Wiley and Sons, Inc. New York USA.

Burton, J. G. A. (2002). Sediment quality criteria in use around the world. Limnology, 3(2), 65–76. https://doi.org/10.1007/s102010200008.

Carrier, N. (2005a). ''The need for speed: Constructing Time Frames in the social life of Kenyan Miraa'', 75 (4): 539-558.

Carrier, N., (2005b). ''Miraa is cool: The cultural importance of Miraa (khat) for Tigania and Igembe Youth in Kenya''. *Journal of African Cultural Studies,* 17 (2): 201-218.

Clement, R.E. (1992). Environmental sampling for trace analysis. *Analytical Chemistry*, *64*(22), 1076A-1081A.

Chiou, C. T., Malcolm, R. L., Brinton, T. I., and Kile, D. E. (1986). Water solubility enhancement of some organic pollutants and pesticides by dissolved humic and fulvic acids. *Environmental Science & Technology*, 20(5), 502–508. https://doi.org/10.1021/es00147a010

Cox, S., Niskar, A. S., Narayan, K. M., and Marcus, M. (2007). Prevalence of self-reported diabetes and exposure to organochlorine pesticides among Mexican Americans: Hispanic health and nutrition examination survey, 1982-1984. *Environmental health perspectives, 115*(12): 1747–1752.

Cox, J.C. (2002). Sampling for pesticide residue analysis. In Grant IF and Tingle CCD (Eds), Ecological monitoring methods for the assessment of pesticide impact in the tropics. 125–147 Natural Resources Institute, Chatham, UK.

Daba, D., Hymete, A., Bekhit, A.A., Mohamed, A.M., Bekhit, A.E., (2011). Multi residue analysis of pesticides in wheat and khat collected from different regions of Ethiopia. *Bull Environ Contam Toxicol,* 86 (3): 336-41.

Daly, G. L., Lei, Y. D., Teixeira, C., Muir, D. C., Castillo, L. E., Jantunen, L. M., and Wania, F. (2007). Organochlorine pesticides in the soils and atmosphere of Costa Rica. *Environmental Science & Technology,* 41(4), 1124–1130. https://doi.org/10.1021/es062349d.

Danso, G., Drechsel, P., Wiafe-Antwi, T., and Gyiele L. (2002). Income of farming systems around Kumasi, Ghana. *Urban Agriculture Magazine.* 7: 5–6.

Date, J., Tanida, N., and Hobara, T. (2004). Khat chewing and pesticides: a study of adverse health effects on people of the mountainous areas of Yemen. *Int. J Environ Heal Res*, 14 (6): 405-14.

De Bleecker, J. L. (2008). Organophosphate and carbamates poisoning, Handbook of Clinical Neurology. 91**:** 401-432.

Drum, C., (1980). Soil chemistry of pesticides, PPG Industries, Inc. USA.

Eskenazi, B., Bradman, A., and Castorina, R. (1999). Exposures of children to organophosphate pesticides and their potential adverse health effects. *Environmental health perspectives*,107 Suppl 3(Suppl 3), 409–419.

EURL. (2013). Guidance document on analytical quality control and validation procedures for pesticide residues analysis in food and feed. (SANCO/12571/2013). https://www.eurlpesticides.eu/library/docs/allcrl/AqcGuidance_Sanco_2013_12571.pdf.

FAO, (1989). International code of conduct on the distribution and use of pesticides, Rome, Italy.

Fosu-Mensah, B. Y., Okoffo, E. D., Darko, G., and Gordon, C. (2016). Assessment of organochlorine pesticide residues in soils and drinking water sources from cocoa farms in Ghana. *Springer Plus,* 5(1). https://doi.org/10.1186/s40064-016-2352-9.

GOK. (1985). Pest Control Products Act, Chapter 346. Kenya Law Reports. http://extwprlegs1.fao.org/docs/pdf/ken63608.pdf.

Gunasekara, A.S. (2004). Environmental fate of pyrethrins. Environmental monitoring branch department of pesticide regulation 1001 I Street Sacramento, CA95812 November.

Hagmar, L., Rylander, L., Dyremark, E., Klasson-Wehler, E., and Erfurth, E. M. (2001). Plasma concentrations of persistent organochlorines in relation to thyrotropin and thyroid hormone levels in women. *International archives of occupational and environmental health,*74(3), 184–188.

Harrison, M., Beatrice, S., Hudson, A.L., Dawson, N., and James, M. (2019). Improvement in coffee production and economic gains by the farmers through support of coffee cooperative societies in Kenya. *Journal of Agricultural and Crop Research, 7*(4), 47–54.

Hassall, A.K. (1990). The chemistry and uses of pesticides, structures metabolism, mode of action and uses in crop protection, Macmillan Press limited. pp .5-40.

Hassan, N.A., Gunaid, A.A., and Murray-Lyon, I. M. (2007). Khat (*Catha edulis*): health aspects of khat chewing. *Eastern Mediterranean health journal, 13*(3), 706–718.

Hatcher, J. M., Pennell, K. D., Miller, G. W. (2008). Parkinson's disease and pesticides a toxicological perspective. *Trends Pharmacol Sci.,* 29(6): 322-9.doi: 10.1016/j.tips.2008.03.007.

Hay, A. (2012). DDT and the American Century: Global health, environmental politics, and the pesticide that changed the world. *Journal of American History,* 99(2), 678–679.

Hu, W., Wang, T., Khim, J. S., Luo, W., Jiao, W., Lu, Y., Naile, J. E., Chen, C., Zhang, X., and Giesy, J. P. (2010). HCH and DDT in Sediments from Marine and Adjacent Riverine Areas of North Bohai Sea, China. *Archives of Environmental Contamination and Toxicology,* 59(1), 71–79.

IARC, (1991). Occupational exposures in insecticide application, and some pesticides. IARC Working Group on the Evaluation of Carcinogenic Risks to Humans. Lyon, 16-23 October 1990. (1991). IARC monographs on the evaluation of carcinogenic risks to humans,53, 5–586.

IUPAC, (2010). History of pesticide Use. International Union of Pure and Applied Chemistry.https://agrochemicals.iupac.org/index.php?option=com_sobi2&sobi2Task=sobi2Details&catid=3&sobi2Id=31.

IUPAC, (2003). Regulatory Limits for pesticide residues in water. *Pure and Applied Chemistry,* 75(8): 1125-1156.

Jablonowski, N. D., Linden, A., Köppchen, S., Thiele, B., Hofmann, D., and Burauel, P. (2012). Dry–wet cycles increase pesticide residue release from soil. *Environmental Toxicology and Chemistry,* 31(9), 1941–1947. https://doi.org/10.1002/etc.1851.

Jiang, Y.F., Wang, X.T., Jia, Y., Wang, F., Wu, M.H., Sheng, G.Y., and Fu, J.M. (2009). Occurrence, distribution and possible sources of organochlorine pesticides in agricultural soil of Shanghai, China. *Journal of Hazardous Materials*, *170* (2): 989-997.

Jones, D. V., Hovorka, A., Zeeuw, H., and Njenga, M. (2009). Women feeding cities: mainstreaming gender in urban agriculture and food security. *Journal of Agricultural and Environmental Ethics, 23*(5), 495–497.

Joyce, G. N. (2013). Distribution of chlorpyrifos and some organochlorine pesticide residues In the Upper Tana River Catchment. http://erepository.uonbi.ac.ke/handle/11295/57925.

Junakova, N., and Balintova, M. (2012). Assessment of nutrient concentration in reservoir bottom sediments. *Procedia Engineering,* 42, 165–170.

Jurewicz, J., and Hanke, W. (2008). Prenatal and childhood exposure to pesticides and neurobehavioral development: Review of epidemiological studies. *International Journal of Occupational Medicine and Environmental Health,* 21(2). https://doi.org/10.2478/v10001-008-0014-z.

Kabasenche, W.P., Skinner, M.K. (2014). Epigenetic harm and transgenerational environmental justice. *Environ Health* 13**:** 62 https://doi.org/10.1186/1476-069.

Kaiser, J. (2000). Endocrine disrupters: Panel cautiously confirms low-dose effects. *Science,* 290:695–697.

Kalix, P. (1988). Khat: a plant with amphetamine effects. *Journal of Substance Abuse and Treatment,*5,163–169.

Karlaganis, G., Marioni, R., Sieber, I., and Weber, A. (2001). The elaboration of the 'Stockholm Convention' on Persistent Organic Pollutants (POPs): A negotiation process fraught with obstacles and opportunities. *Environmental Science and Pollution Research,* 8(3), 216–221. https://doi.org/10.1007/bf02987393.

Kassim, S., Dalsania, A., and Nordgren, J. (2015). Before the ban - an exploratory study of a local khat market in East London, U.K. Harm Reduct J12,19.

Kenya Meteorological Services, (2015). Advisory on the climate conditions in June- August period over Kenya issued on 30.06.2015. Ministry of Environment, Water and Natural Resources. Nairobi. Kenya.

King, H., Aubert., R.E., and Herman., W.H. (1998). Global burden of diabetes, 1995-2025: prevalence, numerical estimates, and projections. *Diabetes care, 21*(9), 1414–1431.

Kishimba, M., and Mihale, M. J. (2009). Levels of pesticide residues and metabolites in soil at Vikuge farm, Kibaha district, Tanzania – A classic case of soil contamination by obsolete pesticides. *Tanzania Journal of Science,* 30(2). https://doi.org/10.4314/tjs.v30i2.18402

Kishimba, M.A., Henry, L., Mwevura, H., Mmochi, A.J., Mihale, M., and Hellar, H. (2004). The status of pesticide pollution in Tanzania.*Talanta*,64(1), 48–53.

Klein, A., Beckerleg, S., and Hailu, D. (2009). Regulating khat--dilemmas and opportunities for the international drug control system. *The International journal on drug policy,* 20(6), 509.

KNBS, (2019).2019 Kenya Population and Housing Census 1. Population by County and Sub-County.

Lans-Ceballos, E., Padilla-Jiménez, A. C., and Hernández-Rivera, S. P. (2018b). Characterization of organochloride pesticides residues in sediments from the Cienaga Grande of the lower Sinú river of Colombia. *Cogent Environmental Science,* 4(1), 1436930.

Lee, D.H., Lind., P.M., Jacobs, D.R., Salihovic, S., Van Bavel B. L., (2011). Polychlorinated biphenyls and organochlorine pesticides in plasma predict development of type 2 diabetes in the elderly the prospective investigation of the vasculature in Uppsala Seniors (PIVUS) study. *Diabetes Care,* 34(8), 1778-1784.

Leena, S., Choudhary, S. K., and Singh, P. K. (2012). Pesticide concentration in water and sediment of River Ganga at selected sites in middle Ganga plain. *International Journal on Environmental Sciences,* 3(1), 260–274.

Ligani, S., and Hussen, A. (2014). Determination of organochlorine pesticide residue levels in chewable parts of the khat (*Catha edulis*) plant. *Bulletin of Environmental Contamination and Toxicology*, 93(5), 591–595. https://doi.org/10.1007/s00128-014-1385-4.

Macharia, J. W., Abongo, A. D., Wandiga, S., Osoro, E., and Madadi, V. O. (2016). Organochlorine Pesticides Residues in Water and Sediment from Rusinga Island, Lake Victoria, Kenya. *Journal of Applied Chemistry,* 09(09), 56–63.

Madadi, O.V., Wandiga, S.O., and Jumba, I.O. (2006). The status of persistent organic pollutants in Lake Victoria catchment. In E Odada, DO Olago (eds), Proceedings of the 11th World Lakes Conference. Vol. 2, Nairobi. pp 107– 112. Retrieved from https://aquadocs.org/handle/1834/1475.

Mahugija, J. A., Nambela, L., and Mmochi, A. J. (2018). Levels and distribution of pesticide residues in soil and sediments in Eastern Lake Tanganyika environs. *International Journal of Biological and Chemical Sciences,* 11(5), 2537.

Marete, G. M., Lalah, J. O., Mputhia, J., & Wekesa, V. W. (2021). Pesticide usage practices as sources of occupational exposure and health impacts on horticultural farmers in Meru County, Kenya.Heliyon,7(2), e06118.

Martin H., (1968) Pesticides Manual, British Crop Protection Council, London UK

Martinez, F. D., Trejo-Acevedo, A., Betanzos, A., Espinosa-Reyes, G., Alegría-Torres, J. A., and Maldonado, I. P. (2011). Assessment of DDT and DDE levels in soil, dust, and blood

samples from Chihuahua, Mexico. *Archives of Environmental Contamination and Toxicology,* 62(2), 351–358.

Mathew, L.L. (2012). Organochloride Pesticide Toxicity. Drugs, Diseases and Procedures. Medscape References.

Mawussi, G., Júnior, R. P. S., Dossa, E. L., and Alaté, K. A. (2014). Insecticide residues in soil and water in coastal areas of vegetable production in Togo. *Environmental Monitoring and Assessment,* 186(11), 7379–7385. https://doi.org/10.1007/s10661-014-3934-z.

Meeker, J. D., Altshul, L., and Hauser, R. (2007). Serum PCBs, *p, p*'-DDE and HCB predict thyroid hormone levels in men. *Environmental research,*104(2), 296–304.

Mekonen, S., Ambelu, A., Negassa, B., and Spanoghe, P. (2017). Exposure to DDT and its metabolites from khat (*Catha edulis*) chewing: Consumers risk assessment from southwestern Ethiopia. *Regulatory Toxicology and Pharmacology,* 87, 64–70.

Messaros, B. M., Rossano, M.G., Liu, G., Diamond, M.P., Friderici, K., Nummy-Jernigan, K., Daly, D., Puscheck, E., Paneth, N., and Wirth, J.J . (2009). Negative effects of serum *p, p*'-DDE on sperm parameters and modification by genetic polymorphisms. *Environ Res,*109**:** 457-464.

Miglioranza, K. S. B., De Moreno, J. E. A., and Moreno, V. J. (2003). Dynamics of organochlorine pesticides in soils from a southeastern region of Argentina. *Environmental Toxicology and Chemistry,* 22(4), 712–717. https://doi.org/10.1002/etc.5620220405.

Miller, J.N., and Miller, J.C. (2010). Statistics and chemometrics for analytical chemistry.

Momanyi, V.N., Keraka, M., Abong'o, D.A., Warutere, P. (2019). Farmers' compliance to pesticide use standards in Mwea Irrigation Scheme, Kirinyaga County, Kenya. *International Journal of Innovative Research and Advanced Studies (IJIRAS)*, (6)10, 67-72.

Muir, P. (2002). The History of Pesticides Use, Encyclopedia of Chemical Techn. Oregon State University Press, USA.

Mueller, J.F., Harden, F., Toms, L.M., Symons, R., and Fürst, P. (2008). Persistent organochlorine pesticides in human milk samples from Australia. *Chemosphere,* 70(4): 712-720.

Mungai, T. M., and Wang, J. (2019). Occurrence and toxicological risk evaluation of organochlorine pesticides from suburban soils of Kenya. *International Journal of Environmental Research and Public Health,* 16(16), 2937.

Mureithi, P., Waswa, F., and Kituyi, E. (2011). Assessment of occupational safety concerns in pesticide use among small-scale farmers in Sagana, Central Highlands, Kenya. Innovations as Key to the Green Revolution in Africa, 001 10.1007/978-90-481-2543-2_100, © Springer.

Mwagha, S.M., and Ntong'ondu, H.K. (2014). An agricultural product e-business system: Case of khat e-business in Kenya. *International Journal of Business, Economics and Management Works Kamboh well Publisher Enterprises,* 1(2), 30–34.

Mwoga, G.M. (2014). Topo-sequence analysis of climate variability and land use changes among smallholder farmers in Meru County, Kenya. *Semantic scholar,* 40–106.

Nantongo, M. F., Edebe, J., Otachi, E. O., and Kipkemboi, J. (2023). Organochlorine pesticide residues in water, sediments and Nile tilapia (*Oreochromis niloticus*) of Lake Nakuru, Kenya and implications for its fishery. *Wiley Online Library,* 28(1).

Ndunda, E. N., Madadi, V. O., and Wandiga, S. O. (2018). Organochlorine pesticide residues in sediment and water from Nairobi River, Kenya: levels, distribution, and ecological risk assessment. *Environmental Science and Pollution Research,* 25(34), 34510–34518.

NRC, (1982). Aldrin/Dieldrin. In An Assessment of the Health Risks of Seven Pesticides Used for Termite Control. (pp. 23–28). *National Academy of Sciences*. https://doi.org/10.17226/665.

Ogbeibu, A., Omoigberale, M. O., Ezenwa, I. M., Eziza, J. O., and Igwe, J. O. (2014). Using Pollution Load Index and Geoaccumulation Index for the assessment of heavy metal pollution and sediment quality of the Benin River, Nigeria. *Natural Environment,* 2(1),1. https://doi.org/10.12966/ne.05.01.2014.

Okworo, E. K. (2017). Assessment of the fate of selected pesticides on vegetables in Naivasha area. *Semantic Scholar,* Corpus ID: 133677314.

Padungtod, C., Savitz, D.A., Overstreet, J.W., Christian, D.C., Ryan, L.M., and Xu, X. (2000). Occupational pesticide exposure and semen quality among Chinese workers. *J Occup Environ Med.* 2 42(10): 982-992. Doi: 10.1097/00043764-200010000-00004.

Padungtod, C., Hassold, T.J., and Millie, E. (1999). Sperm aneuploidy among Chinese pesticide factory workers: scoring by the FISH method. *Am J Ind Med,* 36: 230–8.

Padungtod, C., Lasley, B.L., and Christiani, D.C. (1998). Reproductive hormone profile among pesticide factory workers. *J Occup Environ Med*, 40:1038–47.

PCPB, (2015). Pest control products registered for use in Kenya, 9th Edition © 2015 Pest Control Products Board, Nairobi, Kenya.

Prakash, O., Suar, M., Raina, V., Dogra, C., Pal, R., and Lal, R. (2004). Residues of hexachlorocyclohexane isomers in soil and water samples from Delhi and adjoining areas. *Current science,* 87(1).

Ravindran, J., Megha, P., and Sreedev, P. (2016). Review Article. Organochlorine pesticides, their toxic effects on living organisms and their fate in the environment. *Interdisciplinary Toxicology,* 9(3–4), 90–100. https://doi.org/10.1515/intox-2016-0012.

Reemtsma, T., Savric, I., and Jekel, M. (2003). A potential link between the turnover of soil organic matter and the release of aged organic contaminants. *Environmental Toxicology and Chemistry,*22(4):760-6.

Richardson, E. R., and Seiber, J. N. (1993). Gas chromatographic determination of organophosphorus insecticides and their dialkyl phosphate metabolites in liver and kidney samples. Journal of Agricultural and Food Chemistry, 41(3), 416–422.

Rozpondek, K., Rozpondek, R., and Pachura, P. (2017). Characteristics of spatial distribution of phosphorus and nitrogen in the bottom sediments of the water reservoir Poraj. *Journal of Ecological Engineering,* 18(4), 178–184. https://doi.org/10.12911/22998993/74277.

Rusiecki, J., Baccarelli, A., Bollati, V., Tarantini, L., Moore, L. E., and Bonefeld-Jørgensen, E. C. (2008). Global DNA hypomethylation is associated with high serum-persistent organic pollutants in Greenlandic Inuit. *Environmental Health Perspectives,* 116(11), 1547–1552. https://doi.org/10.1289/ehp.11338.

Saadati, N., Abdullah, P., Zakaria, Z., Rezayi, M., and Hosseinizare, N. (2012). Distribution and fate of HCH isomers and DDT metabolites in a tropical environment–case study Cameron Highlands–Malaysia. *Chemistry Central Journal,* 6(1). https://doi.org/10.1186/1752-153x-6-130.

Sagiv, S.K., Thurston, S.W., Bellinger, D.C., Tolbert, P.E., Altshul, L.M., and Korrick, S.A. (2010). Prenatal organochlorine exposure and behaviour associated with attention deficit hyperactivity disorder in school-aged children. *American Journal of Epidemiology;* 171 (5): 593–601.

Sang, S., Petrovic, S., and Cuddeford, V. (1999). Lindane – A review of toxicity and environmental fate, World Wildlife Fund Canada, Toronto.

Schecter, A., Colacino, J., Haffner, D., Patel, K., Opel, M., Päpke., and Birnbaum, L. (2010). Perfluorinated compounds, polychlorinated biphenyls, and organochlorine pesticide contamination in composite food samples from Dallas, Texas, USA. *Environmental Health Perspectives,* 118(6): 796.

Sharma, V., Sharma, K.K., and Sharma, A. (2013). Sediment characterization of lower sections of a central Himalayan River. *International Research Journal of Environmental Sciences,* (2) pp. 51–55. 2013.

Sheiner, E. K. (2003). "Effect of occupational exposures on male fertility: literature review". Ind Health 41 (2): 55–62.

Simcox, N.J. (1995). Pesticides in household dust and soil: exposure pathways for children of agricultural families. *Environ Health Perspect,* 103 (12): 1126–1134.

Simmons, M.P., Cappa, J.J., Archer, R.H., Ford, A.J., Eichstedt, D., and Clevinger, C.C. (2008). Phylogeny of the *Celastreae* and the relationships of *Catha edulis* (qat) inferred from morphological characters and nuclear and plastid genes. *Mol Phylogenet Evol*, 48(2):745-57.

Sinaii, N., Cleary, S. D., Ballweg, M. L., Nieman, L. K., and Stratton, P. (2002). High rates of autoimmune and endocrine disorders, fibromyalgia, chronic fatigue syndrome and atopic diseases among women with endometriosis: a survey analysis. *Human Reproduction,* 17(10), 2715–2724.

Snedeker, S. (2001). Pesticides and breast cancer risk: A Review of DDT, DDE, and Dieldrin. *Environmental Health Perspectives,* 109, 35-47. doi:10.2307/3434845.

Son, H.K., Kim, S.A., and Kang, J.H. (2010). "Strong associations between low-dose organochlorine pesticides and type 2 diabetes in Korea". *Environment International,* 36(5): 410–414.

Sohail, E., Waseem, A., Chae, W.L., Jong, J.L., and Imitiaz, H. (2004). Endocrine disrupting pesticides: A leading cause of cancer among rural people in Pakistan. *Experimental oncology,* 26(2): 98–105.

Sosan, M. B., Akingbohungbe, A. E., Ojo, I. A. O., and Durosinmi, M. A. (2008). Insecticide residues in the blood serum and domestic water source of cacao farmers in Southwestern Nigeria. *Chemosphere,* 72(5), 781–784. https://doi.org/10.1016/j.

Spark, K. M., and Swift, R. S. (2002). Effect of soil composition and dissolved organic matter on pesticide sorption. *The science of the total environment, 298*(2002), 147–161. https://doi.org/10.1016/S0048-9697(02)00213-9.

Stuyt, R.J.L., Willems., S.M. Wagtmans, M.J. and VanHoek, B. (2011). Chewing khat and chronic liver disease. *Liver international,* 31: 434–436.

Subramaniam, K., and Solomon, J. (2006). Organochlorine pesticides BHC and DDE in human blood in and around Madurai, India. *Indian Journal of Clinical Biochemistry,* 21(2), 169–172. https://doi.org/10.1007/bf02912936.

Székács, A., Mörtl, M., and Darvas, B. (2015). Monitoring pesticide residues in surface and ground water in Hungary: Surveys in 1990–2015. *Journal of Chemistry,* 2015, 1–15. https://doi.org/10.1155/2015/717948.

Szöcs, E., Brinke, M., Karaoglan, B., and Schäfer, R. B. (2017). Large scale risks from agricultural pesticides in small streams. *Environmental Science & Technology,* 51(13), 7378–7385. https://doi.org/10.1021/acs.est.7b00933.

Taiwo, A. M. (2019). A review of environmental and health effects of organochlorine pesticide residues in Africa. *Chemosphere,* 220, 1126–1140.

Tano, Z.J. (2011). Identity, physical and chemical properties of pesticides, pesticides in the modern world - Trends in pesticides analysis, Dr. Margarita Stoytcheva (Ed.), ISBN: 978-953-307-437-5.

Taylor, M.D.S., Klaine, F.P. Carvalho, D., and Barcelo, J. (2003). Pesticide residues in coastal tropical ecosystems. Distribution, fate and effects. Taylor & Francis Publ., CRC Press, London.576pp., (ISBN: 0-415-23917-6).

Tiryaki, O., and Temur, C., (2010). The fate of pesticide in the environment. Erciyes University, Seyrani Agriculture Faculty, Plant protection department, 38039 Kayseri J. Biol. *Environ. Science,* 4(10): 29-38.

Tsiantas, P., Tzanetou, E. N., Karasali, H., and Kasiotis, K. M. (2021). A Dieldrin case study: another evidence of an obsolete substance in the European soil environment. *Agriculture,* 11(4), 314. https://doi.org/10.3390/agriculture11040314.

Torres-Sánchez, L., Schnaas, L., Cebrián, M.E., Hernández, M., Del, C., Valencia, E.O., Hernández, R.M.G., and López-Carrillo, L., (2009). Prenatal dichlorodiphenyldichloroethylene (DDE) exposure and neurodevelopment: A follow-up from 12 to 30 months of age. *Neurotoxicology,* 30(6): 1162–1165.

Turusov, V., Rakitsky, V., and Tomatis, L. (2002). Dichlorodiphenyltrichloroethane (DDT): ubiquity, persistence, and risks. *Environmental health perspectives,* 110(2), 125–128. https://doi.org/10.1289/ehp.02110125.

Trust for African Rock Art. (2008a). Treasures of Northern Kenya. Trust for African Rock Art.

Turyk, M.E., Anderson, H.A., Freels, S., Chatterton, R. J., Needham, L.L., Patterson, D. G, J., Steenport, D.N., Knobeloch, L., Imm, P., and Persky, V.W. (2009). Associations of organochlorine with endogenous hormones in male Great Lakes fish consumers and nonconsumers. *Environmental Research,* 102**:** 299–307.

Tzanetou, E. N., and Karasali, H. (2022). A Comprehensive review of organochlorine pesticide monitoring in agricultural soils: The silent threat of a conventional agricultural past. *Agriculture,* 12(5), 728.

Unsworth, (2010) History of pesticide use. International Union of pure and applied chemistry (IUPAC). 2010.

USEPA, (2016). Chlordane pesticide [Published measurements of chlordane enantiomers in the environment].

USEPA, (2010). Endosulphan health effects Divion's human health risk assessment.2010.EPA DP Barcode: D372569 Docket No.: EPA-HQ-OPP-002-0262-0178.

USEPA (United States Environmental Protection Agency), (1996). Method 3510C, Separatory funnel liquid–liquid extraction. Revision 3. SW846 CH 4.2.1.

USEPA, (2007). U.S Environmental Protection Agency: Method 1699: Pesticides in water, soil, sediment, biosolids, and tissue by HRGC/HRMS: USEPA, Washington, DC, EPA-821-R-08-001, 96 p.

USEPA, (2006). Organophosphorus cumulative risk assessment – pg. 174-178.

USEPA, (2001). Methods for collection, storage and manipulation of sediments for chemical and toxicological analyses: Technical manual. EPA 823-B-01-002. U.S. Environmental Protection Agency, Office of Water, Washington, DC.

USEPA (United States Environmental Protection Agency), (1996). Method 3510C, Separatory Funnel Liquid–Liquid Extraction. Revision 3. SW846 CH 4.2.1.

Van Drooge, H., Groeneveld, C., and Schipper, H. (2001). Data on application frequency of pesticide for risk assessment purposes. *Annals of occupational hygiene,* 45, S95–S101. https://doi.org/10.1016/s0003-4878(00)00112-5.

VanWendel de Joode, B., Wesseling, C., Kromhout, H., Moge, P., Garcia, M., and Mergler, D. (2001). Chronic nervous-system effects of long-term occupational exposure to DDT. *Lancet,* 357**:** 1014–1016.

Von der Ohe, P. C., and Goedkoop, W. (2013). Distinguishing the effects of habitat degradation and pesticide stress on benthic invertebrates using stressor-specific metrics. *Science of the total environment;* 444**:** 480–490.

Wabe, N. T. (2011). Chemistry, pharmacology, and toxicology of khat (catha edulis forsk): a review. *Addiction & health,* 3(3-4), 137–149.

Wandiga, S.O, Yugi, P.O, Barasa, M.W, Jumba, I.O, Lalah, J.O. (2002). The distribution of organochlorine pesticides in marine samples along the Indian Ocean coast of Kenya. *Environ Technol,* 23(11): 1235– 1246.

Wania, F., Mackay, D., (1995). A global distribution model for persistent organic chemicals. *Science of the Total Environment,* 160-161**:** 211-232.

Wasswa, J., (2008). Characterization of selected pesticides in sediments of the Ugandan side of Lake Victoria. PhD Thesis Makerere University, Uganda.

WHO, (2011). Guidelines for Drinking-water Quality, Fourth Edition.

WHO, (2008). Clinical management of acute pesticide intoxication: Prevention of suicidal behaviours: Management of mental and brain disorders Department of mental health and substance abuse.

WHO (2003). Total dissolved solids in Drinking-water Background document for development of Guidelines for Drinking-water Quality.

WHO, (1997). Guidelines for drinking-water quality, 2nd ed. Vol. 3. Surveillance and control of community supplies. Geneva, World Health Organization.

WHO, (1995). Vector control for malaria and other mosquito borne diseases, WHO tech.

WHO/UNEP, (1990). Public health impact of pesticides use in agriculture, Geneva, Switzerland.

Woldetsadik, D., Simon, M. P., Knuth, D., Hailu, H., Gebresilassie, A., Dejen, A., and Düring, R. (2021). Exposure to DDT and HCH congeners and associated potential health risks through khat (*Catha edulis*) consumption among adults in South Wollo, Ethiopia. *Environmental Geochemistry and Health,* 43(9), 3597–3613. https://doi.org/10.1007/s10653-021-00846-w.

Yusuf, B. (2011). The health risks of khat and influences it has on integration issues (OFH024: Thesis in public health sciences). Mälardalen University. https://www.diva-portal.org/smash/get/diva2:766652/FULLTEXT01.pdf.

Xu, X., Dailey, A. B., Talbott, E. O., Ilacqua, V., Kearney, G. D., and Asal, N. R. (2010). Associations of serum concentrations of organochlorine pesticides with breast cancer and prostate cancer in U.S. adults. *Environmental health perspectives,*118(1), 60–66. https://doi.org/10.1289/ehp.0900919.

Zhang, G., Chakraborty, P., Li, J., Sampathkumar, P., Balasubramanian, T., Kathiresan, K., Takahashi, S., Subramanian, A., Tanabe, S., and Jones, K. C. (2008). Passive atmospheric sampling of organochlorine pesticides, polychlorinated biphenyls, and polybrominated diphenyl ethers in urban, rural, and wetland sites along the coastal length of India. *Environmental science and technology,* 42(22), 8218–8223. https://doi.org/10.1021/es8016667.

Zhou, R., Zhu, L., Yang, K., and Chen, Y. (2006). Distribution of organochlorine pesticides in surface water and sediments from Qiantang River, East China. *Journal of Hazardous Materials,* 137(1), 68–75.

APPENDICES

APPENDIX I

A questionnaire to find out farmer's and agrovet dealers' knowledge on importance and safety of use of pesticides on *miraa* plants**.**

RESPONDENT NO…………………………. DATE………….

VILLAGE………………

Please tick the correct answer or state the answer.

SOCIAL DEMOGRAPHIC CHARACRERISTICS

1. Age of client in years

2.15-19 () 20-24 () 30-34 () 35-39 () 40 and above ()

2.Level of education

None () primary1-8 () year of drop out ()

Secondary 1-4 () year of drop out ()

Tertiary (Polytechnic, college or university) ()

4. Occupation

- None ()

- Self-employment ()

- Formal employment ()

Knowledge of importance and safety of pesticides use on miraa plants

1.According to you, why is it important to use pesticides on miraa plants?

2. What are the pesticides used on miraa plants? (Please list)

3.How often do you apply the pesticides?

4. How do you apply the pesticides?

5.Do you use any protective gear? Tick

Yes ()

No ()

•Sometimes ()

6. If yes, which ones?

7. After application, when do you harvest?

8. How long have you used the pesticides.

9.Have you received any training on the safety measures on handling of pesticides?

Yes

No

If yes, how many times?

10.How do you apply the pesticides on the tall plants if you have any?

The 17 Organochlorine pesticides standard calibration chromatogram