





# LEVELS OF SELECTED WATER QUALITY PARAMETERS, HEAVY METALS AND PESTICIDE RESIDUES IN WATER, SEDIMENTS AND NILE TILAPIA OF LAKE NAKURU, KENYA

#### Master thesis

By

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This thesis is submitted in partial fulfilment of the requirements for the joint academic degree of Master of Science in Limnology and Wetland Management jointly awarded by

the University of Natural Resources and Life Science (BOKU), Vienna, Austria the UNESCO-IHE Institute for Water Education, Delft, the Netherlands

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# **DECLARATION AND RECOMMENDATION**

# **Declaration**

This master thesis is my original work and has not been presented for the award of any other degree elsewhere.

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## Recommendation

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# **DEDICATION**

This thesis is dedicated to the very special people in my life; my dear parents: Mr and Mrs. Vincent Kafeero, my spiritual father: Rev Emmanuel Kalerangabo, my love: Albert, Alicia, Julie and Zam.

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#### **ABSTRACT**

The discharge of industrial effluents, raw sewage wastes, increased use of fertilizers and pesticides in agriculture have resulted in increased release of pollutants into the natural environment. These pollutants tend to accumulate and undergo food chain magnification thus ending up in aquatic fauna at the top of the food chain which are consumed by humans. This study was conducted to assess the levels of selected water quality parameters, heavy metals and pesticide residues in water, sediments and Nile tilapia and the potential health risk to humans who consume the fish of Lake Nakuru. Nine water, nine sediment and thirty fish samples were collected from five representative sites within Lake Nakuru between December 2020 and January 2021 and analysed. Heavy metal analysis was conducted using an Atomic Absorption Spectrophotometer (AAS) at Lake Nakuru Water Quality and Testing Laboratory whereas Organochlorine Pesticide (OCP) residue analysis was done using Gas chromatography - Mass Spectrophotometer (GC-MS) at the Directorate of Veterinary Services (DVS) laboratory, Kabete. The pH ranged from 9.52 at Mid lake point to 9.72 at Sewage discharge point. The dissolved oxygen concentrations ranged from 4.58 mg/L at Sewage discharge point to 8.62 mg/L at River Njoro mouth. Electrical conductivity was lower for such a saline system with values of 4470 - 5226 µs/cm measured during the study period. The salinity range of 2.39 - 2.81 % at Sewage discharge and Mid lake point respectively was comparable to that of a freshwater system. There were no significant differences in mercury concentrations across sites whereas chromium and lead showed significant differences across sites p < 005 in water samples (One - Way ANOVA). No significant differences in mean chromium and mercury levels was recorded whereas arsenic and lead showed significant differences across sites p < 0.05 in sediment samples. For heavy metals in fish samples, there were no significant differences in mean concentrations of mercury and lead whereas arsenic and chromium showed significant differences across sites p < 0.05 (One - Way ANOVA). All the 16 OCPs targeted in this study were detected except for aldrin. The OCP residue levels ranged from BDL to  $7.44 \pm 0.66 \,\mu\text{g/L}$ , BDL to  $6.39 \pm 1.10$  $\mu g/kg$  ww and BDL to 319.74  $\pm$  66.94  $\mu g/kg$  ww in water, sediment and fish samples, respectively. The levels of lead and chromium in fish were above the WHO and EU limits while the residue level of endosulfan was above the EU standard hence not safe for human consumption. The present results show that most of organochlorine pesticides though banned in Kenya are still detected in the environment and this may have longterm hazards to humans.

Based on the results, the study recommends an environmental monitoring program and mitigation strategies of reducing pollutant input into the lake to be put in place and an immediate ban on harvesting and consumption of fish from Lake Nakuru.

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#### LIST OF ABBREVIATIONS AND ACRONYMS

AAS Atomic Absorption Spectrophotometer

ANOVA Analysis of variance

APHA American Public Health Association

As Arsenic

ATSDR Agency for Toxic Substances and Disease Registry

BDL Below Detection Limit

CAC Codex Alimentarius Commission

CCME Canadian Council of Ministers of the Environment

Cd Cadmium

Cr Chromium

DCM Dichloromethane

DVS Directorate of Veterinary Services

EC European Commission

EPA Environmental Protection Agency

EU European Union

FAO Food and Agricultural Organisation

FDA Food and Drug Administration

GDP Gross Domestic Product

GC Green Cross

GC-MS Gas Chromatography Mass Spectrophotometer

HCH Hexachlorocyclohexane

Hg Mercury

IARC International Agency for Research on Cancer

ILEC International Lake Environment Committee

IUPAC International Union of Pure and Applied Chemistry

KEBS Kenya Bureau of Standards

KMFRI Kenya Marine and Fisheries Research Institute

LEL Lowest Effect Level

LOD Limit of detection

MRL Maximum Residue Level

NAWASSCO Nakuru Water and Sanitation Services Co. Ltd

NEMA National Environment Management Authority

OCPs Organochlorine Pesticides

Pb Lead

PCPB Pesticide Control and Products Board

PE Pure Earth

PEL Probable Effect Level

p,p,'- DDD p,p'-Dichlorodiphenyl dichloroethane

p,p,'- DDE p,p'-dichlorodiphenyldichloroethylene

p,p,'- DDT p,p'- dichlorodiphenyltrichloroethane

SDGs Sustainable Development Goals

SEL Severe Effect Level

SQGs Sediment Quality Guidelines

TEC Threshold Effect Concentration

THQ Target Hazard Quotient

USEPA United States Environmental Protection Agency

WHO World Health Organisation

WQTL Water Quality Testing Laboratory

ww wet weight

dw dry weight

#### **CHAPTER ONE**

#### INTRODUCTION

#### 1.1 Background information

Environmental pollution is on the rise globally (Hazrat et al., 2019; PE & GC, 2016). This pollution is largely attributed to anthropogenic activities such as agriculture, urbanization, industrial effluents and release of poorly treated sewage to aquatic ecosystems (Lakherwal, 2014; Murtala et al., 2012; Pandey & Singh, 2019; Rai et al., 2019). Aquatic ecosystems tend to be the ultimate sink for pollutants and there is a likelihood that compounds produced on an industrial scale get into the aquatic environment at one point in time (Murty, 1986). Some of the pollutants commonly reported in aquatic environments include: nutrients (nitrogen and phosphorus), organochlorine pesticides, heavy metals, microbial contaminants and biodegradable organic matter (Kanangire et al., 2016; Kundu et al., 2014).

Of the above listed pollutants, heavy metals and organochlorine pesticides (OCPs) are considered among the most dangerous in as far as public health is concerned (Fu et al., 2014). It is further estimated by World Health Organization (WHO) that over a hundred million people are at risk from toxic pollution at levels above the international health standards worldwide (WHO, 2019). The bioaccumulation tendency of these contaminants in aquatic organisms at lower trophic level poses a serious threat to the consumers of those organisms on the top of the food chain such as humans due to the health hazards associated with them (Ayangbenro & Babalola, 2017; Dixit et al., 2015). The health hazards include: tissue damage, disruption in growth and reproduction, immunological effects, neurological damage, severe brain and kidney damage, cancer, cerebrovascular diseases and even death (Njuguna et al., 2017; WHO, 2003).

In Kenya, heavy metal and pesticide pollution in aquatic environments has been reported in various studies (Gitahi et al., 2002; Nzeve et al., 2018; Tenai et al., 2016). These studies confirm that these pollutants are of concern in many Kenyan aquatic ecosystems that need to be monitored from time to time. Organochlorines such as DDT, dibromochloropropane, chlorodimeform, chlordane, heptachlor, toxaphene and endrin were banned in Kenya whereas lindane, aldrin and dieldrin were put under restriction (Omwenga, 2013; Ondiere, 2016). Despite their ban, residues of these pesticides in sediments, soil, water and biota have continually been reported in different studies (Abong'o, 2009; Olutona et al., 2014; Omwenga et al., 2016). The different researchers attributed the continuous detection of

pesticide residues to illegal use or persistence in the environment from the time of their ban (Lalah et al., 2003).

Lake Nakuru was Kenya's first Ramsar site designated in 1991, was Africa's first bird sanctuary in 2009 and a UNESCO designated World Heritage in 2011(Kiogora et al., 2020; Odada et al., 2004). Additionally, it is listed among the protected conservation areas in Kenya. However, the lake has continued to face a lot of impacts from catchment activities. The increase in human population has led to increased contamination of the lake due to anthropogenic activities in its catchment. The Lake Nakuru catchment being a high potential agricultural area, the use of fertilizers and pesticides to increase yields is of utmost importance (Junjiro & Masahisa, 2005). All these have led to release of persistent pollutants into the environment that finally find their way into the lake. It is reported that Lake Nakuru catchment is among the most industrialised and impacted by human activities considering other saline lakes in the Kenyan Rift Valley system (Ndetei & Muhandiki, 2005).

Over the past few years, the water levels in rift valley lakes in Kenya have risen significantly leading to unusual hydrologic and limnologic changes. There is no doubt that the increasing water levels in Lake Nakuru could have led to a change in water quality parameters through dilution hence the introduction and survival of the reported fish species that are known to be freshwater namely: Nile tilapia (*Oreochromis niloticus*), Blue spotted tilapia (*Oreochromis leucostictus*) and Victoria tilapia (*Oreochromis variabilis*) (Kiogora et al., 2020). Though Kiogora et al. (2020) did some work covering several aspects on abiotic and biotic parameters in the lake, the study was just a snapshot of the lake status. Additionally, their report was not published thus this information cannot be accessed by the public.

Therefore, there is a paucity of knowledge regarding the safety of this fish for human consumption following the recent emerging fishery of the lake. This is because Lake Nakuru is a protected area and thus there is no formal exploitation of its recent fishery. In addition, there is limited studies on the chemical pollution of the lake in the current positive water balance state. The aim of this study therefore was to determine selected water quality parameters, heavy metals and organochlorine pesticide residue levels in water, sediments and Nile tilapia (*Oreochromis niloticus*) of Lake Nakuru following the hydrological changes noticed and assess the health risk posed to fish consumers from this lake. The current study focused on the most abundant species of fish in the landed catches that is Nile tilapia.

#### 1.2 Statement of the problem

Lake Nakuru has for long been regarded as a saline lake largely without any fishery apart from the little fish species: Tilapia grahami (*Alcalicus grahami*), which is not suitable for exploitation. Furthermore, the lake is in a protected wildlife area. However, the recent rise in water levels in the lake leading to an expansion of the lake area beyond the protected zone and emergence of new fish species (*Oreochromis niloticus*, *Oreochromis variabilis* and *Oreochromis leucostictus*) have led to an advent of a fishery industry within the lake's vicinity. Consequently, communities around the lake and others from Lake Naivasha and Lake Victoria have moved into the lake's vicinity to fish from the inundated areas outside the protected area. There is a dearth of information on the safety of the fish harvested for human consumption. Therefore, there is an urgent need for assessing the safety of the fish from this lake by examining the different lake matrices for these persistent pollutants in addition to selected water quality parameters. This study intends to contribute to the knowledge on the safety of the emerging fishery with an emphasis on the two most hazardous pollutant groups to human health that is heavy metals and organochlorine pesticides.

#### 1.3 Objectives

#### 1.3.1 General objective

To determine the levels of selected water quality parameters, heavy metals and pesticide residues in water, sediments and in relation to Nile tilapia fishery in Lake Nakuru, Kenya.

#### 1.3.2 Specific objectives

- i. To determine the levels of selected water quality parameters (dissolved oxygen, temperature, salinity, conductivity and pH) from the various selected sites in the lake;
- ii. To determine the levels of selected heavy metals (arsenic, cadmium, chromium, lead, and mercury) and organochlorine pesticide residues (DDT and its metabolites, heptachlor, heptachlor epoxide, endosulfan 1, endosulfan 2, endosulfan sulfate, endrin, lindane, aldrin, dieldrin, methoxychlor, hexachlorocyclohexanes (alpha, beta, gamma, delta)) in water, sediments and fish samples in the various selected sites;
- iii. To evaluate the safety of the emerging fishery in relation to the safety reference standards.

#### 1.4 Hypotheses

- i. H<sub>0</sub>1: There are no significant differences in selected water quality parameter levels (dissolved oxygen, temperature, salinity, conductivity and pH) from the various selected sites;
- ii. H<sub>0</sub>2: There are no significant differences in concentrations of the selected heavy metals and organochlorine pesticide residues in water, sediments and fish samples from the various selected sites;
- iii. H<sub>0</sub>3: The concentrations of the selected pollutants are not significantly different from the safety reference standards.

#### 1.5 Justification

Pollution of aquatic ecosystems with persistent chemical pollutants such as heavy metals and organochlorine pesticides is a public health concern. Lake Nakuru is an aquatic ecosystem of a high ecological and economic value. Previous studies have reported the occurrence of pollution with these persistent pollutants in Lake Nakuru, however following the recent phenomena of thriving fishery in the lake, it is essential to study the safety of fish harvested and subsequently consumed or supplied to local markets. This study will focus on assessing the concentrations of selected pollutants and evaluate if they are within the maximum permissible limits deemed safe for human consumption. The results from the study will contribute to knowledge on public health concerns surrounding the human consumption of the fish from the lake and form a basis for policy direction. Furthermore, the study will contribute to the achievement of Nakuru County Integrated Development Plan (NCIDP) 2018 - 2022, Kenya's vision 2030 especially the economic pillar where agriculture is one of the six major sectors targeted and in which fisheries management and development falls. Both NCIDP and Kenya's vision 2030 look at the fisheries as a potential sector to enhance food security. Moreover, the study will contribute to the realisation of the Big Four Agenda item on food security and the Sustainable Development Goal 3 (Good health and well-being) hence reduction in the number of deaths and illnesses from hazardous chemicals.

#### CHAPTER TWO

#### LITERATURE REVIEW

#### 2.1 Overview of heavy metal pollution

Heavy metals pollution has been studied widely including their occurrence, toxicity, and fate in the environment at a global scale (Su, 2014). Some heavy metals such as copper, manganese and zinc are essential for normal body growth and are very harmful when they exceed a certain threshold (Adelekan & Abegunde, 2011; Inoti et al., 2011). On the other hand, heavy metals like cadmium, chromium, nickel and lead are highly toxic to human and aquatic organisms even at low concentrations (Khan et al., 2013; Ouyang et al., 2002). International bodies such as World Health Organisation (WHO) have regularly reviewed the effects of heavy metals on human health (Wu et al., 2016). When these chemical pollutants are released into the aquatic environment, they accumulate in soil, sediments and biota of water bodies. The aquatic organisms at the lower food chain transfer them to higher trophic levels including fish.

Despite the well documented adverse effects of heavy metals to human health, exposure to them is still on the rise in some parts of the world more so in the developing continents like Africa and Asia. For many years, Africa was deemed safe from heavy metal pollution (Biney et al., 1994). However, the perception is no longer valid considering the evidence from a review study of heavy metal pollution in Africa (Yabe et al., 2010). Whereas the trend of heavy metal pollution has been decreasing in developed countries over the years following reduction in their release into the environment, the reverse is true in developing countries. This has been attributed to the rapid industrialisation, increased use of pesticides containing heavy metals and limited resources for environmental management (Järup, 2003; Xiao et al., 2013).

#### 2.2 Overview of pesticide pollution

The International Code of Conduct on the Distribution and Use of Pesticides defines pesticides as: "Any substance or mixture of substances intended for preventing, destroying or controlling any pest, including vectors of human or animal disease, unwanted species of plants or animals causing harm during, or otherwise interfering with the production, processing, storage, transport, or marketing of food, agricultural commodities, wood and wood products or animal feedstuffs, or which may be administered to animals for the control of insects, arachnids or other pests in or on their bodies" (FAO, 2001). Most pesticides have been used in crop pest and disease vector control thus they have greatly benefited mankind

worldwide. According to the world worst pollution problems report, one-third of agricultural crops are produced with use of pesticides (Blacksmith Institute, 2012). On the other hand, the increasing threat on the environment arising from pesticide pollution cannot be overemphasized. Pesticides have been listed among the emerging pollutants that need to be studied (Kanangire et al., 2016). It is estimated that 4.6 million tons of pesticides belonging to 500 different types are applied on crops per year and yet only 1% is utilized effectively (PE & GC, 2016). As a result, the biggest percentage of the applied pesticides end up in different environmental compartments causing pollution. Due to the health hazards related with pesticide pollution, the Food and Agricultural Organisation (FAO) in collaboration with the World Health Organization came up with permissible limits of pesticide residues in food, drinking water, export products such as fish, horticultural products and fruits (FAO/WHO, 1994).

Agriculture accounts for about 24 % of Kenya's GDP with an estimated 70 % of the rural population working in the sector either directly or indirectly (Birch, 2018). Agriculture being the backbone of the economy, the use of pesticides, fertilizers and acaricides is a common practice (Saoke, 2005). As of 2017, the pesticide application rate in Kenya was estimated at 0.25 kg/ha taking position three after South Africa (2.16 kg/ha) and Zimbabwe (0.53 kg/ha) in sub-Saharan Africa (Roser, 2019). Pesticide use in Kenya started in 1946 when dichlorodiphenyltrichloroethane (DDT) was prominently used in mosquito control especially in Lake Victoria basin (Abong'o, 2009). The undesirable features of organochlorine pesticides led to many countries worldwide both developed and developing to do away with them. For example, the United States of America (USA) stopped their use in 1972 and more countries followed thereafter (Teklit, 2016). Kenya banned and restricted the use of some organochlorine pesticides in 1986 and in subsequent years. For example, the use of hexachlorocyclohexane isomers, DDT, heptachlor and endrin was stopped in 1986; aldrin and dieldrin in 2004; whereas lindane was restricted for use only in seed dressing in 2004 (PCPB, 2008).

# 2.2.1 Classification of pesticides

Pesticides can be classified based on: chemical nature (functional groups in their molecular structure) for example organo - nitrogen, organo - halogen like organochlorines and organophosphates (Njogu, 2011). They can also be classified based on: application requirement for example agriculture, domestic, public health and based on: target organism

for example fungicide, insecticide, herbicide. This study will focus on organochlorine pesticides:

#### (a) Organochlorines

Organochlorine pesticides are synthetic, non - polar, toxic and environmentally persistent dichlorodiphenylethanes, cycodienes or chlorinated benzenes used in pest control (Ogunfowokan et al., 2012). Organochlorine pesticides were on a high demand before their official ban and have continually been used illegally because of their effectiveness in pest control coupled with the relatively low cost (Teklit, 2016; Wandiga et al., 2002). According to FAO (2005), organochlorine pesticides are the most used class of pesticides. It further reports that 40 % of all used pesticides belong to the organochlorine group. However, organochlorine pesticides are lipophilic in nature. Consequently, they are an environmental hazard due to their persistence, toxicity and bioaccumulative effect posing serious adverse impacts on various organisms (terrestrial and aquatic) and public health (Calvert et al., 2010). Organochlorine pesticides accumulate in sediments and their residues finally get into the associated biota such as fish (Ssebugere et al., 2010; Werimo et al., 2009).

# (b) Organophosphates

The term organophosphate refers to all the organic compounds containing phosphorus. Hundreds of organophosphate compounds are in existence and they are derivatives of phosphoric, phosphonic, or phosphinic acid (Gupta, 2006). Organophosphates are unstable, non-persistent in the environment though toxic to vertebrates. They are relatively environmentally friendly as compared to organochlorines because they degrade rapidly by hydrolysis when exposed to soil, air and light (Njogu et al., 2011; Ondiere, 2016).

#### (c) Carbamates

Carbamates are organic compound derivatives of carbamic acid. Carbamates are used as pesticides in agriculture crops and gardens as therapeutic drugs in human medicine (Gupta, 2006). The insecticide mechanism of action is through reversible inactivation of the enzyme acetylcholinesterase. They breakdown in the environment within weeks or months. They have a low mammalian oral and dermal toxicity and a broad spectrum of insect control (Jayaraj et al., 2016).

#### 2.3 Sources of heavy metals and pesticides into the aquatic environment

Unlike organochlorine pesticides, heavy metals are released into the environment by both natural and anthropogenic pathways. Natural sources include: weathering of minerals, erosion and volcanic activities, evaporation from soil and water surfaces and biogenic sources (Dixit et al., 2015; He et al., 2013). On the other hand, anthropogenic sources of aquatic pollution with heavy metals and pesticides both globally and on national level are more or less the same and they include: industrialisation, fertilizer application, municipal sewage discharge, livestock manure, increased use of pesticides and mining (Omwenga et al., 2014). In comparison to natural sources, anthropogenic sources are pointed out as the major causes of the rising environmental heavy metal and organochlorine pesticide pollution. Heavy metals and organochlorine pesticides arising from anthropogenic sources get into the aquatic environment through; industrial effluents, domestic sewage and agricultural runoff (Hazrat et al., 2019). Additionally, these persistent pollutants can also be carried by surface runoff during precipitation with a consequent contamination of the receiving aquatic system (Mahurpawar, 2015).

The sources of chemical pollution of Lake Nakuru mainly stem from its location downstream of Nakuru town which has a fast population growth with a remarkable degree of industrialisation (Odada et al., 2004). Moreover, agriculture is widely carried out in the Lake's catchment hence a possible contamination source more so with pesticides and fertilizers carried in sediments by the influent streams like Rivers: Njoro, Nderit, Larmudiak and Makalia. Heavy metals such as mercury, lead, cadmium, chromium, and a metalloid arsenic have been pointed out by the World Health Organisation as metals of public health concern. An overview of the occurrence and sources of the most hazardous heavy metals and organochlorine pesticides of public health concern is given below:

#### 2.3.1 Arsenic

Arsenic is a ubiquitous metalloid that occurs in soil, rock, water, air and as a solitary element with various allotropes in the earth's crust. It occurs in both organic and inorganic forms in the environment. The inorganic form is present in groundwater whereas the organic form is majorly found in fish (WHO, 2001). The inorganic forms of arsenic are more toxic than the organic forms (Alissa & Ferns, 2011). The major sources of arsenic pollution into the environment are: atmospheric deposition, mining, pesticide usage, rock sedimentation, wood preservatives and smelting of non - ferrous metals and fossil fuel energy production (Ayangbero & Babalola, 2017).

#### 2.3.2 Cadmium

Cadmium is a non - essential, highly toxic element that usually substitutes mercury, copper and zinc in sulphide minerals. In the aquatic environment, cadmium exists in two forms either the dissolved or in particulate form (Keil et al., 2011). In the particulate form,

cadmium is either adsorbed onto surface sediments, chemically bound to organic matter, precipitated or even bioaccumulates in organisms (Jarup, 2003). It readily forms complexes in solution with halides, cyanides and ammonium species, and has a strong affinity for organic matter. At elevated temperatures, cadmium tends to volatilize hence giving a mechanism for it to enter the hydrological cycle through atmospheric deposition downwind of industrial regions (Kubier et al., 2019). Cadmium occurrence in the environment is attributed to both natural and anthropogenic processes. Cadmium enters the environment through wastewater discharge, industrial air emissions and the widespread application of phosphate fertilizers that are eventually washed into aquatic systems. The industrial sources include: paints and pigments, plastic stabilizers, electroplating and battery manufacture (Kim et al., 2015).

#### 2.3.3 Chromium

Chromium (Cr) is regarded as the seventh most available element that occurs naturally on the earth's crust (Blacksmith Institute, 2012; Carolin et al., 2017). The element exists in several oxidation states when in natural state namely: chromium (0), chromium (III) and chromium (VI). The sources of chromium in the environment are both natural e.g. weathering of rocks and anthropogenic (Murray et al., 2005). However, industrial sources such as leather, textile, electroplating, tanning, mining, stainless steel manufacturing, paint and pigment producing, pulp and paper producing industries take lead in the anthropogenic sources (Reid, 2011). The main pathway of pollution of aquatic systems with chromium is discharge of improperly treated industrial waste and direct discharge of wastewaters into waterways.

#### 2.3.4 Lead

As the case with many of the heavy metals, the increased concentration of lead in the environment is more associated with anthropogenic sources than natural sources. Vehicular emission is pointed out as one of the major sources of environmental pollution with lead (Jan et al., 2015; Wu et al., 2016). Anthropogenic sources of lead into the environment include: aerial emission from combustion of leaded fuel, batteries waste, insecticide and herbicide usage, wastewater discharge from electroplating, electrical, steel industries, additives in gasoline and pigment (Jaishankar et al., 2014; Mahurpawar, 2015).

## **2.3.5** Mercury

Mercury occurs in two forms namely: inorganic mercury and organic mercury for example methylmercury (Baby et al., 2010). It is on record that organic mercury is more toxic

than inorganic mercury. Poisoning from eating fish from water that is contaminated with methylmercury has also occurred (Smith, 2017). Anthropogenic sources of mercury environmental pollution include: silver-gold mining, coal combustion, paper and pulp industries, plastic industries, oil refineries and medical wastes (Carolin et al., 2017).

# 2.3.6 Sources of organochlorine pesticides into the aquatic environment

The major source of organochlorine pesticides into the environment is anthropogenic activities including deliberate application to control weeds, insects and disease vectors, improper disposal of wastes and containers from agriculture, industrial usage and public health, accidental spillage from industrial, agricultural sites, domestic and industrial effluents, atmospheric deposition as well as dumping of sewage sludge, municipal, agricultural and industrial solid wastes on land and inland waters (Osibanjo, 2003; Wasswa et al., 2011).

#### 2.4 Harmful effects of heavy metals and organochlorine pesticides to public health

Increased intake of arsenic especially the inorganic form above the recommended standard by WHO is associated with gastrointestinal problems, cardiovascular and central nervous systems' disorders, peripheral vascular disease with eventual death. Moreover, there is a high risk of dying from lung, kidney and bladder cancer of individuals exposed via drinking arsenic contaminated water (WHO, 2019). Other health hazards include: hearing loss, reproductive toxicity, hematologic disorders, developmental abnormalities (Mohammed et al., 2011). Arsenic was associated with abortion, still births and cardiovascular problems by the World Health Organisation (WHO, 2010). Due to the health hazards linked to arsenic contaminant exposure, the World Health Organization recommends arsenic levels in drinking water not to exceed  $10 \mu g/L$  (WHO, 2001).

According to Alissa and Ferns (2011), the most toxicological feature of cadmium is its extremely long half - life in the human body given its low excretion rate. Cadmium affects calcium regulation by interfering with its metabolism and this consequently leads to diseases of cartilage or bone fractures resulting from calcium deficiency. Other effects related to cadmium pollution of public health concern include: carcinogenic, mutagenic, endocrine disruptor and lung damage. Due to cadmium toxicity, a maximum permissible intake was set at  $7 \mu g/kg$  of body weight by the World Health Organisation (WHO, 2003).

Whereas the trivalent form of chromium is less toxic, the hexavalent form is carcinogenic and in high amounts can even cause death (Murray et al., 2005). Exposure to chromium contamination whether through dietary intake, inhalation or any other pathway is

of public health concern. It causes skin inflammation, nausea, ulcers, perforation of nasal septum, respiratory cancer and hair loss (Muharpawar, 2015; Obasi & Akudinobi, 2020).

Lead is very toxic to humans and is associated with health hazards such as red blood cell chemistry interference, body organ and system damage for example kidney, liver, reproductive system, nervous system, urinary system and immune system (Njuguna et al., 2017). Acute exposure is reported to lead to a slight increase in blood pressure in some adults. According to Sharma and Pervez (2003), chronic exposure to lead leads to cerebrovascular disease while lifetime exposure causes cancer. Furthermore, impaired development, reduced intelligence, short-term memory loss, learning disabilities and coordination problems in children have been linked to excessive exposure to lead (Dixit et al., 2015).

Inhalation of elementary mercury vapour has been associated with memory loss, headaches, neuromuscular changes, insomnia. Castro-González and Méndez-Armenta (2008) pointed out auto immune diseases, tremors, brain damage, hair loss, drowsiness, vision impairment, fatigue, kidney and lung failure as the health hazards associated with mercury contamination. Exposure to methylmercury poisoning leads to nervous system damage with consequent loss of sensation at extremities and around the mouth areas, loss of coordination, slurred speech and loss of hearing. Blindness, comma and death have been associated with severe poisoning to methylmercury (Bakir et al., 1973). Additionally, methylmercury has been reported to be a potent neurotoxin that interferes with human brain development (Barkay & Wagner-Döbler, 2005). Moreover, mercury exposure to pregnant women is of great concern because it readily passes through the placental barrier. The International Agency for Research on Cancer regards mercury a probable carcinogen (IARC, 1999).

The high solubility coupled with the persistence nature of organochlorine pesticides aggravates the problems associated with their bioconcentration and biomagnification in organisms and finally in humans. In addition, organochlorine pesticides have been associated with adverse health effects to humans such as high risk of cancer, neurologic problems, behavioural changes, and disruption of reproductive ability of organisms (Abong'o et al., 2014; Kleanthi et al., 2008). DDT has been reported to cause infertility, intrauterine growth retardation and neurologic development distortion (Diamanti-Kandarakis et al., 2009). Moreover, the escape of organochlorine pesticide residues into the environment results in acute and chronic ecological damage through deterioration of water quality hence being a potential hazard to aquatic organisms for example eggshell thinning in birds and humans who may use that water.

#### 2.5 Heavy metal and organochlorine pesticide studies in Kenya

In Kenya, heavy metal pollution in soil, water, sediments and aquatic organisms has been reported in several studies conducted across the country. The concentrations of heavy metals varied across studies, with high concentrations exceeding the recommended level recorded in some studies and low concentrations in other studies. The contrasts in the different studies were attributed to differences in sampling sites, seasons, environmental factors and land use within the sampling sites (Hicks, 2012; Muohi et al., 2007; Ndungu et al., 2019; Njogu et al., 2011; Njuguna et al., 2017; Nzeve et al., 2018; Ochieng et al., 2007; Omwenga et al., 2014; Ondiere, 2016; Otachi et al., 2015; Tenai et al., 2016 among others).

Similarly, different researchers have studied organochlorine pesticide occurrence in the Kenyan environmental matrices (Abong'o, 2009; Gitahi, 1999; Gitahi et al., 2002; Lalah et al., 2003; Lincer et al., 1981; Njogu, 2011; Ogwok et al., 2009; Omwenga et al., 2016; Osoro et al., 2016; Wandiga & Mutere, 1988). There has been an increasing trend in pesticide usage in Kenya mainly in agriculture and public health sector. According to PCPB (2008), about 8,749 tonnes of different types of pesticides were imported into the country in 2006 of which 36 % was fungicides, 28 % was insecticides and acaricides, 22 % herbicides, and 14 % other pesticides. In many countries like Kenya, food production has been enhanced due to extensive pesticide use. However, the pesticides in one way or another get into the environment where they accumulate thus posing a threat to non-target organisms such as humans, invertebrates, wildlife, birds, pollinators among others (Larson et al., 2005; WHO, 2020). Therefore, regular environmental monitoring to establish the level of chemical pollution is necessary to determine the concentration of pollutants and act accordingly.

## 2.6 Status of heavy metals and OCPs in Lake Nakuru

#### 2.6.1 Heavy metal pollution in Lake Nakuru

Several studies on heavy metal pollution have been conducted in Lake Nakuru in the last four decades (Kairu, 1999; Kiogora et al., 2020; Koeman et al., 1972; Nelson et al., 1998; Tenai et al., 2016; Yang et al., 2017). Results from the studies show an increasing trend in heavy metal pollution of the lake over the years. The recorded concentrations were mainly attributed to natural sources as opposed to anthropogenic sources in baseline studies (Koeman et al., 1972). The increasing trend of pollution is attributed to population growth and increased use of pesticides in the lake's catchment given that some of them contain heavy metals and improper sewage discharge (Yang et al., 2017). Few of the conducted studies investigated heavy metal pollution in all the three lake matrices namely: water, sediments and

biota in combination (Mavura & Wangila, 2003). Therefore, more studies such as this that examine all the lake matrices for heavy metal pollution are very crucial.

Furthermore, with the exception of one study (Kiogora et al., 2020), all studies were conducted prior to the recent hydrological and limnological changes associated with increased lake water levels hence a need for more studies to investigate heavy metal pollution with the current hydrological changes. Additionally, Lake Nakuru being a protected area, the fish of the lake has not been exploited until recently when freshwater species were reported in the catches and thus there is scanty information on the safety of this fish for human consumption. The latest study conducted by Kiogora et al. (2020) reported presence of heavy metals in some of the fish samples analysed and recommended further studies on chemical pollution of the Lake. Therefore, this study also sought to further their work based on their recommendations.

#### 2.6.2 Pesticide pollution in Lake Nakuru

Studies on pesticide residues in different matrices of Lake Nakuru have been conducted over the years (Greichus et al., 1978; Kairu, 1994; Kairu, 1999; Koeman et al., 1972; Lincer et al., 1 981; Mayura & Wangila, 2003). Compared to other classes of pesticides, organochlorines have been studied most given their persistence, toxicity, and bio accumulative nature. Generally, low - high concentrations of pesticide residues have been reported in various studies since the time of their ban and restriction. This indicates that illegal uses of some of the banned pesticides could still be ongoing. It is reported that despite the ban of DDT for agricultural use, it is still used in public health sector in the control of malaria vectors and it is still marketed under a non - revealing trademark (Lalah et al., 2003). Therefore, there is a need for continuous monitoring of these pollutants' concentrations to establish their levels in the environment and take necessary action. Unlike heavy metals, there has been no study conducted on the status of pesticide pollution in the different lake matrices for the last 15 years. Additionally, there is need to undertake a study on the safety of fish harvested and subsequently consumed or supplied to local markets regarding OCPs and find out whether their levels are within the maximum permissible limits deemed safe for human consumption.

#### CHAPTER THREE

#### MATERIALS AND METHODS

#### 3.1 Study area

#### 3.1.1 Description and location

Lake Nakuru is a shallow endorheic lake situated in the Eastern arm of the Rift Valley. It is a regular - shaped basin with gentle slopes with a nearly flat bottom (Leichtfried & Shivoga, 1995; Odada et al., 2004). It is located in Nakuru County, south of Nakuru town approximately 157 km from Nairobi, Kenya's capital. The lake has a surface area of 70 m<sup>2</sup> with a total catchment area of 1800 m<sup>2</sup> (Figure 1). Lake Nakuru lies at an altitude of 1759 m above sea level and is located at latitude 0° 23' S and longitude 36° 7' E within Lake Nakuru National Park (Iradukunda et al., 2020).

According to Kiogora et al. (2020), the lake originally had a mean depth of 2.5 m with the deepest point having a maximum depth of 4.5 m. Following the increase in lake water levels, the deepest point is currently approximated at 9.5 m. Lake Nakuru is fed by freshwater springs and five rivers namely: Njoro, Nderit, Larmudiak, Makalia and Naishi in addition to direct rainfall and ground water (Jirsa et al., 2013; Kimaru et al., 2019). The lake's catchment is bordered by Menengai crater in the North, in between the lake and the crater is Nakuru town, Bahati highlands in the North east, Mau escarpment in the West, Eburru crater to the South and grasslands between Nakuru and Elementeita in the East (Odada et al., 2004). Prior to the recent limnological changes, Lake Nakuru was famous for providing habitat to one of the largest population of lesser flamingos globally.

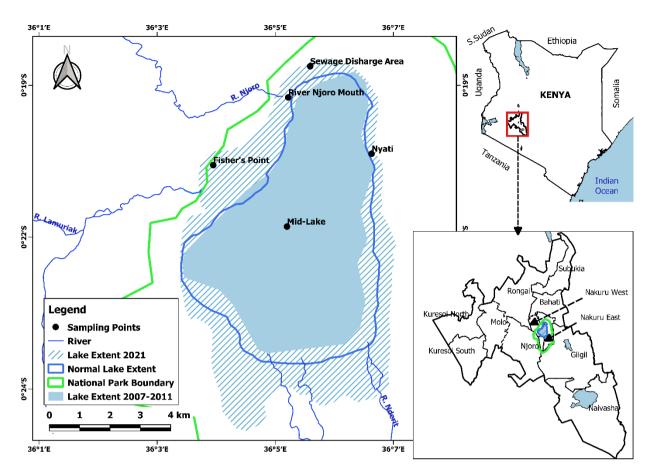


Figure 1: A map of Lake Nakuru showing the sampling points (Source: Author)

#### **3.1.2** Climate

The climate ranges from cold and humid to arid and semi-arid typical of the Rift Valley floor. Climate is strongly influenced by seasonal migration of Inter Tropical Convergence Zone, (ITCZ) and the coinciding precipitation pattern (Kimaru et al., 2019; Nicholson, 1996). Rainfall associated with the transition of the ITCZ follows the highland sun in March and September with a lag of three to four weeks (Nicholson, 2000). Therefore, the basin receives most of its precipitation during the long rains in April to May and the short rains in November. A third lesser precipitation maximum occurs in September, when the Congo air masses transport moisture from the Congo basin to East Africa (Vincent et al., 1979). Mean annual rainfall is 950 mm/yr whereas evaporation is about 1736 mm/yr (Kenya Meteorological Department, 2000).

Isohyetal analyses show general decrease in rainfall from the crest of the catchment towards Lake Nakuru, which is located in a rain shadow (Odada et al., 2004). The rainfall occurs in the afternoon as heavy storms and is quite erosive. The amount of rainfall is strongly linked to topography. Thus, the highest rates are obtained in the high elevation parts of the basin in the west and east, whereas the lower areas are relatively dry. The maximum

temperature in Nakuru district is about 30 °C with December to March being the hottest months. July is the coldest month with an average temperature of 23.90 °C (Government of Kenya, 1997). According to the East African Meteorological Department there is a temperature decrease of 0.56 °C for every 100 m of increase in elevation.

# 3.1.3 Geology

The geology of the Lake Nakuru basin consists of volcanic rocks of the tertiary - quaternary age, which have been affected by a series of faulting (Thompson & Dodson, 1963; Vareschi, 1982). The soil also is of volcanic origin and due to its high porosity, permeability and loose structure, is highly susceptible to erosion, land subsidence and fractures commonly during or after heavy rain (Ngecu & Nyambok, 2000). The geology in the region can be described in relation to the main geomorphologic units observed; the Mau and Bahati Escarpments to the west and east respectively, the Menengai Crater to the North, Eburru volcanic cone to the south, and the centrally located Rift Valley plains. Geology varies significantly from one geomorphologic setting to another, a phenomenon linked to the regional tectonic setting of the area (Kanda, 2010).

#### **3.1.4 Land Use**

Land use in the Lake Nakuru watershed has been changing over the years starting from large scale colonial farmers' settlement on the middle reaches of the watershed and later in the 1970's and 1980's by Kenyan farmers. The basin comprises of various river basins that form local watersheds with diverse vegetation cover and land - use. For example, River Njoro is 60 km in length emanating from indigenous forests in the upper reaches and contributes about 302 km² of the Lake Nakuru watershed (Shivoga et al., 2005). The most common resources utilized in the basin include: timber, stones, gravel, sand, firewood, fodder, medicinal herbs, firewood, ground and surface water as well as cultural uses. Horticulture, subsistence hunting for bush meat for the riparian and forest tribes coupled with grazing grounds for the maasai pastoralists are the commonest activities in the same arid areas.

Land degradation in the catchment has been on the rise and mainly attributed to forest degazettement and encroachment by agricultural communities. Reports show that forest cover reduced by approximately 50 % between the years 1970 and 1987. Currently, the forest cover is estimated at less than 15 % in the Lake Nakuru basin. An approximate 30 % increase in farmland, 20 % increase in urban settlements have been reported whereas small scale farmers constitute 70 % of land use (Shivoga et al., 2005). According to Jenkins et al. (2005), approximately 50 % of the population in River Njoro watershed lives below poverty line

hence an increased demand on natural resources such as water. Over the years, Lake Nakuru basin has been transformed from a sparsely populated and densely forested area into a region that is greatly settled, extensively cultivated, and rapidly urbanizing. The substantial increase in the human population, resulting from both past and continuing extensive resettlement has been the key driving force (Kanda, 2010).

#### 3.1.5 Ecology of Lake Nakuru

The biota of the lake is degraded, although persistent populations of the cyanobacteria, *Spirulina platensis* occur, forming the base of the food chain and supporting large concentrations of lesser flamingos (*Phoeniconaias minor*) (Vareschi, 1978). Until the recent report of introduction (sources unknown) and survival of freshwater fish species in Lake Nakuru, only one saline fish species was found in the lake: The Lake Magadi tilapia (*Alcolapia grahami*), a filter feeding cichlid introduced into Lake Nakuru in 1953 to combat mosquito breeding (Vareschi, 1979). The introduction of fish substantially increased the diversity of the lake ecosystem by extending the food chain to over 30 species of fish - eating birds. Other organisms, found in varying abundance, include three species of rotifers (*Brachionus dimidiatus*, *B. plicatilis*, and *Hexartha jenkinae*), three species of water bug (*Micronecta jenkinae*, *M. scutellaris* and *Sigara hieroglyphica kilimanjaronis*), a copepod (*Lovenula africana*) and a chironomid (*Leptochironimus deribae*) (Thampy, 2002).

Lake Nakuru is surrounded by a buffer zone, which together with the lake constitutes Lake Nakuru National Park. The park is a popular local and international tourist destination that receives close to 200,000 visitors annually. Although the park provides habitat for over 50 species of mammals and 500 floral species, it is best known for its bird life, and for the spectacular assemblages of lesser flamingos that congregate on the shores of the lake (Nurmi, 2010). Lesser flamingos account for approximately 78 % of the world's total flamingo population, and the alkaline lakes of southern Kenya regularly hold between one quarter and one half of this population (Brown, 1959). Until recently, the high primary productivity of Lake Nakuru made it a key feeding ground for this species (Vareschi, 1978). Since 1993, however, frequent dry outs, accompanied by decreased primary production, have rendered the lake unsuitable for feeding, resulting in the migration of lesser flamingos to healthier systems such as Lake Bogoria, located 70 km to the north (Krienitz & Kotut, 2010; Ndetei & Muhandiki, 2005). Apart from the flamingos, over 51 species of waterfowl and water - associated birds inhabit the lake and its littoral fringe, and a further 350 terrestrial bird

species inhabit the buffer zone. The lake is also a staging site and wintering ground for several species of Palearctic ducks and geese (Thampy, 2002).

#### 3.2 Study design

The current study was a fieldwork and observational one with focus on spatial variability of pollutants. The sampling was focused on the northern part of the lake having locations influenced by urban areas, agricultural areas and river mouth. Additionally, it is from the northern part of the lake where fish was being caught by the community in the lake's vicinity. Sampling was conducted three times on a fortnight basis between December 2020 and January 2021.

# 3.3 Location of sampling points

Water and sediment samples were collected from three sampling points that is; River Njoro mouth, Sewage discharge point and Mid Lake Nakuru whereas fish samples were obtained from: Fisher's point, Nyati, River Njoro mouth and Sewage discharge point (Table 1). Fisher's point refers to the point outside the protected area where the community in the vicinity of Lake Nakuru were mainly fishing from.

Table 1: GPS coordinates of sampling sites in Lake Nakuru

Site	GPS location	Altitude	Depth
River Njoro mouth	00° 19' 21.1''S and 36° 04' 39.9''E	1772 m	3 m
Sewage discharge point	00° 18' 29.6''S and 36° 05' 39.4''E	1774 m	2.8 m
Mid lake point	00° 21' 24''S and 36° 04' 53.5''E	1779 m	9.5 m
Nyati	00° 20' 06''S and 36° 06' 50.8''E	-	1.9 m
Fisher's point	00° 20' 12''S and 36° 03' 41.9''E	1772 m	3.5 m

Altitude units are metres above sea level. Depth: approximate depth obtained at the time of the present study.

## 3.4 Data and sample collection

#### 3.4.1 Water quality parameters

Data on water quality parameters such as pH, dissolved oxygen, conductivity, salinity and temperature was generated through *in situ* measurement at the selected sites during each sampling occasion. The measurements were conducted according to APHA (2012) using a multiprobe water quality meter and probes at approximately 10 cm below the water surface.

#### 3.4.2 Water sampling for heavy metals

A total of nine (9) water samples for heavy metal analysis were collected from River Njoro mouth, Sewage discharge point and Mid lake point following standard methods by APHA (2012). At each sampling point, 500 ml of a composite water sample was collected and filtered *in situ* using a filter pump fitted with Whatman GFC filters of 0.47 μm size into a pre acid washed plastic bottle. The sample was then acidified with 2.5 ml of concentrated nitric acid (69%) to avoid precipitation of the metals and adsorption to the surface of the bottles following the standard methods for water and wastewater examination (APHA, 2012). The water samples were transported to Lake Nakuru Water Quality Testing Laboratory (WQTL) for heavy metal analysis in a cool box with ice packs.

#### 3.4.3 Water sampling for pesticide residue analysis

A total of nine (9) water samples for pesticide analysis were collected from River Njoro mouth, Sewage discharge point and Mid lake point following standard methods by APHA (2012). Two and a half (2.5) litres of a water sample was collected in amber glass bottles from each of the sampling points. Each water sample was labelled and treated with 1g of mercuric chloride to dehydrate microorganisms that could degrade the pesticides. The samples were stored in a cool box while in the field and during transportation to Analytical Chemistry and Food safety laboratory at the Directorate of Veterinary Services (DVS), Kabete for temporary storage before analysis at the end of the entire sampling period.

#### 3.4.4 Sediment sampling

A total of eighteen (18) composite sediment samples were obtained from River Njoro mouth, Sewage discharge point and Mid lake point, 6 from each site using stainless Ekman grab sampler (IAEA, 2003). Special care was taken not to obtain the samples from those directly in contact with the surface of the Ekman grab sampler to avoid any form of contamination. Following the standard methods by IAEA (2003), approximately 300 g of a sediment sample was scooped from each of the sampling points and packed in labelled sterile plastic containers. The sediment samples were then placed in the cool box and nine (9) of the

sediment samples were transported to each of the laboratories that is: Lake Nakuru Water Quality Testing Laboratory (WQTL) and Analytical Chemistry and Food safety laboratory at the Directorate of Veterinary Services (DVS), Kabete for heavy metal and pesticide residue determination respectively.

#### 3.4.5 Fish sampling

A total of thirty (30) fish samples (*Oreochromis niloticus*) were collected from the identified sampling sites of Lake Nakuru. Ten (10) fish samples from River Njoro mouth, eleven (11) from Fisher's point, five (5) from Sewage discharge point and 4 from Nyati. Fish samples were obtained with the help of KMFRI team by setting gill nets at 6 pm in the evening and retrieving them the following morning at 6 am. The fish samples were placed in a cool box and transported to the Department of Biological Sciences, Egerton University for tissue extraction. In the laboratory, the fish were first rinsed with double distilled water and sexed. This was followed by taking total lengths (TL) measurements in centimetres (cm) using a measuring board following the description by Weber and Govett (2009). The weights of the fish were also measured in grams (g) using an electronic weighing scale (Model ED 4202S, Sartorius AG, Germany). Using a ceramic knife, the fish skin was removed from the dorsal part and muscle tissue obtained from both sides. The muscle tissue from both sides was mixed, partitioned into two and placed inside plastic vials and then stored at a temperature of -20 °C prior to analysis.

#### 3.5 Heavy metal determination in water, sediment, and fish muscle tissues

#### 3.5.1 Digestion of water samples

Following standard methods by APHA (2012), 100 ml of each of the water samples was measured using a clean measuring cylinder into a clean beaker. The sample was then acid digested with 5 ml of 69 % analytical grade nitric acid. 50 ml of double distilled water was added to the digested sample and immediately heated on a hot plate stirrer at 440 °C in a fume hood for one hour and evaporated to approximately 25 ml. The solution was cooled and filtered while diluting with double distilled water to a final volume of 100 ml using Whatman filter paper into a volumetric flask ready for heavy metal analysis.

#### 3.5.2 Digestion of sediment samples

Sediment samples were dried to a constant mass in the oven at 100 °C after which they were crushed using a mortar and pestle into fine particles. The samples were then sieved to remove debris and rock particles following the standard methods by APHA (2012). A sub

sample (2 g) of the homogenized sediment was accurately weighed, digested, and diluted the same way as the water sample.

# 3.5.3 Homogenization of fish muscle

In the laboratory, the extracted muscle was dried to a constant mass in the oven at a temperature of 100 °C. After cooling, the fish muscle was homogenized using a mortar and pestle for pesticide and heavy metal analysis as described by APHA (2012).

## 3.5.4 Digestion of fish samples

Following the same procedure as for the water and sediment samples, 2 g of homogenised fish muscle was accurately weighed and digested. The digestion of fish samples involved addition of 5 ml of sulphuric acid to the weighed sample in beakers. The samples were then placed on a hot plate in a fume hood and hydrogen peroxide was added to each of the samples until the reaction ceased. The digested samples were then transferred into glass tubes and topped up with double distilled water and then stored with caps prior to analysis for heavy metals.

## 3.5.5 Heavy metal measurement in water, sediment, and fish samples

Heavy metal concentrations were determined in the digested water, sediment and fish samples by using a direct aspiration Atomic Absorption Spectrophotometer (AAS-S series, United Kingdom) at wavelengths of 357.9, 217, 193.7, 253.7 and 228.8 nm for chromium (Cr), lead (Pb), arsenic (As), mercury (Hg), and cadmium (Cd) respectively. The heavy metal concentrations were calculated using the equations obtained from the standard calibration curve. The accuracy of the instrument was checked by triplicate analysis of samples. After every five samples, both a standard and a blank sample were run to check instrumental drift. A serial dilution of a working solution (100 mg/L) made from analytical grade stock solutions (1000 mg/L) acquired from Merck KGaA, Germany was used to prepare standards for instrument calibration. Recovery tests were also conducted using Canadian Reference Materials that is DORM for fish samples and Merck, Germany for sediment samples. The recovery rates obtained were 97 % for As, 104 % for Hg, 107 % for Cr, 102 % for Cd and 98 % for Pb and these were all in the recommended range.

## 3.6 Water, sediment and fish samples preparation for pesticide analysis

# 3.6.1 Extraction and removal of co-extractives of water

Water samples were extracted by solvent-solvent extraction following EN 15662 method. 250 mls of a water sample was transferred into a 1 L separatory funnel and pH adjusted to neutral. This was followed by an addition of 50 mls of dichloromethane and 5 g of

anhydrous sodium sulphate to aid in salting out the organochloride pesticides (OCPs) from the aqueous phase. The solution was shaken vigorously for two minutes (with venting intervals) and collecting the extracts. The extraction process was repeated using 50 ml of triply distilled dichloromethane (DCM). The combined extracts were eluted into conical flasks followed by drying using anhydrous sodium sulphate. The extracts were concentrated in the LABCONCO rotary evaporator at a temperature of 70 °C. Twenty - five (25) mls of isooctane was added into the concentrated sample and sonicated for proper mixing. The mixture was filtered into a glass vial ready for GC - MC analysis.

# 3.6.2 Extraction of sediment samples

The sediment samples were thawed for about six hours before extraction. Extraction was done using the Soxhlet technique following EN 15662 method. Fifteen (15) g of homogenised sediment sample was weighed into a 50 ml centrifuge tube. Fifteen (15) ml of an extraction solvent in a ratio of acetic acid/acetonitrile of 1:99 was added. This was capped and shaken for 1 minute, after which 10 g of an extraction salt (sodium acetate) was added. The mixture was shaken vigorously for 1 minute followed by centrifuging it at 5000 rpm for 5 minutes at 4 °C. A 6 ml aliquot of upper acetonitrile layer was transferred into a 15 ml centrifuge tube containing a clean-up salt (150 mg MgSO4, 25 mg PSA, 25 mg C18E). The mixture was capped and shaken for 1 minute after which it was centrifuged at 5000 rpm for 5 minutes. One (1) ml of the extract was transferred into another tube and dried by Nitrogen flow at 40 °C. This was followed by re - dissolving with 1 ml of isooctane and filtered through a nylon syringe filter of size 0.22 μm. The filtrate was then transferred into a10 ml glass vial with cap and stored in the refrigerator at a temperature of 4 °C prior to GC-MS analysis.

# 3.6.3 Extraction of fish samples

The fish samples were thawed for about six hours before extraction. Extraction was done using the Soxhlet technique following EN 15662 method. 10 g of homogenised fish sample was weighed into a 50 ml centrifuge tube. 10 ml of an extraction solvent (acetonitrile) was added. This was capped and shaken for 1 minute, after which an extraction salt (6 g of MgSO<sub>4</sub>, 1.5 g NaOAc) was added. The mixture was shaken vigorously for 1 minute followed by centrifuging it at 5000 rpm for 5 minutes at 4°C. A 6 ml aliquot of the upper acetonitrile layer was transferred into a 15 ml centrifuge tube containing 1200 mg MgSO<sub>4</sub>, 400 mg PSA, 400 mg C18E. The mixture was capped and shaken for 1 minute followed by centrifuging it at 5000 rpm for 5 minutes. One (1) ml of the extract was transferred into another tube

containing a clean-up salt and dried by Nitrogen flow at 40  $^{\circ}$ C. This was followed by redissolving with 1ml of isooctane and filtered through a nylon syringe filter of size 0.22  $\mu$ m. The filtrate was then transferred into a10 ml glass vial with cap and stored in the refrigerator at a temperature of 4  $^{\circ}$ C prior to GC-MS analysis.

# 3.6.4 GC-MS Analysis

A Shimadzu Gas Chromatography Mass Spectrophotometer (GC-MS/MS) TQ8040 was used for the analysis of the OCPs in water, sediment and fish samples. The injection port temperature was maintained at 250 °C. Nitrogen was used as the carrier gas and make-up gas with a constant flow rate of 30 ml/min. The sample injection volume was 1 μl with a pulsed split less injection mode. The column was a high-performance capillary column, HP5 (5% phenyl methyl siloxane) with dimensions of 30 m long, internal diameter of 0.25 mm and film thickness of 0.25 μm. The temperature limit was -60 °C to 325/350 °C.

# 3.6.5 Preparation of calibration curves

Standard calibration curves were prepared from pesticide standard stock solutions containing the OCPs. Sample analysis was carried out by injecting 1 µl sample size into the GC in split less mode. The resulting chromatograms were analysed for OCPs following external standard method. Retention times of sample peaks were matched with those of the reference standards to identify the specific congeners while standard calibration curves were used for quantitative analysis.

## 3.6.6 Sediment quality guidelines

The pollutant concentrations in sediments were compared with sediment quality guidelines (SQGs) such as Lowest Effect Level (LEL), Severe Effect Level (SEL), Threshold Effect Concentration (TEC), Shale and Probable Effect Level (PEL). The guidelines are set out to define levels of ecotoxic effects and are based on the chronic, long term effects of contaminants on benthic organisms. These levels are: 1- A No Effect Level at which no toxic effects have been observed on aquatic organisms. This is the level at which no biomagnification through the food chain is expected. Other water quality and use guidelines will also be met at this level. 2 - A Lowest Effect Level (LEL) indicating a level of sediment contamination that can be tolerated by the majority of benthic organisms. 3 - A Severe Effect Level (SEL) indicating the level at which pronounced disturbance of the sediment-dwelling community can be expected. At this level, the sediment is considered heavily polluted and likely to affect the health of sediment-dwelling organisms (Persaud et al., 1993). 4 - Threshold Effect Concentration (TEC), the contaminant concentration below which a toxic

response is not expected. 5 - Probable Effect Level (PEL), the concentration above which a toxic response is expected. If the pollutant concentrations measured in the sediment are below TEC, heavy metals and OCP residues are not expected to have any adverse effects on organisms. However, if the pollutant concentrations in the sediment are above PEC, toxic effects are likely to occur (CCME, 2001; Doyle et al., 2003).

## 3.6.7 Quality control and assurance

Quality control and accuracy was ensured by having several blanks together with the analysis of reference materials (WDNR, 1996). Field blanks and method blanks were also incorporated to check contamination during sampling, transportation and laboratory preparation procedures (UNEP, 1993). Recovery tests were carried out using the reference pesticide standards to determine the methodology performance (EC, 2000).

#### 3.7 Health risk assessment

The obtained concentrations of the different pollutants in the samples analysed were compared with the recommended reference standards deemed safe for public health such as World Health Organisation and European Union. Target Hazard Quotients (THQ) for both heavy metal and organochlorine pesticide concentrations as per USEPA (2012) to evaluate the human health risk of consuming fish contaminated with heavy metals and OCPs was conducted. The THQ being defined as the ratio between the possible exposure to a substance and the reference dose. The THQ can be computed from the equation according to USEPA (2012) as follows:

$$THQ = \frac{EFr \times EDr \times IRFa \times C}{RfDo \times BW \times AT}$$

Where, THQ is non-carcinogenic risk. EFr is the exposure frequency (350 days/year), EDr is the exposure duration (30 years) because some of the adverse effects are experienced after a prolonged exposure to heavy metals, IRFa is the fish consumption per day (0.0123 kg/day) because per capita fish consumption is 4.5 kg/year in Kenya (KMFRI report, 2017), C is the concentration of a pollutant in edible part of fish (milligrams per kilogram wet weight (ww)), RfDo is the reference dose, oral (milligrams per kilogram per day, according to the updated 2017 Regional Screening Level (RSL) in the fish ingestion table (USEPA, 2017). For example, the RfDo for Arsenic is 0.0003 mg/kg/day, Chromium is 0.003 mg/kg/day, Lead is 0.004 mg/kg/day and Mercury is 0.0001 mg/kg/day. BWa is the body weight of an adult male (63.9 kg) and female (61.8 kg) for Kenya (WorldData, n.d), AT is the averaging time for non-carcinogens (365 days/year).

## 3.8 Data analysis

All data collected was stored in Microsoft office excel. Statistical tests were done using R statistical software version 3.6.3. Normality of the data was tested using Shapiro Wilk test and wherever the data was normally distributed, a parametric test was conducted. The concentrations of heavy metals and OCP residues in the analysed samples were presented as mean with standard deviation (mean  $\pm$  standard deviation). One-way analysis of variance was used to test the differences in mean concentrations of the selected pollutants in the different lake matrices (water, sediments and fish) across sampling points. A correlation was conducted to find out the relationship between water quality parameters and pollutants in the different matrices. All statistical tests were performed at a significance level ( $\alpha$ ) of 0.05.

## **CHAPTER FOUR**

#### RESULTS

# 4.1 Water quality parameters

The pH ranged from 9.52 - 9.72 with Mid Lake point and Sewage discharge point recording the lowest and highest values, respectively. The dissolved oxygen concentrations ranged from 4.58 mg/L at Sewage discharge point to 8.62 mg/L at River Njoro mouth. The highest temperature was recorded at the River Njoro mouth (25.7 °C) and the least at the Sewage discharge point (23.40 °C). The Mid lake point recorded the highest conductivity (5226.7  $\mu$ s/cm) whereas the Sewage discharge point recorded the least (4470  $\mu$ s/cm). Salinity range was 2.39 - 2.81 % at Sewage discharge and Mid lake points respectively (Table 2). None of the differences in mean pH, dissolved oxygen, temperature, conductivity and salinity levels across the different sampling points were significant p > 0.05 (One-way ANOVA, pH ( $F_{2.6} = 0.6$ , p = 0.58), dissolved oxygen ( $F_{2.6} = 3.05$ , p = 0.12), temperature ( $F_{2.6} = 1.71$ , p = 0.26), conductivity ( $F_{2.6} = 0.08$ , p = 0.93) and salinity ( $F_{2.6} = 0.10$ , p = 0.90)).

**Table 2**: Means and ranges of water quality parameters recorded for Lake Nakuru during the entire study period (n = 9)

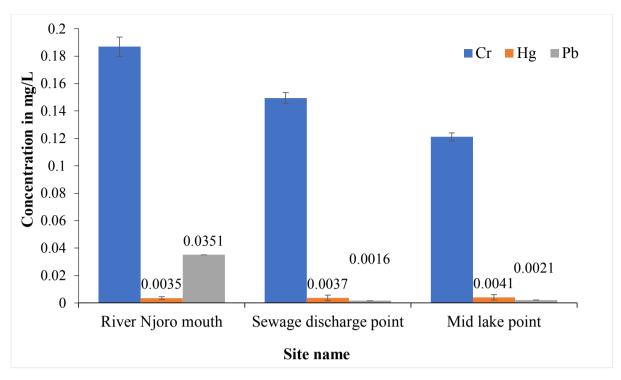
Source		River Njoro mouth	Sewage discharge point	Mid lake point
Parameter			-	-
Temperature (°C)	Mean	$24.9 \pm 0.9$	$23.7 \pm 0.6$	$24.6 \pm 0.7$
	Range	23.83 - 25.7	23.40 - 24.40	23.93 - 25.4
рН	Range	9.59 - 9.71	9.58 - 9.72	9.52 - 9.69
Dissolved oxygen (mg	/l) Mean	$7.5 \pm 1.5$	$5.5 \pm 0.8$	$6.9 \pm 0.5$
	Range	5.85 - 8.62	4.58 - 6.20	6.46 - 7.51
Conductivity (µs/cm)	Mean	$4758.9 \pm 350.5$	$4760.0 \pm 384.9$	$4856.7 \pm 321.4$
	Range	4483.3 -5153.3	4470 - 5196.7	4646.7 -5226.7

Salinity (‰)	Mean	$2.6 \pm 0.2$	$2.5 \pm 0.2$	$2.6 \pm 0.2$
	Range	2.41 - 2.79	2.39 - 2.76	2.46 - 2.81

# 4.2 Heavy metal concentrations

# 4.2.1 Heavy metal concentrations in water

The heavy metal concentrations in water as obtained for different sampling sites are presented as mean  $\pm$  SD (Figure 2). Among the five heavy metals measured, arsenic and cadmium were below detection in all the water samples for all sites (Appendix A.1). Chromium was highest at River Njoro mouth  $(0.19 \pm 0.01 \text{ mg/L})$  and least at Mid lake point  $(0.12 \pm 0.003 \text{ mg/L})$ . Lead was obtained in very low levels in all sites with River Njoro mouth (0.035± 0.00 mg/L) recording the highest. Mercury was highest at the Mid lake point  $(0.0041 \pm 0.002 \text{ mg/L})$  and least at the River Njoro mouth  $(0.0035 \pm 0.001 \text{mg/L})$ . There were no significant differences in mercury concentrations across sites p > 0.05 (One - way ANOVA, mercury ( $F_{2.6} = 0.02$ , p = 0.98) whereas chromium and lead showed significant differences across sites p < 005 (One - way ANOVA, chromium ( $F_{2.6} = 0.31$ , p = 0.03) and lead  $(F_{2.6} = 2.26, p = 0.01)$ ). A post hoc using the Tukey HSD test showed that the mean chromium concentration for River Njoro mouth was significantly different from that of Sewage discharge point and Mid lake point. Similarly, the mean chromium concentration of Mid lake point was significantly different from that of Sewage discharge point p < 0.05 (p =0.00). The mean lead concentration at River Njoro mouth was significantly different from that of Sewage discharge point and Mid lake point p < 0.05 (p = 0.00).



**Figure 2**: Heavy metal concentrations in water samples from Lake Nakuru for different sampling sites.

Irrespective of site, the mean heavy metal concentrations obtained in the lake water in this study are also presented and compared with the maximum permissible limits for different bodies on a national and international level (Table 3). Chromium levels exceeded the WHO and KEBS limits in water whereas mercury levels in water exceeded KEBS and NEMA limits.

**Table 3**: Heavy metal concentrations obtained for water samples from Lake Nakuru in comparison with the WHO maximum permissible levels, KEBS and NEMA water quality standards (mg/L) (n = 9)

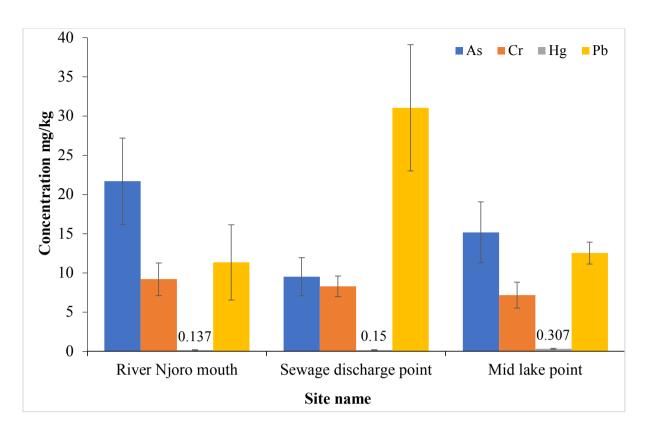
Element	Water (mg/L)	LOD	WHO	KEBS	NEMA
Arsenic	BDL	0.001	0.01	0.01	0.01
Cadmium	BDL	0.02	0.003	0.01	0.01
Chromium	0.150	0.01	0.05	0.05	NG
Lead	0.013	0.004	0.01	0.01	0.05
Mercury	0.004	0.0005	0.006	0.001	0.001

BDL: Below detection limit, LOD: Limit of Detection; NG: Not given, KEBS: Kenya Bureau of Standards, (2014), NEMA: National Environment Management Authority, (2006), WHO: World Health Organization, (2011).

# 4.2.2 Heavy metal concentrations in sediments

The heavy metal concentrations in sediments as obtained for different sampling sites are presented as mean  $\pm$  SD (Figure 3). Unlike for water samples, in sediments four out of the five heavy metals measured were present except for cadmium in all sites. Arsenic was highest in the sediment samples from River Njoro mouth (21.67  $\pm$  5.5 mg/kg dw) and least at the Sewage discharge point  $(9.5 \pm 2.43 \text{ mg/kg dw})$ . River Njoro mouth recorded the highest chromium concentration (9.19  $\pm$  2.08 mg/kg dw) whereas Mid lake recorded the least (7.16  $\pm$ 1.66 mg/kg dw). Lead was highest at Sewage discharge point (31.04  $\pm$  8.05 mg/kg dw) and least at River Njoro mouth (11.33  $\pm$  4.79 mg/kg dw). The highest mercury concentration in sediments was obtained at the Mid lake point  $(0.31 \pm 0.06 \text{ mg/kg dw})$  whereas the least was at River Nioro mouth (0.14  $\pm$  0.07 mg/kg dw) (Appendix A.2). There was no significant difference in mean chromium and mercury levels across sites p > 0.05 (One - way ANOVA, chromium  $(F_{2.6}=1.05, p=0.41)$  and mercury  $(F_{2.6}=0.54, p=0.61)$ ) whereas arsenic and lead showed significant differences across sites p < 0.05 (One - way ANOVA, arsenic ( $F_{2.6} =$ 1.80, p = 0.02) and lead ( $F_{2.6} = 2.82$ , p = 0.031). A post hoc using the Tukey HSD test showed that the mean arsenic concentration for River Njoro mouth was significantly different from that of Sewage discharge point p < 0.05 (p = 0.004). The mean lead concentration at River Njoro mouth was significantly different from that of Sewage discharge point and the mean lead concentration of Sewage discharge point was significantly different from that of Mid lake point p < 0.05 (p = 0.00).

Generally, there was a weak negative relationship (Pearson's r = -0.213, p = 0.01) between all water quality parameters (temperature, dissolved oxygen, pH, salinity and conductivity) and heavy metals in sediments at 0.05 level of significance (Appendix A.4).



**Figure 3**: Heavy metal concentrations in sediments of Lake Nakuru for different sampling sites.

Irrespective of site, the mean heavy metal concentrations of sediments in Lake Nakuru were computed and compared with the lowest effect level in sediment (LEL), threshold effect concentration in sediment (TEC), severe effect concentration in sediment (SEL) and Shale (Table 4). Arsenic levels exceeded all the sediment quality quidelines considered whereas the mercury concentration in sediment was slightly higher than TEC.

**Table 4**: Concentrations of heavy metals in sediment samples from Lake Nakuru in comparison with different sediment quality guidelines (n = 9)

Element	Sediment (mg/kg)	LEL	TEC	SEL	Shale
Arsenic	15.45	6.0	9.79	33.0	13
Cadmium	ND	0.6	0.99	10.0	0.3
Chromium	8.21	26.0	43.4	110.0	90

Lead	18.30	31.0	35.8	250.0	20
Mercury	0.22	0.2	0.18	2.0	0.4

LEL: Lowest Effect Level in sediment, TEC: Threshold Effect Concentration in sediment, SEL: Severe Effect Level in sediment. The sediment quality guidelines are given in mg/kg (Buchman, 2008; Doyle et al., 2003; Persaud et al., 1993; Turekian & Wedepohl, 1961).

# 4.2.3 Heavy metal concentrations in muscle of Nile tilapia

The heavy metal concentrations in muscle of fish as obtained from different sampling sites are presented as mean  $\pm$  SD (Table 5). As the case with water and sediment samples, cadmium was not detected in any of the fish samples. Arsenic was highest in the fish samples caught from Fisher's point  $(2.11 \pm 0.17 \text{ mg/kg dw})$  and least in samples from Sewage discharge point (0.41  $\pm$  0.02 mg/kg dw). The highest mercury concentration was recorded in fish samples caught from Sewage discharge point (0.35  $\pm$  0.06 mg/kg dw) whereas samples from River Njoro mouth had the least  $(0.12 \pm 0.03 \text{ mg/kg dw})$ . River Njoro mouth recorded samples with the highest lead concentration (9.95  $\pm$  0.23 mg/kg dw) whereas samples from Sewage discharge point  $(4.06 \pm 0.09 \text{ mg/kg dw})$  had the least. The highest chromium level was recorded in fish samples caught from Fisher's point (13.06  $\pm$  1.92 mg/kg dw) whereas the least was obtained in samples from Sewage discharge point (3.7  $\pm$  0.96 mg/kg dw). There was no significant difference in mean concentrations of mercury and lead across sites p > 10.05 (One - way ANOVA, mercury ( $F_{3.26} = 2.57$ , p = 0.07) and lead ( $F_{3.26} = 1.83$ , p = 0.17)) whereas arsenic and chromium showed significant differences across sites p < 0.05, (One way ANOVA, arsenic ( $F_{3,26} = 1.39$ , p = 0.007) and chromium ( $F_{3,26} = 1.43$ , p = 0.002)). A post hoc using the Tukey HSD test showed that the mean arsenic concentration for fish samples of River Njoro mouth was significantly different from that of Sewage discharge point. Similarly, the mean arsenic concentration of fish samples from Fisher's point was significantly different from that of Sewage discharge point p < 0.05 (p = 0.004). The mean chromium concentration of fish samples of Fisher's point was significantly different from that of Sewage discharge point p < 0.05 (p = 0.00).

**Table 5:** Mean concentrations of heavy metals in muscle of Nile tilapia samples caught from 4 sites of Lake Nakuru in mg/kg dw

Site	RNM	SDP	FP	NYATI
Element				

Arsenic	$1.85 \pm 0.14$	$0.41 \pm 0.02$	$2.11 \pm 0.17$	< 0.001
Cadmium	< 0.02	< 0.02	< 0.02	< 0.02
Chromium	$4.17 \pm 2.80$	$3.7 \pm 0.96$	$13.06 \pm 1.92$	$6.65 \pm 2.48$
Lead	$9.95 \pm 0.23$	$4.06 \pm 0.09$	$6.05 \pm 2.50$	$9.30 \pm 1.47$
Mercury	$0.12 \pm 0.03$	$0.35 \pm 0.06$	$0.13 \pm 0.02$	< 0.0005
n	10	5	11	4

RNM: River Njoro mouth, SDP: Sewage Discharge point, FP: Fishers' point. An assumption of no fish movement between sites was made.

# 4.3 Organochlorine pesticide results

# 4.3.1 Multi-level calibration curves

OCP calibration curves were developed using seven different concentrations of 16 OCPs standard solution mixture. All the calibration curves were linear and all the obtained R-squared values were above 0.99 indicating a high linearity between instrument response and analyte concentration. A sample calibration curve of endrin is presented (Figure 4) while the rest are in Appendix B.

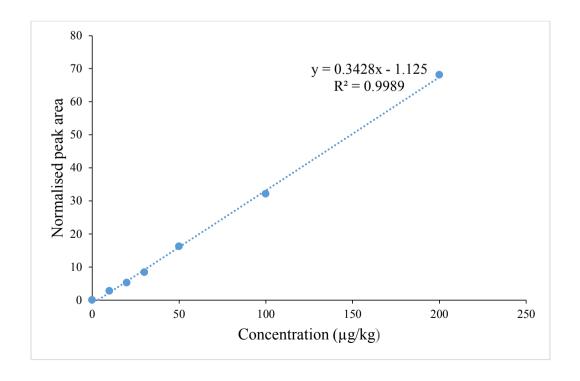


Figure 4: Sample calibration curve for endrin.

# 4.3.2 OCPs recoveries and limits of detection

The mean recoveries for the 16 OCPs ranged from 80 % to 108 %. This was found to be within the acceptable range of 70 % and 110 %, hence the results were not corrected (EC, 2000). The recoveries for the pesticides in water, sediments and fish samples analyzed are summarized in Table 6.

**Table 6**: Percentage recoveries of pesticide residues in water, sediment and fish samples from Lake Nakuru (mean  $\pm$  SD) (n = 3)

Organochlorine pesticide	Percentage recoveries				
	Water	Sediment	Fish		
Alpha - HCH	$107.92 \pm 2.21$	$100.98 \pm 1.12$	$92.84 \pm 1.03$		
Beta - HCH	$100.72 \pm 1.09$	$102.98 \pm 3.17$	$98.87 \pm 1.06$		
Gamma - HCH	$108.67 \pm 0.56$	$93.00 \pm 1.36$	$90.20 \pm 1.01$		
Delta - HCH	$100.86 \pm 2.01$	$90.51 \pm 2.13$	$81.75 \pm 2.19$		
P,P'-DDD	$102.29 \pm 4.25$	$87.50 \pm 2.70$	$84.92 \pm 1.21$		

P,P'-DDE	$102.97 \pm 1.11$	$94.07 \pm 2.22$	$90.25 \pm 0.87$
P,P'-DDT	$104.83 \pm 3.32$	$102.05 \pm 3.44$	$100.31 \pm 1.05$
Endosulfan 1	$92.58 \pm 4.31$	$88.84 \pm 1.60$	$98.81 \pm 2.03$
Endosulfan 2	$86.75 \pm 3.22$	$92.58 \pm 5.65$	$80.86 \pm 1.63$
Endosulfan sulfate	$95.28 \pm 2.25$	$98.03 \pm 1.00$	$83.38 \pm 2.48$
Aldrin	$105.62 \pm 3.05$	$96.89 \pm 4.11$	$83.72 \pm 1.54$
Endrin	$103.09 \pm 2.64$	$88.01 \pm 2.96$	$85.68 \pm 2.08$
Dieldrin	$101.96 \pm 2.96$	$97.55 \pm 3.77$	$88.04 \pm 1.08$
Heptachlor	$94.29 \pm 4.12$	$83.70 \pm 3.55$	$97.67 \pm 2.96$
Heptachlor Epoxide	$81.22 \pm 2.41$	$89.06 \pm 4.58$	$80.75 \pm 1.11$
Methoxychlor	$86.17 \pm 3.16$	$84.23 \pm 3.49$	$80.77 \pm 2.06$

The limits of detection (LOD) for the different OCPs ranged from 0.0011  $\mu g/L$  for alpha - HCH, endosulfan 1, heptachlor and heptachlor epoxide to 0.0036  $\mu g/L$  for aldrin (Table 7). OCPs whose concentration was below LOD were reported as below detection limit (BDL).

Table 7: Limits of detection for the different OCPs analysed in this study from Lake Nakuru

ОСР	LOD (µg/L)	ОСР	LOD (µg/L)
Alpha - HCH	0.0011	Endosulfan sulfate	0.0021
Beta - HCH	0.0016	Aldrin	0.0036
Gamma - HCH	0.0016	Endrin	0.0022
P,P'-DDD	0.0016	Dieldrin	0.0031
P,P'-DDE	0.0018	Heptachlor	0.0011
P,P'-DDT	0.0017	Heptachlor Epoxide	0.0011
Endosulfan 1	0.0011	Methoxychlor	0.0016
Endosulfan 2	0.0015		

#### 4.3.3 Organochlorine pesticide concentrations in water

All the 16 OCPs were detected in all the water samples examined in this study except for aldrin (Figure 5). Hexachlorocyclohexane (HCH) isomers were generally low in all water samples for all sites with concentrations ranging from  $0.03 \pm 0.00~\mu g/L$  to  $0.07 \pm 0.02~\mu g/L$ . Gamma - HCH recorded the highest  $(0.07 \pm 0.02~\mu g/L)$  concentration at the Sewage discharge point whereas beta - HCH recorded the least  $(0.03 \pm 0.00~\mu g/L)$  at River Njoro mouth. DDT and its metabolites residue levels ranged from  $0.03 \pm 0.00~to~0.18 \pm 0.03~\mu g/L$  with DDE recording the highest concentration at Sewage discharge point. The parent compounds: endosulfan 1 and 2 concentrations ranged from BDL to  $2.05 \pm 1.31~\mu g/L$  at Mid lake and River Njoro mouth respectively. In all sites the concentrations of endosulfan sulfate were generally low compared to the parent compounds' concentrations.

Endrin concentrations ranged from  $0.22 \pm 0.06~\mu g/L$  to  $0.68 \pm 0.41~\mu g/L$ . The highest endrin and dieldrin concentrations were recorded at Sewage discharge point whereas Mid lake point recorded the least. Heptachlor concentrations ranged from  $0.12 \pm 0.05~\mu g/L$  to  $0.19 \pm 0.02~\mu g/L$  at Mid lake point and Sewage discharge point, respectively. Heptachlor epoxide concentrations ranged from  $1.50 \pm 0.41~\mu g/L$  to  $7.44 \pm 0.66~\mu g/L$  at Mid lake point and Sewage discharge point respectively. Methoxychlor was highest at Sewage discharge point  $(4.54 \pm 0.35~\mu g/L)$  and least at Mid lake point  $(2.07 \pm 0.52~\mu g/L)$  (Appendix B.1). There were no significant differences in mean concentration of some organochlorine residues in water samples across sites at p > 0.05 whereas significant differences were recorded for delta - HCH ((One - way ANOVA,  $F_{2,6} = 9.15$ , p = 0.015), DDD ( $F_{2,6} = 52.31$ , p = 0.0002), DDT ( $F_{2,6} = 14.2$ , p = 0.005), endosulfan 1 ( $F_{2,6} = 7.36$ , p = 0.02) and heptachlor epoxide ( $F_{2,6} = 78.89$ ,  $p = 4.92 \times 10^{-5}$ )). A post hoc using Tukey HSD test showed significant differences in mean residue levels across sites for some OCPs in water (Appendix C.2).

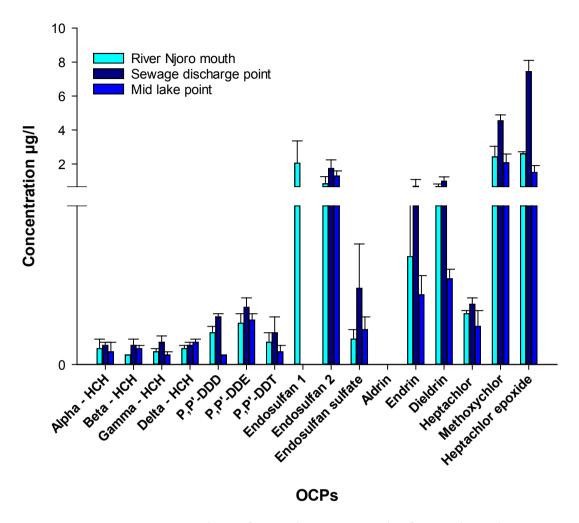


Figure 5: Average concentrations of OCPs in water samples from Lake Nakuru.

Irrespective of site, the mean organochlorine concentrations obtained in the lake water in this study were computed and compared with the maximum permissible limits for different bodies on a national and international level (Table 8). All OCP concentrations in water were below the maximum permissible limits except for heptachlor epoxide that exceeded WHO, EPA and Australian standards in water.

**Table 8**: Average organochlorine pesticide residue concentrations for water samples from Lake Nakuru in comparison with the WHO maximum permissible levels (WHO, 2008) EPA natural potable water limits and Australia water quality standards (IUPAC, 2003) (n = 9)

Pesticide	Concentration	WHO	EPA	Australia
	μg/L			
Alpha HCH	0.05	-	-	-
Beta HCH	0.05	-	-	-
Delta HCH	0.05	-	-	-
Gamma HCH	0.06	20	0.2	0.5
P,P'-DDD	0.09	-	-	-
P,P'-DDE	0.15	-	7	-
P,P'-DDT	0.10	50	200	60
Endosulfan 1	1.75	20	-	-
Endosulfan 2	1.45	20	-	-
Endosulfan sulfate	0.16	-	-	-
Aldrin	ND	10	-	10
Endrin	0.41	2	2	-
Dieldrin	0.47	0.3	-	-
Methoxychlor	2.27	20	40	20
Heptachlor	0.15	0.3	0.4	0.5
Heptachlor	3.68	0.3	0.2	0.5
Epoxide				

<sup>(-);</sup> value not provided. The WHO, EPA and Australian guideline values were given in mg/L but have been converted to  $\mu g/L$  for purposes of comparison.

# 4.3.4 Organochlorine pesticide concentrations in sediments

All the 16 OCPs were detected in all the sediment samples examined in this study except for aldrin. The concentrations of all OCPs considered in this study in the sediments was generally low (Figure 6). Hexachlorocyclohexane (HCH) isomers were generally low in all sediment samples for all sites with concentrations ranging from  $0.03 \pm 0.00 \,\mu\text{g/L}$  to  $0.08 \pm 0.03 \,\mu\text{g/kg}$  ww. Delta - HCH recorded the highest  $(0.08 \pm 0.03 \,\mu\text{g/kg}$  ww) concentration at

River Njoro mouth whereas beta - HCH recorded the least  $(0.03 \pm 0.00 \ \mu g/kg \ ww)$  concentration at Mid lake point. DDT and its metabolites residue levels ranged from BDL to  $1.36 \pm 0.05 \ \mu g/kg$  ww with DDE recording the highest concentration at Sewage discharge point and DDD recording the least at Mid lake point. The parent compounds: endosulfan 1 and 2 concentrations ranged from  $0.97 \pm 0.26 \ \mu g/kg$  ww at Mid lake point to  $6.39 \pm 1.10 \ \mu g/kg$  ww at Sewage discharge point. Endosulfan 2 recorded the highest residue level where as endosulfan sulfate residue level was the least  $(0.13 \pm 0.00 \ \mu g/kg \ ww)$  at Sewage discharge point. In all sites the concentrations of endosulfan sulfate were generally low compared to the parent compounds' concentrations.

Endrin concentrations ranged from  $0.07 \pm 0.02$  µg/kg to  $0.28 \pm 0.18$  µg/kg ww. The highest endrin concentration was recorded at Sewage discharge point whereas River Njoro mouth recorded the least. Dieldrin was highest at Mid lake point  $0.41 \pm 0.01$  µg/kg ww and least at Sewage discharge point  $0.09 \pm 0.03$  µg/kg ww. Heptachlor concentrations ranged from  $0.09 \pm 0.00$  µg/kg to  $0.28 \pm 0.02$  µg/kg ww at River Njoro mouth and Sewage discharge point, respectively. Heptachlor epoxide concentrations ranged from  $2.88 \pm 1.20$  µg/kg to  $3.31 \pm 0.80$  µg/kg ww at Sewage discharge point and River Njoro mouth, respectively. Methoxychlor was highest at Sewage discharge point ( $5.22 \pm 1.41$  µg/kg ww) and least at the Mid lake point ( $0.76 \pm 0.17$  µg/kg ww) (Appendix B.2). There were no significant differences in mean concentration of some organochlorine residues in sediment samples across sites at p > 0.05 whereas significant differences were recorded for DDE ((One - way ANOVA,  $F_{2,6} = 178.9$ ,  $p = 4.49 \times 10^{-6}$ ), endosulfan sulfate ( $F_{2,6} = 5.28$ , p = 0.047) and dieldrin ( $F_{2,6} = 25.67$ , p = 0.00115)). A post hoc using Tukey HSD test showed significant differences in mean residue levels across sites for some OCPs in sediments (Appendix C.4).

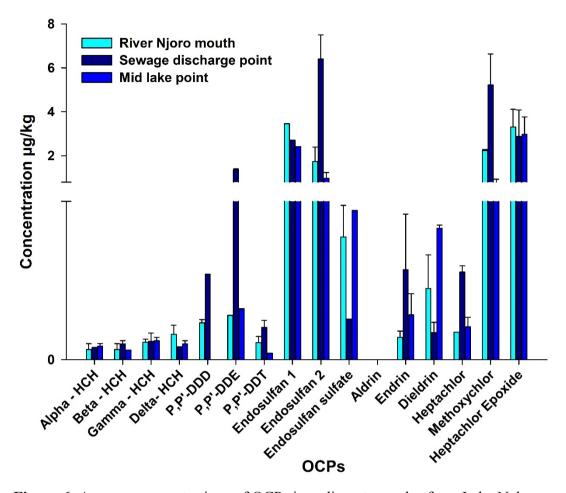


Figure 6: Average concentrations of OCPs in sediment samples from Lake Nakuru.

Irrespective of site, the mean organochlorine pesticide residue concentrations of sediments in Lake Nakuru were computed and compared with sediment quality guidelines including LEL, TEC, SEL and PEL (Table 9). All the OCP residue concentrations in sediments were below the sediment quality guidelines except for heptachlor epoxide whose concentration exceeded TEC and PEL values.

**Table 9**: Concentrations of organochlorine pesticide residues in sediment samples from Lake Nakuru in comparison with different sediment quality guidelines (n = 9)

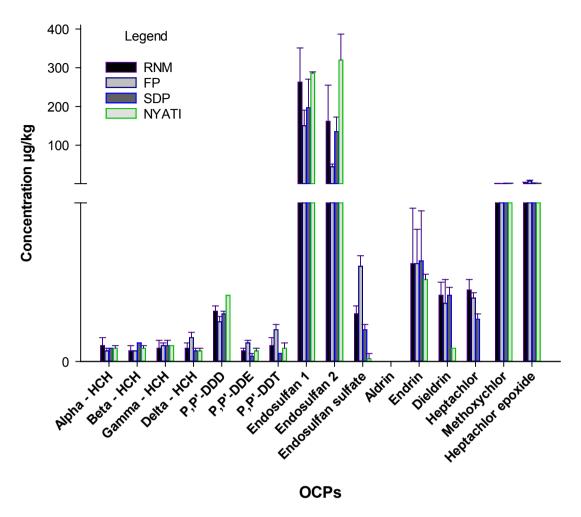
Pesticide	Concentration in sediments µg/kg	LEL	SEL	TEC	PEL
Alpha HCH	0.04	6	100	-	
Beta HCH	0.04	5	210	5	-
Delta HCH	0.06	3	120	3	
Gamma HCH	0.06	3	10	2.37	1.38
P,P'-DDD	0.13	8	60	4.88	8.51
P,P'-DDE	0.55	5	190	3.16	6.75
P,P'-DDT	0.09	8	710	4.16	4.77
Endosulfan 1	2.86	-	-	-	-
Endosulfan 2	3.04	-	-	-	-
Endosulfan sulfate	0.33	-	-	-	-
Aldrin	BDL	2	80	2	
Endrin	0.17	3	1300	2.22	62.4
Dieldrin	0.24	2	910	1.9	6.67
Methoxychlor	2.74	-	-	-	-
Heptachlor	0.16	-	-	-	-
Heptachlor Epoxide	3.05	5	50	2.47	2.74

LEL: Lowest Effect Level in sediment, TEC: Threshold Effect Concentration in sediment, SEL: Severe Effect Level in sediment, PEL: Probable Effect Levels, BDL: Below Detection Limit, (-): value not provided. The sediment quality guidelines are given in μg/kg (Buchman, 2008; Doyle et al., 2003; Persaud et al., 1993).

# 4.3.5 Organochlorine pesticide concentrations in fish samples

The organochlorine pesticide concentrations in the muscle of fish as obtained from different sampling sites are presented as mean  $\pm$  SD (Figure 7). As the case with water and sediment samples, aldrin was not detected in any of the fish samples. Hexachlorocyclohexane (HCH) isomers were generally low in all fish samples for all sites with concentrations ranging from  $0.04 \pm 0.00~\mu g/kg$  to  $0.09 \pm 0.02~\mu g/kg$  ww. Delta - HCH recorded the highest concentration in fish samples caught from Fisher's point whereas beta - HCH recorded the least. DDT and its metabolites residue levels ranged from  $0.02 \pm 0.01~\mu g/kg$  to  $0.25 \pm 0.00~\mu g/kg$  ww with DDD recording the highest concentration in fish samples caught from Nyati. Unlike other OCPs, endosulfan 1 and 2 concentrations were very high in all fish samples irrespective of site. They ranged from  $44.30 \pm 7.15~\mu g/kg$  ww in fish samples caught from Fisher's point to  $319.74 \pm 66.94~\mu g/kg$  ww in fish samples caught from Nyati. In all sites the concentrations of endosulfan sulfate ranged from  $0.02 \pm 0.01~\mu g/kg$  ww at Nyati to  $0.36 \pm 0.04~\mu g/kg$  ww at Fisher's point.

Fish samples caught from Sewage discharge point recorded the highest mean endrin concentration (0.38  $\pm$  0.19 µg/kg ww) whereas those samples from Nyati recorded the least  $(0.31 \pm 0.02 \,\mu\text{g/kg ww})$ . The highest mean dieldrin concentration was recorded in fish samples caught from River Njoro mouth  $(0.25 \pm 0.05 \,\mu\text{g/kg ww})$  whereas samples from Nyati recorded the least  $(0.05 \pm 0.00 \mu g/kg \text{ ww})$ . Heptachlor mean concentrations in all fish samples ranged from BDL at Nyati to  $0.27 \pm 0.04 \,\mu\text{g/kg}$  ww in samples from River Njoro mouth. Heptachlor epoxide mean concentrations ranged from  $1.72 \pm 0.09$  µg/kg to  $7.07 \pm$ 2.68 µg/kg ww in fish samples caught from Nyati and Fisher's point respectively. Methoxychlor was highest in fish samples caught from Nyati (1.48  $\pm$  0.47 µg/kg ww) and least in samples from Fisher's point  $(0.80 \pm 0.28 \,\mu\text{g/kg ww})$  (Appendix B.3). There were no significant differences in mean concentration of some organochlorine residues in fish samples across sites at p > 0.05 whereas significant differences were recorded for Alpha - HCH ((One - way ANOVA,  $F_{3.26} = 4.27$ , p = 0.01), DDT ( $F_{3.26} = 13.11$ ,  $p = 2.08 \times 10^{-5}$ ), endosulfan 2 ( $F_{3.26}$ = 7.10, p = 0.001) and methoxychlor ( $F_{3,26} = 6.50$ , p = 0.002)). A post hoc using Tukey HSD test showed significant differences in mean residue levels across sites for some OCPs (Appendix C.6).



**Figure 7**: Average concentrations of OCPs in fish samples from Lake Nakuru (RNM; River Njoro mouth, FP; Fishers' point, SDP; Sewage discharge point).

# 4.4 Heavy metal and pesticide pollution and safety of Nile tilapia from Lake Nakuru

# 4.4.1 Heavy metal pollution and safety of Nile tilapia

Irrespective of site, the mean heavy metal concentrations obtained in the fish samples from Lake Nakuru in this study were computed and are presented in comparison with the maximum permissible limits for different bodies on a national and international level (Table 10). Chromium and lead levels in the muscle of Nile tilapia by far exceeded the FAO and EU maximum permissible limits in fish and fishery products.

**Table 10**: Heavy metal concentrations in muscle of Nile tilapia samples from Lake Nakuru in comparison with the WHO maximum permissible levels and EU fish and products quality standards (mg/kg) for food safety (n = 30)

Element	Fish (mg/kg dw)	FAO (mg/kg)	EU	
Arsenic	1.46	-	-	
Cadmium	ND	2	$0.05^{a}$	
Chromium	7.01	0.05	$0.05^{a}$	
Lead	5.84	0.5	0.3°	
Mercury	0.15	0.5	0.5 <sup>b</sup>	

<sup>(-):</sup> value not provided; <sup>a</sup> European Union (EU), (2006); <sup>b</sup> EU, (2011); <sup>c</sup> EU, (2015); FAO, 2003.

Target hazard quotients for heavy metals were also computed. Arsenic had the highest THQ in both male and female human fish consumers followed by chromium, lead and lastly mercury. The THQs for all metals were slightly higher for female when compared to male consumers (Table 11). The THQs for all metals exceeded the THQ of 1 as given by USEPA (2017).

**Table 11:** Target hazard quotients (THQs) for male and female Lake Nakuru human fish consumers for the four heavy metals detected in this study

Element	Consumer	Arsenic	Chromium	Lead	Mercury
THQ	Males	26.53	13.95	10.00	8.17
	Females	27.91	14.68	10.52	8.60

# 4.4.2 Organochlorine pesticide pollution and safety of Nile tilapia

Some of the OCP residue concentrations obtained in fish were compared with maximum residue limits (MRLs) as provided by different bodies worldwide (Table 12). All OCP residue levels were below the MRLs except for endosulfan that exceeded the EU MRL of  $100~\mu g/kg$ .

**Table 12**: Comparison of OCP residue levels obtained in fish of Lake Nakuru with maximum residue limits (MRLs) recorded by different organizations (n = 30)

Pesticide	<b>Concentration of OCP</b>	MRLs in μg/kg	Reference
	in fish in μg/kg ww		
Gamma-HCH	0.06	200	CAC, 2009
(Lindane)			
P,P'-DDE	0.04	5000	FDA, 2001
P,P'-DDT	0.06	5000	FDA, 2001
Endosulfan	168.27	100	EU, 2011
Endosulfan sulphate			
Aldrin	ND	300	FDA, 2001
Endrin	0.33	200	CAC, 2009
Dieldrin	0.20	300	FDA, 2001
Heptachlor	0.22	200	CAC, 2009
Heptachlor epoxide	3.12	200	FAO/WHO,
			1983

The maximum residue levels were given in ppm and have been converted to  $\mu g/kg$  for purposes of comparison.

Target hazard quotients for organochlorine pesticides were also computed. Heptachlor epoxide recorded the highest THQ for both male and female human fish consumers and it is the only OCP whose THQ exceeded 1 as given by USEPA (2017) whereas alpha - HCH and beta - HCH recorded the least. A slightly higher THQ was recorded in the female than in male human fish consumers for all OCPs (Table 13).

**Table 13**: Target hazard quotients (THQs) for Lake Nakuru adult male and female human fish consumers for organochlorine pesticide residues

Pesticide	THQ- Males	THQ- Females
Alpha – HCH	3.41E-05	3.58E-05
Beta – HCH	1.41E-05	2.62E-05
Gamma – HCH	1.09E-03	1.15E-03
P,P'-DDD	2.91E-05	3.06E-05
P,P'-DDT	1.64E-03	1.72E-03
Endosulfan 1	1.63E-01	1.71E-01
Endosulfan 2	1.43E-01	1.50E-01
Endosulfan sulfate	1.27E-04	1.34E-04
Endrin	6.00E-03	6.31E-03
Dieldrin	2.18E-02	2.29E-02
Heptachlor	2.40E-03	2.52E-03
Methoxychlor	1.33E-03	1.40E-03
Heptachlor Epoxide	1.31	1.38

#### **CHAPTER FIVE**

#### **DISCUSSION**

# 5.1 Water quality parameters

Generally, the conductivity range of 4470 - 5226  $\mu$ S/cm obtained in this study irrespective of site was low compared to earlier studies. According to classification of lakes based on conductivity by Talling and Talling (1965), the obtained conductivity for Lake Nakuru falls within a range of 600 - 6000  $\mu$ S/cm which is linked to moderately saline lakes. They classified lakes with a conductivity of < 600  $\mu$ S/cm as freshwater whereas those with a conductivity > 6000  $\mu$ S/cm as saline lakes. The conductivity range obtained in this study was lower than what was reported by other earlier studies in the same lake such as Kairu (1994), Leichtfried and Shivoga (1995), Nelson et al. (1998), Ochieng et al. (2007), Oduor and Schagerl (2007), Raini (2009) and Vareschi (1982). For example, Vareschi (1982) reported a conductivity range of 10,000 - 160,000  $\mu$ S/cm. The differences in conductivity values obtained could be attributed to the difference in sampling seasons, sites and time. Ndetei and Muhandiki (2005) pointed out that conductivity tends to decline under wet conditions more so in unstable saline rift valley lakes of Kenya including Nakuru, Elementeita and Magadi.

The salinity range of 2.3 - 2.8 ‰ obtained in this study is very low when compared to that from previous studies in the same lake. For example, Oduor and Schagerl (2007), Raini (2009) and Schagerl et al. (2015) reported higher mean salinities of 18 ‰, 15.37 ‰ and  $29.3 \pm 13.4$  ‰ respectively. The differences could be attributed to dilution arising from the present increase in lake water levels.

The pH of the lake water in this study ranged between 9.52 and 9.72. These pH values are comparable to what has been reported for other freshwater lakes for example Ochieng et al. (2007) reported a mean pH of  $9.15 \pm 0.21$  for Lake Naivasha. Otachi et al. (2014) also reported a pH of 9 for Lake Naivasha. The mean pH of 9.6 obtained in this study is slightly lower than what was reported by earlier studies in the same lake such as Jirsa et al. (2013), Nelson et al. (1998), Oduor and Schagerl (2007) and Raini (2009). The pH range obtained in this study indicates that Lake Nakuru is tending towards freshwater lake as the pH of alkaline lakes is reported to be >10 (Ochieng et al., 2007). The survival of freshwater fish species like Nile tilapia in this originally known saline lake could also justify this.

The mean temperature of 24.4 °C obtained in this study was lower than for some previous studies like Nelson et al. (1998) of 29 °C, Raini (2009) of 27.30 °C and comparable to that reported by Schagerl et al. (2015) of 25.1  $\pm$  1.9 °C in the same lake. The variations

could be attributed to differences in sampling season, sites as well as time of the day when data was collected. The highest temperature being recorded at the mouth of River Njoro could be attributed to the low turbidity and low depth such that the heat from the sun could easily penetrate the water.

Dissolved oxygen ranged between 4.7 and 9.0 mg/L with the highest amount being recorded at the mouth of River Njoro. This could be attributed to the clear fresh water coming into the lake after most of the impurities have settled thus allowing for free circulation of oxygen from the atmosphere. However, this study reported a lower mean dissolved oxygen concentration (6.6 mg/L) when compared to previous studies such as Oduor and Schagerl (2007) who obtained a mean dissolved oxygen concentration of 17 mg/L from the same lake. The differences could be attributed to variations in sampling time as well as season. Furthermore, dilution has had a significant effect on *Arthrospira* which had dominated the lake and was the main food of lesser flamingos which migrated as a result. *Arthrospira fusiformis* is known to form a high algal crop due to its high photosynthetic capacity (Schagerl et al., 2015). This could also have led to the low levels of dissolved oxygen recorded in the present study. Generally, the current results for selected water quality parameters differ from those reported by earlier studies and the variation is mainly attributed to the increased dilution from a rise in lake water levels.

#### 5.2 Status of heavy metal and pesticides pollution in Lake Nakuru

#### **5.2.1** Heavy metal concentrations in water

Generally, the water samples recorded lower concentrations of heavy metals as compared to sediments and fish samples. Arsenic and cadmium were not detected in any of the water samples and this agrees with the findings of Barasa et al. (2017) who did not record the two elements in their study in Lake Nakuru. They associated the finding to the increase in water levels in the saline rift valley lakes of Kenya. However, the finding of arsenic absence in water samples is contrary to the findings of Tenai et al. (2016) who obtained 0.002 mg/L of arsenic and Yang et al. (2017) who obtained arsenic levels of 0.006 mg/L in the same lake. The known sources of cadmium into the environment include; wastewater discharge, industrial air emissions and the widespread application of phosphate fertilizers that are eventually washed into aquatic systems. It was interesting not to detect cadmium in any of the samples given that the Lake Nakuru catchment is largely agricultural. This could be because cadmium was not in a bioavailable form. Cadmium tends to form stable complexes with

organic matter (Kubier et al., 2019). According to Berrow and Mitchell (1980), 99% of the metal content of the soil solution may be present in complexed forms.

The mean Cr concentration of 0.15 mg/L obtained in this study is higher than that reported by Nelson et al. (1998) of 0.067 mg/L, Ochieng et al. (2007) of 0.06 mg/L and Tenai et al. (2016) of 0.005 mg/L in the same lake. The high concentration of chromium in all sites sampled in this study could be attributed to discharge of wastes rich in Cr more so through the inflowing rivers like River Njoro (Akan et al., 2010). More still, the level of Cr obtained in this study is contrary to the findings of Yang et al. (2017) who did not detect chromium in the water samples from the same lake. However, Barasa et al. (2017) reported a higher Cr concentration in water of 0.80 mg/L in Lake Nakuru than the current study. The differences in findings regarding Cr for Barasa et al. (2017) and Yang et al. (2017) could be attributed to the differences in analysis method used. Whereas the former used Atomic Absorption Spectrophotometry (AAS), the later used Inductively coupled plasma-mass spectrometry (ICP-MS). Comparing the heavy metal concentrations obtained in this study with World Health Organisation permissible limits (WHO, 2011) and Kenya Bureau of Standards (KEBS, 2014), chromium exceeded the benchmark values of both WHO and KEBs. This could indicate that Lake Nakuru water is contaminated with chromium. The relatively high Cr level obtained even at the Mid lake point could justify that indeed the lake is polluted with Cr.

The mean lead level of 0.013 mg/L obtained in this study was comparable to that obtained by Tenai et al. (2016) from the same lake of 0.01 mg/L. Higher lead concentrations were reported by Nelson et al. (1998) of 0.02 mg/L and Ochieng et al. (2007) (0.29 mg/L) in the same lake. However, Barasa et al. (2017) and Yang et al. (2017) reported lower concentrations of lead of 0.0002 mg/L and 0.002 mg/L respectively in water samples from Lake Nakuru. The lead concentrations were within WHO, KEBS and NEMA permissible limits in water.

A mean mercury concentration of 0.004 mg/L was obtained in the water samples in this study. However various studies conducted in Lake Nakuru have not considered studying mercury levels in water except for a few such as Yang et al. (2017) who obtained a Hg concentration comparable to the current study of 0.003 mg/L. On the contrary, Mavura and Wangila (2003) reported a higher mean Hg concentration of 2.48 mg/L in water samples from the same lake. The differences in mercury concentrations obtained in this study and Mavura's could be attributed to the dilution effect such that the rate of input of Hg into Lake Nakuru currently is slightly low compared to 2003 and the Hg that gets into the lake is further

diluted by increased water levels. The mean mercury concentration obtained in this study was within WHO limits but exceeded KEBS and NEMA permissible limits in water.

## 5.2.2 Heavy metal concentrations in sediments

The concentration of heavy metals obtained in the sediments of Lake Nakuru from the highest was Pb > As > Cr > Hg. The mean lead concentration (18.30 mg/kg dw) obtained in this study was higher than what Barasa et al. (2017), Mavura and Wangila (2003) and Ochieng et al. (2007) obtained in Lake Nakuru of 11.89 mg/kg, 14.36 mg/kg and 16 mg/kg respectively. More still, the mean Pb concentration in this study was far much higher than what was reported by Tenai et al. (2016) of 0.43 mg/kg in the same lake. The relatively high lead concentration in the present study despite the increased water levels could indicate a continued input of lead into the lake with a consequent accumulation into the sediments.

The mean arsenic concentration (15.45 mg/kg dw) obtained in the sediments of this study was higher than what was reported by Tenai et al. (2016) of 0.35 mg/kg and Barasa et al. (2017) who did not detect arsenic in sediment samples from the same lake. Similarly, Jirsa et al. (2013) reported a lower mean arsenic concentration of 6.1 mg/kg in Lake Nakuru sediments. The variations could be linked to difference in sampling time, analytical methods and seasons by the different studies. The observed trend of arsenic levels compared to earlier studies could indicate a continued input of the pollutant into the lake. The mean arsenic concentration exceeded all the sediment quality guidelines considered for heavy metals that is TEC, LEL, SEL as well as Shale. This indicates that Lake Nakuru sediments are heavily polluted with arsenic. The probable sources of arsenic into the Lake could be linked to pesticide usage in the Lake Nakuru catchment as well as atmospheric deposition.

The chromium concentration (8.21 mg/kg dw) obtained in this study was much lower than what Jirsa et al. (2013) and Tenai et al. (2016) obtained in Lake Nakuru of 57.85 mg/kg and 23.8 mg/kg respectively. However, Barasa et al. (2017), Mavura and Wangila (2003) and Ochieng et al. (2007) reported lower concentrations of Cr in sediments of Lake Nakuru. The variations could be attributed to differences in methods of analysis. The observed levels of Cr in sediments could be attributed to anthropogenic input more so municipal and domestic discharges from the nearby Nakuru town.

The mean mercury concentration (0.22 mg/kg dw) reported in the current study was lower than what was reported by Mavura and Wangila (2003) of 3.06 mg/kg in sediments of the same lake. However, Barasa et al. (2017) did not detect mercury in all sediment samples

considered in their study. The Hg concentration in the sediments could indicate a reduced input of the metal into the lake comparing the finding of this study to Barasa's finding.

The mean concentrations of all heavy metals considered in this study were compared with the sediment quality guidelines. Lead and chromium had concentrations below LEL, TEC, SEL and Shale values of sedimentary rocks. However, mercury had concentrations similar to LEL and TEC whereas arsenic mean concentration in sediments exceeded LEL, TEC and Shale. Therefore, regarding Cr and Pb, the sediments of Lake Nakuru did not show any sign of pollution based on the sediment quality guidelines by Turekiann and Wedepohl (1961). However, the concentrations of As and Hg obtained in the sediments of Lake Nakuru indicated pollution given that they were not within the normal background level in the earth's crust.

The obtained correlation results of heavy metals in sediments with water quality parameters can be explained by, for example pH greatly affects the speciation of heavy metals which in turn influences their migration and transformation in water and sediments (Riba et al., 2004). Furthermore, the mobility of all metals from sediments to the water column is known to increase with decreasing pH values. Zhang et al. (2018) pointed out that at high pH, certain heavy metals such as cadmium tend to precipitate forming complexes which determine metal toxicity in water and sediments hence the negative weak relationship observed.

# 5.2.3 Heavy metal concentrations in muscle tissues of Nile tilapia

The concentration of heavy metals obtained in fish samples of Lake Nakuru from the highest was Cr > Pb > As >Hg. The Cr level (7.01 mg/kg dw) obtained in this study was higher than what Mavura and Wangila (2003) reported in Tilapia grahami (*Alcalicus grahami*) (1.05 mg/kg) from the same lake. Unfortunately, many earlier studies that studied heavy metal contamination in fish of Lake Nakuru such as Kairu (1999) and Koeman et al. (1972) did not include chromium. Elsewhere, this study recorded lower Cr levels than what Ngesa et al. (2019) reported in the muscle of *Enteromius paludinosus* (22.09 mg/kg) in Lake Naivasha. The relatively high levels of chromium in Nile tilapia of Lake Nakuru could be attributed to discharge of improperly treated industrial waste and direct discharge of wastewaters into the lake mainly through the inflowing rivers (Reid, 2011). This could be justified by the relatively high levels of chromium in water samples obtained from River Njoro mouth as compared to the other sites.

The mean lead concentration obtained in the muscle tissues of Nile tilapia (5.84 mg/kg dw) in this study was higher than what was reported by Mavura and Wangila (2003) in Tilapia grahami (*Alcalicus grahami*) of Lake Nakuru (3.22 mg/kg). Unfortunately, Lake Nakuru being a protected area, not so many studies have investigated heavy metal pollution in fish. Elsewhere, Otachi et al. (2015), reported lower mean Pb concentration (0.024 mg/kg) in the muscle of *Oreochromis leucostictus* from Lake Naivasha compared to the present study. The high levels of Pb in the fish muscle indicates high levels in the lake and these could be attributed to the automobile batteries disposed of near the lake and vehicular emission (He et al., 2013; Mavura & Wangila, 2003). This finding concurs with the findings of Yabe et al. (2010) who found out that heavy metal pollution in different environmental matrices in Africa was on an increase to levels exceeding international limits and pointed out lead as one of the metals that are widespread.

The mean mercury level (0.15 mg/kg dw) obtained in this study was lower than what was reported by earlier studies such as Mavura and Wangila (2003) who reported a mercury concentration of 3.34 mg/kg in fish from the same lake. On the contrary, the mercury concentration of this study was higher than what was reported by Kairu (1999) (< 0.01 mg/kg) and Koeman et al. (1972) (0.016 mg/kg) in Tilapia grahami (*Alcalicus grahami*) caught from Lake Nakuru. Elsewhere, the mean mercury concentration of this study was higher than what Hollamby et al. (2004) reported in Nile tilapia (0.01 mg/kg) from Lakes: Mburo and Victoria, Uganda.

In comparison to other heavy metals considered in this study, the metalloid As concentration in fish tissues has not been widely studied. However, the mean arsenic concentration (1.46 mg/kg dw) obtained in this study was higher than what Kairu (1999) and Koeman et al. (1972) obtained in Tilapia grahami (*Alcalicus grahami*) of 0.03 mg/kg and 0.086 mg/kg respectively from Lake Nakuru. This finding shows an increased input of arsenic into the lake over the years with a consequent bioaccumulation in fish given that baseline studies recorded relatively lower levels.

#### 5.2.4 Organochlorine pesticide residues in water

All OCPs examined in this study were detected in the water samples except for aldrin with trade names (Aldrec, Aldrex, Aldrex 30, Aldrite, Aldrosol, Altox, Compound 118, Drinox, Octalene, Seedrin). Aldrin was an insecticide that was banned for use in Kenya in 2004 (Appendix B.5). Its absence in the water samples could be an indication that it is no longer used in the Lake Nakuru catchment. All isomers of hexachlorocyclohexane (HCH) were banned in Kenya but unfortunately, they were detected in this study. Though the

concentrations were low, the frequencies in the water samples analysed were very high (100% for alpha & beta HCH, 77% gamma-HCH and 67% for delta -HCH) of all water samples (Appendix B.4). The cyclodienes including dieldrin, endrin, heptachlor, methoxychlor and endosulfan had the highest concentrations followed by DDT and its metabolites and HCHs isomers had the least levels in water samples. The results obtained could be an indication that the cyclodienes have been recently used in the Nakuru catchment.

DDT was banned in Kenya for use in agriculture in 1986 but was restricted in disease vector control in humans. This stemmed from its undesirable effects in the environment for example residues were found in foodstuffs more so of animal origin. The slightly high levels of dieldrin in the water samples could be explained by the recent use rather than the conversion of aldrin to dieldrin by sunlight and bacteria because aldrin was not detected in any of the samples examined (ATSDR, 2002; Mugambi et al., 1989). The concentration of almost all OCPs was below the WHO, EPA and Australian guidelines in water except for heptachlor epoxide. The detection of banned OCPs in this study even in low concentrations could be attributed to continued illegal use (Lalah et al., 2003; Musa et al., 2011).

Unfortunately, earlier studies of OCPs in Lake Nakuru have not looked at their concentrations in water except Mayura and Wangila (2003). All the analysed OCP residues in water in their study that included DDT, DDE, DDD, gamma - HCH, heptachlor and aldrin had higher concentrations when compared to the present study. Wandiga et al. (2002) reported higher concentrations of OCP residues in water samples (0.50 - 9.03 µg/L) along the Indian ocean coast, Kenya except for endosulfan 1 which was lower than what was obtained in the present study. Elsewhere, the concentrations of OCPs obtained in the water samples of this study (BDL - 7.44 µg/L) were generally lower than what was reported by Osoro et al. (2016) in water samples of Rusinga island, Lake Victoria during the short rain season (BDL -15.53 µg/L). More still, the OCP levels of this study were higher than what was reported by Madadi (2017) in water samples obtained from Kargi area, Marsabit county, Kenya (BDL -3.37 µg/L), Nyaundi et al. (2019) in River Kuja catchment, Kenya (BDL - 2.20 µg/L) and Ondiere (2016) in Lake Elementeita drainage basin (BDL - 0.16 µg/L). The results of this study were also comparable to what Njogu (2011) obtained from Lake Naivasha (0.006 - 6.76 μg/L). In a study by Getenga et al. (2004), relatively high OCP levels were reported in the water samples (BDL - 1240 µg/L) obtained from River Nyando drainage system - Lake Victoria. The authors concluded that the banned OCPs were still in use.

# 5.2.5 Organochlorine pesticide residues in sediments

The OCP residues in sediments were higher than in water samples. This finding concurs with the findings of Wandiga et al. (2002) who reported residue concentration trend in fish > sediments > water. In comparison to other studies, Mayura and Wangila (2003) recorded higher residue levels of OCPs in sediments of Lake Nakuru than what was obtained in the current study. Bettinetti et al. (2011) also reported higher residue levels of DDT and its metabolites in sediments of another saline rift valley lake (Lake Bogoria) than the present study. However, the trend of DDE >DDD >DDT residue concentrations was similar to the current study. The variations could be attributed to differences in sampling season and analytical method. Whereas, their studies were conducted in dry seasons, there were short rains at the time the present study was conducted. Furthermore, the concentration of OCP residues (BDL - 6.39 µg/kg) recorded in this study were lower than what Wandiga et al. (2002) reported (0.58 - 59 μg/kg) in sediment samples from the Indian ocean coast, Kenya. Elsewhere, Osoro et al. (2016) reported higher residue concentrations (BDL - 24.84 µg/kg) during the wet season in Rusinga island, Lake Victoria than the current study. Similarly, Wasswa et al. (2011) reported higher OCP residue levels (BDL - 15.96 µg/kg) in sediments of Ugandan side of Lake Victoria. Lalah et al. (2003) also reported higher concentrations in sediments of River Sabaki with residue levels of BDL - 108.5 ug/kg in 1998 and of BDL -6.93 µg/kg in 1999 with aldrin and lindane contributing significantly to the levels.

There was no clear trend of OCP residues among sites, but sediments at Sewage discharge point and River Njoro mouth recorded relatively high OCP residues indicating their significant contribution to contaminant input into the lake. According to Mavura and Wangila (2003), there is extensive farming and intense application of pesticides in the River Njoro headwaters region. The slightly higher concentration of p,p'-DDE in sediments as compared to p,p'-DDT could be explained by the fact that DDE is a degradation product of DDT in the environment (Kanja et al., 1986; Njogu, 2011).

The concentration of heptachlor epoxide was high when compared to heptachlor and this can be attributed to degradation. It is reported that heptachlor can be degraded into equal portions of heptachlor epoxide and 1-hydroxy chlordane within 4 weeks (Lalah et al., 2003). Additionally, heptachlor has a half-life of approximately six months in water and sediment whereas its derivative breaks down in about three to seven years (Howard, 1991). Therefore, the presence of heptachlor pesticide residue in this study shows that the pesticide was in current use at the time of sampling because it was banned in Kenya in 1986 (PCPB, 2008).

The observed low concentration of Lindane ( $\gamma$ -HCH) in sediments could be attributed to reduced input into the lake following its restricted use to only seed dressing. The relatively high concentrations of endosulfan, endrin, heptachlor and methoxychlor initially used as insecticides could probably be attributed to their continued illegal use in Lake Nakuru catchment. The mean concentrations of OCP residues obtained in this study were compared with different sediment quality guidelines and all were below LEL (lowest effect level in sediment), SEL (severe effect level in sediment), TEC (threshold effect concentration in sediment) and PEL (probable effect level) values of sedimentary rocks except heptachlor epoxide whose concentration exceeded TEC and PEL. Therefore, with an exception of heptachlor epoxide, there was no sign of pollution in the sediments of Lake Nakuru as far as other organochlorine pesticide residues are concerned.

# 5.2.6 Organochlorine pesticide concentrations in the muscle of Nile tilapia

As the case with water samples and sediment samples, all the 16 OCPs were recorded in the fish samples except for aldrin. The trend from highest to lowest of the residue levels in the OCP groups was the same in all the matrices considered that is cyclodienes > DDT and its metabolites > hexachlorocyclohexanes. This indicates that some, if not all OCPs in the cyclodiene group could still be used in the Lake Nakuru catchment while the other groups (hexachlorocyclohexanes and DDT & its metabolites) are phasing out. The recorded residue levels of the other groups could be attributed to obsolete pesticide stocks which remained in stores after the ban of those pesticides (Saoke, 2005). The obsolete pesticide stocks tend to find their way into the environment thus causing pollution (Murty, 1986).

Endosulfan 1 and 2 residue levels were generally high in fish samples irrespective of site when compared to other OCPs. These high residue levels could be attributed to the frequent use of endosulfan in the Lake Nakuru catchment as well as the bioaccumulation effect. Endosulfan is of environmental importance because of its apparent persistence and toxicity to many non-target organisms such as fish (Nyaundi et al., 2019). The residue concentration of heptachlor was generally lower than that of heptachlor epoxide irrespective of site. This could be attributed to the breakdown of heptachlor into heptachlor epoxide by organisms. Despite heptachlor epoxide being a degradation product, it is as toxic and persistent as the parent compound (Murty, 1986).

In comparison to other studies, higher residue levels of pp' DDT, pp' DDE and dieldrin were reported in Tilapia grahami (*Alcalicus grahami*) of Lake Nakuru by Koeman et al. (1972). The levels obtained in their study of below 7 µg/kg ww for all the 3 compounds were higher than what was obtained in this present study. Similarly, in a study conducted to

evaluate the extent of organochlorine pesticide contamination of fish in Lake Nakuru, Greichus et al. (1978) reported very low residue levels in Tilapia grahami (*Alcalicus grahami*). Kairu (1999) reported higher residue levels of alpha - HCH, lindane, beta - HCH and DDE in Tilapia grahami (*Alcalicus grahami*) from the same lake when compared to the current study. Like the current study, the study did not detect aldrin in the fish samples and contrary to the findings of this study, dieldrin was not detected. Elsewhere, Mwevura et al. (2002) reported relatively high frequencies of OCPs during wet season giving frequencies of p, p'-DDT (81%), p,p'-DDE (100%), dieidrin (100%) and  $\gamma$ -HCH (6%) in samples of fish from the coastal area of Dar es Salaam, Tanzania.

# 5.3 Heavy metal and pesticide pollution and safety of Nile tilapia from Lake Nakuru

The mean lead (Pb) level in the muscle of Nile tilapia obtained in this study was above the WHO/FAO and EU maximum permissible levels. The THQ value for Pb was 8.37 for female and 7.96 for male human fish consumers with both values exceeding 1 thus consumption of Nile tilapia from Lake Nakuru poses a serious health risk to humans in regard to Pb levels. The consumers of this fish are prone to body organ and system damage for example kidney, liver, reproductive system, nervous system, urinary system and immune system (Njuguna et al., 2017). Additionally, chronic exposure to lead has been associated with cerebrovascular disease while lifetime exposure causes cancer (Sharma & Pervez, 2003).

The chromium (Cr) level recorded in the muscle of Nile tilapia exceeded the WHO/FAO and EU maximum permissible limits fish and fishery products, an indication that this fish was contaminated with chromium. Though the THQs for chromium were the lowest for both female (6.86) and male (6.52) human fish consumers, they still exceeded the benchmark THQ of 1 (USEPA, 2012) indicating a potential health risk to consumers of this fish. The health risks associated with Cr ingestion include: respiratory and gastrointestinal impairment, skin inflammation, nausea, ulcers, perforation of nasal septum, respiratory cancer and hair loss (McCartor & Becker, 2013; Muharpawar, 2015).

Although, the mercury concentration (0.15 mg/kg dw) obtained in the muscle tissues of Nile tilapia in this study was below the EU (2006) and WHO/FAO (2011) maximum permissible levels, the THQs were very high. THQ values of 8.18 and 8.60 were recorded for adult male and female human fish consumers respectively regarding mercury concentration indicating a potential health hazard to consumers of this fish over time. The consumers are likely to suffer from immune diseases, brain damage, vision impairment, kidney and lung

failure as a result of exposure to mercury contamination (Castro-González & Méndez-Armenta, 2008).

Unfortunately, the WHO/FAO did not provide the maximum permissible limits of arsenic (As) in Nile tilapia. The THQ values of As were 26.53 and 27.91 for adult male and female human fish consumers respectively. The THQs having exceeded 1 indicate a potential health risk to fish consumers of this lake regarding As concentration. Therefore, fish consumers of Lake Nakuru are liable to reproductive toxicity, hematologic disorders, developmental abnormalities, gastrointestinal problems, cardiovascular and central nervous systems' disorders, peripheral vascular disease with eventual death (Mohammed et al., 2011; WHO, 2010).

The residue levels of OCPs in fish recorded in this study were lower than the maximum residue levels set by international organisations except for endosulfan which exceeded the EU standard of residue levels in fish. Unfortunately, endosulfan is not among the OCPs banned or with restricted use in Kenya but it is known to be toxic to the kidney once in the human body. Additionally, several studies have shown that endosulfan, alone or in combination with other pesticides, may bind to estrogen receptors and perturb the endocrine system (WHO, 2008).

Although the pesticide residues measured in fish were lower than the recommended maximum permissible residue levels for fish and fishery products, their long-term impact may be of significance due to their high potential of biomagnification through the food chain. The THQ values calculated for the different OCP residue levels in fish were all below 1 (USEPA, 2012) except for heptachlor epoxide indicating no potential health hazard to Lake Nakuru fish consumers regarding OCP contamination.

### **CHAPTER SIX**

### CONCLUSIONS AND RECOMMENDATIONS

### **6.1 Conclusions**

The levels of water quality parameters from Lake Nakuru were generally lower than the levels reported by earlier studies. The study concludes that dilution resulting from increased water levels has changed the lake from saline towards freshwater.

Chromium levels were above the recommended standards in water samples, arsenic exceeded the sediment quality guidelines whereas chromium and lead exceeded the WHO and KEBS permissible limits for fish and fishery products. Organochlorine pesticide residues analysed were detected in low concentrations in all matrices considered in this study except for aldrin that was not detected

The study concludes that Nile tilapia from Lake Nakuru is not safe for human consumption. Its safety is limited by elevated levels of chromium, lead and endosulfan as well as THQs exceeding 1 for all metals and an OCP: heptachlor epoxide.

### 6.2 Recommendations

Since the water quality status has indicated that the lake is tending towards freshwater, this study recommends an assessment of all the abiotic and biotic parameters of the lake and a possible reclassification of the lake.

Policy makers should put in place an environmental monitoring program and mitigation strategies of reducing pollutant input into the lake and hence manage the water quality status of the lake which has serious implications to the aquatic life.

Since the findings of this study indicate that Lake Nakuru fish is not safe for human consumption, the study recommends an immediate ban on fish harvesting and consumption from Lake Nakuru.

The current study did not embark on the sources of the pollutants into the lake therefore future studies could consider investigating the sources of these contaminants for example the role of inflowing rivers in pollutant input into the lake.

Future studies could also consider investigating factors such as water temperature, conductivity, pH, and organic matter content among others which affect heavy metal concentration in water.

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### **APPENDICES**

### **APPENDIX A**

**Appendix A.1**: Mean ± SD for selected heavy metals in water from three sites of Lake Nakuru in mg/L

Site Element	River Njoro mouth	Sewage discharge point	Mid Lake point
Arsenic	BDL	BDL	BDL
Cadmium	BDL	BDL	BDL
Chromium	$0.1869 \pm 0.007$	$0.1494 \pm 0.004$	$0.1211 \pm 0.003$
Lead	$0.0351 \pm 0.000$	$0.0016 \pm 0.00$	0.0021±0.00
Mercury	$0.0035 \pm 0.001$	$0.0037 \pm 0.002$	$0.0041 \pm 0.002$

**Appendix A.2**: Mean  $\pm$  SD for selected heavy metals in sediments from three sites of Lake

### Heavy metal concentration mg/kg

# Nakuru in mg/kg

Site Element	River Njoro mouth	Sewage discharge point	Mid Lake point
Arsenic	$21.67 \pm 5.5$	$9.5 \pm 2.43$	$15.17 \pm 3.88$
Cadmium	< 0.02	< 0.02	< 0.02
Chromium	$9.19 \pm 2.08$	$8.28 \pm 1.31$	$7.16 \pm 1.66$
Lead	$11.33 \pm 4.79$	$31.04 \pm 8.05$	$12.53 \pm 1.40$
Mercury	$0.137 \pm 0.07$	$0.15 \pm 0.04$	$0.307 \pm 0.06$

**Appendix A.3**: Length-weight of the fish samples analysed for heavy metals in the entire study period in Lake Nakuru

Site	SAMPLE ID	Sex	Total length (cm)	Weight (g)	Arsenic	Mercury	Chromium	Lead	Cadmium
Sewage	SW1	F	20	148.8	ND	0.17	3.30	6.02	BDL
point						***			
	SW2	M	24.5	249.45	0.85	0.23	3.74	1.17	BDL
	SW3	M	22.0	200.89	0.30	0.25	2.74	BDL	BDL
	SW4	M	19.7	151.48	0.55	0.30	3.42	BDL	BDL
	SW5	M	22	206.8	0.35	0.80	5.30	13.10	BDL
River	R1	M	16.2	96	5	0.28	7.48	20.36	BDL
Njoro									
mouth									
	R2	M	16.9	81.07	2.85	0.070	10.33	44.39	BDL
	R3	M	14.3	60.04	1.6	BDL	5.40	0.80	BDL
	R4	F	22	212.92	3.55	0.17	0.95	4.50	BDL
	R5	M	21.3	184.55	2.4	0.09	3.00	3.85	BDL
	R6	M	20.8	167.01	BDL	BDL	2.70	1.25	BDL
	R7	M	19.3	156.56	BDL	0.12	2.68	4.23	BDL
	R8	M	20	155.58	2.10	0.05	2.95	5.70	BDL
	R9	F	20.3	161.48	BDL	BDL	2.80	1.65	BDL
> T	R10	F	20	144.81	0.95	0.40	3.38	12.74	BDL
Nyati	271		1.5.5	640	DDI	nn.	0.200	10.40	DD1
	N1	M	15.5	64.9	BDL	BDL	8.280	12.42	BDL
	N2	M	15.4	71.01	BDL	BDL	9.130	14.83	BDL
	N3	M	15.7	76.6	BDL	BDL	5.380	9.07	BDL
F: 1 ,	N4	F	18.1	123.7	BDL	BDL	3.810	0.51	BDL
Fisher's point									
	G1	F	23.5	279.37	1.05	0.17	6.00	6.85	BDL
	G2	M	25.5	308.05	BDL	0.75	4.65	8.45	BDL
	G3	M	24.5	271.18	BDL	0.44	3.80	3.15	BDL
	G4	M	23.5	285.91	7.50	BDL	3.07	BDL	BDL
	G5	M	26	363.11	3.60	0.03	16.05	0.054	BDL
	G6	F	19.1	136.89	BDL	BDL	32.59	BDL	BDL
	G7	M	22.5	179.14	BDL	BDL	13.01	BDL	BDL
	G8	M	22.5	217.35	8.50	BDL	41.78	0.091	BDL
	G9	F	22.3	207.24	2.60	0.02	0.71	BDL	BDL
	G10	M	23.9	208.27	BDL	BDL	0.78	BDL	BDL
	G11	M	22.4	224.66	BDL	BDL	1.2	BDL	BDL

**Appendix A.4**: Correlations of levels of  $\Sigma$ heavy metals with water quality parameters in water, sediments and fish from Lake Nakuru

		Wat	Sedime	Fis	Temperat	pН	DO	Salini	Conducti	
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		er	nts	h	ure		<u> </u>	ty	vity
Water	Pearson	1	0.038	-	-0.059	-	-	-	-0.056
	Correlati			0.0		0.059	0.059	0.056	
	on			54					
	Sig. (2-tai	led)	0.649	0.5 24	0.481	0.484	0.482	0.502	0.502
	N	144	144	144	144	144	144	144	144
Sediment	Pearson	0.03	1	0.0	213*	-	-	-	212*
S	Correlati on	8		91		.213*	.213*	.212*	
	Sig. (2-tailed)	0.64 9		0.2	0.01	0.01	0.01	0.011	0.011
	N	144	144	144	144	144	144	144	144
Fish	Pearson	-	0.091	1	-0.063	177	177	177	-0.063
L1911	Correlati	0.05	0.091		-0.003	0.063	0.063	0.063	-0.003
	Sig. (2-tailed)	0.52	0.28		0.166	0.166	0.166	0.167	0.167
	N	144	144	480	480	480	480	480	480
Temperat	Pearson	-	213*	-	1	1.000	1.000	.998*	.998**
ure	Correlati	0.05		0.0		**	**	*	
	on	9		63					
	Sig. (2-tailed)	0.48 1	0.01	0.1 66		0	0	0	0
	N	144	144	480	480	480	480	480	480
pН	Pearson	-	213*	-	1.000**	1	1.000	.998*	.998**
1	Correlati	0.05		0.0			**	*	
	on	9		63					
	Sig. (2-tailed)	0.48 4	0.01	0.1 66	0		0	0	0
	N	144	144	480	480	480	480	480	480
DO	Pearson	-	213*	-	1.000**	1.000	1	.998*	.998**
	Correlati	0.05		0.0		**		*	
	on	9		63					
	Sig. (2-tailed)	0.48	0.01	0.1 66	0	0		0	0
	N	144	144	480	480	480	480	480	480
Salinity	Pearson Correlati	0.05	212*	0.0	.998**	.998*	.998*	1	1.000**
	on	6		63			,		
	Sig. (2-	0.50	0.011	0.1	0	0	0		0
	tailed)	2	0.011	67	U	U			
	N	144	144	480	480	480	480	480	480
Conducti	Pearson		212*	-	.998**	.998*	.998*	1.000	1
vity	Correlati	0.05	.212	0.0	.,,,,,	*	*	**	1
· ity	on	6		63					
	Sig. (2-	0.50	0.011	0.1	0	0	0	0	
	tailed)	2	0.011	67					

	N	144	144	480	480	480	480	480	480
* Correlation is significant at the 0.05 level (2-tailed).									
** Correlation is significant at the 0.01 level (2-tailed).									

# APPENDIX B

**Appendix B.1**: Mean  $\pm$  SD for OCP levels in water from three sites of Lake Nakuru in  $\mu$ g/L

Site	River mouth	Njoro	Sewage discharge point	Mid point	Lake
OCPs					
Alpha - HCH	0.05	± 0.03	$0.06 \pm 0.01$	0.04 ±	± 0 03

Beta - HCH	$0.03 \pm 0.00$	$0.06\pm0.02$	$0.05 \pm 0.01$
Gamma - HCH	$0.04\pm0.01$	$0.07 \pm 0.02$	$0.03 \pm 0.01$
Delta - HCH	$0.05\pm0.01$	$0.06 \pm 0.01$	$0.07 \pm 0.01$
P,P'-DDD	$0.10 \pm 0.02$	$0.15 \pm 0.01$	$0.03 \pm 0.00$
P,P'-DDE	$0.13 \pm 0.03$	$0.18 \pm 0.03$	$0.14 \pm 0.02$
P,P'-DDT	$0.07\pm0.03$	$0.10 \pm 0.05$	$0.04\pm0.02$
Endosulfan 1	$2.05 \pm 1.31$	BDL	BDL
Endosulfan 2	$0.83 \pm 0.42$	$1.73 \pm 0.51$	$1.29 \pm 0.30$
Endosulfan sulfate	$0.08 \pm 0.03$	$0.24 \pm 0.14$	$0.11 \pm 0.04$
Aldrin	BDL	BDL	BDL
Endrin	$0.34 \pm 0.25$	$0.68 \pm 0.41$	$0.22 \pm 0.06$
Dieldrin	$0.67 \pm 0.15$	$0.98 \pm 0.26$	$0.27 \pm 0.03$
Heptachlor	$0.16 \pm 0.01$	$0.19 \pm 0.02$	$0.12 \pm 0.05$
Methoxychlor	$2.42 \pm 0.62$	$4.54 \pm 0.35$	$2.07 \pm 0.52$
Heptachlor Epoxide	$2.60 \pm 0.12$	$7.44 \pm 0.66$	$1.50 \pm 0.41$

Appendix B.2: Mean  $\pm$  SD for OCP levels in sediments from three sites of Lake Nakuru in  $\mu g/kg$ 

Site	River-Njoro	Sewage	Mid-Lake
OCPs	mouth	discharge point	point
Alpha - HCH	$0.03 \pm 0.02$	$0.04 \pm 0.00$	$0.04 \pm 0.01$

Beta - HCH	$0.03\pm0.02$	$0.05 \pm 0.01$	$0.03 \pm 0.00$
Gamma – HCH	$0.05 \pm 0.01$	$0.06 \pm 0.03$	$0.06 \pm 0.01$
Delta - HCH	$0.08 \pm 0.03$	$0.04 \pm 0.00$	$0.05 \pm 0.01$
P,P'-DDD	$0.12 \pm 0.01$	$0.27 \pm 0.00$	BDL
P,P'-DDE	$0.14 \pm 0.00$	$1.36 \pm 0.05$	$0.16 \pm 0.00$
P,P'-DDT	$0.05 \pm 0.02$	$0.10 \pm 0.02$	$0.02 \pm 0.00$
Endosulfan 1	$3.46 \pm 0.00$	$2.71 \pm 0.00$	$2.41 \pm 0.01$
Endosulfan 2	$1.74 \pm 0.65$	$6.39 \pm 1.10$	$0.97 \pm 0.26$
Endosulfan sulfate	$0.39 \pm 0.10$	$0.13 \pm 0.00$	$0.47 \pm 0.00$
Aldrin	BDL	BDL	BDL
Endrin	$0.07 \pm 0.02$	$0.28 \pm 0.18$	$0.14 \pm 0.07$
Dieldrin	$0.22 \pm 0.10$	$0.09 \pm 0.03$	$0.41 \pm 0.01$
Heptachlor	$0.09 \pm 0.00$	$0.28 \pm 0.02$	$0.10 \pm 0.03$
Methoxychlor	$2.23 \pm 0.05$	$5.22 \pm 1.41$	$0.76 \pm 0.17$
Heptachlor Epoxide	$3.31 \pm 0.80$	$2.88 \pm 1.20$	$2.98 \pm 0.79$

Appendix B.3: Mean  $\pm$  SD for OCP levels in fish samples from four sites of Lake Nakuru in  $\mu g/kg$ 

Site	RNM	SDP	FP	NYATI
OCPs				
Alpha - HCH	$0.06 \pm 0.03$	$0.05 \pm 0.00$	$0.04 \pm 0.01$	$0.05 \pm 0.01$

Beta - HCH	$0.04 \pm 0.02$	$0.07 \pm 0.00$	$0.04 \pm 0.00$	$0.05 \pm 0.01$
Gamma- HCH	$0.05\pm0.03$	$0.06\pm0.02$	$0.06 \pm 0.01$	$0.06\pm0.00$
Delta - HCH	$0.05\pm0.02$	$0.04 \pm 0.01$	$0.09\pm0.02$	$0.04 \pm 0.01$
P,P'-DDD	$0.19 \pm 0.02$	$0.18 \pm 0.01$	$0.15 \pm 0.02$	$0.25 \pm 0.00$
P,P'-DDE	$0.04 \pm 0.01$	$0.02 \pm 0.01$	$0.07 \pm 0.01$	$0.04 \pm 0.01$
P,P'-DDT	$0.06\pm0.03$	$0.03 \pm 0.00$	$0.12 \pm 0.02$	$0.05\pm0.02$
Endosulfan 1	262.91± 88.07	$196.65 \pm 73.66$	$150.29\pm40.18$	$286.07 \pm 3.16$
Endosulfan 2	161.46± 93.68	$135.08 \pm 37.59$	$44.30 \pm 7.15$	$319.74 \pm 66.94$
Endosulfan sulfate	$0.18 \pm 0.03$	$0.12 \pm 0.02$	$0.36\pm0.04$	$0.02 \pm 0.01$
Aldrin	BDL	BDL	BDL	BDL
Endrin	$0.37 \pm 0.21$	$0.38 \pm 0.19$	$0.37 \pm 0.13$	$0.31 \pm 0.02$
Dieldrin	$0.25\pm0.05$	$0.25 \pm 0.03$	$0.22 \pm 0.09$	$0.05\pm0.00$
Heptachlor	$0.27\pm0.04$	$0.16 \pm 0.02$	$0.24\pm0.02$	BDL
Methoxychlor	$0.9 \pm 0.3$	$1.41 \pm 0.2$	$0.80\pm0.28$	$1.48 \pm 0.47$
HeptachlorEpoxide	$3.11 \pm 1.3$	$2.00 \pm 0.73$	$7.07 \pm 2.68$	$1.72 \pm 0.09$

SDP: Sewage discharge point, RNM: River Njoro mouth, FP: Fishers' point.

**Appendix B.4**: Percentage detection frequency of organochlorine pesticides in water, sediment and fish samples from Lake Nakuru analysed in this study

ОСР	Detection frequency (%)						
	Water $(n = 9)$	Sediment $(n = 9)$	Fish (n = 30)				
Alpha – HCH	100	66.7	70				

Beta – HCH	100	66.7	70
Gamma – HCH	77.8	66.7	76.7
Delta – HCH	66.7	44.4	60
P,P'-DDD	44.4	44.4	40
P,P'-DDE	77.8	77.8	73.3
P,P'-DDT	88.9	55.6	76.7
Endosulfan 1	22.2	33.3	53.3
Endosulfan 2	66.7	66.7	76.7
Endosulfan sulfate	77.8	44.4	43.3
Endrin	100	88.9	86.7
Dieldrin	100	77.8	63.3
Heptachlor	66.7	55.6	40
Heptachlor epoxide	66.7	88.9	86.7
Methoxychlor	100	100	100

**Appendix B.5**: A list of organochlorine pesticides banned in Kenya and those under restricted use

	COMMON NAME	USE	YEAR OF BAN
1.	5 Isomers of hexachlorocyclohexane (HCH)	Herbicide	1986

2.	DDT (Dichlorodiphenyl Tichloroethane)	Agriculture	1986
3.	Endrin	Insecticide	1986
4.	Heptachlor	Insecticide	1986
5.	Aldrin	Insecticide	2004
6.	Dieldrin	Insecticide	2004

# PESTICIDES UNDER RESTRICTED USE

1.	DDT	Mosquito control in public health
2.	Lindane	Restricted for seed dressing only

(PCPB, 2008)

**Appendix B.6**: Concentrations of organochlorine pesticide residues in water, sediment and fish samples from Lake Nakuru analysed in this study (Ranges in  $\mu$ g/L for water and  $\mu$ g/kg for sediments and fish samples)

OCPs		Ranges	
	Water $(n = 9)$	Sediments $(n = 9)$	Fish (n = 30)
Alpha - HCH	BDL - 0.09	BDL - 0.35	BDL - 0.10
Beta - HCH	BDL - 0.49	BDL - 0.05	BDL - 0.27
Gamma - HCH	BDL - 0.07	BDL - 0.09	BDL - 0.61
Delta - HCH	BDL - 0.08	BDL - 0.08	BDL - 0.18
P,P'-DDD	BDL - 0.15	BDL - 0.20	BDL - 0.37
P,P'-DDE	BDL - 0.17	BDL - 1.53	BDL - 0.25
P,P'-DDT	BDL - 0.25	BDL - 0.16	BDL - 0.09
Endosulfan 1	BDL - 3.03	BDL - 3.46	BDL - 897.14
Endosulfan 2	BDL - 2.29	BDL - 6.39	BDL - 646.52
Endosulfan sulfate	BDL - 0.37	BDL - 0.48	BDL - 0.43
Aldrin	-	-	-
Endrin	BDL - 1.01	BDL - 0.40	BDL - 0.80
Dieldrin	BDL - 1.17	BDL - 0.46	BDL - 0.39
Heptachlor	BDL - 0.21	BDL - 0.30	BDL - 0.37
Heptachlor Epoxide	BDL - 19.75	BDL - 4.27	BDL - 9.67
Methoxychlor	0.01 - 4.78	0.37 - 9.04	BDL - 2.00

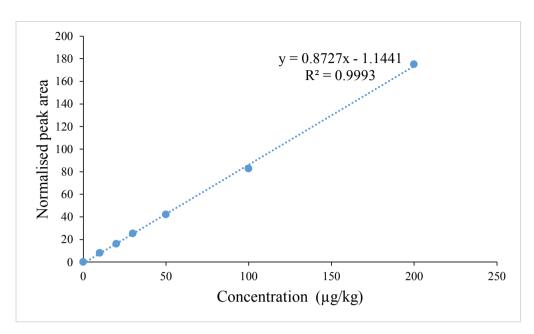


Figure B.1: A calibration curve for Alpha - HCH.

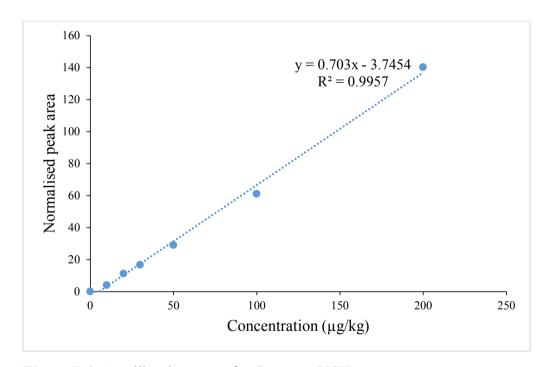
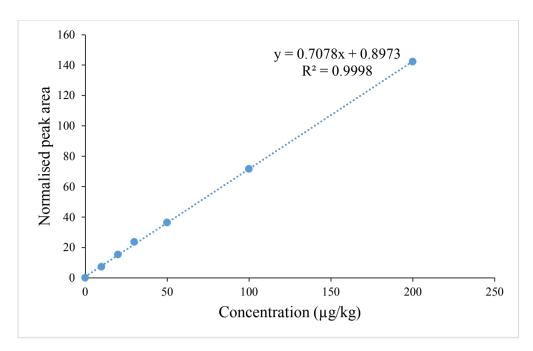


Figure B.2: A calibration curve for Gamma - HCH.



**Figure B.3:** A calibration curve for methoxychlor.

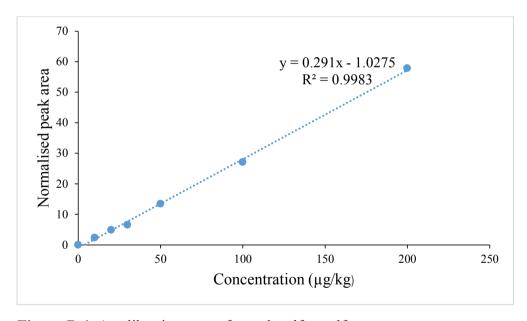


Figure B.4: A calibration curve for endosulfan sulfate.

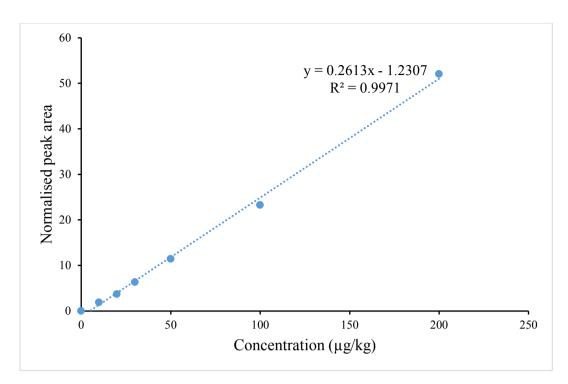


Figure B.5: A calibration curve for dieldrin.

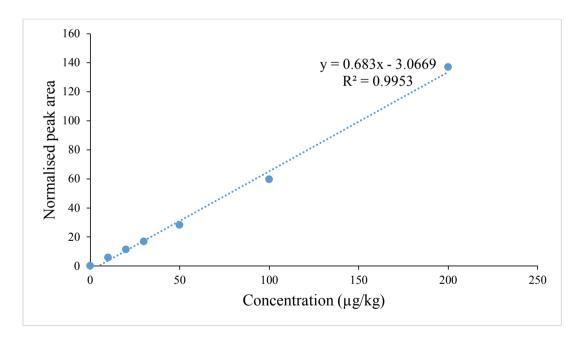


Figure B.6: A calibration curve for DDT.

APPENDIX C

Appendix C.1: One-way ANOVA summary table for comparison of means (OCP residue concentrations in water samples) across sites

ОСР		Df	Sum Sq	Mean Sq	F value	P value
Delta -HCH	Site	2	0.0013387	0.0006694	9.153	0.015 *
	Residuals	6	0.0004388	0.0000731		
DDD	Site	2	0.02005	0.010023	52.31	0.00016 *
	Residuals	6	0.00115	0.000192		
DDT	Site	2	0.03689	0.018446	14.2	0.0053 *
	Residuals	6	0.00779	0.001299		
Endosulfan 1	Site	2	8.415	4.207	7.356	0.0243 *
	Residuals	6	3.432	0.572		
Heptachlor epoxide	Site	2	67.55	33.77	78.89	4.92e-05 *
	Residuals	6	2.57	0.43		

Significant codes: 0.05 '\*'

**Appendix C.2**: Tukey HSD summary table showing adjusted p-values that indicated significant differences of OCP residue concentrations in water across sites (P < 0.05)

ОСР	Sites that showed differences in residue levels	p- values
Delta - HCH	River Njoro mouth and mid lake point	0.01
DDD	River Njoro mouth and mid lake	0.003
	River Njoro mouth and sewage discharge point	0.01
	Sewage discharge point and mid lake	0.00
DDT	River Njoro mouth and sewage discharge point	0.015
	Sewage discharge point and mid lake	0.006
Endosulfan 1	River Njoro mouth and mid lake point	0.037
	River Njoro mouth and sewage discharge point	0.037
Heptachlor epoxide	River Njoro mouth and sewage discharge point	0.00
	Sewage discharge point and mid lake	0.00

**Appendix C.3**: One-way ANOVA summary table for comparison of means (OCP residue concentrations in sediment samples) across sites

ОСР		Df	Sum Sq	Mean Sq	F value	P value
DDE	Site	2	3.534	1.7671	178.9	4.49e-06 *
	Residuals	6	0.059	0.0099		
Dieldrin	Site	2	0.17269	0.08635	25.67	0.00115 *
	Residuals	6	0.02019	0.00336		
Endosulfan	Site	2	0.2249	0.11244	5.281	0.0475 *
sulfate						
	Residuals	6	0.1278	0.02129		

Significant codes: 0.05 '\*'

**Appendix C.4**: Tukey HSD summary table showing adjusted p-values that indicated significant differences of OCP residue concentrations in sediment samples across sites (P < 0.05)

OCP	Sites that showed differences in residue levels	p - values
DDE	River Njoro mouth and sewage discharge point	0.00
	Sewage discharge point and mid lake	0.00
Dieldrin	River Njoro mouth and mid lake	0.03
	River Njoro mouth and sewage discharge point	0.02
	Sewage discharge point and mid lake	0.00
Endosulfan sulfate	Sewage discharge point and mid lake	0.04

**Appendix C.5**: One-way ANOVA summary table for comparison of means (OCP residue concentrations in fish samples) across sites

ОСР		Df	Sum Sq	Mean Sq	F value	p - values
Alpha- HCH	Site	3	0.009002	0.0030008	4.271	0.014 *
	Residuals	26	0.018267	0.0007026		
DDT	Site	3	0.04857	0.016189	13.11	2.08e-05 *
	Residuals	26	0.03210	0.001235		
Endosulfan 2	Site	3	139456	46485	7.104	0.00122 *
	Residuals	26	170128	6543		
Methoxychlor	Site	3	2.319	0.7729	6.499	0.00199 *
	Residuals	26	3.092	0.1189		

Signif. codes: 0.05'\*'

**Appendix C.6**: Tukey HSD summary table showing adjusted p-values that indicated significant differences of OCP residue concentrations in fish samples across sites (p < 0.05)

OCP	Sites that showed differences in residue levels	p - values
Alpha- HCH	River Njoro mouth and fishers' point	0.02
DDT	Nyati and fishers' point	0.006
	River Njoro mouth and fishers' point	0.00
	Sewage discharge point and fishers' point	0.00
Endosulfan 2	Nyati and fishers' point	0.002
	River Njoro mouth and fishers' point	0.01
Methoxychlor	Nyati and fishers' point	0.01
	Sewage discharge point and fishers' point	0.01
	River Njoro mouth and nyati	0.03

**Appendix D**: Research permit granted by the National Commission for Science, Technology and Innovation (NACOSTI) to conduct a study in Lake Nakuru



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